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Increasing diffuse agricultural phosphorus losses

Diffuse agricultural losses of phosphorus to the River Main (the main tributary of Lough Neagh) show an increase over 20 years to the extent that the major reductions in sewage works discharges now appear as a comparatively minor change.

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Ecological water quality polishing and reuse

A constructed wetland system for nutrient removal from the wastewater treatment plant servicing the Empuriabrava community provides both a new wetland area and purified water for the prestigious Aiguamolls de l'Emporda nature reserve.

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The artifical wetlands, July 2000: See: Costa Brava Spain, page3

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WATER POLICY

NORTHERN IRELAND

Increasing diffuse agricultural phosphorus losses

River phosphorus loads in the River Main are calculated from concentration and flow measurements over the period 1974-1995 and compared with estimated inputs from sewage works, populations not connected to sewage works, agricultural manure production and diffuse losses from agricultural soils.

River phosphorus loads were calculated from available weekly sampling results (Smith 1977). The samples were taken from the river near to the point where it flows into Lough Neagh and three phosphorus fractions were analysed : soluble reactive phosphorus (SRP), total soluble phosphorus (taken to be the total phosphorus after 0.45µ filtration) and total phosphorus (TP). Daily river flows were available from continuous river level monitoring data. Daily phosphorus concentrations were then estimated from regressions of daily flow against weekly measured concentrations. From these concentrations, annual river phosphorus loads were then calculated.

Phosphorus inputs to the river from sewage were calculated from sewage works discharge data, and from statistics concerning the catchment population and the % connection to sewage works. The proportion of phosphorus as SRP was estimated by applying fixed ratios based on discharge monitoring for the different types of sewage works in operation (65% of TP as SRP for sewage works without phosphorus removal, 39% for those with).

Phosphorus inputs from non-connected households were estimated by calculating the per capita phosphorus input to waste waters (human plus detergent phosphates) and then assuming 40% retention in soils in soakaways. This proportion was derived from regression equations of annual SRP loads against urban and total populations presented by Smith (1977) : non-sewered populations were less variable for these rivers than urban populations served by sewage works, so that the contribution of the river load from the non-sewered population could be estimated at nearly 1 mgP/day. This is turn could be compared with the per capita value estimated for the population in this study of around 1.5 mgP/day, giving an estimate of around 40% retention in the septic tank and in the soil in the soakaway systems.

Land use, human and farm animal populations

Human populations for the catchment were obtained from census and electoral roll numbers. Land use and farm animal numbers were estimated from the Department of Agriculture for Northern Ireland (DANI) annual farm censuses: these cover rural districts or the county, so were converted to catchment values by using area ratios. Estimated animal numbers were then used to calculate phosphorus inputs by taking standard manure P *per capita* figures for the different animals, as used in farm nutrient management plans by the Republic of Ireland.

Statistics for external imports of phosphorus as mineral fertilisers and in animal feeds are only available covering the whole of Northern Ireland.

Increasing river phosphorus loads, despite sewage works P-removal

Significant reductions in sewage works phosphorus discharges occurred after 1981 (around 50%) following introduction of phosphorus removal, but within a few years river SRP loads had risen back up to their 1978 – 1979 level, and ten years later they had reached around twice their 1974 level at nearly 80 tonnes of phosphorus (SRP) per year. The inputs from unsewered populations altered little over this period (estimated 10% reduction), so the increase in river loadings must have been the result of increases in diffuse sources (mainly agricultural inputs). The river SRP load from non sewage works sources thus approximately tripled over the 1974 – 1995 period.

The authors note that the river SRP load of diffuse origin is positively correlated with annual river flow, and that high flows in the early 1990’s and low flows in the 1970’s may explain some of the SRP load increase.

These data-based calculations of river phosphorus loads (as SRP) and of sewage works discharges, were then compared with catchment estimates of phosphorus generated by agricultural sources.

Animal manure production in the catchment increased 18% from 1974 to 1995, mainly as a result of increased numbers of poultry (increase of 240 tonnes of phosphorus in chicken manure over the period), with the Main catchment now having 16% of Northern Ireland’s total chicken numbers for only 5% of the farmland area. Cattle manure increased by around 1%, and although sheep numbers tripled, they still only contributed 9% of total manure phosphorus by 1995.

The expansion of the broiler chicken sector after 1986 corresponds to the observed increased in river phosphorus load. However, manure phosphorus was not significantly correlated to river SRP loads in regression analysis, and the authors suggest that the modest increase in manure production cannot be considered to be the dominant variable associated with the tripling of the diffuse river SRP load.

Phosphorus in fertilisers and animal feed

The authors calculated that, **for the whole of Northern Ireland, the surplus of agricultural phosphorus inputs in mineral fertilisers and animal feeds over outputs in meat, milk, eggs and harvested crops was, for the study period, 1.3 tonnes P/year per km^2 of agricultural land**. This is much greater than the increase in annual non sewage works SRP-phosphorus load in the Main river over the 1974-1995 period, 0.06 tonnes P/year/km^2.

The authors suggest that this is because most phosphorus is retained in the soil. However, **the increase of diffuse inputs of phosphorus to the Main river (and thus to Lough Neagh) is very considerable in limnological terms**, even taking into account that a part of this may be related to local concentrations of chicken production and to fluctuations in river flow. Over the 20+ years of monitoring, the impact of phosphorus removal in sewage works now appears a minor change in river SRP loads compared with increasing diffuse agricultural releases.

The authors conclude that, even if much of the phosphorus inputs to agriculture are retained in soil, the increases in agricultural phosphorus releases will have a dramatic cumulative effect on lake and river ecology and that management policies will increasingly have to examine agricultural phosphorus use.

"Contributions of diffuse and point sources to the phosphorus loads in the River Main over a 22-year period", Boreal Environmental Research 5, 2000, pages 27-37.

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COSTA BRAVA, SPAIN

Ecological water quality polishing and reuse

A major project for reuse of reclaimed municipal wastewater in the Costa Brava area, near Girona, on Spain's North East coast, includes the supply of water for irrigation to four golf courses and some agricultural plots and also for a constructed wetland system in the Aiguamolls de l'Empordà nature reserve area. For the golf courses and the agricultural users, information concerning the nutrient content of the water allows the managers to adjust the application of mineral fertilisers. In the nature reserve, the lagoon system constructed for nutrient reduction of the effluent from the Empuriabrava sewage works both itself constitutes a new ecosystem attractive for bird life and also provides good quality water for the reserve's natural lagoons. The amount of reclaimed water in the ongoing projects in the Costa Brava area will reach 1,200,000 m^3 by the end of this year.

In the Costa Brava area, in the project developed by the Costa Brava Water Council (Consorci de la Costa Brava, CCB), municipal secondary effluents are being reclaimed through a disinfection or filtration/disinfection treatment and reused for irrigation at four golf courses and in some agricultural orchards. In another location, water is also being reclaimed in a constructed wetland system and reused for environmental purposes at a nature reserve area. The amount of water reused totalled nearly 1,100,000 m3 in 1999, of which around 40 % was used for the golf courses, 50 % for environmental purposed and 10 % for agricultural irrigation. The CCB operates 18 treatment plants under the commission of the Catalan Water Agency (Agència Catalana de l'Aigua), and they treat around 30 hm3/year of municipal wastewater. Water reclamation and reuse is currently being performed in 6 wastewater treatment plants, but there are four other reclamation treatment schemes to start operation by early year 2001.

The reuse started in 1989 and since then user satisfaction has steadily increased because the summer supply is more reliable than from other water sources. Also, water reuse gives a "green" image for golf courses whose water consumption can otherwise pose environmental problems in dry areas, but which are a positive attribute in this tourist centre. Apart from this, golf green-keepers and farmers also value the fertiliser contribution brought by the reclaimed water, which allows them to save on mineral fertilisers. Another positive side effect of water reuse is the decrease in the amount of effluents discharged in the sea, which helps to maintain a good bacteriological quality in the local beaches.

Water reuse for eutrophication abatement

At the Golf d'Aro (formerly Golf Mas Nou, in Platja d'Aro) the nitrogen, phosphate and potassium contained in the filtered and disinfected effluent used for irrigation **save an estimated 20 – 25,000 Euros in fertiliser costs** and cover over 50% of fertiliser requirements. The project organisers emphasise that the use of reclaimed water for irrigation changes agronomic and fertiliser management practices, because of the dose of nutrients present in each irrigation application, this dose increasing with irrigation quantities. Regular information is therefore necessary concerning the nutrient content of the reclaimed water supplied, but this management effort is now perceived as worthwhile because of the economic savings that it produces.

Water reused for agriculture undergoes filtration and disinfection (except for that used on a poplar tree plantation without public access) and applications include orchards and vineyards. Larger major agricultural reuse projects in the lower part of the Muga and Tordera river basins (2 - 3 hm3/year each) are currently being discussed and may start operation by late spring 2001 if everything falls into place.

For all these irrigation applications, except the one mentioned above, a target level of less than 100 faecal coliforms per litre is consistently achieved. Disinfection is mainly done with chlorine, but UV radiation is increasingly being used in the newest projects. However, even in the latter case, a post-chlorination step is maintained in order to provide a residual disinfectant effect and preserve its microbiological quality while the water is being transported to the use point.

Reclaimed water to save a natural wetland

The **Aiguamolls de l'Empordà is a Natura 2000 and International Bird Conservation Area** classified wetland, and one of the most prestigious wetlands in

Northern Spain for birdlife. The main lagoon, El Cortalet, however was facing problems of falling water levels and drought in summer, because of agricultural irrigation pumping upstream in the river feeding the nature reserve. There were also risks of saltwater intrusion into the lower reaches of the Muga river, and thus potentially into groundwater. A possible solution was identified as the reuse of the effluent water from the Empuriabrava wastewater treatment plant, which services the holiday resort of the same name, after removal of remaining nutrients. This would also have the advantage of eliminating the discharge from this sewage works into the Muga river, thus improving the quality of the lower reaches of this river and of its discharge into the sea near bathing beaches. **Because Empuriabrava has high tourist numbers in spring and summer, the sewage works effluent has the advantage of supplying higher flows of water to the natural wetlands particularly in the seasons when their water levels need maintaining.**

The Empuriabrava sewage works was inaugurated in 1995 and treated around 300-600 m3/day in winter and up to 2,400 m3/day in summer, increasing to a maximum of 6,600 m3/day with the connection of the northern sector of Empuriabrava community in 1997. The total volume of water treated is currently around 700,000 m3/year. The works has two parallel lines, each originally consisting of a prolonged aeration tank, a decanter-sludge recirculation tank, two sludge ageing lagoons and a finishing lagoon. In summer 2000, a mechanical dehydration system for continuous sludge processing and removal was installed, which has improved the overall performance of the plant. After the cleansing of the old sludge ageing lagoons, due for late 2000, these other four lagoons will be available to be used for the clarified wastewater to start the polishing process. This treatment plant consistently achieves good suspended matter and BOD removal (down to 4 and 7 mg/l respectively) but nutrient removal is not enough for the intended use of the water. For this reason, it was considered necessary to further reduce nutrient levels in the effluent before reusing the water to supply the Cortalet lagoon natural wetland. This project was approved and funded by the European Union Cohesion Funds in 1995 and the latest construction phase was completed in 1998.

Creation of a new wetland area

It was decided to ensure the required nutrient removal by constructing an **artificial wetland area next to the sewage works, thus providing a completely new wetland zone for the Aiguamolls natural park**. This artificial wetland consists of three small lagoons (cells) of impervious clay each of around 8,000 m^2 and around 40 centimetres of average depth. The impervious bottoms of these cells prevent any risk of percolation of nutrients into the aquifer. The three cells function in parallel and discharge into another larger, shallower lagoon (Europa lagoon, 44,000 m^2, depth of less than 20 cm), intended to provide further nutrient removal, enable oxygenation of the water and also to diversify the habitats created. Small predatory fish were introduced in order to limit mosquitoes, given the proximity of these wetlands to the Empuriabrava holiday urbanisation, situated just the other side of the Muga river. **The newly created wetlands have already proved a great success and are widely used both by migrant and wintering birds, as well as by residents including such prestigious species such as flamingos (*Phoenicuopterus ruber*) and the purple gallinule (*Porphyrio porphyrio*).** The final outflow from the Europa lagoon is taken by a 2.4 km pipeline to the Cortalet lagoon, near the nature reserve's visitors centre. This pipe also has other outlets, allowing if required irrigation or flooding of water meadow areas of the reserve. The reserve's managers can interrupt or modify flow from the Europa lagoon or divert it back to the Muga river, as a function of the reserve's water needs and of the quality of the water flowing out of the lagoon.

Public access and wildlife observation

The creation of the new artificial lagoons near the Muga river have enabled the nature reserve to create a path between them and the visitors' centre, thus developing a new itinerary accessible to the public, through a number of different habitats. Several birdwatching hides have been installed overlooking the new lagoons and these have already become popular. At the same time, the bridge carrying the sewage pipe from the Empuriabrava holiday resort over the Muga river to the sewage works has been adapted to create a footbridge, allowing access for the built up area to the new lagoons, and thus onwards to the main nature reserve. A scientific programme has been following the results of the artificial wetland nutrient removal system, and after an initial stabilisation period during which vegetation colonised the lagoons, **good nutrient removal has been achieved, fully compatible with the reuse of the water in the nature reserve habitats**.

Performance of the Empuriabrava constructed wetlands

The Empuriabrava constructed wetlands have treated 310,000 m^3 of secondary effluent from April to September 2000, the most critical season in terms of water availability for the Cortalet lagoon. Experience until today has shown that the constructed wetland is very effective at denitrifying the effluent, which means that it is quite critical to achieve a good nitrification rate in the Empuriabrava wastewater treatment plant. The polishing ponds in the treatment plant itself have also proved to be a key element in order to provide enough dissolved oxygen to the water before entering the wetland cells, where aeration is rather limited. Submerged macrophyte *Zanichellia palustris* has spontaneously colonised some areas of the wetland cells and has also improved the nutrient removal treatment. On the other hand, duckweed has had to be mechanically removed because it does not provide any beneficial treatment, but blocks the penetration of the light into the water and the diffusion of air, which makes the system tend to undesired anoxia.

By making sure that the wastewater treatment plant was effectively nitrifying the effluent and by removing the duckweed in the constructed wetland cells, these have

Average performance of the Empuriabrava constructed wetland system from April to September 2000

Parameter	*Inlet (secondary effluent)*	*Outlet (constructed wetland effluent)*
Dissolved oxygen, % saturation	*41*	*56*
pH	*7,5*	*8,9*
Ammonia, mg N/l	*3,0*	*0,4*
Nitrite, mg N/l	*0,3*	*0,2*
Nitrate, mg N/l	*6,1*	*1,4*
Total inorganic nitrogen, mg N/l	*9,4*	*2,0*
Soluble orthophosphate, mg P/l	*2,5*	*1,8*

remained aerobic throughout the summer and they have taken their performance capabilities to a maximum, as proven by the results in the table above.

Given the success of these different water reuse projects, discussions are currently underway (late 2000) to develop reuse from a further four sewage works in the Costa Brava area. This water will be reused for agricultural irrigation and for urban non-potable uses. At a smaller level, discussions have also started with two other golf courses in the area.

Material compiled from various publications from the Consorci de la Costa Brava and the paper presented at the 3rd International Water Association's International Symposium, Paris, July 2000 "Cultural eutrophication control through water reuse".

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ECOSYSTEM BALANCE AND EUTROPHICATION

MARINE ECOLOGY

Estuary nutrient balance

The author presents a summary of current knowledge of estuarine nutrient ecology. Man's activities have increased nitrogen loadings since the turn of the century often by 1.5 – 4.5 times, and phosphorus loadings even more by 2 – 6 times. These increases correspond to loadings 18 – 150 times higher than pristine conditions for phosphorus, and 6 – 50 times higher for nitrogen. On the other hand, dams on rivers have probably decreased dissolved silicon loadings in a number of cases (by retaining diatom algae). Phosphorus is often limiting in Spring in estuaries, with nitrogen becoming limiting in Summer, with the result that discharges of both nutrients probably have to be reduced to successfully improve water quality. Reductions of phosphorus inputs only is likely to result in the "export" of nitrogen-stimulated eutrophication problems into adjacent marine waters.

Few estimates are available to compare current estuary nutrient loadings with pristine conditions. The author has however assembled estimates for four estuarine systems for pristine conditions, for the turn of the century and for the present day : the Baltic Sea, Chesapeake Bay USA, Narragansett Bay and Phison Rver/ Eden Bay. This enables him to make the estimates of loading increases given above.

Because increases of phosphorus loadings are generally much higher than those of nitrogen, the N:P ratio has been significantly reduced. The form of nutrient loadings has also been changed by man's activities. Natural ecosystems will tend to export nutrients essentially in organic forms, because inorganic nitrogen and phosphorus, in short supply, are efficiently retained by river vegetation.

Marine nitrogen limitation

The general consensus is that nitrogen is most often the most limiting nutrient for algal development in marine waters, although of course in many situations light and temperature are the factors controlling algal growth. This is justified by the low N:P ratios in marine waters (as compared to the "Redfield ratio" of cells' requirements) and is supported by recent ecosystem-level nutrient limitation experiments (Oviatt *et al.* 1995) and the recent compilation study by Nixon *et al.* 1996 which compares primary production to nitrogen loading per m^2.

In 1986, D'Elia *et al.* first showed the Chesapeake bay estuary to be **phosphorus limited in Spring but nitrogen limited in summer.** A number of other studies since then have reached similar conclusions in other estuaries : Baltic Sea, Roskilde Fjord Denmark, Brest Bay France, Delaware Estuary USA, Neuse River Estuary USA. This behaviour is not observed in all estuaries, however : the low salinity Bothnian Bay in the Northern Baltic is phosphorus limited all year round, whereas higher salinity areas of the Baltic are nitrogen limited all year. The seasonal switch in limiting nutrients appears to occur only in areas of the Baltic receiving fresh water inflows.

In other cases, algal development has been observed to

be controlled by dissolved silicate concentrations : for example for the Chesapeake Bay spring diatom bloom (Conley & Malone, 1992) or in the Brest Bay, France, which has recently changed from nitrogen to dissolved silicate limitation (Del Amo *et al*. 1997).

Explaining changes in nutrient limitation

The author proposes several explanations for the differences in nutrient limitation processes between freshwater and marine ecosystems. Firstly, there are differences in the balance between the "fixing" of atmospheric nitrogen by blue-green algae and the loss of bioavailable nitrogen by bacterial denitrification. Denitrification losses from fresh and marine waters are similar, although it has been observed that estuarine denitrification rates are significantly lower in the summer and higher in winter and spring. However, nitrogen fixation rates can be much higher in freshwater systems, so that phosphorus can often be the limiting nutrient, even in cases of low N:P loading ratios in freshwaters.

Another important difference is in **sediment phosphorus retention.** Unlike in freshwaters, nearly all the phosphorus deposited in estuarine sediments is remineralised each year and returns in a bioavailable form to the water column. In estuaries, sediment phosphorus release is strongly temperature dependent and is highest in summer, because of increased sulphate reduction rates causing the release of ion-bound phosphorus. The release of dissolved silicon from sediments is also temperature dependent (being related to the decomposition of diatom algae debris).

Management policies

Many coastal water management policies have concentrated on reducing phosphorus inputs, not least because **point sources can be readily dealt with (in particular, by phosphorus removal in sewage works)**. Danish estuaries (Odense and Rsokilde Fjords) have seen significant reductions in phosphorus and smaller reductions in nitrogen loadings, achieved by improved sewage treatment. This has in particular reduced spring blooms of the fast growing nuisance macrophyte *Ulva lactuca*, despite a situation which was already nitrogen limited prior to the phosphorus reductions.

The author concludes that phosphorus loading reductions to estuaries are unlikely to reduce summer chlorophyll levels (algal development), although they may reduce spring blooms. Because the spring is the most important season for the deposit of organic matter to the sediments, this may improve estuary-bed oxygen levels during the summer (less organic matter to decompose).

Even if it did prove possible to reduce phosphorus loadings sufficiently to limit estuarine summer algal growth, this would then reduce the nitrogen retention in the estuary and so "export" the nitrogen eutrophication problem to adjacent coastal waters. This occurred when Stockholm's sewage works was completed: algal blooms previously developing near the city began to occur further out into the archipelago.

The author therefore indicates that coastal water nutrient management policies must target both nitrogen and phosphorus loadings.

"Biogeochemical nutrient cycles and nutrient management policies". Hydrobiologia 410, pages 87-96, 2000.

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CULTURAL EUTROPHICATION

Nutrient impacts and management

This paper reviews the processes and impacts of anthropogenic nitrogen and phosphorus loading to fresh and marine waters, and to terrestrial ecosystems. Case studies of nutrient management of loadings to fresh and marine waters are presented, where in each case the treatment of urban sewage – including nutrient removal installation – proved to be a key factor in ecological restoration. The paper also looks at the issues of nitrogen enrichment of terrestrial ecosystems, concluding that although large increases in nitrogen loadings to terrestrial ecosystems can deteriorate biodiversity, increases in global nitrogen deposition to land and oceans from NO_X generated by fossil fuel burning and from agriculture, potentially may enhance primary production and so CO_2 fixation, buffering to somewhat extent the greenhouse effect.

Man has profoundly modified global nutrient cycles. **Anthropogenic inputs currently add at least as much nitrogen to terrestrial ecosystems as do all natural sources:** 90 -140 million tonnes per year (Mt/y) of nitrogen are naturally fixed from the atmosphere by plants, whereas over 50 Mt/y result from land transformations, 80 Mt/y from agricultural fertiliser inputs (1990) and 40 Mt/y through the cultivation of nitrogen-fixing leguminous crops (peas, beans, clover, alfalfa …). Further, more than 20 Mt/y of nitrogen are released into the atmosphere as N0x of which a significant proportion then returns to the ecosystem as plant-available nitrogen via wet and dry deposition.

At the same time, the addition of phosphate as fertilisers and manures, has resulted in an accumulation of phosphorus in many agricultural soils. These increases in soil phosphorus and changes in livestock management towards intensive production have been accompanied by increases in phosphorus run-off rates into surface waters. Fluxes of phosphorus to the world's oceans are thus estimated to have increased from around 8 MtP/y to around 22 MtP/y.

Increased nutrient loadings to surface waters from atmospheric and agricultural sources and from wastewater disposal systems often result in the development of nuisance algal growth, sometimes with deleterious secondary effects on the biology, chemistry and human use of the water. Phosphorus is the primary limiting nutrient in most lakes and reservoirs, and most eutrophication management programmes have therefore focused on the control of phosphorus loadings. However, input-output models for nitrogen have also been developed.

Successful lake restoration

The paper presents a number of lake restoration success stories. In Lake Washington (Seattle, USA), **the diversion of wastewater effluents led to a profound improvement in water quality**, accentuated by the appearance of large populations of the algae-grazing zooplankton, *Daphnia sp.*

Lake Maggiore, Italy, has also shown considerable decreases of algal biomass, a restoration of phytoplankton biodiversity and changes in zooplankton, invertebrate and fish populations, following the construction of sewage treatment installations with nutrient removal that served 60-70% of the catchment population. Detergent phosphates have also been restricted in Italy, but the impact of this change was augmented by the investments in sewage treatment. Further reductions in nutrient loadings are planned, in particular the construction of sewage treatment facilities to take the proportion of the population covered up to 80%, with the aim of restoring the lake to a condition close to its pre-1950's oligotrophic state. Manca and Ruggia (1998) concluded that changes in algal biomass resulted not only from reduced nutrient loadings, but also from changes in the lake's food web.

Rivers, streams and coastal waters

Many streams and rivers worldwide show elevated nutrient levels. A number of studies suggest that flowing waters are indeed sensitive to anthropogenic inputs of nitrogen and phosphorus. **Enrichment of streams with both nutrients often produces more algal development than with either nitrogen or phosphorus alone (co-limitation).** In other streams, nitrogen alone may be limiting.

Although eutrophication science for streams is more limited than for lakes and reservoirs, new management tools are being developed. The response of streams to nutrients also appears to depend on variables such as watershed area or hydraulic residence time (see for example E. van Nieuwenhuyse *et al.*, SCOPE 30, page 2).

Algal development in many marine coastal and estuarine waters is thought to be generally dependent on external nitrogen loadings. The paper presents as a success story the restoration of Hillsborough Bay, Florida (a subdivision of Tampa Bay). Advanced wastewater treatment was installed and industrial nutrient releases reduced. This resulted almost immediately in significant reductions in algal biomass, improved water transparency and oxygen concentrations, as well as the recovery of seagrass and macroalgal vegetation.

Terrestrial eutrophication

High rates of nitrogen deposition on natural habitats can significantly affect the balance of species and the biodiversity. In Holland, high levels of nitrogen deposition have caused the loss of species-rich heathlands and their conversion to low-diversity grasslands and forests. Experiments in Minnesota showed that nitrogen addition to grasslands caused a loss of plant diversity, the disappearance of native prairie forbs, and dominance by one or two non-native grass species. Long term nitrogen addition to British grassland caused a more than five-fold loss of plant diversity.

Long term experiments at Rothamsted Experimental Station, UK, show that 150 years of nitrogen fertilisation of agricultural soils did not lead to significant changes in soil carbon, compared to unfertilised plots.

Climate change

Many terrestrial and marine ecosystems are effectively nitrogen limited, so that anthropogenic nitrogen enrichment can initially lead to an increase in primary productivity, and thus act as a sink for atmospheric CO_2. This has been confirmed experimentally for certain plant species in fertilisation experiments. The authors present a provisional statistical analysis which suggests that nitrogen enrichment, resulting from fossil fuel burning (generating NO_x) could potentially lead to significantly enhanced global primary production over coming decades, thus buffering increases in atmospheric CO_2.

However, significant nitrogen loading of terrestrial ecosystems, as seen above, is likely to cause dramatic changes in biodiversity, which may then reduce carbon sequestration.

"Eutrophication: impacts of excess nutrients on freshwater, marine and terrestrial ecosystems". Environmental Pollution 100 (1999), pages 179-196.

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ANALYTICAL METHODS

EUROPEAN REFERENCE PROTOCOL

Harmonising analysis methods for phosphorus in sediments

Internal phosphorus loadings to lakes and rivers, resulting from sediment release and sediment cycling, can be a major issue in surface water eutrophication management. The release of phosphorus depends on conditions in the lake water, but also on the different forms in which the phosphorus is present in the sediments : most of the phosphorus is in particulate forms, and only some of it bioavailable and thus likely to be released.

Standard methods exist for quantifying total phosphorus, but not for determining the different forms. Indeed, the sequential extraction methods used imply specific reagents and procedures, so that data are not comparable from one laboratory to another, and so cannot be extrapolated from one ecosystem study to other management situations. In order to improve this situation, the European Commission, through the Standards, Measurements and Testing Programme, launched a collaborative project to :

- assess the different existing published methodologies
- design a harmonised sequential extraction methodology and protocol
- test this in inter-laboratory comparative studies
- certify the extractable phosphorus contents, for different phosphorus forms, of a reference sediment material

The four different existing sequential extraction schemes, published and used in different studies, were tested by the 15 participant laboratories using five different lake sediments and evaluated for ease of application and reliability :

Method :	*Extraction series (numbers refer to concentrations in moles/litre)*
Williams	*NaOH 1, HCl 1, HCl 1 plus calcination,* HCl 3.5 plus calcination
Hieltjes-Lijklema	*NaH4Cl 1, NaOH 0.1, HCl 0.5*
Golterman	*H2O, Ca-EDTA dithionite 0.05, Na2-EDTA 0.1,* H2SO4 0.25, NaOH 2
Ruttenberg	*MgCl2 1, Na3 citrate 0.3 plus NaHCO3 1,* Na-acetate 1, HCl 1, HCl 1 plus calcination

The results from the different laboratories using the same sediment sample showed the large differences in figures generated by the different extraction methods, and also the **variation between laboratories** even when using the same method. This confirmed the need to define one method only to be used if results are to be comparable, and the need to standardise the protocol for that method.

Although the Golterman and Ruttenberg methods delivered more information regarding the phosphorus forms (specific compounds and organic P extraction, distinction between calcium phosphate forms, respectively), they both posed difficulties of practicality and complication, resulting in low reproducibility or cumulative errors. The Hieltjes-Lijklema was relatively simple, but also gave poor reproducibility.

The Williams methodology gave relatively good reproducibility. Its advantages over the Hieltjes method appearing to be the use of higher extractant concentrations, and the fact that it is not a sequential method but the different extractions are carried out in parallel (thus avoiding cumulative errors and reducing overall time).

Williams method

The Williams method was then tested for 3 different sediment types (organic, siliceous and calcareous) by the 15 participant laboratories. The results were generally good (CV generally < 10%) and only a few labs noted problems, which were solved. The digestion method was tested for total phosphorus assessment, but proved problematic (not a routine procedure in most laboratories) without giving significantly different results to those from the standard Williams method, so this was abandoned.

Following this experience, slight modifications were made to the experimental protocol, in order to make it as clear as possible, even for laboratories not accustomed to sequential extraction analysis methods.

Certification

After reaching agreement between the participating labs and the European Commission on the modified Williams protocol, a lake sediment material was selected for certification as a reference material. This sediment come from a shallow bay in an oligotrophic lake receiving significant quantities of phosphorus. It is rather siliceous, with low calcium and organic matter contents (which facilitates the analysis of extractable forms of phosphorus), and around 1.3 mg/kg phosphorus.

The material was tested for within- and between- bottle homogeneity and found to be suitable for certification. No instability of extractable phosphorus forms was found after 1, 3, 6 and 12 month periods and +4, +20 and +40°C, showing that dried freshwater sediments remain stable for analysis over long periods.

The material was tested by the 15 laboratories, each carrying out five independent analyses, using at least two different bottles of the material on at least two different days. These tests enabled certain specifications of the protocol to be refined, or where it was clear that no difference resulted, ranges of values to be allowed (eg. operating temperature 21 +/- 3°C). The variation in the results obtained was satisfactory or low: - see table below.

The authors conclude that the exercise was very efficient in terms of defining and validating a standard method for the analysis of different forms of phosphorus in freshwater sediments, in order to enable results from different sites and different laboratories to become compatible. This is particularly useful as the certification experiments demonstrated the stability of dried sediments over a long period of time. The protocol defined will be a useful tool for laboratories in terms of method and of quality control.

The final validated protocol can be obtained on request from Véronique Ruban as below.

"Selection and evaluation of sequential extraction procedures for the determination of phosphorus forms in lake sediment", paper published in the Journal of Environmental Monitoring (1999, 1: 51-56) submitted in a shortened version to the SCOPE Newsletter by the EU Commission.

V. Ruban, Laboratoire Central des Ponts et Chaussées Division Eau, BP 4129, F44341 Bouguenais Cédex, France. G. Rauret, Universidad de Barcelona Dept. Quimica Analitica, Mari I Franqués 1-11, E08028 Barcelana, Spain. H. Muntau, European Commission Joint Research Centre Environment Institute, I21020 Ispra, Italy. Ph. Quevauviller, European Commission , DG Research (MO73 3/9), rue de la Loi 200, B1049 Brussels, Belgium. Email: **veronique.ruban@lcpc.fr**

Variation in analysis results from 15 labs using defined protocol and reference test material.

	CV based on all data	*CV based on 95% of data*	***sediment content mg/kg as P (average)***
- NaOH-P :	*9.8%*	*3.8%*	*0.550*
- HCl-P :	*9%*	*5.2%*	*0.536*
- inorganic P :	*3.5%*	*2.2%*	*1.113*
- organic P :	*20.6%*	*4.3%*	*0.209*
- concentrated HCl-P :	*4.5%*	*2.5%*	*1.373*

PHOSPHORUS RECOVERY AND RECYCLING

SWEDEN

Phosphorus and nitrogen recovery from urine

Struvite precipitation, induced by magnesium oxide dosing, was tested using both synthetic and real human urine, and proved to effectively removal all phosphorus and 20-60% of potassium. Because the pH induced increase facilitated the conversion of urea to ammonium, this could be efficiently combined with nitrogen recovery by adsorption and 65-80% of nitrogen was fixed in experiments using natural zeolites, clinoptilotile or mixed zeolite, and wollastonite.

The authors explain that around 94% of the N P K nutrients (nitrogen, phosphorus and potassium) in toilet waste waters originate from urine, and that LCA's (life cycle analyses) suggest that urine-separation toilets can offer energy efficiency and nutrient recovery advantages. Toilets allowing separative urine collection have been developed and installed in different eco-villages around the world, including in Sweden.

Fertiliser and soil conditioner

However, the direct recycling of urine by agricultural spreading poses storage, transport, agronomic and social acceptance problems. The paper aims to address these problems by **testing the recovery of the nutrients present in urine by struvite precipitation combined with ammonium adsorption**. The authors suggest that the mixture of struvite crystals and natural mineral ammonium adsorbant zeolites or wollastonite would provide a good slow release fertiliser with soil conditioning properties.

Initial test-tube experiments were carried out using synthetic urine prepared according to conventional urological methods. This solution contained 11 solutes in concentrations equivalent to the average daily urine of normal healthy men. Struvite precipitation was then also tested using real urine from five healthy people.

Struvite precipitation was induced at 20°C by adding magnesium oxide to continuously adjust the pH to values in the range 6.5 – 10. This meant that magnesium ions were present at concentrations greater than the stoichiometric requirement for struvite precipitation of all phosphate ions present. Precipitation of white sediment was visible immediately after adding magnesium oxide, and needle-shaped crystals formed on the test tube walls and base after shaking for 30 – 50 minutes, growing up to 1mm long. Quantitive EDS and XRD analysis confirmed that both the white powder and the crystals were mainly struvite. Calculations showed that all of the phosphorus, 20-60% of the potassium and 3-5% of the sodium from the solution had been precipitated.

The authors note that natural struvite is not generally pure magnesium ammonium phosphate $MgNH_4PO_4.6H_2O$, but that small amounts of calcium, manganese and iron may substitute for the magnesium and potassium may substitute for the ammonium, giving a formula of (Ca, Mg)(K, NH_4)$PO_4.6H_2O$. They also indicate that other minerals such as montgomeryite (calcium aluminium phosphate or calcium aluminium magnesium phosphate), brucite $Mg(OH)_2$ or epsomite (magnesium sulphate) can also form, giving a more complete mineral precipitation.

With pH's varying from 8.55 to 10.4 in synthetic urine, phosphorus precipitation was consistently 100%, but potassium precipitation varied from 22 – 64% and calcium precipitation from 2 – 5.6%.

Ammonium adsorption

Ammonium uptake by the natural minerals was studied using both pure ammonium solutions and synthetic human urine. The ammonium uptake varied with grain size, ion concentration and contact time. 70-80% uptake was achieved with clinoptilolite and 50-60% with wollastonite.

In experiments with synthetic urine and zeolite, nitrogen adsorption was combined with magnesium oxide induced struvite precipitation, either following it or simultaneously. 0.06g of magnesium oxide was added to 25ml of synthetic urine (taking the pH to 9 – 9.5) and 0.5g of natural zeolite was used. With a contact time of 5-10 minutes, 64-67% of nitrogen was removed (to struvite or by adsorbtion) with clinoptilolite and 64-75% with wollastonite. The authors indicate that these high nitrogen removal rates are possible because most of the urea will be transformed to ammonium at pH's above 9.

"Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite". Bioresource Technology 73 (2000) pages 169-174.

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STRUVITE FEASIBILITY

An economic and environmental evaluation of P- recovery

The authors examine different possible configurations for recovering phosphates as struvite (magnesium ammonium phosphate) from municipal sewage, and the economic and environmental feasibility of using this recovered raw material (with or without further chemical processing) in UK fertiliser markets. Economic modelling and simplified Life Cycle Analysis are applied to compare production-distribution costs and environmental impacts with those of triple super phosphate fertiliser or di-ammonium phosphate fertiliser.

The paper reviews different literature concerning the potential for recovery of struvite in sewage works. **An estimated that 29,000 tonnes P/year could theoretically be recovered for recycling as struvite in the UK, 134,000 tonnes P/year in Western Europe, on the basis of 80% recovery of sewage works inflow phosphates and 85% of the population connected to sewage works.** Although certain sewage works configurations are not readily appropriate for P-recovery (eg. trickling filter), increasing requirements for P-removal combined with pressure on sludge disposal may lead to the replacement of such installations with processes compatible with biological P-removal. This would facilitate struvite recovery, as biological nutrient removal processes offer streams with high soluble phosphate and ammonia concentrations, appropriate for struvite precipitation.

The paper assumes, as a reasonable hypothesis configuration, a struvite recovery plant in the form of a dedicated precipitation – clarifier tank with scraper unit, analogous to units typically installed as primary and secondary sedimentation tanks.

Struvite as a fertiliser

The possible uses of recovered struvite as fertilisers are addressed. At present, the authors indicate, both fertiliser manufacturers and fertiliser trade associations are reluctant to define how struvite could fit into existing fertiliser markets, as the product has never been tested in field trials. **1960's research in the US, however, suggests that struvite can be effectively used as a slow-release fertiliser at high application rates without risk of damaging plants**. Suggested uses are diverse and include ornamental plants, young trees in forestry, grass, orchards and potted plants. A recent Dutch publication suggests using struvite as a slow-release, reserve phosphorus supply for container potted plants, with a more soluble fertiliser as the initial supply.

The authors therefore take as an assumption that struvite is indeed effectively suitable for substitution for existing fertiliser products.

The authors also consider processing struvite, with phosphoric acid, to produce a fertiliser containing 2 parts slowly soluble dimagnesium phosphate ($MgHPO_4$) to one part highly soluble di-ammonium phosphate ($(NH_4)_2HPO_4$), referred to as "enhanced struvite".

Production process and distribution analysis

The process flow sheets for the production and distribution of di-ammonium phosphate fertiliser, triple super phosphate fertiliser, recovered struvite and "enhanced struvite" are compared, with the aim of establishing an approximate comparison between the three.

For struvite recovery, it is assumed that magnesium will have to be added at the sewage works to bring concentrations up to the stoichiometry with phosphorus necessary for struvite precipitation. Capital costs, which are a significant element of the recovery costs, are calculated using a 6%/year discount rate. Because of the high level of capital costs compared to recovery operating costs, the economics of recovery will be very dependent on the struvite recovery rate (% of sewage works inflow phosphate recovered), and rates from 13% - 80% are considered.

Costs and environmental impacts take into account estimates, based on crop areas and average distances, of transport requirements to move fertilisers from import arrival ports to the field, and to move struvite from the sewage works to the field (via regional processing centres in the case of "enhanced struvite"). The costs and environmental impact related to the use of recovered struvite therefore depend on the supply/demand ratio : if supply is significantly lower than demand (struvite only replaces existing fertilisers a small part of the potential markets) then transport distances will be lower and thus so will costs and environmental impact.

Total production and distribution costs for struvite and "enhanced struvite" thus compare to at-the-farm prices (market price plus delivery) for existing fertilisers as follows. The highest price range for recovered struvite/"enhanced struvite" assumes a very low recovery efficiency in the sewage works (13%), application in small-medium sewage works (50,000 pe) and a high supply/demand ratio (longer transport distances). The lowest price range assumes 80% recovery efficiency in 250,000 pe sewage works and a lower supply/demand ratio.

Total average cost, at the farm (UK£ per tonne P_2O_5)

triple super phosphate	190-200
di-ammonium phosphate	227-238
phosphate mineral rock	183-195
recovered struvite	146-1195
recovered "enhanced struvite"	217-865

The authors conclude that, where high recovery rates can be achieved, struvite recovery is likely to be cost effective for regional distribution and use of the product, fairly near the recovery site.

At a 49% rate for the efficiency of struvite recovery in sewage works, recovered struvite offers an at-the-farm cost equal to that of di-ammonium phosphate.

Environmental comparison

The relative environmental impacts of producing and distributing existing fertiliser products are compared to those for recovered "enhanced struvite" using a coarse level Life Cycle Analysis (LCA). The burdens of recovered struvite are not analysed, but these would in any case be lower than for "enhanced struvite". Existing fertilisers are taken to be all imported from North Africa, which is the main source and for which data are available, in order to facilitate the approach.

The authors note that the LCA approach used does not strictly conform with ISO 14041 requirements, which require a more detailed assessment as well as peer-review, since the objective is to enable a comparison of relative performance with the hypothetical recovery of struvite.

Assuming a high struvite recovery efficiency in sewage works, the results suggest that the environmental burdens associated with producing and distributing "enhanced struvite" are likely to be at worst equal to, and in many cases lower than those for di-ammonium phosphate or triple super phosphate.

The environmental burdens for "enhanced struvite" are significantly lower than those for triple super phosphate for ozone depletion, winter smog, acidification and heavy metals. They are significantly lower than those for di-ammonium phosphate for all the criteria considered (the above four, plus global warming, carcinogenesis, summer smog and eutrophication).

Furthermore, decreases in the purity of phosphate rock used in manufacturing existing fertiliser products will increase the energy used and the environmental impact of manufacture, thus accentuating differences in favour of "enhanced struvite" or of straight application of recovered struvite.

Struvite is attractive

The authors conclude that, if high recovery efficiencies can be achieved in sewage works and recovered products can be used substitute existing fertiliser products and to meet regional demand, then struvite based products could be cost effective. **In particular, the substitution of struvite for di-ammonium phosphate fertiliser looks especially attractive economically** provided that these conditions are met.

Under these conditions, recovered struvite based products perform well compared to existing fertiliser products in terms of environmental burden.

The authors also note that certain crops require magnesium, which is present in struvite (magnesium ammonium phosphate) and so, for such applications, struvite will offer additional economic and environmental advantages by avoiding the need for a magnesium fertiliser.

"An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from waste water treatment works in existing UK fertiliser markets". Environmental Technology vol. 21 n° 9 pages 1067-1084..

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The SCOPE Newsletter seeks to promote the sustainable use of phosphates through recovery and recycling and a better understanding of the role of phosphates in the environment.

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SCOPE NEWSLETTER

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WATER POLICY

WATER FRAMEWORK DIRECTIVE PAGE 2

European Union water quality policy for coming decades

After 5 years, the content of the European Union's "Water framework Directive" has been finally fixed in Parliament - Council conciliation. The Directive, whose publication is expected this autumn, will instate a catchment-based approach for improving water quality, whilst at the same time maintaining the regulatory requirements of existing EU Directives.

UK PAGE 3

Sewage phosphorous and river ecology

Targeted sewage works phosphorus removal is a key water quality objective, despite the complex response of river ecosystems.

PHOSPHOROUS RECOVERY AND RECYCLING

ITALY PAGE 12

Defining precipitation parameters for phosphorous recovery

Ageing studies, supersaturation tests and a bench pilot reactor were used to establish kinetic and reaction parameters for phosphate precipitation for P-recovery from sewage sludge dewatering liquors.

POLAND PAGE 13

Potential for P-recovery as struvite

Laboratory tests with sewage works liquors demonstrate conditions for struvite precipitation.

JAPAN PAGE 14

Struvite recovery plants in operation

Three Japanese plants currently recover phosphorous from urban sewage for recycling as a fertiliser. The recovered struvite fetches around 2700 Euros/tonne from fertiliser companies.

PILOT PLANT PAGE 15

Using seawater for struvite recovery

A 1,100 litre pilot scale reactor at Hiagari sewage works, Kitakyushi City, Japan, was used to test phosphorous recovery as struvite using seawater to provide magnesium supply

ECOSYSTEM BALANCE AND EUTROPHICATION

LAKE GENEVA PAGE 5

Upstream dams reduce deep lake oxygenation

Dams on the Upper Rhône and its tributaries have reduced sediment transport into Lake Geneva by a factor of at least 2, negatively affecting oxygenation of deep lake waters.

WESTERN IRELAND PAGE 6

Protecting valuable lake eco-systems

Major increases of agricultural phosphorous inputs to the large, ecologically unique and sensitive Western Irish lakes requires a concerted management response.

DAPHNIA AND ROTIFERS PAGE 8

Grazer control of lake algal growth

The natural populations of grazer zooplankton proved able to control algal development in eutrophic lake water mesocosms, in situ, but if only larger grazer species were removed, algal development occurred.

BULGARIA PAGE 9

Nutrient trends in the Black Sea and coastal lakes

Two papers look at changes in nutrient concentrations and ratios in the Bulgarian Black Sea coastal waters and in five coastal lakes.

PHOSPHATE CONCENTRATIONS PAGE 11

Biological cycling of dissolved phosphorous

Concentrations of bio-available phosphorous in lakes are extremely low and depend essentially on biological activity.

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WATER POLICY

WATER FRAMEWORK DIRECTIVE

European Union water policy for coming decades

The proposed EU Water Framework Directive constitutes a "fundamental revue of Community water policy" and is the result of negotiations initiated in 1995. A final text was agreed by the EU Parliament – Council conciliation procedure on 29th June 2000 and now requires only final votes by the Parliament and the Council to come into force this autumn.

The overall aims of the new Directive are to ensure "enhanced protection and improvement of the aquatic environment". In particular, **the text requires Member States to prevent any further deterioration of all surface and ground waters, to ensure that all surface water bodies are brought up to "good status" within 15 years** (except for justified exceptional local situations) and to phase out within 20 years discharges of priority hazardous substances.

Catchment ecosystem approach

One of the key changes which be introduced by the new Directive is the **use of a global ecosystem approach at the catchment level** to assess water quality and to define the actions necessary for its improvement. Existing EU water legislation generally relies on blanket quantitative discharge limits or quality standards for specified substances, rather than encouraging the adoption of management constraints to specific local catchment contexts. Similarly, **the objective of "good ecological status", instead of being defined only by quantitative ceilings for different physico-chemical parameters, is defined by detailed tables of ecological characteristics** and guidelines for different types of aquatic ecosystem as well as by certain chemical quality standards.

Thus, regarding eutrophication, the new Directive defines "good status" for lakes and for rivers as **a situation where there occurs "no accelerated growth of algae … such as to produce an undesirable disturbance to the balance of organisms present …".** Nutrient inputs will thus be considered as compatible with "good status" so long as they do not result in "undesirable" ecosystem unbalance, and will be acceptable if they are compatible with stability of a healthy aquatic ecosystem even where they are higher than natural or background levels might be.

The new Directive requires Member States to achieve "good status" in all surface and ground water bodies within 15 years. In certain specific local cases where this is not technically feasible or would be disproportionately expensive because of natural phenomena, the deadline is extended to 28 years, but the Member State must justify this in published (and so, challengeable) river basin management plans.

Physical modifications

The conciliation process added new safeguards to the Directive text specifying that "new modifications to the physical characteristics of a surface water body or alterations to the levels of groundwater" which are susceptible to prevent good status being achieved must be of "overriding public interest".

This will provide a **significant tool to limit damming, embankment and other damaging modifications to river courses, or indeed to limit the drainage or deterioration of wetlands.**

Catchment management plans

Reflecting the new obligation to define and manage water quality status with a catchment and ecology based approach, the Directive requires river basin assessment, monitoring and management planning systems to be established :

- assessment of river basins and of the impact of human activities, by 2004
- river basin management plans and pollution control programmes, by 2009 and then revised every 6 years

Hazardous substances

The Water Framework Directive's text sets as a principle **"progressive reductions" of emissions of all substances posing significant risks to the aquatic environment or to man via water, and the phasing out of "priority hazardous substances" within 20 years** (this target corresponds to comparable OSPARCOM commitments). The text specifies that the Commission will propose, for all "priority" substances within 2 years of their inclusion on the priorities list, daughter directives defining measures for limiting emissions and setting Environmental Quality Standards (EQS) and product controls.

It is not clear, however, how extensive the priority list of substances considered will be.

The Commission published a list of 32 "priority substances" on 7th February 2000 (see list below) but not all of these may finally be included. This

Commission’s explanation of this selection is included with the list in the Commission’s official proposal document COM(2000)47final available at http://europa.eu.int/eurlex/en/com/pdf/2000/en_500PC0047.pdf

Existing EU water legislation is maintained

The new Directive specifically provides that **the levels of protection established by existing EU environmental and water quality legislation will be at least maintained.** This sets a baseline for the new Directive’s implementation, in that water basin management plants and pollution control programmes will necessarily have to bring "enhances protection and improvement" of the aquatic environment compared to existing legislation.

Thus, **existing EU legislative requirements will in effect continue to be legally binding.** In particular, for nutrients, this means that the requirements of the EU Urban Waste Water Treatment Directive 91/271 concerning sewage collection and treatment, and also the Nitrates Directive 91/676, will remain applicable as minimum obligations.

The 1991/271 Directive effectively requires that sewage is collected and that phosphorus is removed for all towns or groups of villages of more than 10,000 "population equivalent" (generally around 6 – 8,000 people) discharging into "sensitive areas" (that is, surface waters susceptible or potentially susceptible to eutrophication). **This 1991 Directive also requires "appropriate" treatment of sewage in smaller villages, which can be taken to include P-removal in eutrophication susceptible areas.** These requirements should ensure that phosphates in sewage are no longer an environmental problem, once they are implemented by Member States (the implementation deadline was December 1998, but probably around one third of the P-removal capacity still remains to be installed - see SCOPE Newsletter n° 34).

The local water basin management plans established under the new Water Framework Directive will thus legally have to take the above requirements as a minimum obligation as regards P-removal from sewage, but will also have to take an overall catchment approach and thus tackle other sources of phosphorus and in particular agriculture, which is now the main nutrient source for most surface waters.

Information on the final conciliation process agreed text for the proposed Water Framework Directive : ENDS (Environmental Data Services) Magazine n° 305, June 2000, pages 50 – 52. The joint text approved by the Conciliation Committee. The "Joint text approved by the Conciliation Committee" is available from conciliation@europarl.eu.int refs. 1997/0067(COD) C5-0347/00 document PE-CONS 3639/00 and annexes. The proposed list of priority substances COM 2000(47)final is available in at : http://europa.eu.int/eur-lex/en/com/pdf/2000/en_500PC0047.pdf.

The EU Commission’s proposed list of "priority substances" (from COM(2000)47final)

Alachlor, anthracene, atrazine, benzene, brominated diphenylether, cadmium and its compounds, C_{10-13}-chloroalkanes, chlorfenvinphos, chlorpyrifos, 1,2-dichloroethane, dichloromethane, di(2-thylhexyl)phthalate (DEHP), diuron, endosulfans, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclohexane (inc. Lindane), isoproturon, lead and its compounds, mercury and its compounds, napthalene, nickel and its compounds, nonylphenols, octylphenols, pentachlorobenzene, pentachlorophenol, polyaromatic hydrocarbons (inc. benzopyrenes, benzoperylenes, fluoranthenes, pyrenes), simazine, tributylin compounds, trichlorobenzenes, trichloromethane (chloroform), trifluralin.

UK

Sewage phosphorous and river ecology

"Phosphorus and river ecology – tackling sewage inputs" is the title of a document intended for water company and regulator staff jointly produced by the UK Environment Agency and English Nature (March 2000). The document builds on the Environment Agency's National Eutrophication Strategy 2000 to provide technical information for local decision makers. The need to reduce phosphorus towards natural concentrations, an order of 10x lower than current levels, is emphasised. Sewage works discharges are identified as the priority target for reducing phosphorus loads because of their contribution to bioavailable phosphorus during summer low-flow periods. The cost and sludge production related to phosphorus removal is related to discharge target concentrations, so that targeted action should be defined at the catchment level. Phosphorus recovery for recycling is presented as an important future option.

The 46-page technical document provides not only a strategic overview for local decision makers of the impacts and management issues of river phosphorus loadings, but also gives a range of operational information on areas such as nutrient limitation of plant growth, algal growth, trophic states, indicator species, phosphorus budgets, sewage phosphorus removal processes and associated costs, agricultural and soil management, different forms of phosphorus and their ecology …

Complexity of river ecosystem response

The document's first message is the complexity of river phosphorus dynamics, resulting from transformations of phosphorus forms and exchanges between the water column (subject to downstream movement), sediments, plants and algae. Furthermore, the complexity of competition within plant and algal communities and ecosystem interactions with other man-made impacts mean that **the ecological results of phosphorus reductions cannot be predicted with any certainty.**

The confounding impacts on plant communities are detailed, including changes in sediment particle size (increased silting because of soil erosion or other causes, or because of reduced river flow and channel modifications), current velocity, organic content of sediments (often related to sewage works discharge of particulate organics or livestock), turbidity (sediment re-suspension by boat traffic or channel modifications, particulate discharges), shading, water residence times, trace nutrients, changes in grazing of floating or surface algae by zooplankton, molluscs or crayfish. **Sewage discharges have been shown to contain many biologically active chemicals liable to stimulate algal growth**, for example Vitamin B12 and thiamine.

Low natural phosphorus levels

Natural phosphorus concentrations are addressed and **estimated to be generally below 0.03 mgP/l** in all except very specific stretches of UK rivers. The concept of "background" phosphorus concentrations is considered to be not well defined, and is taken to be the natural level plus minimal agricultural and other anthropogenic inputs such that the ecological balance is only modified to a limited extent.

Current phosphorus concentrations in most UK rivers are an order of 10x higher than the natural concent-rations, at 0.2 – 0.3 mgP/l, but phosphorus levels in sediments are also an important factor.

The authors suggest that river phosphorus concentrations should be reduced to as near background levels as possible.

Because point discharges, in particular sewage works, contribute soluble (bioavailable) phosphorus forms to the water column during the summer low-flow period (reduced dilution), when algal growth potential is high, they represent the priority target for management actions.

Point and diffuse sources

Figures are given for the relative contribution of different sources to the total phosphorus annual loadings for four UK rivers. **Sewage works discharges contribute 18 – 84%, mineral fertiliser use 7 – 22% and livestock 7 – 15%** with other sources being less significant.

Although diffuse loads are often strongly related to run-off, and thus occur to a considerable extent at periods of high river flow (high dilution) and low algal growth, phosphorus-rich particles can be retained in the river system, in sediments. The phosphorus may then be subsequently released and contribute to algal growth during the next season. **Diffuse loadings are thus highly significant for lakes and wetlands** fed by rivers where annual total phosphorus loads are the most realistic reflection of the relative importance of different sources.

For river ecosystems, comprehensive measures are thus necessary to minimise phosphorus emissions and point sources should be targeted as a priority in order to minimise emissions during the critical summer period.

Small sewage works

The comprehensive approach should **address smaller point nutrient sources in upstream reaches (small sewage works possibly in agglomerations below the 10,000 pe. definition of the EU Urban Waste Water Treatment Directive 91/271**, livestock farms, etc) as removing phosphorus here may be of more ecological significance than for larger downstream sources, because nutrients are carried cumulatively downstream in both the water column and in sediments, and because of higher dilution rates downstream.

When planning phosphorus removal installation in sewage works in a catchment, it is appropriate to start upstream and progress downstream, assessing impact along the way.

As point sources are brought under control, diffuse sources become increasingly important, so that an integrated approach will be necessary to bring water column concentrations down towards natural levels, including reducing agricultural sources, soil and land management, and river system restoration

Phosphorus removal from sewage

A variety of known and tested techniques enable phosphorus to be readily removed from effluent streams, in particular sewage works, but also food industry or livestock discharges. **Concentrations can be brought down to 1 mgP/l or even lower by biological and/or chemical techniques.**

The choice of technique will depend on site-specific questions, but, according to the authors, biological removal offers the best environmental perspective for larger sewage works (little or no additional sludge production, no chemical costs).

Indicative **capital and operating costs for phosphorus removal are given** for different situations. These are considered to depend on the sewage works connected population (volume treated) and not on the inflow phosphorus concentration.

The document indicates that **the volume of additional sludge generated by chemical phosphorus removal is related to the target effluent P-concentrations** (and not to the inflow concentration), with a significant increase in both chemical dosing necessary for effluent P-concentrations below 2 mgP/l, and consequent sludge production.

The authors point out that sewage sludge currently constitutes only around 1% of the total phosphorus applied to agricultural land in the UK, so that even if this were to double with widely implemented phosphorus removal from sludge resulting in increased sludge P-contents, the figure would only reach 2%, with most agricultural phosphorus application coming from manure and mineral fertilisers. The lower **bioavailability of phosphorus in sludges from sewage works using iron chemicals for phosphorus removal** further complicates the issue, providing less phosphorus for the crop but accentuating long-term soil accumulation. In all cases, therefore, managers should try to ensure that the agricultural spreading of phosphorus removed from sewage, in sludges, effectively replaces the application of other forms of phosphorus to agricultural land.

Phosphorus recovery for recycling

One of the document's key messages is that phosphorus recovery from sewage works for reuse in agro-industrial applications is feasible and represents a considerable potential to reduce the mass-transfer of phosphorus into UK catchments by replacing imported rock with recovered phosphates. This will tackle eutrophication at its true source.

Phosphorus recovery for recycling pilot plants in Holland and Japan are referred to and it is concluded that phosphorus recycling for industry or in mineral fertilisers has the potential to replace a non-renewable resource (phosphate rock) with a sustainable reclaimed resource, benefiting the water industry in economic and regulatory contexts. **Active encouragement of this approach, it is suggested, is likely to bring considerable environmental benefits.**

"Phosphorus and river ecology – tackling sewage inputs". Published by the UK Environment Agency and English Nature, March 2000, 46 pages.

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ECOSYSTEM BALANCE AND EUTROPHICATION

LAKE GENEVA

Upstream dams reduce deep lake oxygenation

From 1950-1990 construction of dams on the Upper Rhône and its tributaries considerably modified discharges into Lake Geneva. Today, these reservoirs have a capacity of around 1.2 billion m^3 of water, which is around 1/5 of the total annual Upper Rône river flow. This study assesses the effects of these dams on discharge patterns and sediment transports and suggests that these have resulted in significant negative effects on deep lake water oxygenation, and thus in nutrient release from lake bed sediments.

The 9 major dams on the Upper Rhône and its tributaries were built for hydroelectric production, mainly between 1958 and 1975. A very small dam capacity has been built specifically for flood control or irrigation. Less than 2% of the total 1.2 billion m3 dam capacity is "dead" volume, that is not destined to be filled and emptied.

The Upper Rhône's natural flow patterns are dominated by snow melt and upstream glaciers, with high flows from May through to the Autumn high-altitude freeze-up. Annual discharges averaged 187 m^3/s for 1915-1994, with a range of annual averages from 136 – 234 m^3/s.

The hydroelectric dams have drastically modified discharge patterns, with water being stored in the summer and released for electricity generation in the winter. Winter average flow has more than doubled from 50-60 m^3/s before 1950 to 120 m^3/s in the 1980's. Summer average flow has fallen significantly from over 400 to 300-350 m^3/s.

One overall result of these changes is the elimination of extreme low and high (spate) flows. Flooding related to glacier melting has thus apparently disappeared, but very large floods nonetheless did occur in 1987 as a result of heavy rain storms in the Swiss Alps.

Loss of sediment transport

The number of days with particularly high flow rates has thus been significantly reduced : flows > 600 m^3/s have nearly disappeared and the frequency of flows > 400 m^3/s have been reduced by a factor of 3. Lower flow rates have a lower velocity and thus a reduced capacity to carry sediment both in terms of grain size and of quantity.

The authors assessed changes in sediment transport by comparing different literature data for the Upper Rhône (1892, 1964, 1966, 1971, 1989), taking into account the different sampling methods used in the past, with theoretical calculations based on flow rates. They conclude that whereas **before dam construction summer suspended solid loads were much higher than in winter, this has now been reversed.**

Sediment loads of around 1,000 mg/l were observed at flows of 300 m^3/s before the dams, whereas such loads are now only found at significantly higher flows (500 m3/s). The size of particles will also have changed as a result of dam construction: a 1964 study showed that 50% of sediment load consisted of particles > 200 µm for a flow of 500 m^3/s, but only 12% for a flow of 200 m^3/s.

Several small spate flows do not carry as much sediment as one very high flow, so that the double effect of the dams is thus to reduce sediment load for a given flow rate but also to reduce the incidence of high flow rates (which carry high sediment load). By summing estimated loads and flow frequencies, the authors estimate that overall the annual suspended sediment load has dropped from 2-5 million tonnes before the 1960’s to 1 – 2.5 millions tonnes today.

This reduction is the result not only of reduced flooding and reduced soil erosion, but also of the retention of sediments behind the dams themselves.

Underflow currents and lake floor oxygenation

The occurrence of currents of river water moving over the bed of Lake Geneva is generally related to the relative density of inflowing water compared to the lake’s water. This is affected by three parameters : temperature, dissolved salts and suspended solid concentration. Such undercurrents sometimes may also result from channel collapses in the delta area where the Upper Rhône enters the lake.

Using estimates of comparative temperature and salt concentrations, the authors suggest that the Upper Rhône’s inflowing water in summer will be denser than the lake water only when inflowing suspended solid concentrations are greater than approximately 450 mg/l. This corresponds to flow rates of perhaps 400 m^3/s.

From the 1920’s to the 1960’s, the frequency of flows > 400 m^3/s fell from around 55 to 15 days/year, as a result of decreases in the glacier area in the watershed and of dam construction.

Underflows bring oxygen-rich river waters to the lake’s deep waters, ensuring their re-oxygenation. Fahrini and Rapin (1986) estimated that underflows carried in this way around 15% of the total oxygen stock of the lake’s deep waters each year. The oxygenation of the deep waters is essential in controlling phosphorus release from sediments, as this occurs if anoxic conditions appear on the lake bed surface. Furthermore, the suspended particulate matter carried by river water undercurrents can also block phosphorus release by settling onto the lake bed.

The authors conclude that the construction of dams on the Upper Rhône and its tributaries may have reduced by a half the oxygen supply to Lake Geneva’s deep waters, with significant implication in terms of increased sediment phosphorus release.

"Evolution of the Upper Rhône discharge and suspended sediment load during the last 80 years and some implications for Lake Geneva"" Aquatic Sciences n° 62, pages 54-67, 2000.

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WESTERN IRELAND

Protecting valuable lake eco-systems

This paper looks at nutrient management policies which are being developed to try to protect two of the large Western Irish lakes, Loughs Mask and Conn, in County Mayo. These lakes offer some of the finest brown trout fisheries in Europe, as well as holding a variety of other exceptional species. A large increase of phosphorus inputs, essentially as a result of agricultural activities and other land use changes, is causing considerable concern.

The concerted nutrient management and land use strategy developed is outlined.

Lough Conn has been subject to significant water quality changes due to agricultural intensification - with a doubling of agricultural phosphorus inputs - over the period 1980-1990. Although mid-lake chlorophyll levels have not been shown to have increased, ecological changes have appeared which include an apparent increase in shoreline algae and the disappearance of the Arctic Charr (Salvelinus alpinus L) population.

Pristine lakes

Lough Conn has a surface of 50 km^2 and a drainage catchment of 414 km^2 with an average runoff of 12 m^3/s. Drainage operations in the 1960's caused a significant lowering of the lake's water level with consequent changes in the shoreline and bordering areas.

Lough Mask has an area of 882km^2 and can be considered the most pristine of the Western Irish lakes. These lakes are relatively shallow, subject to turbulent mixing, and are fed by naturally fast-flowing tributaries which are in many cases still clean and unpolluted, thus providing considerable salmonid spawning and nursery areas (yielding up to 0.1 salmonid parr/m^2).

The lakes hold a number of noteworthy glacial relict species as well as the Arctic Charr, including macro-invertebrates such as Mysis relicta, specific floral assemblages including stoneworts, and unique fish populations The latter include stocks dating from the ice age and local sub-populations of the wild brown trout.

The Arctic Charr population of Lough Conn suffered a dramatic decline in the late 1980's, to near extinction in the lake, as did another Western Irish lake, Lough Corrib. Lough Mask, on the other hand, still holds a large Arctic Charr population.

Because of the shallow, well mixed nature of the lakes, oxygen depletion does not occur in the lake water even near the lake floor, so that this cannot have been the cause of the Arctic Charr's decline.

Sediment studies do suggest increasing algal abundance, in both Lough's Conn and Mask during the 1960's, but open lake monitoring over the period 1975-1996 showed **no statistically significant trends in chlorophyll concentrations (algal development)**, Secchi disk depth (water clarity) or nutrient chemistry (and in particular, no increase trend for total phosphorus).

In Lough Conn, however, an apparent increase in shoreline algal growths was noted over this period, with accumulation of Anabaena (cyanobacteria). Significant deposis of senescent Oscillatoria and filamentous Mougeotia were noted on stony shorelines suitable for Arctic Charr spawning. This could be the cause of the fish's decline, because of the known sensitivity of their eggs.

Increase P inputs

Comparison of studies of Lough Conn's tributaries over the period 1979-1982 with a survey in the early 1990's showed a striking change in phosphorus runoff patterns. Whereas in the earlier studies phosphorus concentrations were not related to rainfall or stream flow for any tributary, they were strongly correlated in the second survey for two of the Lough's larger tributaries, the Dee and the Adergoole rivers (246 and 40 km^2 catchments). **This was considered to be the result of diffuse agricultural runoff, and accompanied a doubling of the total phosphorus load to Lough Conn from 18 to 65 tP/year from 1980 to 1990 (compared to an estimated natural loading of 9 tP/year).**

A very large proportion of the Lough's phosphorus load was estimated to come from agriculture by the early 1990's : over 20 tP/year from agriculture, compared to less than 2 tP/year for each of the other identified anthropogenic sources (forestry, rural and town sewage, peat extraction).

The increase in agricultural nutrient loads is considered to be the consequence of changes in agricultural practices resulting from application of the European Union's Common Agricultural Policy. This has caused a move away from traditional extensive animal husbandry (grazing, hay making, cattle kept outside over winter) to intensive fertilisation, silage making, cattle kept in sheds with spreading of the resulting animal manures.

In response to this situation, the Lough Conn Management Committee was created in 1992, bringing together representatives of different stakeholders and regulators. The guideline to the Committee's action, in order to obtain acceptability with the main target – the farming sector, was that all sectors should reduce their nutrient releases, even those responsible for only small contributions.

The paper outlines the different policies defined for each sector. These include **upgrading of municipal sewage works** to install P-removal even in small sewage works (in particular, at the Crossmolina sewage works, 1,100 pe.) and encouraging the use of P-free detergents in the intermediate period before these sewage works investments were brought on line. Domestic discharges were also addressed by recommendations concerning the maintenance of septic tanks and changes to planning regulations to prevent building developments in areas near water courses and not connected to sewage treatment works.

Wide-ranging recommendations were developed to attempt to improve agricultural practices, including in particular the development of "nutrient management planning", better management of animal manures (for example : ensuring the inclusion of slurry nutrient loads in fertilisation calculations, avoiding nutrient application in the autumn or winter, or before expected rainfall …), avoidance of runoff of dirty farmyard waters, preventing cattle access to streams (which causes not only the direct deposit of manures in the water, but also the destabilisation of banks which leads to erosion), use of vegetation buffer strips and silt/nutrient traps along streams …

Other recommendations outlined in the paper include **improved forestry management (reducing conifer plantation, avoidance of clear-felling …)** and better control of pollution from peat workings.

Following the development of this action programme around Lough Conn, a similar Management Committee was set up for Lough Mask, with the aim or pre-empting and avoiding the ecological deterioration observed Lough Conn. This Committee has developed a targeted approach : by comparing intensively farmed sub-catchments with polluted tributaries, certain farms have been identified where action is particularly urgent and likely to bring significant results.

The paper ends by noting that Irish environmental law offers local authorities the powers to require farmers to prepare nutrient management plants to control nutrient losses, and indeed to prosecute farmers who fail to do so and polluters.

"Keeping pristine lakes clean: Loughs Conn and Mask, western Ireland". Hydrobiologia 395/396, pages 455-469, 1999.

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DAPHNIA AND ROTIFERS

Grazer control of lake algal growth

The ability of natural grazer zooplankton populations to control algal development aver 5 days was tested using 30 litres mesocosms floating in situ in a eutrophic oxbow lake in Hungary (460 54' North). Three situations were tested : with the full natural population of grazer zooplankton, with larger zooplankton (mainly Daphnia magna) removed, and with all grazers removed. Unfortunately the removal of all grazers also effectively removed the dominant algal species (the filamentous cyanobacteria Anabaena spriroides). The results showed significant algal develop-ment (nearly doubling) but only increased marginally in the mesocosm in which both grazers and the dominant algal species had been removed, and not significantly in the mesocosm with the full natural grazer zooplankton population.

The experiments were carried out in late Spring (end of June) and involved filling 30 litre mesocosms, consisting of transparent floating plastic bags, with water collected from the lake water column using a plastic bucket. Regrettably, nutrient concentrations, temperature and light intensity in the lake water are not given.

The "no zooplankton" configuration was obtained by filtering the water through a 45µm net, which also removed the dominant filamentous algal species ; the "small zooplankton only" configuration was obtained by filtration at 180µm. This 180µm filter removed nearly all cladocerans, copepod adults and copepodids. **The dominant zooplankton in the lake water were Daphnia magna** (around 42 individuals/litre and 95% of zooplankton biomass, removed in both the "no" and "small" zooplankton configurations) and Keratella cochlearis (around 65 individuals/litre, removed in the "no" but retained in the "small" zooplankton configuration). The "small" zooplankton configuration thus retained only 10% of the zooplankton biomass of the unfiltered configuration.

For each of the three configurations, three mesocosms were used (duplicates) making a total of nine. The experiments were carried out for a duration of five days, long enough for algal response to be established but short enough to avoid significant growth of periphyton on the bag surfaces.

Zooplankton and phytoplankton species and densities were counted in the bags at the start and at the end of the 5 day experiment and biovolumes estimated in each case.

Algal development when large grazers removed

In the "small" zooplankton configuration, significant algal development occurred (+87% biovolumes, increasing from an initial value of just over 2 to over 4 µm3/ml (the chlorophyll-a concentrations are not given), mainly due to the development of the filamentous Anabaena spiroides. **Algal biovolumes did not develop significantly in the lake itself, nor in the mesocosm with the full natural grazer zooplankton populations**. In the mesocosm with "no" zooplankton, there was a small algal biovolume development close to the bounds of duplicate variation. It is to be noted that in the 45µm filtered "no" zooplankton configuration, the dominant A. spiroides alga was also removed and the initial algal biovolume reduced from just above 2 to around 1.6 µm3/ml.

The authors suggest that the differences in algal development between the different mesocosms may result from the **effective grazing control of algae, and in particular of the filamentous A. spiroides by Daphnia magna in the natural lake waters.** The smaller zooplankton, in particular Keratella cochlearis are unable to graze the filamentous algae, allowing its development in the "small" zooplankton mesocosm.

The authors suggest that the higher algal development in the "small" zooplankton configuration, compared to the "no" zooplankton mesocosm, may be the result of nutrient cycling by the smaller zooplankton (grazing on bacteria and smaller algal species and excreting nutrients which are then available for growth of larger algal species, such as A. spiroides). This effect may also, however, be the consequence of the reduction in initial algal populations and in particular the removal of the dominant filamentous A. spiroides in the "no" zooplankton 45µm filtered mesocosm.

The results clearly demonstrate the importance of larger zooplankton, such as Daphnia magna in controlling algal populations, and the ability of natural lake densities of such grazers to prevent algal development.

Effect of large- and small-bodies zooplankton on phytoplankton in a eutrophic bow". Journal of Plankton Research, vol. 20 n° 10, pages 1989 – 1995, year 1998.

I. Grigorsky, C. Mathé and G. Borbély, Dept. Botany PO Box 14 and S. Nagy, A. Toth and Z. Müller, Dept. Ecology PO Box 71, L. Kossuth Univeristy, H-4010 Debrecen, Hungary.

BULGARIA

Nutrient trends in the Black Sea and coastal lakes

A study of nutrient trends in the Bulgarian Black Sea coastal areas reaches significantly different conclusions from a study published at the same time of five Bulgarian coastal lakes. Whilst in the coastal waters phosphate and dissolved silicate levels have decreased over the last decade, the lakes are tending to become nitrogen limited (in particular the shallow ones).

The papers both suggest that changes in phosphate loads can be related to modifications in zooplankton communities, but that other factors such as the sun's activity or global climate change can play an important role. Changes in agricultural management should take into account the need to reduce phosphorus inputs and accumulated phosphorus levels.

Decreasing phosphates and silicates in the Black Sea

The North West part of the Black Sea is strongly affected by land-based agricultural, industrial and municipal discharges. Various authors have estimated that the combined inputs of nutrients and dissolved organic compounds from the Danube, Dniepar and Dniestar rivers increased tenfold from 1950 – 1980, reaching **annual loads of 0.6 – 0.8 million tonnes/year of total inorganic nitrogen, 0.023 – 0.032 million tonnes/year of total phosphorus and 0.15 – 0.3 million tonnes/year of dissolved silicates.**

Since the early 1990's, **nutrient loads are believed to have begun to fall due to the economic collapse of industrial and agricultural activities.**

The published paper is based on monthly monitoring data from stations located in the Varna Bay and 3 nautical miles offshore of Cape Galata. Comparison with seasonal values for 1951 – 1974 Rojdestwenskyi, 1986) showed an increase in dissolved oxygen for all four seasons in the Varna Bay (surface waters) and in the Spring and Summer at the Galata station (zero, 10 and 22 m depths). The average annual BOD^5 did not differ significantly from the 1950 – 1980 levels.

In the 1995-1996 monitoring, soluble phosphate was typically lowest at 10m depth, often being undetectable here. Low concentrations were generally found in the summer months because of high phytoplankton uptake. Compared to past data, at the Galata station (3 nautical miles offshore) there was **an evident trend of decreasing soluble phosphate concentrations for all seasons,** whereas in Varna Bay the decrease is only apparent for the summer levels.

Dissolved silicates also showed a trend for a general decrease in concentrations at both sites, probably related to the reduction in levels in the Danube.

No reduction in nitrates

Nitrate concentrations, on the other hand, did not show a downward trend compared to past values. Changes in analytical methods make comparisons with data obtained before 1990 impossible, but a trend for concentrations to increase for all seasons was apparent since that date.

The seasonal pattern for nitrate concentrations had nonetheless changed, with the lowest seasonal concentrations being found in the summer, rather than seeing seasonal maxima in the summer as previously. This is considered by the authors to correspond to a trend towards more natural seasonal patterns.

Improving phytoplankton balance

A comparison with 1983 – 1986 data showed a decrease in the dominance of phytoplankton communities by

Dinophyta species, an increase in diatoms, a move towards more frequent Bacillariophyta dominance and a general increase in taxonomic diversity.

These positive changes are thought to be related to a shift in nutrient ratios towards a phosphorus limited ecosystem.

The annual average biomass for the coastal zone fell by more than one half between 1983-1986 and 1996-1996. The proportion of this annual average represented by the summer bloom also dropped from around 60% to near 30%. This corresponds to trends in summer nutrient concentrations.

When spring – summer blooms are related to the variability of zooplankton (grazer species) biomass, N scintillans cell density, or the sun's activity, there is evidence that these factors could play an important role, and that **the trends in nutrient concentrations and ratios are not the only factors responsible for changes in algal communities.**

Increasing nutrient loads to coastal lakes

For five coastal lakes, recent measured concentrations of nutrients and chlorophyll were compared with literature data for concentrations in the same lakes from various periods from 1963 through to the 1990's. The lakes studied are all at around 43° North and are characterised as follows :

area km^2	*max. depth*	*m*	*salinity %*
Dourankoulak	*3.3*	*4*	*0.2 – 0.4*
Ezerets	*0.7*	*9*	*0.1 – 0.2*
Shabla	*0.8*	*9.5*	*0.06 – 0.15*
Bourgas	*27*	*1.3*	*0.17 – 4.5*
Mandra	*5*	*5*	*0.023 – 3.3*

Soluble phosphate concentrations increased over the study period in all five lakes, but this increase was more apparent for the deeper lakes. **The nitrate concentration, on the contrary, decreased in all five lakes**. At the same time ammonium concentrations increased (which is indicative of worsening oxygen availability), particularly in the two shallower lakes.

The shallower lakes showed phosphate concentrations corresponding to hypereutrophic conditions for both early and recent data. The two deeper lakes had reached hypereutrophic levels by the time of the more recent data.

Nitrate levels in the lakes, with the exception of Bourgas, however corresponded to only mesotrophic or eutrophic conditions.

The phytoplankton / chlorophyll-a levels in recent monitoring data corresponded to a state somewhere between that to be expected from the phosphate and that to be expected from the nitrate levels.

Nutrient ratios

The three deeper lakes could be considered as phosphorus deficient in the period 1960 – 1970, but had changed to become nitrogen limited by the 1990's (whereas the nutrient ratios in the two shallower lakes remained close to the optimal ratio for plants' needs). **The authors indicate that his change in the deeper lakes' nutrient balance is due to the intensive use of mineral fertilisers** in the Dobroudzha Plain where the Ezerrets and Shabla Lakes are situated. The influence of fertiliser use on the Dourankoulak Lake seems to be less significant, maybe because of a lack of recent data, or because of more mixing with sea water (higher salinity). Also, fresh spring water inflow to the Shabla Lake is diverted for use for drinking water supply.

As a result of these changes in nutrient balance, blue green algae have tended to appear and diatoms to be less prominent. This has resulted in an increase in dissolved silicate concentrations, as these are no longer taken up by diatoms which use them in their structure.

The authors conclude that, today, these five lakes are highly productive ecosystems and represent important fisheries, as well as holding endemic species and significant biodiversity. The changes shown by this study of nutrient trends with the more or less continuous increase of trophic status over the last 30 years give cause for serious concern. **Farming and other activities in the areas around the lakes should take into consideration the need to reduce phosphorus inputs and to reduce the stock of accumulated phosphorus**, in order to restore the aquatic ecosystems to a state of phosphorus limitation or nutrient balance.

"Changes in chemical parameters in the Bulgarian Black Sea coastal areas as an indication of the ecological state of the environment". Wat. Sci. Tech. vol 39 n° 8, pages 37-45, 1999.

G. Shtereva, S. Moncheva, V. Doncheva, O. Christova and I. Shterev, Institute of Oceonology, Bulgarian Academy of Science, Varna, PO Box 152, Bulgaria.

"Long-term eutrophication development in five coastal lakes of the Bulgarian Black Sea". Wat. Sci. Tech. vol. 39, n° 8 pages 1-7, 1999.

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PHOSPHATE CONCENTRATIONS

Biological cycling of dissolved phosphorous

This paper presents results of a new steady-state radiobioassay method which shows dissolved (bio-available) phosphate concentrations in aquatic ecosystems to in fact be orders of magnitude lower than is generally estimated by conventional chemical and radiochemical techniques. Concentrations in a variety of lakes are shown to range from 27 to 885 picomoles of dissolved P. They are essentially dependent on rates of biological cycling : even minute concentrations of dissolved phosphorus can support high productivity, and algal productivity is similar (on a per-unit biomass basis) across a wide range of total phosphorus levels.

The authors calculated actual concentrations of bio-available phosphorus using a new steady-state radio bioassay method based on measurement of the regeneration rate (rate of cycling of phosphorus from algal cells back to the dissolved form) and the uptake constant "k", and by then assuming that the [measured] regeneration rate = [not measured] uptake rate = [measured] k x dissolved P concentration [thus calculated].

Dissolved phosphorus concentrations were determined for 56 lakes from three different geoclimatic areas : the Rocky Mountains, the US interior plains and the Canadian shield. These were compared with literature concentrations for soluble phosphorus for 14 of the lakes. The lakes studied had total phosphorus levels in the range 0.058 – 4.5 µMP (that is, total concentrations of phosphorus in the water column, including both dissolved and particulate P and organic forms within living cells and other organic matter).

When three outlying lakes were excluded from the data set, the calculated dissolved phosphorus concentrations varied from 27 to 885 picomoles (0.027 – 0.885 x 10-3 µM).

The authors explain that conventional measurements of dissolved phosphates in aquatic ecosystems (as "SRP" = soluble reactive phosphorus) considerably and systematically overestimate concentrations, because of two errors introduced by the experimental method itself :

- some organically bound P is released to a soluble form during the necessary filtration step, prior to analysis
- the reagents used to determine SRP themselves acidify the filtrate leading to further dissolution of bound phosphorus forms

The widely used Rigler bioassay method also over-estimates dissolved P concentrations because of the unknown effect on the P uptake rate of the artificial addition of soluble phosphate (half saturation constant).

Phosphate uptake concentrations "k" were rapid (0.02 – 1.1 / minute) indicating that phosphorus was limiting algal growth in all of the 56 lakes.

The concentrations of phosphorus determined by the authors' steady state method were **3-4 orders lower than the literature "SRP"** values for the 14 lakes where a comparison of this type was possible, and around 2 orders lower than Rigler bioassay estimates made in two of the lakes.

The authors' method assumes a steady state for dissolved phosphorus : uptake by algae equal to regeneration. There may be cases where this does not hold, for example where the plankton community is increasing and drawing dissolved phosphorus concentrations down, uptake would then presumably exceed regeneration. The authors suggest however that such errors are likely to be small as total plankton biomass does not change rapidly in the timescale of phosphorus regeneration (several minutes).

The concentrations of dissolved phosphorus calculated by the authors are **the lowest concentrations ever reported for an aquatic ecosystem** but are comparable to concentrations of micronutrients such as iron, manganese and zinc found in the open sea.

These very low concentrations confirm that in many ecosystems algal development is fundamentally limited by the biological mechanism of phosphorus uptake, rather than by actual phosphorus concentrations. The picomolar concentrations of bio-available phosphorus demonstrated by the authors, in a wide range of lake types, are probably very close the physiological limits of algal uptake.

"Phosphate concentrations in lakes" Letters to Nature, Nature 406, pages 54-56, July 2000.

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PHOSPHOROUS RECOVERY AND RECYCLING

ITALY

Defining precipitation parameters for phosphorous recovery

Dewatering liquor from the belt press treating anaerobic digester sludge from an 85,000 pe sewage works at Falconara, Italy, (operating a pre denitrification/nitrification process) was used to investigate phosphate precipitation by natural liquor ageing, phosphate supersaturation curves and P-recovery reactor operating parameters (using a 58 mm diameter, 42 cm high bench reactor). The authors conclude that supersaturation curves play a key role in defining reaction parameters and demonstrated good phosphorus removal by crystal growth can be achieved in with a process time of around 100 minutes (time spent in the fluidised bed reactor and stripper). They suggest however that the chemistry kinetics should allow good P-recovery rates to be achieved in a reaction time of 2-3 times the theoretic half time, ie. 2-3 x 7 minutes.

For the natural ageing experiments, the anaerobic digester sludge dewatering liquors from the sewage works were variously enriched using sodium phosphate to different soluble phosphorus concentrations from 2 to 54 mgP/l (as PO_4). Natural ageing in 5000ml beakers at 25°C. After 2 – 8 days of ageing, soluble phosphorus concentrations fell by 43 – 96%. The % reduction was considerably greater for the higher initial soluble phosphorus concentrations : over 80% for initial concentrations > 32 mgP-PO_4/l, below 50% for initial concentrations below 5 mgP-PO_4/l.

With ageing, as well as soluble phosphorus concentrations falling, the pH rose (from around 7.2-7.6 to 7.9-8.4), bicarbonate alkalinity fell (by 0.9 – 7.6 meq/l) and carbonate alkalinity rose slightly (by 0.2-0.6 meq/l). Changes in dissolved calcium and magnesium ion concentrations were measured, enabling conclusions to be drawn regarding the fate of the phosphorus ions removed from solution.

Four different liquor samples taken from the sewage works over a six month period were used for the ageing experiments, showing somewhat variable physico-chemical characteristics. Of these, for two, the stoichiometry of the changes in calcium and magnesium ion concentrations during ageing, compared with that of soluble phosphorus, suggested that the phosphorus removal was the result of struvite precipitation with association calcium phosphate coprecipitation. One of the other liquors (sample "E") however showed ion concentration changes suggesting mainly precipitation of calcium phosphates, along with precipitation of calcium as a non-phosphate salt, perhaps calcium carbonate (for this liquor, the precipitation was also more rapid).

Supersaturation curves

Supersaturation was evaluated by adding different concentrations of sodium phosphates to the sewage works liquors in 1000ml beakers and then increasing progressively the pH by adding alkali (NaOH) or by aeration whilst measuring turbidity (by transmission of 400 nm). When light transmission dropped to below 80%, this was considered to be due to the formation of small precipitated particles and was taken to correspond to the point of supersaturation. The changes in concentrations of soluble phosphorus, calcium and magnesium ions during the experiments were measured.

The "E" sample liquor, which had shown different behaviour in the ageing tests, also proved different in the supersaturation experiments, with its supersaturation occurring at lower pH's than for the other liquors tested (supersaturation at around pH 7.3 at 16 mgP-PO_4/l for liquor "E", compared to around 8.3 for the other liquors at the same soluble phosphorus concentration).

The changes in ion concentrations showed that in two of the tested liquors, struvite only was forming ; that for one liquor a mixture of struvite and calcium phosphates were forming ; but that for the "E" liquor (as with the ageing experiments) there was a notable formation of calcium salts.

The authors draw a number of conclusions comparing the supersaturation curves experimentally obtained with the different liquors, the ratio between the conditional solubility products for HAP (hydroxyapatite ($Ca_5(PO_4)_3OH$)) and struvite (magnesium ammonium phosphate (NH_4MgPO_4)) and the supersaturation curves obtained from synthetic pure struvite and hydroxyapatite or combinations of the two. They conclude that calcium phosphate’s supersaturation curve is predominately influenced by calcium concentrations, that struvite supersaturation curves are at a higher pH, but that the presence of calcium accelerates struvite formation at lower pH’s.

Pilot fluidised bed reactor

Phosphate crystallisation experiments were carried out using a glass column, 58mm diameter, 42 cm high pilot fluidised bed reactor. The reactor was filled with quartz sand (0.21-0.35 mm diameter) as a seed material to 15cm depth, and this was expanded to a 30cm fluidised bed by a liquid upflow of 0.11-0.3 m^3/hour. A stripping tank (volume 5 l) was utilized with an air flow rate of 0.9 m^3/hour. The reactor was operated in batch mode with the column full of liquid being recirculated and was tested with nine different sludge dewatering liquor/phosphate concentration combinations.

Good removal of phosphates (62 – 90%) from solution was obtained with high soluble phosphate concentration liquors (24-48 mgP-PO_4/l) with around 100 minute process time, but a significant proportion of the phosphate was precipitated as fines (<0.45 µm) instead of being crystallised onto the sand or larger particles. The soluble phosphate concentration was progressively reduced as pH progressively rose in the same way as in the ageing experiments, but over shorter times. Runs at lower soluble phosphate concentrations (12-18 mgP-PO_4/l) also achieved acceptable P-removal rates of 63-83% and in this case with a low loss as fines (<5%).

The authors conclude that supersaturation curves are the key to understanding and controlling the phosphate crystallisation reactions. Operation at higher pH's or nearer the supersaturation concentration (eg. high soluble phosphorus concentrations) will reduce reactor residence times, but risk resulting in precipitation of non-recoverable fine phosphate particles instead of crystallisation onto recoverable larger particles. The ratio of conditional solubility products controls the formation of struvite or calcium phosphates, with struvite forming up to a ratio of around 0.54.

The authors suggest a saturation model (equation 1) that links the efficiency of P-recovery (precipitation of phosphates onto the seed material in the reactor) (E) to the maximum crystallization yield (E_m), the reaction time (RT) and the half time $T_{1/2}$ (defined as the reaction time which guarantees half of the maximum efficiency). The model is directly derived from second order kinetics.

$$E = \frac{RTxE_m}{T_{1/2} + RT}$$

According to this model a maximum of around 80% of soluble phosphorus can be recovered and a reaction time of 2-3 times the half time $T_{1/2}$ is needed to obtain satisfactory results.

The equation 2 defines the relation between the reaction time RT (time of crystallisation on seed material) and the process time t (time spent in the fluidised bed reactor and stripper):

$$RT = HRT?n = t?\ V/V_s$$

where HRT is the hydraulic retention time, n is the number of solution cycles in the reactor, V is the volume of the expanded bed in the reactor, V_s is the liquor volume of the system (stripper volume plus liquid column volume).

"Struvite crystallisation : a feasible and reliable way to fix phosphorus in anaerobic supernatants". Wat. Res. vol. 34, n° 11, pages 3033-3041, 2000.

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POLAND

Potential for P-recovery as struvite

Sewage and anaerobic digester sludge liquor (outflow from the filter press treating digester sludge) from three Polish sewage works, each operating biological phosphate removal, were studied to assess magnesium concentrations and to test the feasibility of struvite precipitation.

The magnesium concentration in the supernatant obtained by settling raw sewage was determined using atomic absorption spectrometry and found to be in the range **10-14 mg Mg/l** for the three plants studied. If the sewage was first filtered (using a 45µm filter), however, the concentration fell to around half these values.

The difference presumably suggests that around half the magnesium in raw sewage supernatant is attached to small, non-settling particles. The study does not indicate figures for the magnesium content of the solid sludge material obtained by settling the sludge, which could be obtained for example by digesting these solids prior to analysis.

Struivte stoichiometry

When magnesium concentrations were determined at different stages of the waste water treatment process as the sewage moved through the different anaerobic and then aerobic plant zones towards the final effluent discharge, all of the three investigated treatment plants showed an initial increase (the authors suggest that this could be due to the return of magnesium in sludge cycling) followed by a decrease of around –2 mg Mg/l on average. The authors suggest that this decrease may be caused by the **spontaneous formation of insoluble struvite crystals** (magnesium ammonium phosphate).

For reasons which the authors cannot explain, **magnesium concentrations in the digester sludge**

dewatering liquors from the three plants are considerably higher, ranging from 50 – 120 mg Mg/l.

The initial magnesium concentrations of 10-14 mg Mg/l would correspond (on a 1:1 molar basis) to 13-18 mg P/l, which is likely to exceed the influent concentration of phosphorus in most sewage works. This indicates that there is sufficient available magnesium to allow, in theory, removal of phosphorus by struvite precipitation.

Laboratory struvite precipitation

In order to assess the feasibility of struvite precipitation processes, laboratory experiments were carried out using the digester sludge dewatering liquors.

The liquors were subjected to aeration for 3 hours and pH, turbidity, magnesium, ammonia and phosphorus (soluble phosphate) concentrations were measured.

After 3 hours, pH had increased from 7.9 to 8.8, magnesium decreased from 21.7 to 8.5 mg Mg/l and soluble phosphorus from 31 to 14 mg P/l (these changes in concentrations are approximately 1:1 stoichiometric). The amount of ammonia removed from solution was considerably higher than a 1:1 stoichiometry, presumably because of ammonia stripping with the aeration and pH increase.

Over the 3 hours, turbidity increased by a factor of 10. The authors conclude that the turbidity increase is the result of **struvite forming as small particles**, which corresponds to the stoichiometric magnesium and phosphorus removal.

"Phosphorus recovery – laboratory scale experiments". Polish-Swedish Seminar, May 2000, Krakow.

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JAPAN

Struvite recovery plants in operation

Operating experience from three full-scale phosphorus recovery plants in Japan is presented. The reactors (capacities : 170 – 500 m3/day) produce granules of struvite (magnesium ammonium phosphate) from return liquors from the sludge processing of sewage works with biological phosphorus removal.

The three plants operating are situated at Shimane Prefecture (Lake Shinji East Sewage Works), Fukuoka Prefecture (East Water Treatment Centre) and at Osaka South Ace Centre (Japan Sewage Works Agency). They each use magnesium addition (magnesium hydroxide or chloride) and pH adjustment (to pH 8.1 – 8.9) to cause struvite precipitation. The fine crystals of struvite formed are grown to 0.5-1 mm granules by air stirring or recirculation stirring over an average 10 day residence time. The extracted granules are separated (fine crystals are returned to the reactor) and either left to stand or air dried down to 10% water content. The Shimane Prefecture reactor **removes 90% of soluble phosphates** from the treated liquors.

Plant :	*Capacity:*	*Soluble phosphate concentration of treated liquors PO_4-P*
Shimane Prefecture	*500 m^3/day*	*100-150 mgP/l*
Fukuoka Prefecture	*170 m^3/day*	*70-150 mgP/l*
Osaka South	*266 m^3/day*	*30-50 mgP/l*

Advantages for bio-P processes

The authors indicate that the process has advantages for the operation of sewage works using biological P removal : during anaerobic digestion of sludge (which enables energy recovery as methane and reduces sludge volumes as well as improving characteristics for disposal), phosphorus is released back into soluble form, and has to be returned to the sewage works inflow, deteriorating P-removal performance. At the Shimane Prefecture sewage works, prior to installation of the struvite recovery process, iron precipitants were added to the sludge digestion liquor to remove phosphorus before its return to the sewage works. Nonetheless, the return liquor still contributed some 70% of phosphorus inflow to the biological P-removal process and aluminium precipitant chemicals had to be added in the aeration tanks.

After installation of the struvite process (which reduces the soluble P content of the return liquors from over 100 to around 10 mgP/l), the sewage works has been able to achieve over 90% P-removal and to meet its discharge limit of 0.4 mgP/l by biological P-removal only (no addition of precipitant chemicals).

Struvite as a fertiliser

The struvite granules recovered at Shimane Prefecture showed ammonia-N, phosphate and magnesium contents near the theoretical values for struvite with 29.5% citric acid soluble phosphate.

Heavy metal levels were lower than regulatory standards for fertilisers, at 48 ppm arsenic and 6 ppm cadmium. Nickel, chromium and lead were not detectable.

The fertiliser value of the granules was tested at the Shimane Prefecture Agricultural Laboratory and was shown to be similar to standard fertilisers, with no harmful effects. The authors indicate that struvite is currently sold as a quality fertiliser for 1 – 200,000 Euros/tonne and suggest that 2 500 Euros/tonne is the approximate market price which the fertiliser companies will therefore pay for the product from recovery plants.

On this basis, the struvite recovery plants can be estimated to pay for themselves within 10 years.

The authors estimate that there are around 60,000 tonnes/year of phosphorus in Japanese domestic sewage and that if this were fully recovered as struvite it could cover around 20% of the country's current phosphorus use (mainly fertilisers), which is at present supplied from imported phosphate rock.

"Development of phosphorus resource recycling process from sewage". Paper presented at the First World Water Congress, International Water Association, 3-7 July 2000.

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PILOT PLANT

Using seawater for struvite recovery

9-10% seawater (containing 1250 mg Mg/l) was added in an aeration stirred 1,100 litre pilot (3.7 m high) reactor in order to enable struvite precipitation from digester sludge dewatering liquor at the Hiagari sewage works (which operates biological phosphorus removal). The reactor influent varied from 7 – 58 m^3/day and the soluble phosphorus concentration averaged 64, 70 and 110 mgP/l for the three different runs. pH was controlled by adding sodium hydroxide NaOH in some periods.

The three different experimental runs, lasting 18, 6 and 28 weeks, used slightly different influent liquors : different combinations of centrifuge, belt filter press filtrate and filter wash liquors.

The reactor was made up of an inner (99 litre) cylinder in which aeration caused mixing of the influent liquor and seawater in an upflow, an outer 218 litre cylinder, and a 792 litre settling zone around the top of the outer cylinder. The linear velocity of the inner cylinder was 9.5 – 76 m^3/m^2/h and the air supply 130 m^3/m^2/h. Struvite particles then sank to the bottom of the outer cylinder and were drawn off and separated by a 0.2 – 0.3 mm screen.

Power consumption for the reactor was 1.4 kWh/kg struvite produced.

70% P-removal

In all three experimental runs, **over 70% removal of dissolved phosphorus was achieved**, considered adequate to enable the biological P-removal process at the sewage works to achieve the sewage works' effluent quality standard of 0.5 mgP/l.

The 70% P-removal performance could be reliably achieved with a reactor residence time of 10-12 minutes and a pH of 8.03, or with a residence time of 29 minutes and a pH of 7.77.

Total phosphorus removal ratios were lower in the first experiment, when suspended solid concentrations were high (over 100 mgSS/l), probably because fine struvite particles were leaving in the reactor outflow. Removal of total phosphorus was also slightly lower at higher suspended solids concentrations (falling below 70% above 100 – 200 mgSS/l) because of fine struvite particles flowing out in the effluent.

Soluble phosphorus removal is also lower at lower influent soluble phosphorus concentrations, falling below 70% for soluble phosphorus levels below around 80 mgP/l.

There was no clear relation in the pilot plant experiments between magnesium:phosphorus ratios and soluble phosphorus removal. Previous beaker studies, however, had suggested that P-removal was improved with higher magnesium concentrations, so the seawater addition was regulated during the experiments at 1.5x stoichiometric concentrations with the aim of ensuring >70% P-removal. The addition of seawater at around 10%, necessary to achieve this, was calculated to increase ion concentrations in the mainstream of the sewage works (and so presumably in the sewage works effluent) by 4 mg/l for sodium, 7 mg/l for chloride and 0.3 mg/l sulphur (as sulphate).

Recyclable struvite

The struvite granules produced were hard and white, around 1mm in diameter (the larger the diameter, the harder the material). They contained **5.5% N, 12.5% P, 9.6% Mg and 42% water**, close to theoretical values for struvite $MgNH_4PO_4(H_2O)_6$.

Heavy metal concentrations were **compatible with the use of the recovered struvite as a fertiliser :** cadmium was below detection limits, mercury <0.003 ppm and arsenic 0.7 ppm

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"Phosphorus removal from sidestreams by crystallisation of magnesium ammonium phosphate using seawater". J. CIWEM, 2000 – 14 – August, pages 291-296.

Y. Matsumiya, Japan Institute of Wastewater Engineering Technology, Toshima-ku, Tokyo, Japan. T. Yamasita, Environmental Bureau of Kitakyushu City, MN803-8501 1-1 Shirouchi, Kokura-Kita-ku, Kitakyushu, Japan. Y. Nawamura, Nishihara Environmental Sanitation Research Corportation Ltd., MN108-0023 3-15-9 Shibaura, Minato-ku, Tokyo, Japan.

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The SCOPE Newsletter seeks to promote the sustainable use of phosphates through recovery and recycling and a better understanding of the role of phosphates in the environment.

The SCOPE Newsletter is open to input from its readers and we welcome all comments or information. Contributions from readers are invited on all subjects concerning phosphates, detergents, sewage treatment and the environment. You are invited to submit scientific papers for review.

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SCOPE NEWSLETTER

NUMBER THIRTY EIGHT **AUGUST 2000**

SEWAGE TREATMENT AND PHOSPHORUS RECOVERY

HISTORICAL STRUVITE RECOVERY PAGE 2

The Grace/Dearborn chemical companies tested P-recovery in 1960's

A report for the US authorities dated July 1969 presents a process for recovering struvite from sewage for use as a fertiliser.

EXPERIMENTAL RESULTS PAGE 3

Struvite precipitation reactor

A 3-litre lab-scale fluidised bed reactor was tested to precipitate struvite, with the aim of avoiding deposit problems in sludge handling circuits. The relatively pure struvite crystals produced could permit phosphorus recycling.

JAPAN PAGE 4

Heavy metals removed from sludge utilising phosphoric acid

8% phosphoric acid + 2% hydrogen peroxide achieved efficient removal of heavy metals from sewage sludges.

STRUVITE RECOVERY PAGE 6

Ammonia removal from landfill leachate

Struvite precipitation proves an effective process at near neutral pH for removing ammonia from landfill leachate

USA PAGE 6

Ammonium recovery process

Innovative technology allows ammonium sulphate for fertiliser to be recovered from anaerobic sludge digestion centrate

VIEWPOINT PAGE 17

Struvite – Problem or Resource?

Simon Parsons & James Doyle, of the School of Water Sciences, Cranfield University UK, present a summary of current thinking on struvite recovery.

NUTRIENT SOURCES

IRELAND PAGE 8

Dominance of agricutlural P sources

Analysis of 24 years' nutrient data shows near doubling of soluble phosphorus in Lower Lough Erne, Northern Ireland, caused by diffuse agricultural inputs.

SWEDEN PAGE 9

Drainage loss of phosphorus from fields

Drainage water was collected from four experimental plots in South-West Sweden over four years and showed total phosphorus loss of 105 - 201 gP/ha/year of which dissolved orthophosphates were 42 – 81 gP/ha/year.

EUTROPHICATION AND ECOSYSTEM BALANCE

HOLLAND PAGE 10

Lake restoration

Control of external nutrient loadings has not resulted in the desired improvement in quality in Dutch shallow lakes. A comprehensive ecosystem approach may be required for effective lake restoration.

CLAY TREATMENT PAGE 12

Australia tests "Phoslock" river treatment

Testing of a new method for removing phosphorus from surface waters in Australia, using a thin layer of absorbent clay on the bed.

AUSTRALIA PAGE 12

State of knowledge on limiting nutrients

A Australian National Eutrophication Management Program workshop has lead to a paper presenting, for water managers, the state of current knowledge on the links between nutrients and other factors and algal development. The conclusion is that nutrient concentrations are of limited value in predicting algal growth limitation, that often nutrients are not limiting, and that nitrogen is as likely to be limiting as phosphorus.

CULTURAL OLIGOTROPHICATION PAGE 15

The need for sustainable nutrient management

The authors suggest that choices must be made between clear water and sustainable fishery productivity. Phosphorus recycling and a new nutrient management philosophy will be required.

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SEWAGE TREATMENT AND PHOSPHORUS RECOVERY

HISTORICAL STRUVITE RECOVERY

The Grace/Dearborn chemical companies tested P-recovery in 1960's

A WR Grace & co. – Dearborn Chemical Division report from 1969, for the US Department of the Interior, presents a process to recover phosphates from sewage. Orthophosphate release from sewage sludges was studied, followed by phosphate precipitation from the solution utilising magnesium salts and pH control (pH raised). The precipitated phosphate (primarily a mixture of struvite and calcium phosphate) was found to be readily available for plant uptake and hence suitable for incorporation into fertilisers.

Phosphate precipitation from digester supernatant was also studied, caused either by increasing the pH or simply by application of heat and/or vacuum.

The report presents a considerable body of experimental work covering the release of orthophosphate from waste activated sludge when subjected to acidification and anaerobic conditions. This phenomenon has since been extensively researched, particularly with the development of biological phosphorus removal processes, and in the management of P-rich sludges from such plants.

On the other hand, the work on phosphate precipitation, from the orthophosphate solution generated by this treatment of sludge, or in the sludge digester supernatant, remains of considerable interest today as little other comparable work has been published in this area to date.

Struvite precipitation

The main objective of the work was to precipitate struvite (magnesium ammonium phosphate: $MgNH_4PO_4.6H_2O$) from waste streams containing 50-100 mgP/l as orthophosphate (dissolved inorganic phosphate), with emphasis placed on the type and quality of the precipitated solids. **The aim was to "yield a solid by-product with economic value".**

Preliminary studies were carried out using de-ionised water with P (phosphoric acid), Mg (magnesium sulphate) and Ca (calcium chloride), to which ammonium hydroxide was added to increase pH and provide ammonium ions. The neutralisation phase was about 15 minutes, with a stirred reaction time and a settling time of one hour each.

With an initial concentration of 100 mgP/l and 77 mgMg/l, **41% of phosphate was precipitated at pH 8.5, 85% at pH 9 and 93% at pH 10. Nearly all the phosphate was precipitated as struvite.**

In systems containing a relatively low concentration of calcium (13 mgCa/l to 100 mgP/l), the phosphate and magnesium precipitation were not significantly affected. At higher concentrations, the phosphate precipitation rate was improved. Optimum phosphate precipitation was achieved at pH 9.5.

Further experiments were carried out using magnesium at 25% or 50% above phosphorus stoichiometric requirements. The following conclusions were reached in this case:

- a high phosphate precipitation (95%) is obtained at pH9 when magnesium concentration is above stiochiometry
- phosphates tend to precipitate as calcium phosphates rather than struvite at a pH of 8.5
- higher initial calcium concentrations lead to linearly lower magnesium precipitation (precipitation of calcium phosphates instead of struvite)
- at higher pH and relatively low calcium concentrations, most phosphate precipitates as struvite

Ammonium concentrations above those necessary for pH adjustment also lead to enhanced struvite precipitation.

The re-use of precipitated struvites as a seeding material did not appear to significantly improve phosphate precipitation.

Preliminary studies are also presented using a variety of sludge release products. These showed that **phosphate precipitation rates of over 95% were also achieved in liquids containing nearly 1% solids and significant concentrations of soluble organics.**

P-recovery processes

Two processes were tested at the 5-litre tank scale to assess the feasibility of phosphate recovery, as struvite, from sludge digester supernatant.

The supernatant used was from the Libertyville sewage works, and contained 71-258 mgP/l total Phosphorus, 42-90 mgP/l orthophosphate (average 60 mgP/l), 36-490 mg/ calcium (average 100 mgCa/l), a total Kjeldahl nitrogen average of 360 mg/l, an average 740 mg/l suspended solids and an average chemical oxygen demand of 1,230 mg/l.

At pH 9 and higher, 93% phosphate precipitation was achieved by a pH increase only (no addition of magnesium or ammonium), because the supernatant itself contains fairly high concentrations of both magnesium and calcium.

Results from a number of experiments using different chemical addition combinations are given (pH, magnesium, ammonium).

Phosphate precipitation efficiency was also assessed at different temperatures, and showed an to increase at higher temperatures (up to 70°C)

The authors noted during experiments at higher temperatures (>60°C) and by using high speed agitation (around 1,000 rpm) or a vacuum, the pH could be increased without the addition of a base chemical (presumably by driving off CO_2 and by decomposition of ammonium bicarbonate, releasing ammonium for struvite precipitation). Phosphate precipitation efficiencies of 94 – 97% were obtained by this method (with the pH reaching 8.4 – 8.9), without addition of chemicals (as indicated above, the supernatant contained relatively high magnesium and calcium concentrations).

After the heat precipitation process (65°C experiments), the supernatant phosphate concentrations had been reduced to 2-9 mgP/l total P and nitrogen concentrations to 8 – 45 mgN/l.

Plant available recovered phosphates

The recovered phosphate materials were amorphous under X-ray analysis. In synthetic solutions with ion concentrations comparable to those in the Libertyville supernatants and precipitated using excess magnesium, the solid contained approximately 16% struvite, 45% magnesium phosphate and 37% calcium phosphate.

Solids precipitated from the actual supernatants contained roughly 20% phosphate (P_2O_5) and 2% - 4% nitrogen (N), corresponding to a roughly 50% "dilution" of the phosphates in the precipitate by suspended solids, including organic nitrogen compounds which are precipitated with the phosphates.

Both the synthetic solution and the real supernatant precipitates were tested by the "AOAC" procedure (American Organisation of Agricultural Chemists) and it was found that the phosphates in these solids were completely available for plants.

"Ultimate disposal of phosphate from waste water by recovery as fertilizer – phase I – final report". WR Grace & co. – Dearborn Chemical Division. Prepared for the US Department of the Interior, Federal Water Pollution Control Administration. July 15, 1969.

K. Ries, M. Dunseth, M. Salutsky, J. Shapiro. Grace & co., Merchandise Mart Plaza, Chicago, Illinois 60645.

EXPERIMENTAL RESULTS

Struvite precipitation reactor

A lab-scale struvite ($MgNH_4PO_4.6H_2O$) precipitation reactor was built and tested, under different operating conditions, in order to assess the feasibility of using such a process in sewage works to prevent struvite deposit problems in sludge treatment circuits. This work follows investigation of the precipitation chemistry of struvite presented in SCOPE n° 36 (page 6).

Struvite accumulation in sewage works piping and other equipment has been documented as a significant problem at a number of plants across the world. The Sacramento Regional Wastewater Treatment Plant in Northern California (685,000 m^3/day), with which the authors worked, has extensive struvite deposit problems, leading to the replacement of a 5.6 km section of piping in the post-digestion sludge storage and treatment system.

The development of biological nutrient removal systems (which transfer phosphorus to sludge from which it can readily be released in anaerobic conditions) and increasing requirements for advanced sludge treatment, mean that **the potential for struvite accumulation problems is increasing.**

One promising way of preventing such problems is to remove the struvite by controlled precipitation from sludge supernatent, thus allowing recovery of phosphorus.

Scientific chemistry approach

The authors' previously published work (see SCOPE 36) indicates that struvite precipitation is controlled primarily:

- ***at the nucleation stage*** (formation of nuclei of new crystals): mainly by concentrations of orthophosphate, ammonium, magnesium and pH, with an inherent supersaturation-related lag period.
- ***at the growth stage*** (on the surface of existing crystals): mainly by transport mechanisms (that is, growth is accelerated with mixing).

Struvite solubility decreases with increasing pH in the range pH 6-10, with a minimum at pH 10.5 – 11 (authors' previous paper).

For these reasons, the authors suggested that an efficient struvite precipitation reactor should be based upon:

- **an increase in pH,** obtained either by aeration (to drive off CO_2) or by chemical addition (NaOH was used).
- use of fine **struvite seed crystals,** to provide a large surface area and bypass the nucleation stage.
- a **high mixing energy,** obtained in this case by using a fluidised bed reactor.

A fluidised bed, in theory, allows extraction of "grown" struvite crystals (which naturally sink to the bottom of the expanded bed as their size increases) and their replacement with small, new seed crystals, in order to maintain the surface area of the seed material and to recover the precipitated struvite.

Lab-scale experimental set-up

Laboratory struvite precipitation experiments were carried out using **sludge storage basin supernatent from the Sacremento sewage works** mentioned above.

The experimental set-up used involved a **1 m high 3.17 litre volume acrylic plastic fluidised bed column** with an unexpanded bed height of 31 cm. The upflow through the column was adjusted to ensure full expansion of the bed, achieved with an upflow rate of 11 cm/second (21 litres/minute).

The pH was adjusted in a separate tank to around 8.3, usually using only aeration to increase it up from the influent pH of 7.8 - 8. In some cases (high flow rates), NaOH addition was necessary to achieve the pH of 8, but this may have been because the aeration equipment was inadequate.

In order to allow a long residence time in the fluidised bed (using the small lab-size column with the necessary upflow rate), the liquid was continuously re-circulated from the top of the column back through the pH adjustment tank to the bottom of the column.

80% orthophosphate removal

Struvite removal rates (as measured by orthophosphate removal) corresponded to the calculations from the chemical constants established in previous work. Calculations demonstrated that the mixing energy in the reactor was theoretically sufficient for optimal struvite crystal growth and the measured growth-rate in the reactor approached that observed in high-energy mixing environments in the field at around 22 m/m^2/day.

With a hydraulic residence time in the reactor of one hour, over 80% removal of orthophosphate from the sludge supernatant was achieved, reducing struvite supersaturation from above one (influent) to 0.8 – 0.9.

Because the experimental runs were relatively short, the mass increases of the struvite seed crystals in the bed were always <1%. **X-ray diffraction analysis showed no evidence of impurities.** The authors note that this process could produce struvite for recovery, some of which would be crushed to provide new seed crystals, but most of which could be marketed as a slow-release fertiliser.

"Postdigestion struvite precipitation using a fluidized bed reactor". Journal of Environmental Engineering, April 2000, pages 361-368.

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JAPAN

Heavy metals removed from sludge utilising phosphoric acid

One of the main obstacles to agricultural recycling of the nutrient and organic values of sewage sludges is heavy metal contamination, which prevents or limits spreading (see article in SCOPE 37 regarding proposed new EU specifications for sludge spreading). Experiments were carried out using different types of acids and hydrogen peroxide to assess removal of heavy metals from sludge filter cake.

Most heavy metals in sewage sludges are accumulated by biosorption, in particular, by ion-exchange reactions on cell surfaces. The heavy metals bind to sites on the cell surfaces which include carboxylates, amines, thiols, phosphates and other functional groups. **The exact mechanism of heavy metal binding but it is clear that most do indeed adhere to mircro-organisms' cell surfaces rather than being integrated into the intracellular structure.**

Heavy metal removal experiments were carried out using a sludge filter cake (75% water) from the municipal activated sludge sewage works serving the industrial area of Kel-Hin. The sludge in the works was dewatered by the addition of a polymer coagulant at 0.6% dry sludge weight.

Heavy metal contents were as follows (mg/kg dry sludge): Cd 15.2, Cr 73.2, Cu 688, Fe 15,800, Hg 266, Mn 328, Ni 67.6, Pb 230, Zn 850, As 680.

Acid removal

Removal of heavy metals was tested by mixing 10g of sludge filter cake with 30ml of acid and stirring for one hour at room temperature. The mixture was then filtered and the heavy metal content of the acid measured. The following acid and hydrogen peroxide mixtures were tested:

1N hydrochloric acid
1N sulphuric acid
1N nitric acid
2.12% - 42.5% concentrations of phosphoric acid
2% - 40% concentrations of phosphoric acid with 2% hydrogen peroxide

1N hydrochloric acid gave better removal rates than 1N sulphuric or nitric acid, but still only achieved 60% removal of chromium, mercury, copper and cadmium.

Removal with phosphoric acid was correlated to pH values, with 8.5% phosphoric acid achieving removal rates comparable to 1N hydrochloric acid (over 80% removal for all the metals considered except copper, iron and zinc and 100% removal of cadmium, chromium and mercury).

Copper extraction

All four acids gave very low removal rates for copper (ranging from 9% removal for 42.5% phosphoric acid to 58% removal for 1N hydrochloric acid) and for iron. The authors suggest that this is because these elements do not combine with the organic matter through a carboxyl bond.

The removal or iron is not a problem, as this element does not pose a problem in sludges, but copper needs to be removed. In order to achieve this, 2% hydrogen peroxide was included in the phosphoric acids used. This also improved zinc removal, but did not significantly affect removal of other metals.

The authors conclude that phosphoric acid plus hydrogen peroxide, at room temperate, enables good heavy metal removal: 40% phosphoric acid plus 2% hydrogen peroxide permits over 80% removal of all heavy metals tested (except iron which is not a sludge management problem).

Phosphoric acid recycling and recovery

The authors also tested the feasibility of re-use of the phosphoric acid, by treating the acid after metal extraction with a cation exchange resin (Amberlite IR 120B). This enabled the heavy metals to be extracted from the acid and the acid – peroxide mix to be successfully used for three successive heavy metal removal runs, with only minimal intermediate addition of acid and peroxide to maintain concentrations.

The authors also demonstrated that the phosphate concentration in the acid solution actually increased following the sludge treatment: the process actually enables recovery of phosphate from the sludge itself.

"Principle and process of heavy metal removal from sewage sludge". Environmental Science and Technology, vol. 34, n° 8, 2000. Pages 1572-1575.

S. Yoshizaki, Yoshizaki Engineer Office, 15-1 Azasotobiraki, Komatsushima, Tokushima 773-0001 Japan. T. Tomida, Dept. Chemical Science and Technology, University of Tokushima, Minamijosanjimacho, Tokushima 770-8506, Japan.

Extract of presented results for metal removal from sludge filter cake:

(% removal)	*As*	*Cd*	*Cr*	*Cu*	*Fe*	*Hg*	*Mn*	*Ni*	*Pb*	*Zn*
42.5% H_3PO_4	88	100	100	9	54	100	80	83	81	72
8.5% H_3PO_4	85	72	35	6	45	46	86	80	65	77
40% H_3PO_4 + 2% H_2O_2	91	96	92	92	50	89	82	87	100	81
8% H_3PO_4 + 2% H_2O_2	87	76	35	78	43	42	85	83	85	92

STRUVITE RECOVERY

Ammonia removal from landfill leachate

Fresh and anaerobically digested samples of leachate from a landfill site in Istanbul, Turkey, were used to test different methods and conditions for ammonia removal. In particular, struvite (magnesium ammonium phosphate) precipitation was tested at different pH's and under varying conditions, and was shown to offer 87% - 91% ammonia removal in the pH range 6.5 – 9.

The landfill leachate and the anaerobically treated leachate sample used contained ammonia concentrations of 1,000 – 2,400 mgN/l (as ammonia) within a total nitrogen level of 1,600 – 2,700 TKN, 7 - 16mgP/l soluble phosphate (PO_4-P) and 6,000 – 14,000 mg/l COD and around 500 mg/l suspended solids.

Ammonia stripping by aeration at near neutral pH had to be continued for 12 hours to achieve 80% removal. Ammonia removal of 85% could also be obtained by stirring at pH 12 for 24 hours. Other authors have demonstrated 65 – 80% nitrogen removal using biological treatment, but high ammonia levels may inhibit such methods.

Struvite precipitation

The aim in testing struvite precipitation as an ammonia removal technique was to provide a rapid and reliable technique for achieving high levels of ammonia removal efficiency.

Struvite was precipitated by the addition of magnesium chloride and hydrogen phosphate at stoichiometric concentrations (stoichiometry of added magnesium and phosphate ions to initial ammonia concentrations in the leachate sample to be treated). The pH was adjusted using sodium hydroxide. In some experiments, ferric chloride was also added before pH adjustment. Precipitation was carried out in 1 litre experimental beakers, kept closed and magnetically stirred for one week to ensure equilibrium.

Ammonia removal efficiencies of 87 – 91% were achieved for the different pH's tested in the range 6.49 – 8.91 (leaving final ammonia concentrations of 185 – 300 mgN/l ammonia). COD removal was generally of the order of 70% for the raw leachate and 30 – 40% for the digested leachate. The addition of 500 – 4,000 mg/l $FeCl_3$ as a coagulant seemed to have no apparent effect on either ammonia or COD removal.

However, at pH 6.09 only 25% ammonia removal efficiency was shown (residual concentration 1,800 mgN/l ammonia), and interestingly also a significantly lower COD removal. This suggested that COD removal was related to struvite precipitation. Suspended solids were also nearly completely removed with the struvite precipitation, contributing to removal of organic nitrogen.

Residual phosphorus levels were significantly lower for all pH's used above 7.2. Residual soluble inorganic phosphorus was in the range 3 – 33 mgP/l for pH's above 7.2 ; 113 mgP/l and 400 – 500 mgP/l for pH's 6 – 6.5 (these levels are often higher than initial leachate soluble phosphate levels, because of the addition of hydrogen phosphate for the struvite reaction).

After struvite precipitation, the treated leachate's ammonia and COD were at a level compatible with aerobic treatment.

"Ammonia removal from young landfill leachate by magnesium ammonium phosphate precipitation and air stripping". Water Science and Technology vol. 41 n° 1, pages 237-240, 2000.

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USA

Ammonium recovery process

An "Environmental Technology Verification Report" has been published for a new process to recover fertiliser, in the form of ammonium sulphate, from sludge digester centrate. The process is called the "Ammonia Recovery Process (ARP)" and has been developed by ThermoEnergy Corporation. The verification report is part of the EPA program for objective audit of innovative, commercially-ready environmental technologies, carried out by the US Civil Engineering Research Foundation (CERF) Environmental Technology Evaluation Center (EvTEC).

The ThermoEnergy ARP process recovers ammonium by ion exchange, followed by concentration and vaporisation phases, leading finally to crystallisation of ammonium sulphate from ammonia gas. The process testing was carried out using anaerobic sludge digester centrate produced by the Oakwood Beach sewage works, Staten Island, New York, from September to December 1998. The sewage works was operated as normal and 48 processing runs treating nearly 100,000 litres of centrate were completed. During this time, the pilot plant operated in very varied weather temperature conditions ranging from +32°C to -4°C.

Ion exchange ammonia removal

The first stage is reversible chemisorption ion exchange (using two 181 litre vessels filled with zinc-impregnated ion-exchange media). The media was regenerated using zinc sulphate in 5% sulphuric acid. This stage enabled concentration of ammonia from 100 - 500 ppm in the digester centrate to around 15,000 ppm in the regenerate solution (this theoretical value was not in fact achieved) and removal of 75% - 99% (average achieved: 89%) of the ammonia present in the treated centrate.

The ion exchange system appeared to be resilient. A settling tank was used upstream of the columns to limit solid soiling and maintain a suspended solids concentration in the treated solution of around 10 mg/l. The ion exchange efficiency was severely affected by accidental ferric chloride contamination (2 incidents) and by polymers, both results of dosing errors at the waste water plant, but in both cases it proved possible to regenerate the ion exchange columns and restore efficiency.

Interestingly, **the resin columns also effectively removed phosphorus, taking concentrations down from 29 – 32 mgP/l in the inflowing digester centrate to 3 – 6 mgP/l.**

The report notes that the Oakwood Beach sewage works has had struvite formation problems in the past, but that these have been resolved in the digester centrate by the addition of ferric chloride. The report authors indicate that this resolves struvite problems by dropping the pH *[SCOPE editor's note: the effect may also be due to removal of reactive phosphorus by precipitating iron phosphates]*. Struvite precipitation is not, in any case expected to cause problems in the ARP process, because of the low operating pH and high alkalinity.

Double salt crystallisation process

The ion exchange regenerate, with concentrated ammonia, was subjected to the following process (batch treatment of around 800 litres) in order to recover ammonium sulphate crystals:

- steam-heated evaporation, to increase ammonia concentrations
- chilling to around 1°C to promote the formation of zinc sulphate crystals
- basket filtration to recover these crystals, the remaining solution being returned to the regeneration system for reuse
- heating of the zinc sulphate crystals in a furnace, initially to drive off water, then to 400°C to convert NH_4^+ to NH_3 and to drive it off as a gas
- the zinc sulphate remaining in the furnace are recirculated to prepare fresh ion exchange column regeneration solution
- the gases driven off were then sent to a wet scrubber unit using sulphuric acid at pH 2-3 at a temperature of 40-70°C to capture ammonium, sulphur trioxide and water vapour
- the resulting solution was then transferred to a batch crystalliser where the temperature was lowered to 10-20°C to precipitate ammonium sulphate crystals, the remaining solution being returned to the scrubber.

Unfortunately the scrubber unit delivered to the project was not as specified. As a consequence, the final ammonium sulphate production stage of the process did not function during the verified test runs, and only around 10 kg of ammonium sulphate crystals were actually produced.

Mass balance and costs

The estimated overall mass balance ammonium recovery efficiency varied from 37 – 73% (not accurately calculated because of the scrubber problem indicated above) and the total treatment cost was evaluated as around 0.75 – 1.5 US$/1,000 litres (not taking into account the potential resale value of the recovered fertiliser product).

"Environmental Technology Verification Report for Ammonia Recovery Process". CERF Report #40458, January 2000.

EvTEC Environmental Technology Evaluation Center, 1015 15th Street NW, Suite 600, Washington DC 20005-2605, USA. www.cerf.org/evtec.

ThermoEnergy ARP Process, 323 Center Street, Little Rock, AR 72201, USA. www.thermoenergy.com.

NUTRIENT SOURCES

IRELAND

Dominance of agricutlural P sources

Northern Ireland has two large lake catchments with long records of nutrient flows: Lough Neigh (385 km^2 lake surface, catchment 4,453 km^2) and Lower Lough Erne (109.5 km^2 lake surface, catchment 4,212 km^2). Nutrient data have been monitored in Lough Neigh since 1969 and in Lower Lough Erne since 1974. Studies of Lough Neigh have pointed to a steady increase in phosphorus inputs from diffuse agricultural sources (Foy et al 1995). This paper looks at trends in phosphorus and nitrogen inputs to Lower Lough Erne and probable origins of these nutrients.

Lower Lough Erne is the third largest lake in the British Isles, situated 54°30' N 7°50'W at an altitude of just under 50m. The maximum depth is 62m and the volume turnover time 0.42 years. The 4,212 km^2 catchment is essentially rural, with a human population of around 128,000, but 83,000 pigs, 420,000 cattle, 72,000 sheep and 4.4 million poultry. Significant areas of the catchment are used for managed forestry. The main industries are linked to agriculture and tourism.

The lake is in an **Area of Outstanding Natural Beauty** and is an important tourist area, used for pleasure cruising and course fishing.

Nutrient data records

From 1974 to 1987, nutrient data (lake water concentrations at the lake inflow and in the open lake at the deepest point) were collected every two weeks in the summer and monthly between October and March. From 1987 onwards, samples were taken every two weeks throughout the year. Total phosphorus, soluble reactive phosphorus and total soluble phosphorus (after 0.45µ filtration) were analysed, as well as total Kjeldahl nitrogen, nitrate- plus nitrite- nitrogen and ammonium nitrogen. Certain missing data were calculated by interpolation.

The range of annual values for nutrient inflows varies widely, from 103 tonnes/year in 1974 to 254 tonnes/year in 1993 for total phosphorus, and from 23 to 107 tonnes/year over the 24 years of data for total nitrogen. **Nutrient inputs were statistically correlated with total flow of water (lower nutrient inputs in dry years) for both phosphorus and nitrogen,** and for all forms of both nutrients except particulate phosphorus.

The absence of a relationship between particulate phosphorus and flow is surprising, as high flows in most river systems result in high particulate transport of phosphorus. This may, in this case, be the result of methodological problems: dates of nutrient samples are not the same as flow analysis, variations in lake water levels (affecting sediment re-suspension through peripheral wave action)…

Increasing soluble phosphorus

Inflow loadings of soluble reactive phosphorus and total soluble phosphorus both showed a strong upward trend over time, explaining the increase in lake water concentrations. Total nitrogen showed a weak upward trend with time. Soluble nitrogen fractions did not show significant trends, and neither did total or particulate phosphorus (but this may be due to the methodological problems indicated above).

The authors conclude that the soluble reactive phosphorus (SRP) load to Lower Lough Erne has been increasing at around 2.0 tonnes SRP/year over the 24 year study period, rising from around 29 tonnes SRP/year in the mid 1970's to 86 tonnes SRP/year in the mid/late 1990's.

They indicate however that **an analysis of (unpublished) chlorophyll-a data does not show a clear upward trend over time**, and that there is no evidence to support the hypothesis that increased P concentrations may have tilted the nutrient ratio in favour of N-fixing cyanobacterial such as *Anabaena* and *Aphanizomenon.*

Responsibility of diffuse agricultural sources

The human population in the Erne catchment has not increased over the period of this study, sources of phosphorus other than riverine inputs are trivial (aerial deposition not more than 2 tonnes P/year) and nutrient release from sediments is small (due to predominantly oxic conditions). **The authors therefore suggest that diffuse agricultural sources are responsible for increasing SRP concentrations.**

The cause is probably not an increasing intensity of agriculture or of fertiliser application, but an ongoing net import of phosphorus to Northern Ireland farmland (Tunney *et al.*, 1997). This leads to **an increase each year in the phosphorus status of soils, which in turn results in increased phosphorus losses to drainage waters.**

"Long-term changes of nitrogen and phosphorus loadings to a large lake in North-West Ireland". Wat. Res. vol. 34, n°3, pages 922-926, 2000.

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SWEDEN

Drainage loss of phosphorus from fields

Surface runoff from agricultural fields has been identified as one of the main contributors of phosphorus to surface waters (Sharpley and Rekolainen, "Phosphorus loss from soils to waters", 1997), but significant levels of phosphorus have also been measured by different authors in agricultural drainage waters (see eg. SCOPE 35, 37). This four-year study measured phosphorus losses in drainage water under four tile-drained experimental field plots in South-West Sweden (Lanna Plain 58°21' N 13°08'E).

Tile drains were installed in the plots in 1935 at a depth of 1m and with a spacing of 3.5m. The field is fairly flat (less than 1% slope) with a structured clay soil (Udertic Haploboroll type). Each plot studied had an area of 0.4 ha. Three had the same standard tillage and fertilisation histories, the fourth had been under zero tillage since 1988. The four plots were used for rotating cultivation of barley, oats and rape, with rye grass also being planted on the tilled plots. Annual precipitation varied over the four years from 444 – 703 mm/year (agrohydrological years from 1 July – 30th June).

Drainage and phosphorus

As could be expected, **drainage discharge was strongly dependent on precipitation.** The amounts of drainage were generally similar for the four plots, although in some cases, the untilled plot showed higher drainage peaks and volumes: this may be the consequence of more effective preferential flow routes in the untilled soil, but may also partly result from horizontal sub-surface water movement, as the plots were not hydrologically sealed at the margins.

Much of the total annual drainage discharge was, in all plots, related to a few high drainage events.

Total phosphorus discharges in the drainage water, averaged over the four years, were 118, 105 and 201 g/ha/year for the tilled plots, and 165 g/ha/year for the untilled plot. The soil P-content of the third plot were slightly higher than for the other plots (P-AL = 5.7 mg/100g compared to 5 mg/100g, for example), but this cannot explain the significantly higher value for total phosphorus discharge from this plot (201 g/ha/year), and this is probably due to spatial variation in soil characteristics and structure.

The authors indicate that these phosphorus discharges are lower than those indicated in other studies for clay soils, for example 110 – 750 g/ha/year in South-West Finland (Turtola and Jaakola, 1995) or 300 – 600 g/ha/year in South and Central Sweden (Ulén, 1997). Where farmyard manure is used, losses can be even higher (Smith *et al.*, 1998)

Dissolved phosphorus

The four-year average PO_4-P discharges varied from 42 – 81 g/ha/year for the four plots (dissolved inorganic phosphorus, which is directly available for uptake by algae and plants in surface waters). Again, the third plot had a high value, but in this case so did the untilled plot. This may be because no-till management conserves soil structure and hence the continuity of macropores which facilitate preferential transport.

The proportion of the total phosphorus discharge which was in the dissolved inorganic PO_4-P (available) form was proportionally higher following fertiliser application.

PO_4-P discharge was not only dependent on the volume of drainage water, it was also related to fertiliser use.

The authors conclude by noting **the difficulty in drawing clear quantitative conclusions, given the pronounced differences in phosphorus discharges over time and between plots and because phosphorus discharges were largely episodic in nature.**

"Temporal and spatial variations of phosphorus losses and drainage in a structured clay soil". Wat. Res., vol. 34, n°5, pages 1687-1695, 2000.

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EUTROPHICATION AND ECOSYSTEM BALANCE

HOLLAND

Lake restoration

Algae-dominated turbid water states may be extremely stable in shallow lakes, so that solely reducing external nutrient loadings tends to be insufficient to attain clear water conditions. This paper addresses the factors which can cause turbid or clear water states to be stable and the buffer and switch mechanisms which can hinder or facilitate lake restoration.

The development of lake restoration strategies started with the “Vollenweider approach”, based on statistical analysis of different lakes, which suggested criteria for external nutrient loading. Lake restoration in Holland has been focused mainly on the control of external phosphorus loading from point sources (sewage works, industry, etc…), but this has not resulted in the desired water quality.

The authors indicate that this is because of the **release of nutrients from sediments (internal loading)** and independent **ecosystem effects which prevent lake recovery** by rendering the algae-dominated turbid water state extremely stable. Furthermore, these biotic ecosystem effects can actually facilitate sediment nutrient release.

In 1975, Shapiro *et al.* indicated the need to treat lakes as ecosystems and not as “containers of algae and phosphorus”.

Algal feedback effects

Algae are a key element of the lake ecosystem, affecting the physical, chemical and biological conditions in the lake. These effects depend on both the species composition and the density of the algal population. Conversely, light penetration, which depends on lake depth, mixing, water quality and algal populations, is itself the limiting factor for algal growth.

The paper outlines the different feedback mechanisms which are essential for defining a lake restoration strategy:

Physical conditions: algal development renders the water turbid and, beyond a certain threshold, leads to the collapse of submerged plant (macrophyte) communities. This can prevent lake recovery: macrophytes are important as they provide refuge for zooplankton (which graze algae), consume nutrients (reducing their availability for algal growth) and protect sediments from disturbance by water movements or fish (thus reducing nutrient release).

Chemical conditions: algal development leads to a high oxygen demand/ (ow redox potential) on the sediment surface, through the decomposition of sinking algae, and increases the pH, through net CO_2 consumption. These factors facilitate phosphorus release from sediments, increasing internal loading and thus further algal development.

Biological conditions: turbid lake conditions and the absence of macrophytes generally lead to domination by planktivorous and benthivorous fish, with reduced populations of piscivorous species, thus reducing zooplankton populations (reducing grazing of algae) and stirring up sediments (accentuating trubidity and internal nutrient loading). Excessive algal development can also favour the appearance of blue-green algal species (cyanobacteria), which show low rates of population loss (low energy requirements/low mortality rates, reduced edibility and so reduced grazing, buoyancy control by gas vacuoles preventing sinking).

Lake resistance to changes in nutrient loading

The authors also indicate a number of other perturbations of the lake ecosystem with can prevent recovery from the algae-dominated, turbid state:

Loss of lake-edge wetlands: resulting either from drainage or simply from stabilisation of the lake’s water level. Marginal wetlands provide spawning areas for piscivorous fish, thus reducing populations of smaller fish which consume algae-grazing zooplankton. Wetlands also play an important role in removing nutrients from incoming or lake water, as well as stabilising and removing sediment particles.

Stocking with fish: high stocks of benthivorous fish (such as bream, carp) can destroy macrophyte populations and accelerate internal nutrient loading from sediments.

Toxic chemicals: can reduce populations of algae-grazing zooplankton.

As a result of these different factors and their interactions, **the response of shallow lakes to nutrient loading tends to be complex, and to be different for the process of eutrophication (increasing nutrient loading) to that of oligotrophication (decreasing loading).** Both clear and turbid lakes are resistant to changes in nutrient loading, and show the phenomenon of hysterisis: only at critical nutrient thresholds does the system show dramatic changes in algal biomass.

The authors describe a series of stages and events for the processes of nutrient enrichment:

Increase in external nutrient loading, but constant low concentrations in the lake water:
Nutrients are absorbed by sediments and by abundant macrophytes. Biomanipulation studies have shown that macrophytes can reduce total nitrogen levels in lake waters, so that nitrogen as well as phosphorus may be important limiting nutrients for algal production.

Increase of total phosphorus concentrations in the lake water, but not of algal biomass:
The clearing of algae by zooplankton grazers (which find refuge in the macrophyte community) control algal development.

Non-linear shift to the algae-dominated, turbid water state:
Macrophytes become overgrown with periphyton, or blooms of (maybe inedible) algae lead to deteriorating light conditions, and macrophytes disappear from significant areas of the lake. Also, nutrient loadings may coincide with increased levels of toxic pollution, reducing algae-grazing zooplanktons or macrophytes.

Increase in algal biomass roughly corresonding to nutrient limitation, then levelling off:
The slope of the phosphorus/chlorophyll ratio varies for different algal species and according to the availability of the phosphorus in the specific lake ecosystem. Above a certain nutrient concentration, this ratio again ceases to apply, as algal biomass is determined by the availability of light (depth, mixing, different factors affecting turbitity).

Phosphorus threshold

The authors suggest, on the basis of field data from Denmark (Jeppesen et al. 1990) that **the clear water state may be stable up to total phosphorus concentrations of around 0.1 mgP/l in larger lakes and even higher concentrations in smaller lakes (< 3 ha) where there is a strong impact of submerged plants.**

The authors develop a comparable series of stages and events for nutrient loading reduction:

Decrease in external nutrient loading, but only a small reduction in summer total P:
Summer total phosphorus concentrations may be largely controlled by internal loading from sediments.

Decrease in total P concentrations, but constantly high summer algal biomass:
Algal growth is limited by factors other than phosphorus levels (nitrogen, light…)

Decrease in biomass corresponding to nutrient load reductions:
Turbidity may decrease progressively, or make jump improvements with switches in algal species composition.

Shift to a clear water state:
If nutrient loadings are reduced to such a low level that algal development is limited and light penetration improves, macrophytes may reappear and the lake may switch back to a clear water state. A total phosphorus concentration of 0.05 mg/l or lower will often have to be achieved to allow this shift, assuming other ecosystem factors preventing lake recovery have been resolved. This shift may be inhibited by the factors indicated in the discussion above. Inedible *Oscillatoria* algae dominated lakes may produce more biomass at given nutrient concentrations than those with a mixed algal population, resulting in a lower nutrient threshold. Macrophyte re-establishment is more difficult in deeper lakes, so that again a lower total phosphorus threshold will have to be achieved to enable recovery.

Perspectives in Holland

Total phosphorus concentrations in Holland's surface waters have been significantly reduced, for example by 50% in the Rhine, but shallow lakes have in many cases not recovered to a clear water state.

The authors indicate that three problems must be resolved, as well as reducing nutrient loading, before restoration can be achieved.

Prevent* Oscillatoria *blooms: in many lakes the 0.25 – 0.5 mgP/l level needed to prevent *Oscillatoria* blooms will be difficult to achieve (Hosper 1997) so that additional switch mechanisms must be used. Flushing the lakes in winter with relatively clear water can be effective in removing *Oscillatoria*.

Prevent the algal-bloom mediated release of phosphorus from sediments: in some lakes, this effect can be avoided by flushing with water rich in carbonate and calcium ions (which reduce phosphorus release from the sediment)

Restore algae-grazing zooplankton and macrophyte populations: a significant reduction in planktivorous and benthic fish populations can in some cases enable recovery of macrophytes and sufficient development of zooplankton to control algal development and permit the return to a clear water state. This strategy is less likely to be successful in lakes dominated by inedible *Oscillatoria* algae. It may also be useful to restore floodable marshlands to provide breeding areas for piscivorous fish (pike) which can then naturally control other fish species. Near colonies, cormorants (fish eating birds) may also play a significant role in controlling fish species and so allowing algae-grazing zooplankton to develop.

"Stable states, buffers and switches: an ecosystem approach to the restoration and management of shallow lakes in the Netherlands". Wat. Sci. Tech. vol. 37 n°3, pages 151-164, 1998.

S. Hosper, Institute for Inland Water Management and Waste Water Treatment (RIZA, PO Box 17, 8200 AA Lelystad, Holland.

CLAY TREATMENT

Australia tests “Phoslock” river treatment

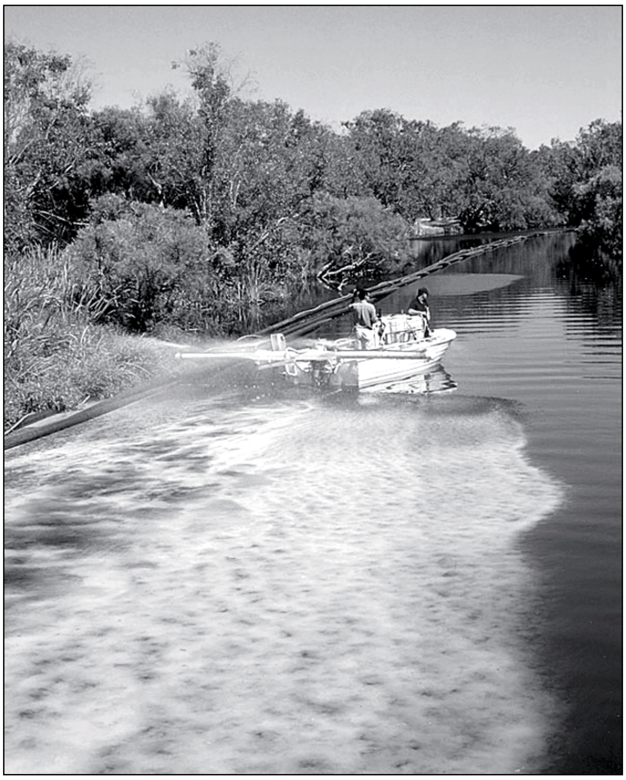
A 700-metre stretch of Perth’s Canning river is being used to test a new method for removing phosphorus from rivers and lakes. A clay-based substance called “Phoslock” is used, in a thin layer, less than a millimetre deep, on the bed. The full scale trial follows lab and large tank tests and will allow field assessment of the effects on phosphorus levels but also possible effects on algae, fish, vertebrates and water quality.

The project has been jointly developed by Dr Malcolm Robb, of the Water and Rivers Commission, and by Dr Grant Douglas; of CSIRO Land & Water. The aim is to prevent blue-green algal blooms by *considerably reducing aquatic phosphorus levels.*

The Canning river suffers not only from significant nutrient inputs, but also from low summer flow “so low that it’s more a lake than a river” according to Malcolm Robb. This results in frequent algal blooms, and often these are of the toxic blue-green classification.

The “Phoslock” clay is diluted and sprayed onto the water surface. It rapidly sinks to the river bed, **absorbing up to 90% of aquatic phosphorus,** and preventing remobilisation of phosphorus from the sediments. In certain stretches of the river, the project also involves oxygenation in order to remove nitrogen.

Within 24 hours after the application of Phoslock dissolved phosphate concentrations were reduced to below detection limits (5 micrograms/l) over a 700m section of the river and this was sustained for at least two weeks after the application (more recent data not yet available).



The Australian scientists emphasise that this treatment can only be an expedient measure, and that “**the most important thing is to understand how each river or lake system functions, how and when the nutrients enter it, how they are released from the sediment, and the conditions that trigger algal blooms**”. In the long term, catchment measures to cut nutrient flows into water are essential.

Press release from CSIRO available at http://www.csiro.au and type “phoslock” in Search.

Dr M Robb, Water and Rivers Commission. Dr Grant Douglas, CSIRO Land & Water, Private Bag, PO Wembley WA 6014, Australia. Grant.Douglas@per.dwr.csiro.au. Further information at: www.clw.csiro.au/staff/GDouglas/

AUSTRALIA

State of knowledge on limiting nutrients

The LWRRDC Occasional Paper 7/99, published by the Australian Land and Water Research and Development Corporation and the Murray – Darling Basin Commission is the outcome of a workshop organised at the Charles Sturt University, Wagga Wagga, in November 1997 by the National Eutrophication Management Program. The aim was to review the current state of knowledge regarding the role of different nutrients and other environmental factors in controlling algal development in fresh waters, particularly in the light of increasing evidence that nitrogen can be as important a limiting nutrient as phosphorus, and to produce a report in plain English for managers.

The papers presented at this workshop, concerning **limitations to algal growth in Australian fresh water systems,** are available from their authors at the addresses given in the appendices to the Occasional Paper at www.lwrrdc.gov.au/publicat/op0799/lnw_7_99.htm.

The LWRRDC Occasional Paper, put together by Alistair Robertson, summarises and explains the conclusions of this workshop.

In theory, the maximum phytoplankton biomass that can be supported by an aquatic ecosystem is determined by the nutrient supply and by light availability. When a nutrient which is essential for plant growth is unavailable (because it has been exhausted, or is locked up in unavailable forms) the phytoplankton growth will be “limited” by that nutrient. **Dissolved inorganic phosphorus and dissolved**

inorganic nitrogen are the key limiting nutrients, according to the literature, when their concentrations fall to around 10 and 100 µg/l respectively. Diatomaceous algae may in some circumstances also be limited by dissolved silicon concentrations, but these are not generally considered a nuisance group. There is no significant evidence of phytoplankton growth being limited by other (trace) elements in Australian fresh waters.

Nutrient limitation has been assessed by three main approaches:

- comparison of chemically-analysed concentrations of nutrients in waters with calculated cellular requirements of the phytoplankton population
- use of algal bioassay experiments where different nutrients are added to samples of water withand the natural phytoplankton population and algal development is recorded
- use of physiological indicators of the health of phytoplankton cells to indicate under-supply of one or more nutrients

Nutrient concentrations "of little value"

The paper emphasises that "**on their own, measurements of nutrient concentrations in water samples are of limited value in determining whether nutrients are limiting the growth and biomass yield of phytoplankton**".

One of the main reasons is that it is extremely difficult to obtain reliable measurements of concentrations of available nutrients. Firstly, when the concentration of the nutrient is low enough to imply cell growth limitation, the concentrations are too low to measure accurately. Secondly, only certain forms of phosphorus and nitrogen are actually available for uptake by algae cells. Thirdly, **the actual measured concentration of the nutrient in different forms is often not indicative of the concentrations actually available to algae,** because of relatively rapid cycling between different forms and between particle and sediment-trapped nutrients and dissolved available forms.

Whereas the dissolved inorganic forms NO_x and NH_4 seem to provide a fairly reliable indicator of nitrogen available for phytoplankton growth, phosphorus speciation is much more difficult because of its reactivity with particles of different sizes in the water. On the other hand, certain species of phytoplankton (blue-greens) can "fix" dissolved nitrogen gas to organic nitrogen, thus avoiding nitrogen limitation.

Chemical analyses of dissolved phosphorus are generally carried out on samples passed through a 0.45µ filter, but this still includes phosphorus associated with very fine particles and colloids, which may not in fact be available for algal uptake. Conversely, **phosphorus linked to large particles and on bed sediment, may be available to "buffer" dissolved phosphorus concentrations: as dissolved concentrations drop through algal uptake, phosphorus may be released from particles to a soluble form.** Low measured nutrient concentrations do not necessarily imply a limited supply, as the concentration can be maintained by cycling of internal sources on an "as required" basis.

A more reliable way to estimate available phosphorus levels is to use iron oxyhydroxide coated filter strips. These will rapidly adsorb available dissolved phosphates, resulting in the release of phosphorus from internal buffer sources, which will in turn be adsorbed to the strips. This method has been applied to a range of waters in the Murray – Darling Basin, showing that the "available" fraction can range from 20% to 100% of the total phosphorus present, with the unavailable fraction remaining attached to particles.

This work showed that the same total phosphorus concentration can correspond to widely differing levels of available phosphorus, and thus by implication to widely different levels of phytoplankton biomass.

The exchangeable phosphorus is desorbed from particles within around 24 hours, well within the time-scale of development of algal populations.

Nutrient ratios

Another widespread approach to predicting nutrient limitation is the comparison of total nitrogen: total phosphorus (TN:TP) ratios to the **Redfield ratio (C:N:P 106:15:1 by atoms).** The authors point out that the TN:TP ratio is only of any significance if phytoplankton growth is indeed nutrient limited, and is not being limited by other factors such as light.

The TN:TP ratio's value as a predictive tool is also strongly reduced by the fact that TN and TP measurements do not necessarily provide reliable estimates of nutrient concentrations actually available to algae (cf. above). In turbid or organic waters in particular, the presence of organic non-dissolved nitrogen forms associated with particles will render use of the ratio invalid. An improved ratio can be established by comparing dissolved inorganic nitrogen with "desorbable" phosphorus (using the iron strip method above).

The TN:TP ratio correctly predicted which nutrient would be limiting (as established by bioassays) in only one out of five samples from the Darling River at Bourke, for example, but DIN: 0.003µm filterable phosphorus gave correct predictions for the five samples.

Where nutrient recycling and re-supply from sediments and other internal sources is significant, the N:P ratio is unlikely to be a reliable tool.

The use of TN:TP ratios to predict blooms of nitrogen-fixing blue-green algae has been subject to substantial debate. Certain authors suggest that blue-green blooms are a risk at TN:TP atom ratios < around 60 but other authors conclude that there is no laboratory or field evidence for such a relation.

Vollenweider P- chlorophyll relation

The simple "Vollenweider" (1968) model which empirically relates summer chlorophyll concentrations to total phosphorus levels for lakes is surprisingly congruent for such a simplistic one-factor relationship, but **individual lakes can deviate markedly from the "expected" relation.** The result is that the **lake ecosystem response to reductions in phosphorus inputs can be disappointing.** Sas (1989) found that for 18 European lakes which had undergone phosphorus input reductions, seven did not show a significant decline in phytoplankton biomass.

Factors, such as light limitation, internal nutrient supply, and non-correspondence between measured nutrient concentrations and bio-availability may cause failure of ecosystems to react as hoped to nutrient load reductions. Consequently, before an expensive nutrient reduction strategy is implemented, it is important to develop and test relationships between phytoplankton biomass and the targeted nutrient(s).

The author also indicates that the Vollenweider relation is not suitable for river systems, because of the continual growth and loss of algae, cycling between organic and inorganic components and sediments, and the permanent supply of new nutrients and changes in concentrations due to flow. Australian rivers, in particular, undergo rapid changes in flow rates which make simple loading models inapplicable.

Nitrogen as often limiting as phosphorus

Bioassays involve taking samples of river water with the natural phytoplankton population and testing the response to the addition of different nutrients. This technique may not accurately measure in situ growth potential, because of nutrient re-supply from sediments which is "lost" in the bioassays. Further distortions occur where bioassays involve removing particles (which can be a significant source of nutrient re-supply) and adding cultured algae.

Nonetheless, bioassays give some insight into nutrient limitation conditions. In a review of a large number of bioassays in North American Lakes, Elser et al. concluded that enrichment with both nitrogen and phosphorus simultaneously almost always resulted in algal growth, whereas **nitrogen or phosphorus enrichment only produced growth in only about half of the cases, with nitrogen as likely to be limiting as phosphorus.** Similar results have been obtained from a range of rivers in the Murray Darling Basin.

Physiological studies provide an immediate indication as to whether the phytoplankton cells in a water sample are nutrient limited. The recently developed "Nutrient Induced Fluorescence Transient" assay (NIFT) uses transient fluctuations in chlorophyll-a fluorescence when a limiting nutrient is added. Application to samples from three Murray – Darling Basin field sites showed that **often neither nitrogen nor phosphorus is limiting, and that nitrogen limitation occurs as often as does phosphorus limitation.**

Other limitations to algal growth

Factors other than nutrient concentrations may often prevent phytoplankton blooms. These include flow, low temperatures, grazing by zooplankton and light limitation.

Sediments play an important role, both in contributing to turbidity during suspension (light limitation) and through release of dissolved nitrogen (through microbial processes) and dissolved phosphorus (both my microbial and inorganic chemical processes).

Small plants and surface bacteria, forming a biofilm on sediments and on other objects (including large water plants) can limit nutrient release from sediments, but if deprived of light, can generate anoxic conditions which accelerate phosphorus release.

Large water plants (macrophytes) can play an important role in the control of zooplankton in Australian aquatic habitats, by their own nutrient uptake from the sediments (through their roots), but more importantly by reducing sediment re-suspension (and thus reducing nutrient release), by providing a substratum for biofilm growth and by themselves subtracting a stock of nutrients into their tissue.

Australian waters are often turbid, with very varying flow rates, so that light availability is often the limiting factor for phytoplankton growth. Conditions that decrease turbidity by decreasing the flow rate and allowing settling, such as weirs and dams, can increase light penetration and lead to algal blooms.

"Limiting Nutrient Workshop 1997", A. Robertson, LWRRDC Occasional Paper 7/1999, published by LWRRDC and the Murray – Darling Basin Commission.

LWRRDC Land and Water Resources Research and Development Corporation, GPO Box 2182, Canberra, ACT 2601, Australia. Available on line at: www.lwrrdc.gov.au/publicat/op0799/lnw_7_99.htm.

CULTURAL OLIGOTROPHICATION

The need for sustainable nutrient management

Under the title "Cultural oligotrophication", the authors examine how changes in man's management of nutrients are leading to a structural impoverishment of upland area ecosystems and a non-sustainable use of mined mineral phosphates in fertilisers. Clean, aesthetically limpid lakes and rivers often imply declining fishery productivity. The authors suggest that it is time to revise current policies of nutrient elimination and to consider "ways of re-introducing nutrients in a balanced and ecologically sensitive way to restore lost production".

Whilst upland ecosystems have always been and continue to be largely susceptible to oligotrophication (lack of nutrients limiting productivity), man's activities over the last centuries have considerably accelerated nutrient transfers towards lowland waters (lowland rivers and lakes, coastal waters). This results from the use of water to transport wastes (sewage systems) and the centralisation of industry, agriculture and urbanisation, which together put an end to the traditional recycling of human and animal wastes to farmland, and from **major changes in land use such as drainage and cultivation of wetlands and intensive forestry.**

Over recent years, the resulting nutrient enrichment of surface waters has been largely targeted as a water management issue. The raised nutrient concentrations of lowland waters, often in combination with other factors such as changes in river flows (dams, weirs, channelization of rives, drainage of wetlands…) and ecosystem deterioration (reduction of grazer or macrophyte populations…), can contribute to algal growth and lead to water quality and amenity problems. **As a result, major investments have been made to remove nutrients from point sources, in particular phosphates from sewage works where they can be readily removed** and transferred to sewage sludge.

Causes of cultural oligotrophication

This has led to a situation where the authors identify a number of widespread causes of cultural oligotrophication:

- ***dams and reservoirs:*** Dams and weirs on rivers significantly increase the rate of retention and degradation of organic material above the obstacle to river flow, thus resulting in the transfer of nutrients to sediments which effectively act as a phosphorus trap. This results in low nutrient levels both in the dam water and reduced transfer downstream.
- ***drainage of wetlands:*** the extensive conversion of wetlands to marginally productive agricultural land over the last centuries, along with the accompanying channelization and straightening (ditching) of small tributary streams, has led to increased soil erosion, reduced water retention in soils, lowering of ground water levels and nutrient enrichment of ground waters. This results in greatly increased phosphorus export from such areas towards downstream, lowland areas. The consequent impoverishment of the newly cultivated soils leads to the need for annual fertiliser application to maintain productivity, further increasing nutrient export to streams and downstream lakes
- ***logging and clearance of forests:*** natural forests are essentially P-recycle systems but forest clearance (conversion to farmland) and modern forestry practices (clear-cut logging, access road and track construction, fertilisation…) have converted large areas into P-export zones. Logging represents a direct export of phosphorus in wood, and also results in nutrient loss from soil erosion because of reduced water retention in the soil of the cut area. In Sweden, the P content of wood exported from a cut coniferous forest was estimated at 10 kgP/ha, a significant proportion of the 40 – 45 kgP/ha estimated as present in the soil humus and mineral layers. Much of the phosphorus exported in wood ends up in saw mill and paper mill wastes and discharges in lowland areas.
- ***fish reductions:*** Migratory fish can represent a significant transport pathway carrying nutrients upstream from the sea back to freshwater streams and riparian zones. Pacific salmon adults, for example, die after spawning, recycling their body content of nutrients to freshwaters and riparian zones, where they can sustain productivity for the development of juvenile migratory and resident fish. The phosphorus imported to rearing lakes by adult salmon can represent more than a half of the total nutrient input to some ecosystems. Factors such as dams blocking fish migration, over-fishing or disappearance of fish populations because of other factors (pollution,…) will prevent this natural "nutrient pump" and lead to oligotrophication of upstream aquatic ecosystems.
- ***removal of anthropogenic nutrients:*** Since the mid-70's, phosphorus inputs to surface waters from point sources have been markedly reduced in developed countries, in particular through connection to sewerage and phosphorus-removal in sewage works. Phosphorus removed from sewage is increasingly not recycled, as agricultural spreading is limited. Large mesotrophic lakes have, as a consequence, shown

significant reductions in phytoplankton production, whereas shallow, lowland lakes have tended to remain eutrophic because of non-point sources and internal loading from anaerobic sediments.

- ***acid rain and climate change:*** Acidification of lakes and rivers, and liming which is often used to counter acidification can contribute to oligotrophication through a variety of mechanisms. These include reduction of phosphorus mineralisation (recycling of organic sediment P) or trapping of phosphorus on soil/sediment aluminium complexes, due to acidification; and precipitation of insoluble calcium phosphates by liming. Climate change is likely to accelerate oligotrophication through the combination of warmer summers and wetter, milder winters, leading to increased lake stratification and reduced water mixing.

Consequences of oligotrophication

The restoration of aquatic ecosystems and the reduction of nutrient inputs have in some cases allowed waters to achieve an aesthetically pleasing "clear" water state. However, this generally implies a relatively unproductive ecosystem, and may not be of benefit for recreational or commercial fishing activities.

The authors indicate that **declining fishery productivity is an "inevitable" consequence of changes in food web structure related to oligotrophication.** Annual primary production declines and is increasingly dependent on internal phosphorus recycling rather than external inputs. In parallel, food webs shift from high nutrient requiring diatom-based, short food chains to longer, less energy efficient picoplankton-based microbial food webs. The authors conclude that the moderately high levels of nutrient inputs necessary to support efficient, short food chains and healthy fisheries in freshwaters are usually incompatible with the low nutrient concentrations necessary to maintain visually "clear" water.

Marked declines in fisheries over the last 20 years in large European and North American lakes have been attributed to oligotrophication.

Evidence from southern temperate reservoirs suggests that **total phosphorus concentrations in water of 80 – 100 µgP/l will support the greatest biomass of game fish.** Other studies suggest that total phophorus concentrations in the 10 – 40 µg/l range would best support salmonid populations. However, this balance is very complex, and actual ecosystem quality and stability may also depend significantly on appropriate N:P ratios.

The authors conclude that it is necessary to move towards processes which enable phosphorus recycling and reduce global oligotrophication, in order to slow down the consumption of non-renewable phosphate rock through fertilisers, to enhance ecosystem CO_2 assimilation and to maintain protein production. This will require moves towards **phosphorus recovery and recycling from sewage works, restorative nutrient administration to upstream oligotrophic ecosystems** and **changes from wetland drainage and clear-fell logging to wetland restoration and sustainable forestry.**

"Cultural oligotrophication". Fisheries, Vol. 25 (5) 2000 pages 7-14

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VIEWPOINT

Struvite – Problem or Resource?

Phosphorus removal has become an essential part of wastewater treatment in many areas due to the implementation of the Urban Wastewater Treatment Directive (91/271). The directive deals with the reduction in nitrogen and phosphorus for effluents discharged into potentially eutrophication "sensitive" waters. The processes of removing phosphorus are well understood and either chemical phosphorus precipitation or biological nutrient removal (BNR) are used. BNR reduces both dissolved nitrogen and phosphorus, and can be either retrofitted or included as the standard design for domestic wastewater treatment plants. What is of particular relevance here is the treatment of the sludges formed as a result of BNR and the sidestream processes employed to stabilise and deal with them.

Phosphorus is normally present in wastewater as orthophosphates; PO_4^{3-}, HPO_4^{2-}, and H_2 PO_4. Normal concentrations of Phosphorus entering a specific works will obviously vary, however 10 mg/l is a reasonable value to expect in the UK. In this form Phosphorus is termed bio-available and during biological treatment processes such as activated sludges of BNR technologies, orthophosphates are taken up and stored as inert polyphosphates within the biomass. **Waste sludge's entering a digester, however, tend to release phosphorus since the polyphosphates are hydrolysed, and this can be followed by the refixation of phosphates as a number of species one of which is magnesium ammonium phosphate or struvite.** Struvite forms quantitatively according to polyphosphate hydrolysis and subsequent Mg availability. As soon as conditions of supersaturation occur, struvite formation will take place.

Struvite formation

Struvite is magnesium ammonium phosphate ($MgNH_3PO_4$) and forms a **hard crystalline deposit** when the molar ratio of $Mg:NH_3:PO_4$ is greater than 1:1:1. Struvite is most likely to form in areas of increased turbulence as its solubility decreases with pH (Figure 1). In the UK most examples of struvite formation have been found downstream of the anaerobic digesters, where high concentrations of released soluble phosphates are present, in the digested sludge or sludge liquor pipelines. Table 1 identifies the processes reported to be prone to struvite formation, Figure 2 shows the severity of the problem where the bore of the pipe reduced to 60 mm from 150 mm over 12 weeks.

Table 1. Impact of struvite forming in pipes and the associated processes.

Process Affected	*Result*
Digested sludge pipeline.	*Bore of pipe reduced from 0.3m to 0.15m.*
Pipeline from sludge holding tank to centrifuges	*Bore of pipe reduced from 100mm to 50mm*
Vertical PVC pipe (digester effluent)	*150 mm diameter reduced by a mean value of 10.65 mm*
Horizontal acrylic pipe (digester effluent)	*142 mm pipe diameter with negligible struvite build up*
90 degree elbow PVC piping (digester effluent)	*by a mean value of 28.38mm 150 mm pipe diameter reduced*
Centrate Discharge line	*150 mm rubber pipe reduced to 60 mm in 12 weeks*
Centrate discharge lines	*Bore of pipe reduced from 203mm to 38mm in 1 month*

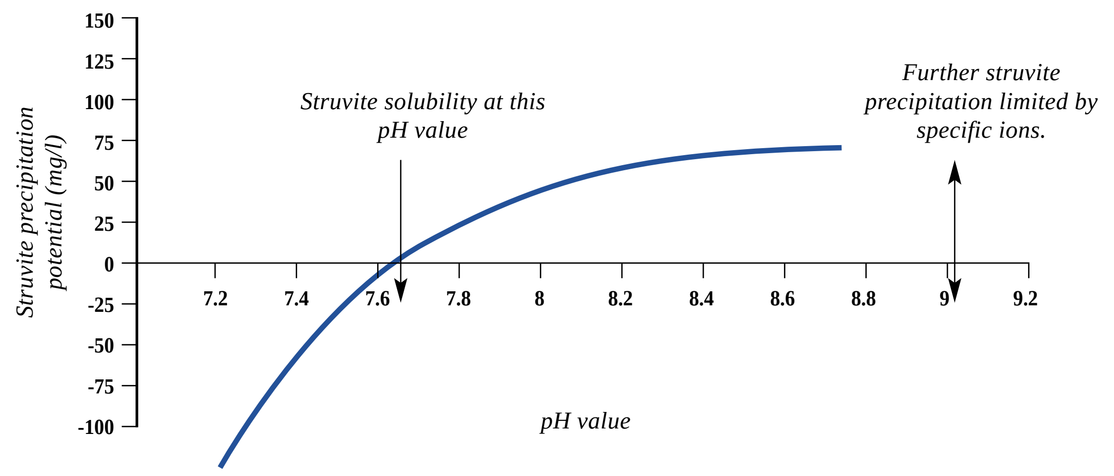

Figure 1. Effect of pH upon struvite formation.

A recent review of struvite formation from wastewater identified the physical attributes of a wastewater treatment plant which contributed to the deposition of struvite. These were:

- a large increase in surface area to volume ratio
- roughness of the internal surface of the pipeline
- pressure drops at bends, venturis and pumps

The first two factors increase the number of crystal growth sites whilst the final factor leads to a driving off of CO_2 which leads to a **pH increase.** Changing the pH in digester supernatant from 7.8 to 8 can lead to double the amount of struvite being formed.

The operational and maintenance problems struvite causes are predictable. Solutions so far have included simply chipping away the scale using a hammer and chisel or dosing acid to dissolve the encrusted material.

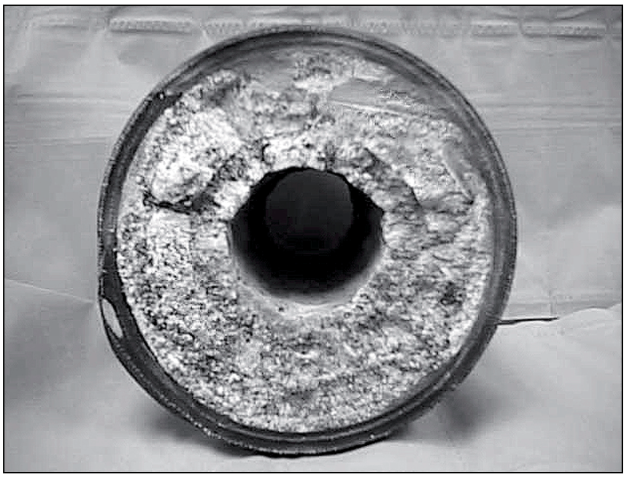

Figure 2. Struvite found in the centrate liquor pipe.

The chemistry of struvite precipitation

The formation of struvite is dependant upon the solubilities of the respective ions in solution. Magnesium and phosphate ions decrease in solubility as the pH increases whereas the ammonium ions are volatilised as ammonia gas forms at pH values greater than 9.8. Struvite formation can be described by the equation below:

$[Mg^{2+}][NH_4][PO_4^{3-}] = K_{sp}$

Essentially this equation says that if the concentrations of magnesium ammonium and phosphate ions are greater than the value denoted by K_{sp} then the solution will be supersaturated with respect to struvite and precipitation will occur.

A number of values have been quoted in the literature with respect to the K_{sp} value. **The application of these literature figures to real sludge treatment processes may not be possible.** The issue regarding K_{sp} values is that a real sludge liquor will contain numerous ions in solution potentially forming complexes with magnesium, ammonium and phosphate ions essentially increasing the solubility of struvite in solution. Furthermore the solubility product is only accurate for a single pH value. Finally when using the K_{sp} value as a basis for calculating the maximum concentration of ions in solution before supersaturation is reached, a series of values is obtained which bares little resemblance to the concentrations and molar ratios of those ions in a real wastewater or sludge liquor (Table 4).

For these reasons a conditional solubility product can be calculated producing a more representative figure upon which to base struvite solubility. These figures can be

Table 2. pK_{sp} values reported by a number of authors and the respective ionic concentrations at the published K_{sp} value.

Author	*pK_{sp}*	*Mg^{2+}(mg/l)*	*NH_4^+ (mg/l)*	*PO_4^{3-} (mg/l)*
Taylor et al., (1963)	*13.15*	*0.993*	*0.745*	*3.93*
Stumm and Morgan (1981)	*12.36*	*1.82*	*1.37*	*7.2*
Bube (1910)	*12.6*	*1.51*	*1.14*	*5.99*
Buchanan et al., (1994)	*12.36*	*1.82*	*1.37*	*7.2*
Ohlinger et al., (1998)	*13.26*	*0.912*	*0.684*	*3.61*
Aage et al., (1997)	*12.94*	*1.17*	*0.875*	*4.62*
Borgerding (1972)	*9.4*	*17.7*	*13.2*	*69.9*

Table 3. Conditional solubility products (pK_{so}) calculated using a series of dissociation constants over a pH range.

pK_{sp}	*Conditional Solubility Product (pK_{so})*				
	pH 7	*pH 7.5*	*pH 8*	*pH 8.5*	*pH 9*
13.15 (Taylor et al., 1963)	*7.44*	*8.17*	*8.76*	*9.26*	*9.65*
12.6 (Bube 1910)	*6.89*	*7.93*	*8.21*	*8.71*	*9.1*
13.26 (Ohlinger et al., 1998)	*7.55*	*8.28*	*8.87*	*9.37*	*9.76*

derived from a series of equations and compared with the figures given in table 2. Changes in the pH will either drive the equations to the left or to the right until equilibrium is reached.

Equations used to determine pK_{so} values:

$MgO + H_2O \rightarrow Mg(OH)_2$

$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^- \quad K=1 \times 10^{-11.3}$

$HPO_4^{2-} + OH \rightarrow PO_4^{3-} + H_2O \quad K=1 \times 10^{-12.37}$

$NH_4 \rightarrow NH_3 + H^+ \quad K= 1 \times 10^{-9.2}$

Control of struvite precipitation.

Struvite can be prevented by both chemical and biological methods. Chemical controls fit into three main categories: those that affect solubility, those that alter the growth mechanisms of the crystals and those that act as dispersants. Since struvite formation is based upon equilibria, most treatments have been based upon either reducing phosphate concentrations by forming other phosphate containing salts, or reducing the pH to one where struvite formation is less prevalent. Dosing with iron(III) salts to remove the phosphorous is the most commonly reported method although can produce large quantities of sludge.

Deliberately dosing with the limiting ion (usually Mg) that is preventing more struvite from forming may provide an effective method of controlling struvite formation. The basic idea being this: **if the water chemistry is such that struvite is going to cause a problem, why not make it form somewhere where it can cause no major problems and can potentially be recovered.**

Struvite may represent a **cheap yet reasonably effective fertiliser due to its chemical attributes namely nitrogen and phosphorus.** Current prices for struvite are around £670 per tonne. From table 1 this would make one litre of water from sites A and B worth 13 p/litre and 7 p/litre respectively. At a reasonable sized works (10 tonnes of sludge per day) this equates to over £7 000 per day. Table 2 shows analytical data for a range of real digester liquors showing the calculated mass of struvite that can precipitate.

Struvite recovery

Struvite has a potential use as a fertiliser. Natural sources of struvite include guano deposits and cow manure and it has been shown to be a highly effective source of nitrogen, magnesium and phosphorus for plants foliar and soil applications.

Struvite recovery from a treatment works not specifically designed for such a purpose would undoubtedly prove challenging. However, it is important to note that full-scale struvite recovery plants have been operating in Japan for several years now, treating industrial wastewaters and sewage. Research is ongoing with respect to the potential recovery and removal of struvite from domestic and industrial wastewaters and a number of pilot plants have been tested Whether struvite recovery will be adopted by the water industry as a routine process in wastewater facilities will surely be determined by economic issues related to sewage plant operation and to the potential market value for recovered struvite.

This article is an update, prepared by the authors for the SCOPE Newsletter, of the article of the same title published in the UK water industry magazine "Wet News" on 15th March 2000.

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Table 4. Concentrations of magnesium, ammonium and phosphate ions found in digester liquors and the potential for struvite formation.

Site of Study	*Mg^{2+} (mg/l)*	*NH_4^+ (mg/l)*	*PO_4^{3-} (mg/l)*	*Struvite formed*	*Value*/litre*
Site A (Durrant et al.,(1999)	*35*	*905*	*1010*	*192 mg/l*	*13*
Site B (Booker, N. 1999)	*20*	*800*	*300*	*106 mg/l*	*7*
Site C (Borgerding, 1999)	*17.5*	*13.1*	*69.5*	*0 mg/l*	*0*
Site D (Doyle et al., 2000)	*25*	*793*	*64.4*	*97 mg/l*	*7*

**Value – potential amount of struvite in 1 litre of digester liquor@£670/tonne*

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SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Sewage sludge disposal

EU considers tighter sludge spreading rules

The European Commission's "Working Document on sludge, 2nd Draft" (12/1/2000 ENV.E.3/LM) proposes to significantly tighten limits for heavy metals and other pollutants in sludge used for agricultural spreading or otherwise spread on soils. The objective is to maintain or improve rates of recycling of sludge nutrients and organic matter, thereby restoring public confidence and ensuring environmental compatibility of sludge spreading.

However, there is a risk that **stricter regulations may, in the short term, push water companies to seriously consider other disposal options, in particular incineration**.

The Working Document not only proposes new limit values (for immediate, medium and long term application) for different contaminants in sludge, it also **defines how sludge can be applied to different types of crop/ land use and requires a certification process** for all sludge spreading, including laboratory analyses. The Document includes not only sludge from municipal sewage works, but also sludges from septic tanks as well as the food, paper and leather (where chromium is not used) industries.

======== Septic tanks ========

Septic tank sludges will not be permitted to be spread directly on land but will have to be transported to sewage works for treatment.

All sludges will have to undergo a minimum processing regime before spreading, involving either thermal drying, thermal treatment or composting, digestion or stabilisation at pre-determined combinations of temperature and time. A three-tier system of treatment classification is established, with spreading on certain crops or in certain situations requiring one of the higher standards of treatment. The spreading of sludge in natural forests and woods is no longer permitted.

Producers will ultimately be responsible for the quality of the sludge supplied, even where there are intermediaries ensuring marketing and spreading. The producers will have to **guarantee "the suitability of sludge for use"** (compatibility with EU requirements). They must also install an independently audited quality assurance system and carry out sampling and analysis of sludges (a table of frequencies and tests is set out in the working document) in a certified laboratory, authorised and monitored by the competent authority.

======== Limit values ========

The Working Document proposes **limit values** for :

- **soils** : spreading prohibited on soils which exceed these values for one or more heavy metals ; also spreading must not result in final soil values exceeding the limit values

- **sludges** : spreading not to take place if one or more sludge heavy metal or listed organic compound limit exceeded (limit values for immediate application are proposed, but also limits to be introduced progressively over the medium and long term)

- maximum annual quantities of **heavy metals** to be applied in sludge per hectare of soil

Limit values proposed by EU Commission working document for contaminants in sludges for use on land (sludge not to be used if one or more value exceeded).

Contaminant	**Directive 86/278**	**proposed immediate**	**proposed medium term**	**proposed long term**
Heavy metals (mg/kg dry matter)				
Cadmium	20-40	10	5	2
Copper	1,000-1,750	1,000	800	600
Mercury	16-25	10	5	2
Nickel	300-400	300	200	100
Lead	750-1,200	750	500	200
Zinc	2,500-4,000	2,500	2,000	1,500
Organic compounds (mg/kg dry matter)				
Sum of halogenated organics (AOX)	not addressed	500		
Linear alkylbenzene suphonates	not addressed	2,600		
Di(2-ethylhexyl phthalate	not addressed	100		
NPE (certain nonylphenol and nonylphenolethoxylates)	not addressed	50		
Sum of certain polycyclic aromatic hydrocarbons (PAH)	not addressed	6		
PCB (sum of indicated polychlorinated byphenils)	not addressed	0.8		
dioxins PCDD/ dibenzofuranes	not addressed	0.1 mg toxic equivalent/kg		

======== Difficulties in meeting targets for UK ========

The UK's Environment Ministry (DETR) has released figures (see ENDS report 301) showing that the UK's 1996/97 90 percentile values are higher than the proposed long term limit values for cadmium, copper, mercury and lead, with mercury 90 percentile values already at the proposed initial limit value.

The UK would have difficulty meeting the limit values. Water companies would have to tighten trade effluent consents for industries, but this would not resolve the issue of copper levels, for which the main problem is copper from domestic plumbing piping.

The **proposed limits for dioxins and PCB's** of 0.1 and 0.8 mg/kg can be compared with new limits proposed by the US Environmental Protection Agency (EPA) in December 1999 of 0.3 mg toxic equivalent/kg for the sum of dioxins, furans and certain coplanar PCBs (see : http://www.epa.gov/ost/biosolids).

======== Realism or consumer confidence ? ========

The objective of the EU Commission's proposals is to **ensure a long-term future for sustainable agricultural use of sewage sludge (recycling or nutrients and organic matter)** by restoring consumer confidence through strict contamination limitation requirements. The risk is that water companies will find it so difficult to meet the stricter limits that they will instead choose to accelerate investments in other sludge disposal routes, in particular incineration.

Reacting to a first draft of the Commission's working paper, which included significantly stricter limits in the short Ð medium term, the UK's Environment Ministry suggested that it would lead to an increase in incineration from 17% of sludge in 1999 to around 35%.

One possibility for avoiding this negative consequence of tighter environmental requirements for agricultural re-use, would be to set recycling targets as well as sludge quality limit values.

The EU Directive 86/278 concerning sewage sludge spreading is available at : http://europa.eu.int/eur-lex/en/lif/dat/1986/en_386L0278.html

The EU Commission's "Working Document on Sludge" is available on request from envinfo@cec.eu.int.

SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Pot trials

Struvite proves a good fertiliser

This study's aim was to look at the reaction products produced in soil by three commercial fertilisers and to study the solubility and fertiliser value of these products. Struvite (magnesium ammonium phosphate), which can be recovered from sewage and other phosphate containing waste streams, was detected as a soil reaction product for two of the fertilisers studied.

The plant phosphorus uptake and growth for the different reaction products identified, which included struvite, were then assessed using 45-day pot trails of gram (Cicer arietinum L.).

Struvite ($MgNH_4PO_4.6H_2O$) appeared as a soil reaction product for APP = ammonium polyphosphate and for DAP = diammonium orthophosphate fertilisers. The pot trials thus compared struvite with these two fertilisers, with SSP (single super phosphate fertiliser), and with three other soil reaction products (each laboratory prepared crystalline precipitates) :

- brushite : $CaHPO_4.2H_2O$
- variscite : $AlPO_4.2H_2O$
- strengite : $FEPO_4 . 2H_2O$

======== Pot trials ========

The pot trials used gram (var. H208), irrigated as required, and harvested 45 days after sowing. The trials used 5 gram plants per pot, with triple random duplication.

The soil used was collected from an upland area of Ranchi, Bihar, India. It was acidic (pH 5.2), loamy and low in organic carbon (0.37%).

At the commencement of sowing, 8mg/kg soil K (as KCl) and 9 mg/kg soil N (as urea) were applied.

The phosphate compound to be tested was added at sowing, in the soil, below the seeds at 6 and 12 mg/kg soil dosages.

======== Struvite as a fertiliser ========

Struvite gave consistently better results for both plant P-uptake and growth (measured as oven-dry plant mass at the end of the 45-day trials), when compared with the three other soil reaction products.

When compared with the three commercial fertilisers, struvite gave the results in Table 1. (see below)

The authors indicate that Lindsay and Taylor (1960) also reported that **struvite was a good source of phosphorus for crops, almost equal in efficiency to monocalcium phosphate.**

They conclude that **struvite “proved to be superior or equally effective” as a source of phosphorus** for gram plants compared to the three commercial fertilisers tested.

Table 1

Product used	Plant dry weight (g/pot)		Plant P uptake (mg/g in plant)	
Phosphorus dosage (mgP/kg soil)	6	12	6	12
struvite	**0.475**	**0.705**	**0.209**	**0.404**
APP ammonium polyphosphate	0.665	0.683	0.167	0.393
DAP diammonium orthophosphate	0.590	0.645	0.218	0.376
SSP single super phosphate	0.605	0.616	0.197	0.338
control	**0.406 at zero added P**		**0.289 at zero added P**	

chick pea

SCOPE Newsletter editor’s note : the performance of struvite is probably dependent on soil pH, and may be better in the acidic soils used for these trials than in many temperate soils.

SCOPE would welcome any information, trial results or literature readers may have regarding the fertiliser value of struvite in different conditions.

KAP Ref: “Characterization of soil-fertilizer P reaction products and their evaluation as sources of P for gram (Cicer arietinum L.)”, Nutrient Cycling in Agroecosystems 46, pp. 71-79, 1996.
Ghosh G., Mohan K. and Sarkar A., Dept. Soil Science and Agricultural Chemistry, Birsa University, Kanke, Ranchi 834006, India
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SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Agricultural leaching

Phosphorus in tile drainage flows

Phosphorus concentrations and forms were analysed in tile drainage waters at 27 sites underneath intensively cropped farmland in the Saint Lawrence lowlands area, southeast of Montreal, Quebec, Canada. The results suggest that flat, clayey soils of medium to rich P status may be particularly at risk of exceeding phosphorus concentration standards for surface waters.

The 27 sampling sites were at drain outlets from underneath nine different neutral to slightly alkaline, poorly drained soil plots, mainly used for maize (Zea mays) and soybean (Glycine max) crop rotation. Tile drains in the area are usually located in the C-horizon, more than 90 cm below the soil surface. Samples were collected in the spring and the autumn of 1994, and in the autumn of 1995. Samples were tested unfiltered for total P (TP), soluble inorganic (reactive) phosphorus (SRP) and for dissolved organic carbon (DOC), and, after 0.45µm filtration, for total P and soluble inorganic phosphorus (SRP). Dissolved organic phosphorus was taken to be the difference, following filtration, between total phosphorus and SRP).

For each site, an A-horizon soil sample was analysed for available P (Meklich-III extractable P):

- 9 exceeded 112 mg $M^{III}P$/kg (excessive available P)
- a further 12 exceeded 53 mg $M^{III}P$/kg (adequate P fertility for maize and soybean).

======== High drainage water phosphorus levels ========

Total phosphorus concentrations in the sampled drainage waters varied widely, from <0.01 to 1.17 mgTP/l, with significantly higher levels in 1994 than in 1995, particularly for the sites sampled in the autumn of 1994 (when sampling came after a significant rain event following a dry month).

Background surface water phosphorus concentrations in the area are < 0.02 mgTP/l and a local “standard” for surface water for phosphorus is 0.03 mgTP/l.

This 0.03 mgTP/l “standard” was exceeded in drainage waters for 14 out of 27 sites in 1994 and for 6 out of 25 sites in 1995 (2 sites could not be sampled in 1995 because the drain outlets were below the ditch water level). 10 of the 14 sites with total phosphorus drainage water levels above 0.03 mgTP/l (1994) were clayey soils.

The implications of these levels of agricultural phosphorus are relatively difficult to assess, particularly as data regarding phosphorus drainage from natural, undisturbed soils in the area are not available.

======== Forms of phosphorus in drainage water ========

The proportion of total phosphorus (TP) present as soluble reactive phosphorus (SRP = inorganic) and dissolved organic phosphorus (DOP) varied widely from site to site and between years. The proportion DOP/TP was however significantly lower in 1994.

Taking site averages from both years, **DRP/TP ranged from 0-59%, DOP/TP from 0-79% and particulate phosphorus from 2-96%**. The authors indicate that the proportion of particulate phosphorus tended to be higher when total phosphorus was high.

The concentrations of phosphorus present as particulates and soluble inorganic (SRP) showed significant variations between 1994 and 1995, whereas dissolved organic phosphorus did not. Also a weak logarithmic correlation was found between dissolved organic carbon and dissolved organic phosphorus. The authors suggest that this may be related to a **relatively constant background level of dissolved organic phosphorus in drainage waters**, attributable to a mobile form of phosphorus. This corresponds to Schoenau and Bettany (1987) who noted that a high proportion of organic phosphorus was associated with the mobile fulvic acid fraction, susceptible to leaching.

Ron Vas et al. (1993) also reported a **strong relationship between DOP and DOC** and suggested that DOP was mobile and might contribute significantly to phosphorus loss to groundwaters. Chardon et al. (1997) found that DOP was the largest fraction of phosphorus below 50 cm depth, even in soil receiving only mineral fertilisers, and that the addition of crop residues increased DOP levels and enhanced phosphorus leaching.

The authors suggest that DOP probably originates from native soil phosphorus fractions and is mobilised by soil microbial activity stimulated by carbon inputs. They conclude that **"the generalised assumption that most mineral soils are not at risk for P leaching needs to be refined. In medium to excessively P-rich, flat and tile drained soils, P loss in subsurface waters is very likely to contribute to the observed eutrophication of surface waters."**

"Forms and concentration of phosphorus in drainage water of twenty-seven tile-drained soils". Journal Env. Quality, 27 pages 721-728, 1998.

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SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Lysimeters

Phosphorus leaching from soils

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20 1m wide, 1.25m deep lysimeters were used at the Falkenburg research centre, Germany, to test phosphorus leaching from two types of soil underneath grassland, winter barley/oats, winter wheat, sugar beet, maize, potato and alternated cultures with different levels of fertiliser application (manure and/or mineral phosphate fertiliser), as well as under fallow land and reforested land.

Soil samples were used to calculate total soil phosphorus and amounts of sequentially extractable forms (total P, resin extractable labile P, $NaHCO_4$ extractable, NaOH extractable, H_2SO_4 extractable, residual P). Soil leachate water was collected and both the volume of leachate and the concentration of total phosphorus, were analysed monthly enabling annual phosphorus leachate loss to be calculated.

Soil phosphorus contents were in the range 435-1134 mg/kg, comparable to those of the soil parent material, indicating no significant anthropogenic phosphorus enrichment. The proportion of labile (resin adsorbed) phosphorus was 8-18%, similar to that reported in other German manured soils (Leibweiner, 1996).

======== Mobile phosphorus in soils ========

Higher contents of very labile phosphorus forms (resin adsorbable) tended to occur under arable cultures whereas the content of relatively available phosphorus ($NaHCO_3$ extractable etc) followed the order grassland >arable land > fallow. This may result from the intense root and rhizosphere effects of grass and larger microbial activity, leading to increased cycling of moderately labile forms of phosphorus.

Soils receiving large mineral fertiliser application rates (25-60 kgP/ha) usually had higher labile phosphorus contents, although the relationship was not linear. Furthermore, as indicated later, this did not apparently result in increased phosphorus leaching.

Overall, grassland on sandy soil and intensive root crop/grain crop rotations on loamy sand showed the largest amounts and percentages of soluble phosphorus fractions.

======== Phosphorus leaching ========

The **mean annual concentrations of phosphorus in the leachate waters collected in the lysimeters reached 0.8 mgP/l (total phosphorus)** in some cases, with an overall average of 0.16 mgP/l. This corresponded to total phosphorus losses of up to 3.2 kgP/ha/year, with an average for all lysimeters (with non zero leachate volume collected) of 0.3 kgP/ha/year.

These values are similar to those reported by Sharpley & Menzel 1987 but are lower than those modelled by Breeuwsma *et al*. 1995 for manured soils in Holland.

In lysimeters using the same soil type and culture, leachate losses did not relate to rates of mineral fertiliser application. However, **leaching was significantly related to the type of agricultural management**, but not in as might be expected. In order of decreasing observed leaching, the authors indicate the following comparison between different types of land management : grassland and arable cultures with mineral fertilisers > less intensively used soils with low fertilise inputs > arable cultures with organic and mineral fertilisers.

$NaHCO_3$ and acid oxalate extractable phosphorus contents of soils were positively correlated with the concentrations of phosphorus in leachates and leaching phosphorus losses.

No significant correlations were found, however, between DLP or H_2O P and leaching losses, which supports doubts about the usefulness of soil P test values (as developed to assess the supply of phosphorus to crops) as a tool for predicting phosphorus leaching.

The authors conclude that **agricultural management which conserves soil organic matter and increases biological activity (such as permanent grassland or manure application) will increase the proportion of labile phosphorus in the soil, desirable for crop nutrition but more susceptible to leaching.**

The lysimeters which showed the lowest phosphorus leaching were those with intensive root crop/grain crop rotations with high phosphorus fertilisation rates. This means that any shift from intensive to extensive land use will need to be gradual and accompanied by management strategies if it is not to result in an increase in phosphorus leaching.

“Management effects on forms of phosphorus in soil and leaching losses”. European Journal of Soil Science, n° 50, pages 413-424, Sept. 1999.

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SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Manures on grassland

Phosphorus leaches to drains through rapid transport pathways

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Flow rates and phosphorus concentrations and forms were studied in the tile drainage water flowing from underneath two sites in the Kleine Aa subcatchment of Lake Sempach, in the central Swiss plateau (altitude 505 - 670 m, slope 5-10%). The sites studied are permanent grassland, used for intensive dairy and pig farming (stock density of 3.0 dairy cow/ha equivalent) and are cut 5-7 times/year, with manure application following cutting.

Tile drains were installed around 100 years ago 50Ð100 cm below the soil surface and the study looked at discharge waters flowing out of the drains into a brook. Whenever significant discharge occurred, samples were automatically collected every 15 minutes and mixed in pairs to give 30 minute averages. Discharge flows from the drains were measured and logged at 15 minute intervals. Precipitation was measured using a rain gauge located between the two sampling sites.

Phosphorus was analysed in the drainage water samples as follows :

- total phosphorus (TP) was assessed before filtration
- soluble reactive phosphorus (SRP, which is mainly inorganic) was measured after 0.45µm filtration
- total P after filtration was used to indicate total dissolved phosphorus (TDP)
- particulate phosphorus (PP) was calculated as the difference in total P before and after filtration
- dissolved organic phosphorus (DOP) was calculated as the difference between TDP and SRP

In one case, the inorganic phosphorus adsorbed to colloids was also assessed, by taking the difference between SRP in 0.45 µm and 0.05 µm filtrates.

The analysis of drainage waters was completed by assessments of the depth distribution of water extractable phosphorus in soils at the sites (these showed that phosphorus was mainly present in the upper 30 cm of soil) and by sprinkling experiments using blue dye to study water flow patterns and speeds within the soils.

======== Drainage flows and P discharges ========

Flows and phosphorus discharges were measured for seven rain events at site I and for 12 at site II, giving a total of 503 sets of 30-minute data. Drainage flow was continuous at site I, even during the driest periods of the year, whereas at site II, it generally stopped a few days after precipitation.

Measured **concentrations of SRP varied from 1.61 to 155 µmol/l, and were correlated with the flow rate for nearly all the discharge peaks**. At site II, which was managed by just one farmer, manure applications were noted and showed some influence on SRP concentrations: two rain events occurring within 1-2 days of manuring showed extremely high SRP concentrations, although other high SRP levels did not show an identifiable relationship to manure applications.

========= Available phosphorus loads =========

Soluble reactive phosphorus (SRP), which is the form most available to plants and so most susceptible to contribute to eutrophication, made up an average of 50% of phosphorus discharges at site I and 70% at site II. Particulate phosphorus (PP) was also significantly present, whereas levels of dissolved organic phosphorus (DOP) were very small despite the regular manure applications. When colloidal phosphorus was assessed, this was found to make up an average of 12% of discharged phosphorus.

A base flow phosphorus discharge concentration of 1.6 µmol/l was estimated for site I. Total phosphorus load from the drainage discharges to the nearby brook was estimated, on the basis of the measured values for the recorded discharge events. This gave estimates of SRP leaching of 227 gP/ha over two and a half months at site I (May, June, October) and 1290 gP/ha at site II over the whole growing season (6 months), respectively arithmetically equivalent to **around 1300 and 2600 gP of SRP/ha/year**.

The figure for site I does not include the major flood event and the series of large discharges which followed it in May, because the site I instrumentation was damaged by this flood, whereas these discharges alone accounted for around 2/3 of all phosphorus losses from site II.

The 95% confidence levels for these estimates are very large, being 21% for site I and 36% for site II.

========= Rapid infiltration pathways =========

Dye sprinkling experiments, with irrigation at levels set to avoid run-off (5 mm/h at site I, 10 mm/h at site II, on 1.5 m x 1.5 m plots), showed that, although the dye only infiltrated 2-5 cm into the general bulk of the soil, a substantial proportion of the dye rapidly penetrated down to a depth of about 80 cm along preferential flow pathways at both sites. **Worm burrows (probably *Lumbricus terrestris L.*) were the dominant penetration pathway**. These were observed to be present in high densities everywhere throughout this area of grassland.

The fate of the dye penetrating these pathways differed between the two sites. At site II, after one day of sprinkling, many of the burrows were full of water, indicating little exchange with the surrounding bulk soil, but dyed water appeared in an open ditch 4.5 m downhill of the sprinkling plot less than two hours after the start of dye sprinkling. The dyed water emerged from pores with a diameter of 1-2 mm, situated below the water level of the ditch. By digging uphill, the lateral transport was shown to be occurring in the water-saturated zone of soil more than 1m below the surface, perhaps in preserved ancient root channels which are specific to the soils in this area.

At site I, on the other hand, large blue patches had developed in the bulk soil underneath the sprinkling plot after one day, showing s**ubstantial lateral transport.**

The authors conclude, as already suggested by Flury (1994), that **in agricultural soils vertical preferential flow is the normal case and not the exception**. The immediate response of SRP concentrations in drainage water to manure application at site II strongly suggests that some of these preferential flow channels are hydraulically connected to the drainage system, allowing phosphorus to pass rapidly from the topsoil to the tile drains.

The study sites are situated in the catchment of Lake Sempach, which is subject to eutrophication. Swiss water quality goals indicate that SRP losses from agricultural land in the catchment should not exceed 400 gP/ha/year on average. However, the authors emphasise that the observed values suggest that **these levels are largely exceeded by the drainage water on its own**, to which must then be added surface run-off.

"Preferential transport of phosphorus in drained grassland soils". J. Environ. Qual. 27, pages 515-522, 1998.

C. Stamm, H. Flühler, J. Leuenberger, H. Wenderli, Institute of Terrestrial Ecology, Soil Physics, Grabenstrasse 3, 8952 Schlieren, ETHZ, Switzerland. R. Gächter, Swiss Federal Institute for Environmental Sciences and Technology (EAWAG), Limnological Research Centre, 6047 Kastanienbaum, Switzerland.

SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Phosphorus cycle

Significance of atmospheric inputs

Dust and aerosols containing phosphorus are transported across the world, from erosion to of phosphorus containing soils, biological processes, combustion and other sources, accentuated by human activities (10-20% of atmospheric phosphorus). The evaluations of atmospheric phosphorus deposition in literature may often be inexact, because of difficulties in measurement or experimental method, but deposition is estimated at 0.04-2 kgP/ha/year.

Atmospheric phosphorus can be found in both organic and inorganic dust particles. Particles of organic origin, such as pollen, will contain phosphorus as do all living organisms. Mineral dust will contain varying levels of phosphorus depending on its source: dust from the Atlas region of North West Africa, for example, contains 0.2%P. Other natural sources are volcanoes, meteorites and, to a limited extent, sea spray.

Phosphorus is also released into the atmosphere by microbial reduction processes which have been shown to generate volatile phosphorus compounds in sewage sludges, faeces, landfill, compost heaps and coastal sediments. Volatile gaseous products such as PH_3 or P_2H_4 may move into the atmosphere and become oxidised and airborne as aerosol droplets.

The main anthropogenic sources of atmospheric phosphorus are probably combustion of coal and forest fires, though certain industries such as concrete furnaces, phosphorus rock mining and intensive fertiliser use may also contribute to some extent.

========= Sampling errors =========

The assessment of the phosphorus content of air is very difficult because of the very small concentrations present and because the phosphorus is generally in aerosol form or associated with very small particles, often below 0.1 µm size. Concentrations in rain may often also be below the detection limit, necessitating concentration before analysis. **Errors in assessing phosphorus concentrations in rain water may also result from methodological differences** of filtering, as the phosphorus will be associated with aerosols and particles, or from errors in the molybdenum blue method resulting from silicate interference (eg. in dusts), or even from phosphate adsorption or release by laboratory glasswear in used sapling and analysis.

Phosphorus deposition needs to take into account both dry deposition and deposition in rain. This introduces further difficulties as dry deposition rates will be higher on a wet surface and the phosphorus content of rain may vary widely. **Fog water, for example, may contain up to ten times higher concentrations of phosphorus than most rain.**

======== Significance of atmospheric deposition ========

The authors quote estimates for annual phosphorus deposition from the atmosphere (kgP/ha) of 0.04-0.1 for the central Amazon basin, 0.1-2 for tropical moist forests, 0.8 for German oak forest and 1 for New Hampshire hardwood forest.

Rain can contribute a significant amount of phosphorus to the photic zone of the Mediterranean Sea during the summer (Bergametti et al., 1992). Atmospheric deposition compensates for 25% of phosphorus loss through sedimentation in some US lakes (Cole et al., 1990) and can contribute up to 30% of all phosphorus input to some Swiss lakes (L. Thšni, personal communication to the authors).

The authors conclude that a**tmospheric deposition is thus a critical input to both terrestrial and aquatic ecosystems**, at least for oligotrophic situations. However, special care in sampling and analysis methodology are necessary to obtain reliable data. Current values given in literature vary widely and some values may be questionable.

"The biogeochemical cycles of phosphorus: a review of local and global consequences of the atmospheric input". Technological and Environmental Chemistry, vol. 67, pages 171-188, 1998.

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SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Lake Constance

Complexity of phosphorus - biomass relations

This paper provides a full assessment of phosphorus fluxes in Lake Constance and examines interactions between different forms and sources of phosphorus and biological productivity (growth of algae, bacteria, zooplankton grazing). In particular, consideration is given to the exchanges between river inflows, surface waters (euphotic layer), deep waters and sediments, and to the biological cycling of phosphorus within the euphotic layer. The paper examines how these relationships have changed with re-oligotrophication of the Lake.

The Lake Constance phosphorus loads have been reduced significantly over the past decade, so that, for example, the phosphorus load flowing out of this Lake in the Rhine has been reduced by 50% for 1985/6 to 1997.

73% of river phosphorus load entering the Lake was in particulate form (1985/86). The authors estimate that **80% of this particulate inflow settles directly as sediment in the Lake and is rapidly and irreversibly buried.**

Although the Rhine River makes the largest contribution to the Lake's total phosphorus load (48%), this is mainly particulate, so that other rivers such as the Schussen carry as much dissolved phosphorus.

The Lake Constance phosphorus budget based on 1985/6 investigations (Wagner and Bührer, 1989) was (tonnes P):

Total phosphorus 1985	2835
+ river particulate load	+1677
+ river dissolved load	+578
+ atmospheric load	+42
- sedimentation losses	- 2086
- outflow (Rhine)	- 406
- other (drinking water extraction, fisheries …)	- 15

Total phosphorus 1986 2625

======== Sedimentation as a P sink ========

Sinking of phosphorus out of the euphotic layer into sediment is mainly caused by the loss of dead organisms, evidenced by the low proportion of living organisms found in the bottom waters. **Zooplankton grazing and then subsequent mortality was estimated to be the cause of 26% of phosphorus loss from the euphotic layer** to the sediment. Other main causes of phosphorus sedimentation were the breakdown of the spring algal bloom, calcite precipitation, and diatom sedimentation in autumn.

Phosphorus sedimentation rates in the pelagic zones of the Lake were estimated as 2-6 mgP/m^2/day, representing per day up to 2% of the total phosphorus concentration in the euphotic layer in the summer (during thermal stratification). Although this is significantly lower than the input to the Lake from rivers, the total phosphorus concentrations in the euphotic layer remain relatively stable, demonstrating that most of the river input is sedimented near the river inlets.

Considerable variations of river phosphorus loads flowing into the Lake have no apparent effect on concentrations in the euphotic layer, probably because of both intense horizontal mixing and the direct movement of river inflow phosphorus into the deep water layer with a reduced impact on the euphotic layer. Wagner and Wagner (1978) indicated that most of the phosphorus load from the Rhine and Bregenzer Ache rivers went into Lake water layers deeper than 10m.

Release rates of phosphorus from the sediments can reach 30-50% of the sedimentation rates and are fairly independent over the long term on whether the sediment surface is aerobic or anaerobic (although a change to anaerobic conditions can lead, in the short term, to an accelerated release). This phosphorus released from the sediments, however, will tend to stay in the deep waters and not reach the euphotic layer.

======== Significance of littoral sediments ========

The rates of phosphorus inflow to the Lake are halved in summer, but epilimnetic phosphorus is not depleted. The authors suggest that this is largely related to the **release of littoral sediments** through wind resuspension and estimate that this source of phosphorus is comparable to river inflow. Phosphorus released from littoral sediments would mix rapidly within the euphotic layer.

======== Biological cycling ========

The authors note that the biological demand for phosphorus in the euphotic layer (calculated from the biomass of bacteria and algae and uptake rates) largely exceeds available phosphorus supply during growth periods (1500 mgP/m^2 compared to 360 mgP/m^2).

In this situation, **bacteria will tend to act as a phosphorus sink**, absorbing phosphorus from water which is then retained as they either sink to the sediment or are grazed by zooplankton. Hence bacteria can effectively compete with algae to take up scarce available phosphorus, rather than - as is often modelled - acting as a source of phosphorus by cycling phosphorus during decomposition.

Experimental observations suggest that **bacteria are superior competitors for phosphorus at low concentrations than algae** and that bacteria have a higher phosphorus content (P:C) ratio than algae.

This leads to a paradox: how can the high algal demand for phosphorus be effectively met during the summer in the Lake's euphotic layer? **Zooplankton grazing may be a key factor in influencing the outcome of this competition.**

======== Importance of biological cycling ========

The authors also indicate that **phosphorus regeneration by grazing of algae and bacteria is probably a very important factor**, perhaps accounting for up to 50% of estimated algal phosphorus demand (grazers excrete part of the phosphorus taken in with prey, only retaining phosphorus for their own growth).

Overall, 70-80% of the phosphorus required for algal biomass production must be provided by regeneration of organic materials within the euphotic layer.

Dissolved organic phosphorus, may be an important phosphorus source in the summer when dissolved inorganic phosphorus remains constantly below the detection limit. The authors note that more than 50% of the dissolved organic phosphorus pool could consist of nucleic acids, which are rather resistant to enzyme breakdown (resulting in a residence time in the water of 10-20 days), whereas concentrations of monomeric nucleotides such as ATP were two orders of magnitude lower (and showed very short turnover times in the water).

To conclude, the authors state that **the links between phosphorus fluxes and biological production is subject to complex biotic and abiotic interactions, so that biological productivity cannot be sufficiently predicted by simple phosphorus load approaches.**

"Phosphorus fluxes in Lake Constance". Arch. Hydrobiol. Special Issues Advanced Limnology n¡ 53, pages 505-544, 1998.

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SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Japan

Algal control by shading

Shading of 40-80% of the surface of small farm irrigation water reservoirs (1,000-1500 m2, approx. 3m maximum depth) was tested in the field as an approach for controlling algal blooms. Three reservoirs were tested using shading of 30-60% of the surface, with one left unshaded as a control, in 1998 and 1999.

Shading was achieved using floating plastic or stick boards, either held together to cover one part of the reservoir, or distributed randomly as they floated over the water surface.

In 1998, after the appearance of the summer algal bloom, 50% shading was added resulting in a 50% drop in COD and water transparency improving to the extent of being able to see the reservoir bottom. In 1999, 30% and 50% **shading used before the appearance of the summer bloom completely prevented its appearance**. In both years, the control reservoir underwent a significant algal bloom, with scum developing on the water surface.

======== Blue-greens ========

In both years, the shading also resulted in an algal species shift from cyanobacteria in the algal blooms to diatoms. This is a very positive response where the reservoir water is intended for the water supply as it avoids risks due to toxins or odour problems.

The author notes that **the algal bloom was avoided both in the shaded and the unshaded areas of the reservoirs.** This does not appear simply to be the result of water mixing (meaning that all of the reservoir's water passes a proportion of its time under shading) since the growth rate of the algae in the unshaded areas of the reservoirs with partial shading was found to be one half to two thirds that of the algae in the control reservoir.

======== Loss of photosynthetic capacity ========

The author explains these results by referring to work by the late Prof. Ichimura, Tsukuba University, Japan, demonstrating that when samples of surface water from a eutrophic lake was stored in the dark or in low-light conditions for 1-5 days, the photosynthetic capacity becomes lower (on returning to light conditions after storage). The loss of photosynthetic activity is greater for longer storage periods and with darker storage conditions. This can be envisaged as a kind of shading memory effect.

In conclusion, the author suggests that up to 80% shading may be necessary to ensure very low algal concentrations necessary for the use of water for drinking supply, but that **40-60% shading would suffice to avoid algal bloom problems whilst maintaining some primary production**, considered necessary for fish production. Because this would imply relatively large areas of shading panels on any lake of significant size, the author suggests that the floating boards could be used to support photoelectric panels thereby also providing a source of renewable energy.

“Algal control of shallow lake by partial shading of surface”. Tsukuba International Aquatic Environment Forum, February 1st 2000.

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SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Thin film gels

Measuring dissolved inorganic phosphorus

Dynamic interactions of phosphorus species in natural systems may result in changes when samples are stored. The technique of diffusive gradients in thin films (DGT) can allow in situ measurements of dissolved inorganic phosphorus in natural waters, sediments or soils.

The DGT technique is based on a simple device consisting of a **phosphorus binding agent fixed behind a thin hydrogel layer which acts as a well defined diffusion layer**. In the work presented in this paper, the binding agent is ferrihydrite fixed in gel behind a 0.8mm thick layer of polyacramide gel, itself behind a membrane filter for protection. A 10 cm x 1 cm window on larger sheets was in contact with the water to be tested.

Phosphorus accumulated by the ferrihydrite was measured by elution with sulphuric acid followed by spectophotometric analysis of molybdenum blue. The rate of diffusion of soluble inorganic phosphorus across the hydrogel layer was assessed experimentally using the diffusion cells and noting times taken to reach equilibration concentrations.

========= Field testing =========

The DGT devices presented were **field tested in a small, still eutrophic pond** on the Lancaster University campus (UK) in April 1997 (suspension for 8 hours) **and also in sediment cores** extracted from Esthwaite Water in June 1997 (24 hours contact time). In both cases, the soluble phosphorus calculated from them (FRP method) was compared with the concentrations in the pond and pore water measured by standard laboratory methods. Nine DGT devices were used in each case: triplicates of three different gel thicknesses.

For the pond water, the DGT-calculated soluble phosphorus concentration gave 100.8 +-3.3 µgP/l (95% confidence limits) and the FRP method 91.6 +-4.5 µgP/l. The 10% difference may be due to variations in the concentration in the water over the 8 hour exposure time (the sample for FRP was taken at one time only) and in any case is such that the **95% confidence limits overlap.**

In the sediment, the DGT device measurements need to be adjusted (equation given in paper) in order to take into account possible re-supply of soluble phosphorus from sediment particles in response to absorption from the pore water into the DGT device. The DGT results from the sediment core show a **well defined curve of increasing concentrations** from below the detection limit at the sediment surface to around 300 µgP/l at a depth of 50-60 cm in the sediment.

========= Interest of DGT method =========

The DGT method will indicate concentrations of soluble phosphorus species which are small enough to diffuse through the hydrogel layer (pore size 2-5 nm), so **that the DGT method will indicate genuinely soluble species only.**

Because the DGT device accumulates phosphorus over time, it can be **deployed for long time periods** (up to 50 days, subject only to problems of biological fouling), and can thus measure (as an average) very low soluble phosphorus concentrations (by accumulating phosphorus in the ferrihydrite) to concentrations measurable by standard laboratory techniques.

In soils and sediments, DGT can provide an indication not only of pore water soluble P concentrations, but, more interestingly, the **capacity of the soil to re-supply soluble phosphorus from particles.** More work is needed to assess the relationship between this DGT measurement of available phosphorus fluxes and possible plant uptake.

"In situ measurement of dissolved phosphorus in natural waters using DGT". Analytica Chimica Acta 370 pp. 29-38, 1998.

H. Zhang, W. Davison, T. Kobayashi, Environmental Science, Lancaster University, Lancaster LA1 4YQ, UK. R. Gadi, ERD Kdmipe, ONGC, Dehradun-249001, India.

SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - LaPlatte River, Vermont

Phosphorus storage

A three year study of the La Platte River (north west Vermont, USA, further details in article below) used a number of techniques to assess phosphorus stocks, phosphorus storage and exchange of phosphorus between different compartments.

The study concentrated on phosphorus dynamics in two contrasting stretches of river:

- **Bacon Dr.**, around 6 km upstream from the mouth of the river (Lake Champlain), with a varied sediment river bed (sand, silt, clay and some pebbles and cobbles) and a macrophyte community covering 75% of the bed by late summer (dominated by *Elodea canadensis Michx* waterweed and two species of pondweed *Potamegon pectinatus L.* and *P. natans l.*)

- **Spear St.**, around 10 km from the river mouth, a quick flowing reach with a substrate mainly of cobbles with some boulders and a few small patches of gravely sand, silt and clay. The macrophyte community covered less than 1% of the river bed of this reach (same dominant species).

========= Phosphorus mass balance =========

Phosphorus dynamics in the river reaches were examined using seasonal stock assessments to estimate uptake and release from the five compartments: water, sediment, epilithon, macrophytes and epiphytes, detritus. Additional experimental assessments of uptake rates were made using radioactively labelled phosphorus in laboratory conditions, and retention rate assessments were made in the river using phosphorus spike and dye addition (see article below).

A phosphorus dynamics simulation model was built and parameters assigned using both the experimental results and map data covering the river basin morphology.

========= Stock assessment =========

Phosphorus stocks for each of the studied compartments were assessed for each season from August 1993 to April 1995. At both reaches, a number of samples were taken from random locations for each compartment and total phosphorus was calculated using chemical analysis along with the calculation of plant matter, detritus weight and suitable epilithon and sediment area.

As might be expected, **the plant and sediment rich Beacon Dr. reach showed significantly higher standing phosphorus stocks** than the Spear St. reach (25-29 compared to 2 - 4 gP/m^2 on average). In both reaches, most of the phosphorus stock was in the sediment (97% and 71% respectively).

Phosphorus uptake rates were estimated by comparing the maximum differences between consecutive seasonal stock estimates, giving 96 and 11 mg/m^2/day respectively for Beacon Dr. and Spear St.

========= Sediment exchange =========

Nearly all of the exchange of phosphorus between sediments and other compartments concerned the **upper layer of sediments** only. The variation in phosphorus concentrations in the upper 0-2 cm of sediment was high (range 0.25 mgP/g sediment = 44% of the mean value) whereas the variation for the remaining 3-5 cm of sediment studied was only 0.07 mgP/g sediment.

In laboratory sediment sorption experiments, the river sediments reached equilibrium with a 1 mg/lP soluble phosphorus solution after 12 hours, with half of the total absorption occurring within one hour. This demonstrated that the **sediments were far from phosphorus saturated under ambient conditions.**

========= River phosphorus dynamics =========

The uptake rates estimated from laboratory radioactive phosphorus experiments (river microcosms with all of the different studied compartments and with epilithon) were consistent with those estimated from the seasonal stock variations in the river, suggesting overall phosphorus uptake rates of 10-100 mgP/m2/day over the year. The rates at the upper end of this range would occur in summer when biologically available phosphorus concentrations are higher and at sediment and plant-rich reaches such as Beacon Dr.

The extrapolation of these phosphorus uptake rates to the whole river (51 ha of river surface) yields a range for **phosphorus uptake between seasons of 600-4,500 kgP**. This is somewhat lower than the estimated annual flux of phosphorus from non-points sources from the LaPlatte River into Lake Champlain (7,600 kgP/year).

Extrapolation of phosphorus stock estimates suggest that the **stock in all compartments of the LaPlatte river lies between 1,400 and 14,000 kgP, with a likely figure being around 8,000 kg, giving a**

load:stock ratio of around one.

«Lake Champlain in transition : from research toward restoration». Water Science and Application, vol. 1, pages 205-223 (American Geophysical Union).

D. Wang, School of Natural Resources, University of Vermont, Burlington, Vermont, 05405 USA. Email : deane.wang@uvm.edu. S. Levine, D. Meals, J. Hoffmann, J. Drake, E. Cassell (addresses see next article).

SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Nutrient ecology

River phosphorus retention

Spikes of dissolved phosphate (orthophosphate) and of dye added to a stretch of the LaPlatte River, north west Vermont , USA (flow 0.2-20 m3/s) showed that over one third of the phosphorus was temporarily retained (not carried downstream after 2.5 hours) in both December and September. However, whereas nearly all the added phosphorus was released during the next 12 hours on 20th December (under ice cover, with minimal biological activity), nearly 40% was still retained 48 hours later on 3rd September when plant growth was abundant.

The LaPlatte River drains a watershed of nearly 14,000 ha and is 24 km long, flowing into Lake Champlain from its headlands in the Green Mountain foothills. Around 20% of the catchment is forested headland area, the remainder being agricultural and suburban, with agricultural land accounting for 47% of the catchment area, mainly dairy farming.

The river has historically experienced heavy agricultural and point source (Hinesburg urban wastewaters) nutrient and sediment loads. Annual average total phosphorus (TP) and soluble reactive phosphorus (SRP) concentrations were 420 and 310 µgP/l respectively in the 1980’s. In 1992, the Hinesburg sewage works was upgraded, resulting in significant reductions in phosphorus concentrations in the river waters at low flow (to 20-140 µgP/l TP and 10-100 µgP/l SRP) although annual average phosphorus loads in the river water at its outflow into the lake have not changed significantly.

The phosphorus spiking experiments were carried out in a 3 km long 3rd order pool and riffle reach of the LaPlatte River near the town of Shelbourne. The pools had a macrophyte community with typically dominant species of Elodea and Potamogeton. Riffles had abundant substrates for epilithic periphyton, with cobbles, boulders and patches of sand, silts and clays. At this point the river was around 10-12 m wide with depths varying from 2m in the pools to <0.3m in riffles. River water flow rates were 0.58 m3/s in the December experiment and 0.24-0.25 m3/s in the September experiment.

The river was spiked both with relatively large doses of phosphorus (890 g of phosphorus in winter, 300g in autumn calculated to give the same concentration in the river as a function of the flow, both as orthophosphate) and Rhodamine WT (a red dye considered to be not significantly absorbable to plants or clays at the doses used). Following spiking and for the first 20-48 hours, samples of the river water were taken 3 km downstream at 10 minute intervals. The first samples gave the background level of phosphorus before spiking, whilst samples, starting with the arrival of the first traces of dye, enabled the phosphorus retention in the river system to be assessed by comparing the distributions over time of concentration and flux of phosphorus and of the dye.

========= Delayed phosphorus transport =========

In the December experiment, when the river was largely covered in ice, the dye pulse was first detected 3 km downstream 380 minutes later (average velocity of leading edge 0.13 m/s) and dye continued to be detected for a further 230 minutes, corresponding to a “plume” length of 1.8 km in the river. Phosphorus, however, although first detected nearly concurrently with the first detection of dye (the small difference was compatible with errors resulting related to differing detection sensitivity), was still detectable above background levels in the last sample taken 550 minutes after its first detection. By extrapolation, the phosphorus plume was calculated to have continued for 830 minutes, corresponding to an overall plume length in the river of 6.5 km.

Background phosphorus levels were 47 µgP/l total phosphorus (TP) and the maximum concentration reached in the sampling 3 km downstream of the spiking was 216 µgP/l.

The flux of phosphorus above background levels leaving the experiment reach was estimated, using measured discharges and comparisons with dye concentrations, as 93% of the mass of phosphorus added in the spike. The 7% “loss” was most probably due to minor errors in estimations of flows and concentrations, so it was deduced that all or nearly all the added phosphorus had been carried out of the experimental reach after the 830 minutes (13 hours), indicating **negligible phosphorus retention in December.**

========= Phosphorus retention =========

In the September experiment, when water temperatures were in the 15-17 °C range, flow rates were significantly lower as was the average velocity of the leading edge of the dye plume, at 0.9 m/s. This resulted in the dye first reaching the lower end of the experimental reach 560 minutes after spiking and continuing to be detectable for a further 670 minutes, giving a 3.6 km long dye plume (three times the length of the dye plume in December).

The first detection of phosphorus above the background level was again concurrent with the first detection of dye, but, unlike for the December experiment, phosphorus concentrations returned to background levels only shortly after the end of dye detection (760 minutes after detection), giving a **phosphorus plume length of 4.0 km, considerably shorter than the phosphorus plume in December.**

Background phosphorus concentrations were in this case 58 µgP/l total phosphorus (TP), and the maximum concentration reached at the sampling point 3 km downstream of the spiking was 98 µgP/l.

When the phosphorus concentrations had returned to background levels (accuracy of measurement 1 µgP/l), it was calculated that **only around 62% of the spiked phosphorus had actually flowed past the sampling site, corresponding to 38% retention in the river system after 48 hours.**

======== Abiotic and biological P retention ========

In both the December and September experiments, the short-term retention of phosphorus was demonstrated, with the phosphorus plume being longer than that generated by the spiked dye. The authors suggest that this is probably due to **the temporary sorption of phosphorus to sediments**, resulting from the relatively higher phosphorus concentrations in the water due to spiking, followed by release as the water P concentration decreases again as the plume moves downstream. The fact that this effect occurred more noticeably in December (longer phosphorus spike) may have been because the phosphorus concentrations resulting from the spiking were in this case higher (concentration below spiking point after initial mixing 13.5 mgTP/l in December versus 10.0 mgTP/l in September).

The shorter phosphorus plume and the significant level of P retention (38%) in September suggest, on the other hand, that the dominant mechanism in this case is **active biotic phosphorus uptake, probably by macrophytes and epilithon**. This was compatible with laboratory measured phosphorus uptake rates for the LaPlatte River epithlon, estimated at 66 mgP/m2/day (Hoffmann et al. 1996).

The authors note that their results are difficult to extrapolate to general conclusions about phosphorus retention in river systems, in particular because the P-spiking method necessarily implies concentrations significantly above natural levels in the river waters, and these are, in turn, susceptible to result in non typical ecosystem responses. They do, however, conclude that **the experiments confirm the capacity of a relatively short stretch of river (in this case a eutrophic river already subject to high nutrient loads) to retain a very considerable proportion of input phosphorus during the growth season**, that is at exactly the time of year when receiving waters (in this case a lake) would be most sensitive to nutrient inflows.

“Retention of spike additions of soluble phosphorus in a northern eutrophic stream”. J. N. Am. Benthol. Soc. 1999 18(2) pages 185-198.

D. Meals (dmeals@wcvt.com), S. Levine, D. Wang, E. Cassell, D. Pelton, H. Galarneau (School of Natural Resources), J. Hoffmann (Dept. of Botany), J. Drake, A. Brown (Geology Dept.), Vermont University, Burlington, Vermont 05405 USA.

SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Rhine and Elbe rivers

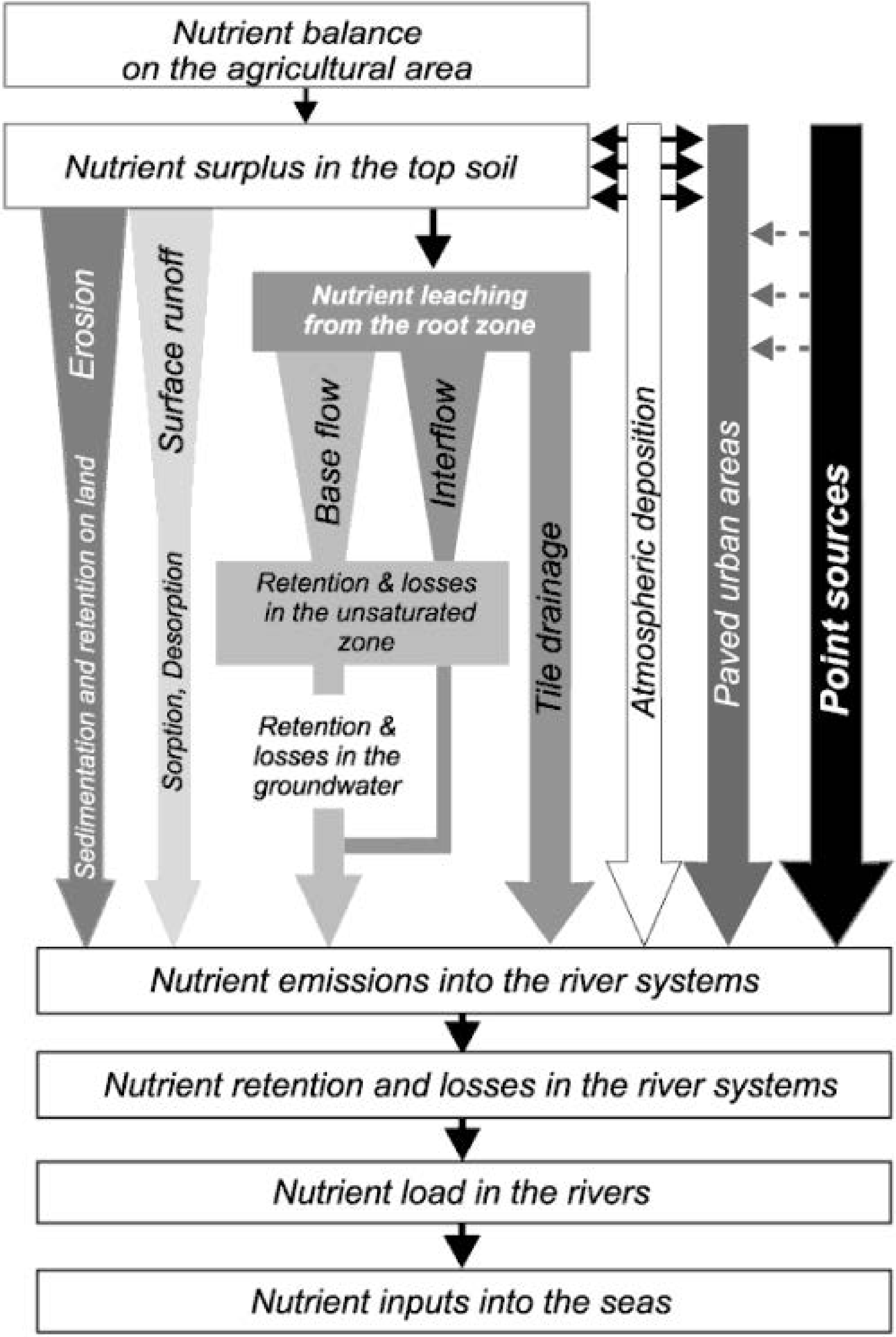
Trends in nutrient loads to German rivers

Both nitrogen and phosphorus inputs to the Rhine and Elbe rivers have been significantly reduced over the last fifteen years, mainly as a consequence of reductions to point source emissions (nitrogen removal in sewage works).

One of the main objectives of the International Geosphere - Biosphere Programme core project LOICZ (Land - Ocean Interactions in the Coastal Zone) was to determine fluxes of nutrients to coastal areas. Most nutrients are carried by medium and large rivers. The MONERIS (Modelling Nutrient Emissions in River Systems) model has been developed to estimate point and diffuse source nutrient inputs into German rivers - see diagram opposite.

The MONERIS model was applied to more than **200 different German river basins** and summarised for the Rhine (159 700 km^2 upstream of the Lobith monitoring station where it flows out of Germany into Holland) and the Elbe (134 900 km^2 upstream of the Zollenspiker monitoring station, the last station not influenced by tides). A detailed description of the model is published in Behrendt, H., Huber, P., Kornmilch, M., Opitz, D., Schmoll, O., Scholz, G. & Uebe, R. (1999): NŠhrstoffbilanzierung der Flu§gebiete Deutschlands. UBA Text 75/99, 288S.

Nutrient inputs from the river basins and nutrient loadings as carried in the river water at the downstream monitoring stations were compared for the periods 1983-1987 and 1993-1997. (see table below)


Nutrient balance on the agricultural area
Nutrient surplus in the top soil
Erosion
Sedimentation and retention on land
Surface runoff
Sorption, Desorption
Nutrient leaching from the root zone
Base flow
Interflow
Retention & losses in the unsaturated zone
Retention & losses in the groundwater
Tile drainage
Atmospheric deposition
Paved urban areas
Point sources
Nutrient emissions into the river systems
Nutrient retention and losses in the river systems
Nutrient load in the rivers
Nutrient inputs into the seas

Pathways and processes within the MONERIS model.

========= Nitrogen loads =========

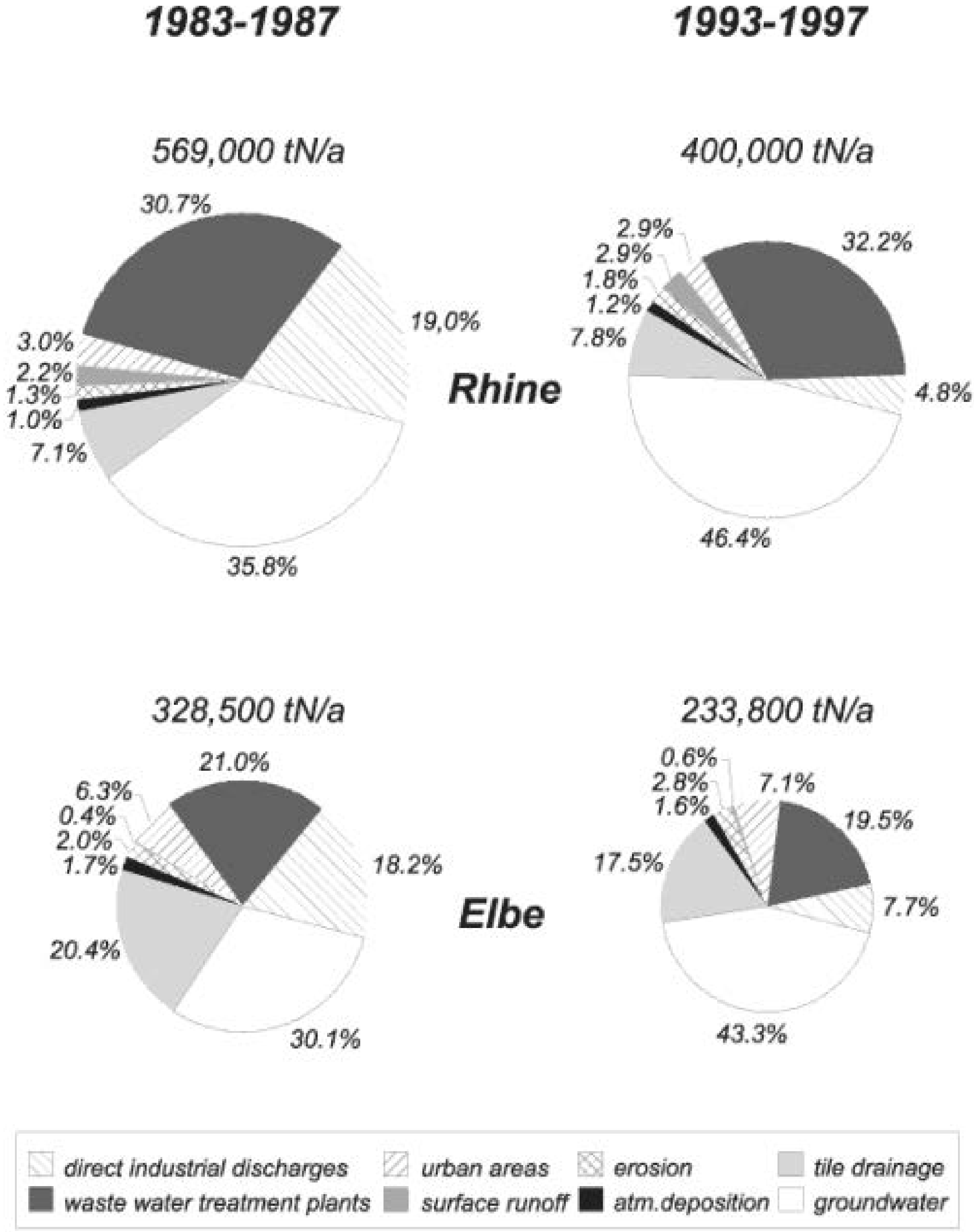
The 1990’s total nitrogen input to the Rhine was 400 000 tonnes N/y, 28% lower than in the 1980’s. **46% of this nitrogen input comes from groundwater**. The reduction results in particular from lower industrial discharges (down to only 4.8% of inputs in the 1990’s) and improved sewage treatment.

The 1990’s total nitrogen input to the Elbe was 233 800 tN/y. The reduction since the 1980’s (29%) was very similar to that for the Rhine, and was again the result of reduced industrial discharges and improved nutrient removal from sewage.

Nitrogen input to the Elbe from agricultural drainage (17.5%) is significantly higher than for the Rhine because of the higher proportion of land with tile drainage.

The decrease in agricultural nitrogen surplus only caused a very limited reduction in nitrogen load during the 1990’s, because of the long residence time of nitrates in the water table, but is expected to lead to a slow decrease in nitrogen inputs from groundwater after 2000.

Nitrogen Emissions



========= Phosphorus loads =========

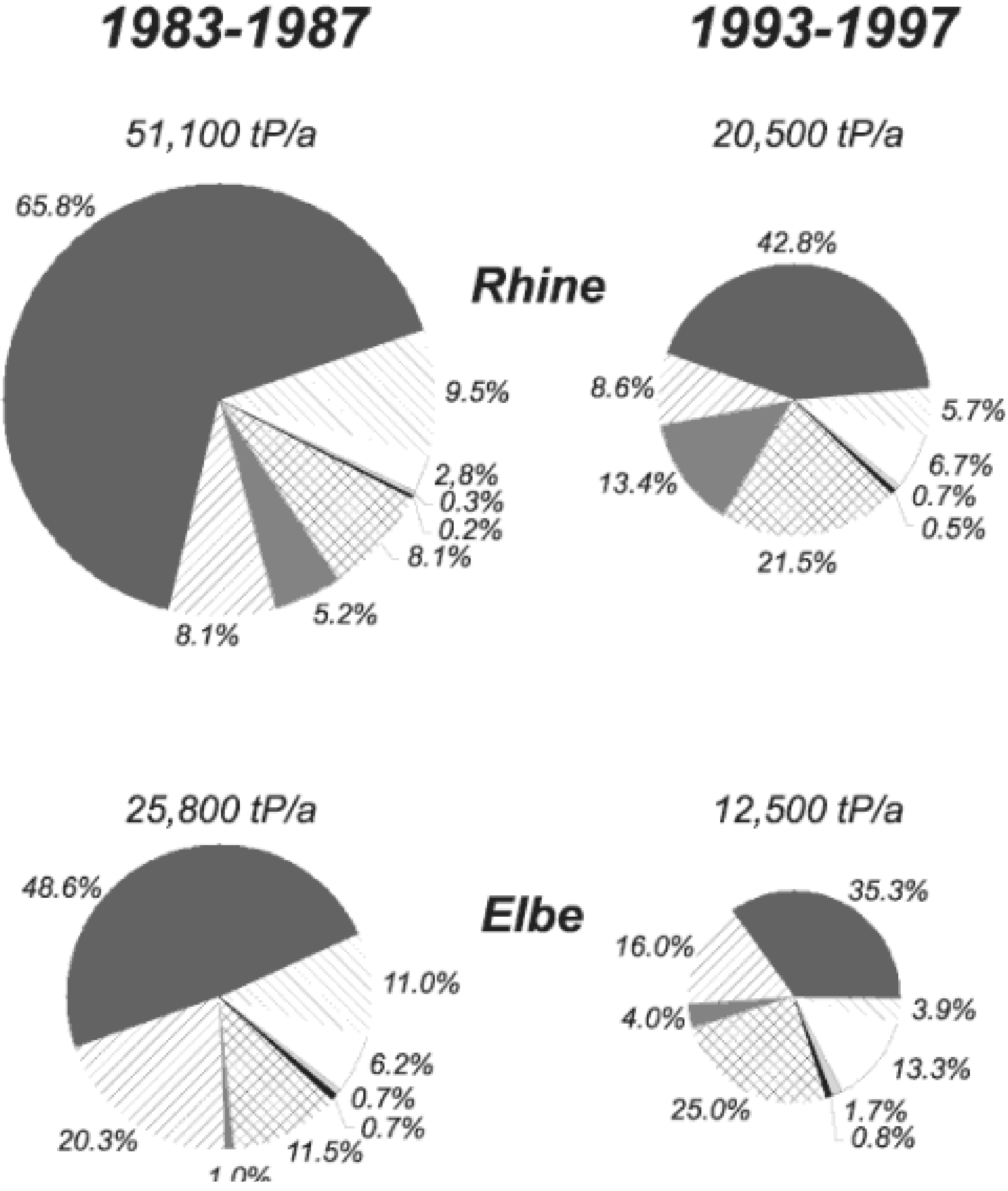
Total phosphorus inputs into the Rhine were very considerably reduced from the 1980’s to 20 500 tP/y in the 1990’s (60% decrease), mainly as a result of **reduced inputs from sewage works (nutrient removal**

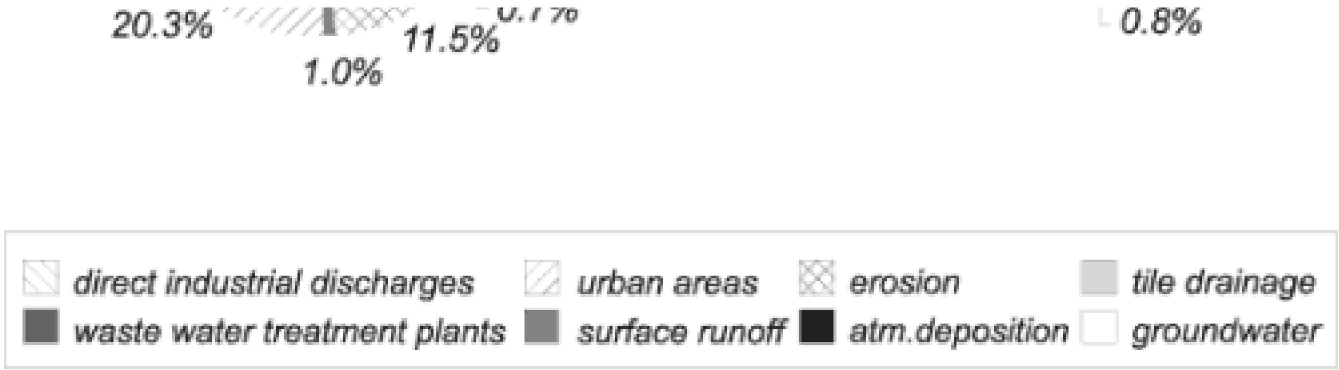
installation). This source still accounted for 42.8% of total P inputs in the 1990’s, however. Industrial discharges also decreased.

For the Elbe, the total phosphorus input of 12 500 tP/y in the 1990’s was a 52% reduction from 1980’s levels, again mainly resulting from reduced emissions from sewage works (64% reduction).

In both the Rhine and Elbe, by the 1990’s, d**iffuse sources were the main inputs of phosphorus** (51.5% and 60.8% respectively).

Phosphorus Emissions





======== Nutrient inputs exceed outflows ========

The observed nutrient loads carried in the river outflow (average concentrations x flow at downstream monitoring stations) are significantly lower than the total inputs to the river : 30-40% lower for both N and P in the Rhine, 50-65% in the Elbe.

However, the reduction in observed loads of both nutrients in the river waters at the monitoring stations is comparable to the reductions in nutrient inputs.

The author suggests that the significant differences between nutrient inputs and monitored river loads are the result of **retention and loss processes in the river** (denitrification, sedimentation, adsorption) - ***see other papers reviewed in this Newsletter.***

The author concludes that, beyond nutrient removal from point sources, additional **measures to reduce diffuse nutrients will be necessary** to meet the target of 50% coastal zone load reductions set by Helcom and Osparcom. Nutrient retention near to or within surface waters should be increased by using **buffer strips and wetland restoration or reconstruction.**

“Estimation of the nutrient inputs into medium and large river basins - a case study for German rivers”, LOICZ Newsletter n¡ 12, September 1999.

H. Behrendt, Institute of Freshwater Ecology and Inland Fisheries, Müggelseedamm 310, D-12587, Berlin, Germany.

SCOPE NEWSLETTER

SCOPE N°37 - 06/2000 - Nutrient retention

Phosphorus loads in rivers lower than inputs

Three recent papers compare inventories of point and diffuse nutrient inputs to different river basins/ sub-basins with observed nutrient load.

Previously, a small number of authors had already **published figures indicating that monitored nutrient loads in rivers were lower than would be expected from total inputs**. Billen *et al.* (1982, 1985) found nitrogen losses between upstream and downstream points of 48% in the Meuse and 73% in the Escaut rivers in Belgium. For phosphorus, Svendson and Kronvag (1993) measured P retention in a small river in Denmark at around 20% and the International Commission for the Protection of the Rhine (1992) found monitored phosphorus loads around 20% higher than total inputs.

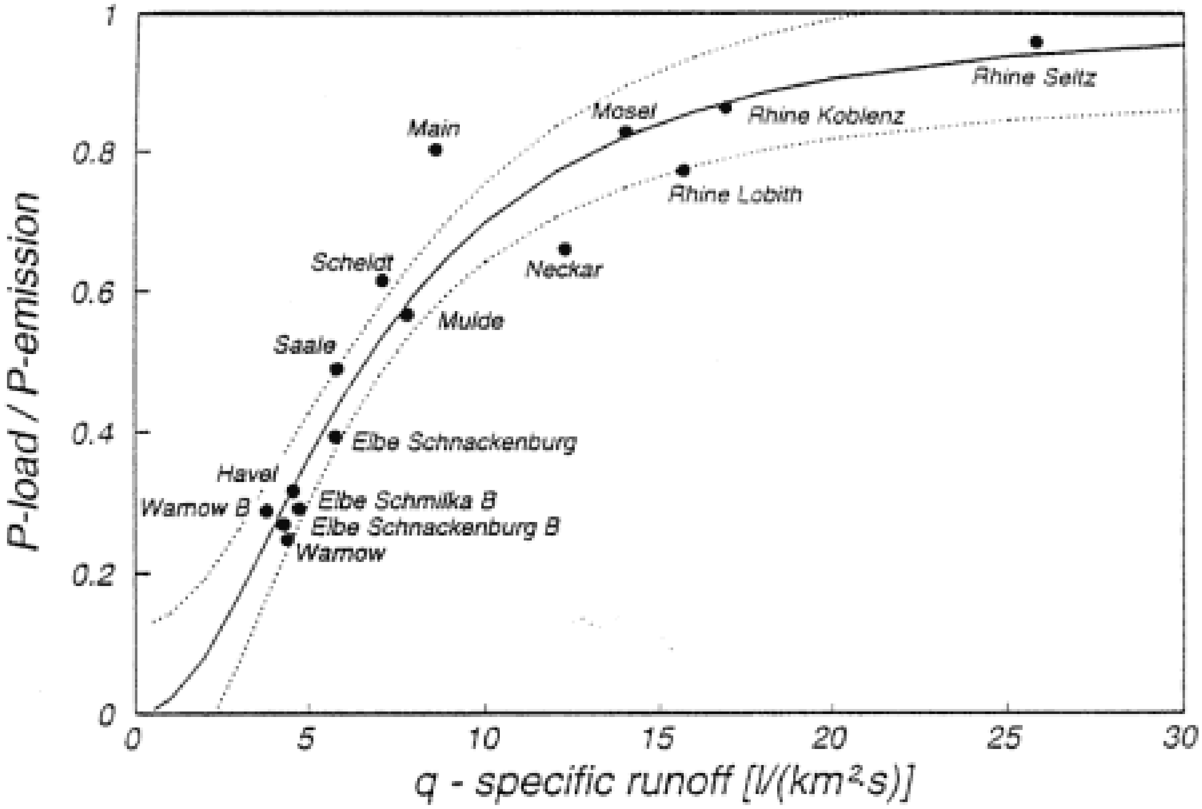
In 1996, Behrendt (ref. below) compared estimated total N and P inputs into the German rivers Rhine and Elbe and their tributaries, and into the smaller river Warnow in North-East Germany.

======== P retention related to run-off ========

The author found significantly larger differences between nutrient inputs and river load for the Elbe river system than for the Rhine and its major tributaries (Mosel, Necker, Main). He suggested a strong inverse relationship, for both nitrogen and phosphorus, between nutrient retention and **specific runoff (average river flow l/s per km^2 river basin).**

Rivers with a relatively low specific runoff (around 5 l/s/km^2) showed phosphorus retention of 60-80% and nitrogen retention/loss of 40-80%.

The author suggests that differences between nutrient inputs and monitored loads cannot be explained by errors in estimates of inputs, although diffuse sources may be overestimated in some cases. He concludes that although nutrient retention mechanisms may not be significant in the small river basins often used for studies, they may be considerable in larger basins.



Dependency of the (phosphorous transported/total emissions) ratio on specific runoff for diffrent Centre European Basins.

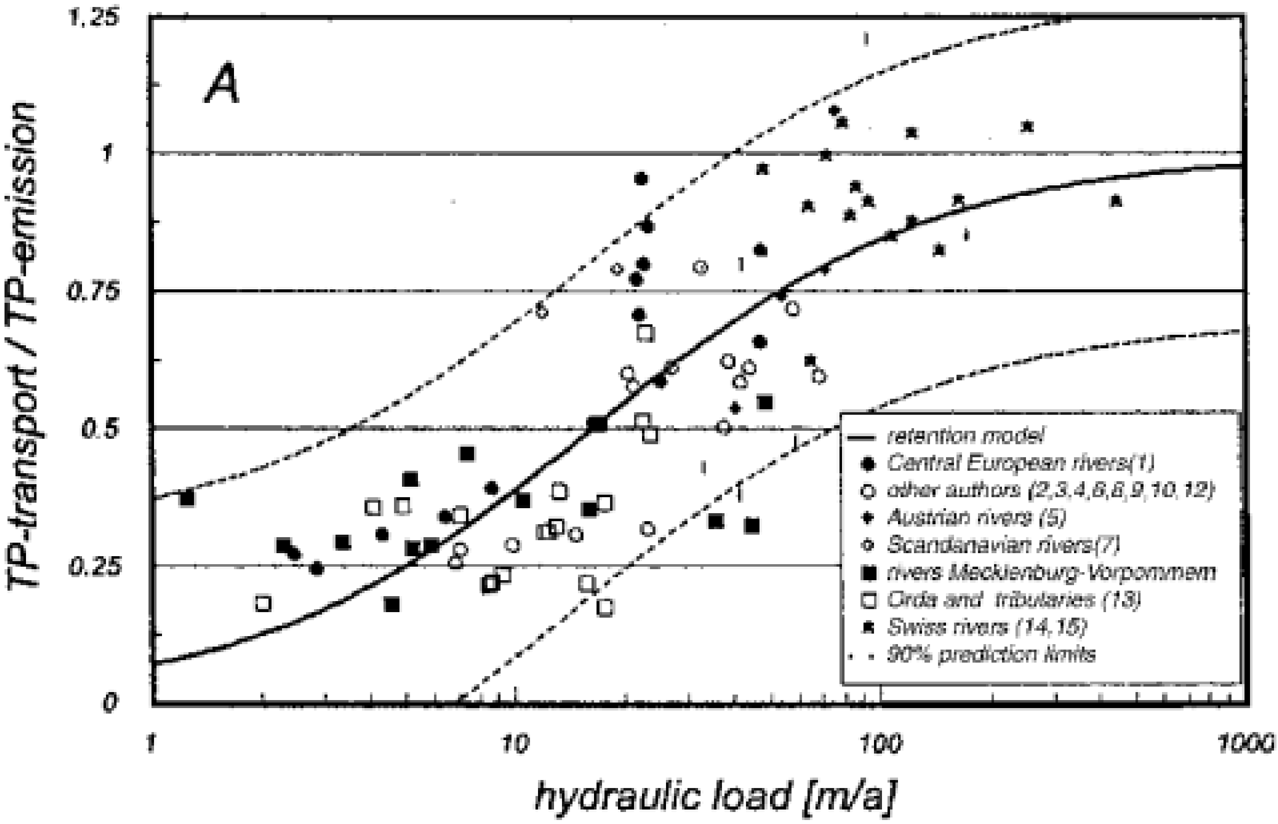
========= 100 river basins =========

In a further study in 1999, Behrendt and Opitz compare nutrient inputs with monitored river load for 100 European river basins with catchments varying from 121 to 194 000 km^2. They showed that the **observed transport of phosphorus is lower than total inputs** for nearly all except five of the river catchments considered, and was often considerably lower.

The authors examined the dependence of the % phosphorus retention (difference between inputs and transport) on two indicators of river system hydrology : the specific runoff (litres/second per km2 catchment area) and hydraulic load (annual average value of the height of water column flowing over one m2 of the river system water surface).

Around 80% of the variation in phosphorus retention is explained by variation in specific runoff, whereas only 61% is explained by hydraulic load. For nitrogen the results are different, with 51% of the variation in N loss/retention only being explained by specific runoff and 65% by hydraulic load. No statistically significant dependence on catchment basin size was found.

The authors derived a statistical model of nutrient loss/retention as a function of specific runoff, water surface area and basin size.



Dependency of the (phosphorous transported/total emissions) ratio on hydraulic load for diffrent Centre European Basins.

========= 40-50% phosphorus retention =========

In a further paper in 1999, Behrendt considers different methods for estimating diffuse source nutrient inputs into rivers. Seven methods of assessment were examined for 14 river basins in North East Germany.

This demonstrates the **difficulties involved in estimating diffuse sources of phosphorus** : the standard deviation for the results of the seven different methods applied to these basins is 60% for phosphorus, compared to only 27% for nitrogen.

The results demonstrate that **methods which assume “zero phosphorus retention” must be excluded**. An overestimation of point sources and underestimation of transported loads for phosphorus is indicated by the statistical analysis, but a large difference between inputs and transported phosphorus nonetheless remains. The authors conclude that river retention processes result in around 40-50% of phosphorus inputs not reappearing in the transported nutrient loads. This retention is clearly dependent on specific runoff.

========= 3/4 of nutrient inputs to the Odra river do not reach the sea =========

In another 1999 paper, Behrendt *et al.* examine nutrient inputs and transport in the Odra river, one of the largest transboundary rivers in Central Europe. The catchment studied is that upstream of Krajnik Dolny : more than 110 000 km^2 with a population of around 15.5 million. Specific runoff is relatively low at 4.5 $l/s/km^2$.

Point sources dominate phosphorus inputs in the basin (73%) with a trend of reductions over the study period 1991-1994.

Compared to nutrient inputs, river transport is low, with an average of around 43-55% of nitrogen and **75% of phosphorus retained / lost in the river system**. River transported phosphorus loads make up less than 50% of identified point source P inputs, even if diffuse sources are ignored !

The authors indicate that the target of a 50% reduction in nutrient load to the Baltic Sea can be achieved for the Odra river for phosphorus if point sources alone are reduced by 70%, which is possible by nutrient removal installation in sewage works.

H. Behrendt : “Inventories of point and diffuse sources and estimated nutrient loads - a comparison of different river basins in central Europe”, Wat. Sci. Tech. vol. 33 n¡ 4-5 pp. 99-107, 1996.

H. Behrendt, D. Opitz : “Retention of nutrients in river systems: dependence on specific runoff and hydraulic load”, Developments in Hydrobiology 410 pp.111-122.

H. Behrendt : “A comparison of different methods of source apportionment of nutrients to river basins”, Wat. Sci. Tech. vol. 39 n¡ 12, pp. 179-187, 1999.

*H. Behrendt, M. Kornmilch, R. Korol, M. Stronska, W-G. Pagenkopf : “Point and diffuse nutrient emissions and transports in the Odra basin and its main tributaries”. Acta Hydrochim. Hydrobiol. 27 n¡5 pp 274-281, 19*99.

H. Behrendt, Institute of Freshwater Ecology and Inland Fisheries, Müggelseedamm 310, D-12587, Berlin, Germany.

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - Sweden

Trends for sewage sludge disposal

Sweden currently recycles around one third of its 180,000 tonnes (dry weight) of sewage sludge, a proportion similar to the EU average. However, increasingly stringent limitations on heavy metal loads to soils as well as other factors are putting considerable pressure on agricultural spreading and are likely to drive the development of wastewater stream separation and resource recovery, such as phosphate recovery for recycling.

Sweden currently has no incineration of sewage sludge, although incineration in domestic waste incinerators has been considered in some cities. Sludge not spread on agricultural land is currently disposed of to landfill or in land restoration. Landfill however will no longer be allowed for organic sludges in the future, in application of European legislation.

The paper presents graphs of metal concentrations in sewage sludges over the period 1986–1996 for Stockholm's largest sewage works. This shows a **significant downward trend** for lead, chromium, nickel and mercury, but not for cadmium. It is also noted that a near doubling of mercury concentrations from 1995–1996 (returning to near 1986 levels) was due to illegal discharges from one small company : this shows how one industrial source can considerably worsen the metal content of sludge for even a large treatment plant.

========= Source control and separation =========

Sewage sludge disposal can be addressed by **separating sources** :

- ensure that harmful substances from industries and households do not enter the domestic sewage system
- install separate collection of urine (not through the sewerage system), as this contains 60% of phosphorus and 80–90% of nitrogen in domestic wastes. The separate collection enables recycling as fertiliser or other applications.

The separation of household streams, however, would imply far-reaching changes in existing waste water infrastructure which would be very costly.

======== Product recovery and phosphate recycling ========

When source separation is not feasible, the paper suggests that sewage sludge can be split into **fractions that can be re-used (nutrients, organic substances for energy, inorganic substances for use in building materials)** and into a small fraction containing the harmful substances which require disposal.

Two existing examples of sludge fractioning processes are cited, both currently functioning in Scandinavia : the Krepro system at Helsingborg, Sweden, and the Cambi system at Hamar, Norway.

The Krepro system uses acids at high temperature. The Cambi system treats sewage sludge before digestion using pressure and steam which releases phosphates and ammonium and making the remaining organic substances more digestible, thus increasing biogas production.

======== Possible phosphate recycling pathways ========

The authors present phosphorus recovery as an important area for resource recovery from sewage sludge fractioning.

Several different pathways are indicated :

- **anaerobic digestion** of sludge leading to a liquid phase rich in soluble phosphate and ammonium which can be treated to precipitate phosphates. Digestion of untreated sludge will render soluble roughly 50% of the phosphorus in the sludge, higher proportions can be achieved by utilising a sludge pre-treatment such as the Cambi process.
- **dissolving of sludge** in acids or bases. Work carried out in the author’s research department indicates that nearly all the phosphate can be rendered soluble by acid at pH2 (for sludges containing iron and aluminium precipitated phosphates)
- **reaction with sulphides.** The same work found that sulphides at neutral pH did not cause phosphate release from the same sludge, but released 80% of phosphates at pH4. Such reactions would pose safety, corrosion and odour problems. Efficiency might be improved by using a two step bacterial process but this has not yet been investigated.
- **heat treatment,** with the aim of developing processes which release phosphates and improve sludge biodegradability at temperatures below 100°C.
- **phosphorus recovery from sludge incineration ash** (see article on work by Erik Levlin of the same research division in this Newsletter)

SCOPE editor’s note : **agricultural spreading of sewage sludge in Sweden has recently come under significantly stronger pressure** with the recent recommendation (Autumn 1999) by one member of the committee responsible for defining sludge quality standards that agricultural spreading should be suspended because of the presence of brominated flame retardants in sludges, the risk of their accumulation in soil and possible effects on organisms.

"Trends in Swedish sludge handling", Proceedings of the Polish – Swedish Seminar on Sustainable Municipal Sludge and Solid Waste Handling, Royal Institute of Technology, Stockholm August 24th 1999.

Bengt Hultmann, Division of Water Resources (Civil and Environmental Engineering), Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden.

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - Recovery and Recycling

Phosphorus in sludge incineration ash

Results are presented for preliminary investigations of phosphate and metal contents of sewage sludge incineration ashes and of leaching of these using acids. Different types of ash, various incineration temperatures, different acid concentrations and leachate phosphorus/metal ratios are studied.

Phosphate contents of 13 ash samples from 6 literature sources are given, showing phosphate levels mainly varying from 9–27% (one third of the samples over 20% phosphates, but also two samples with very low levels).

Investigations of acid leaching of incineration ash were made using three types of ash :

- ***pure sewage sludge incinerated at different temperatures in a laboratory oven (sludge from the Stockholm Himmerfjarden sewage works which uses iron salts for phosphorus removal)***
- ***fly ash from the Igelsta incineration plant burning dewatered Himmerfjarden sludge with biofuel (approx 20% sludge / 80% biofuel)***
- ***bottom ash from the Högdalen incineration plant burning the same sludge with municipal waste (around 10% sludge / 90% waste)***

The phosphorus content of the Igelsta and the Högdalen ashes were 0.44–0.45% respectively, with an estimated 80% of this coming from the input sewage sludge component.

The experimental results presented show that no phosphate can be dissolved from the ashes without acid digestion, roughly half at 0.5 M hydrochloric acid (HCl) and almost all of the phosphate at 1 M HCl or more (see diagrams below).

Matsuo (1996) however indicated that phosphorus can be leached from biological P-removal sludge incineration ash using warm water (see opposite).

========= Metal leaching =========

As well as phosphorus, metals are leached out of the ashes by acid. Metal:phosphorus ratios are

generally significantly better (lower) in the raw sludge than in the Högdalen and Igelsta ashes, but this may be due to the metals present in the municipal waste and biofuels which were co-incincerated with these sludges.

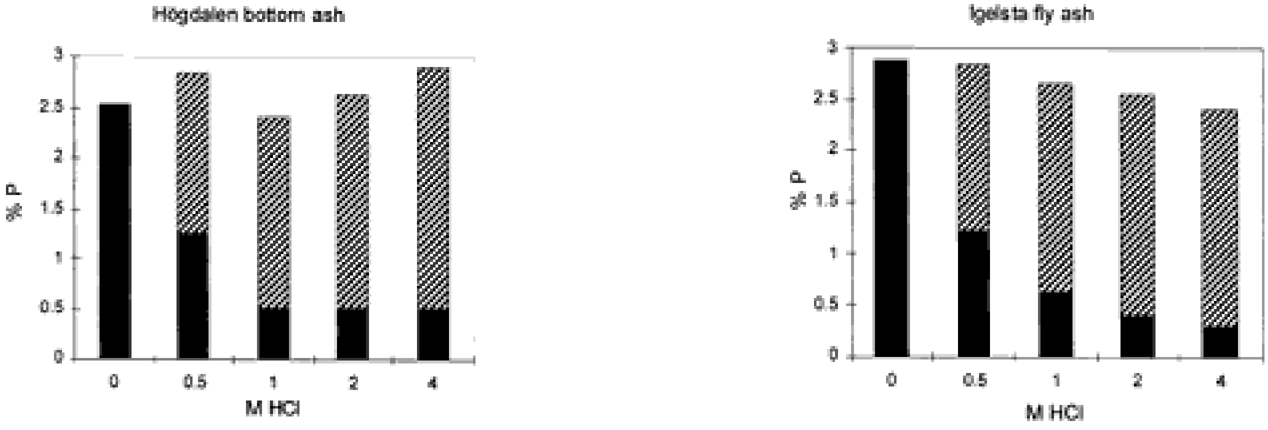
The paper also explores the volatility of the different metals in these ashes. The author suggests that metal contamination of the recovered phosphorus could be avoided by evaporating them during incineration and recovering the phosphorus from the bottom ash.

The paper also summarises possible routes for using sludges or incineration ash in the manufacture of bricks or ceramic materials.

Percentage phosphorus in ash from Högdalen and Igelsta after leaching and dissolved phosphorus versus acidity in M HCl of the leaching liquid.

■ **P in ash after leaching**

▒ **Dissolved P**



"Trends in Swedish sludge handling", Proceedings of the Polish – Swedish Seminar on Sustainable Municipal Sludge and Solid Waste Handling, Royal Institute of Technology, Stockholm August 24th 1999.

Bengt Hultmann, Division of Water Resources (Civil and Environmental Engineering), Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden.

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - Biological P-removal ash

Availability of Phosphorus for Recovery

The study used sludge produced by a laboratory scale Enhanced Biological Phosphorus Removal plant (28 litres/day influent) running on synthetic waste water. The sludge was evaporated, dried and then incinerated in an electric muffle furnace for 2 hours at 670°C.

The bio-P plant removed nearly all the phosphorus from the influent (15–18 mg total P/l), giving a sludge which the authors indicate contained 5–10% P. The P content of the sludge incineration ash is not indicated, but would appear to be roughly 32% (total ash P = approx. 320 mg/l according to graph p410, in a suspension of 40 mg in 40 ml water).

Phosphorus elution

Phosphorus elution was tested by suspending the ash in water, at a given temperature for a certain time, then filtering to separate eluted from non dissolved phosphorus.

The authors state that a large part of the phosphorus in the ash is released in a relatively short time using hot water. The graphs given indicate that around 80% of ash total P is eluted after 4 days using water at 86°C. No results are given for shorter time scales, but it is possible that most of the release might occur in a much shorter period.

Release at a comparable level (around 80%) occurs using lower temperature water at 53°C after around 10 days.

Water at 30°C or 5°C only achieves low P elution rates (less than one third) even after 12 days.

Varying concentrations of ash in suspension were tested (from 0.5 g ash/l to 5 g ash/l) showing reduced proportions of P eluted in the presence of higher concentrations of ash (probably as a result of higher phosphorus concentrations developing in the water).

Orthophosphate

Interestingly, almost all the eluted phosphorus appeared to be in the form of dissolved orthophosphate at 86°C, whereas there was little orthophosphate released at 53°C or lower (eluted phosphorus is assumed to then be inorganic polyphosphate).

The authors indicate that at 86°C the phosphorus is initially eluted as polyphosphates but rapidly hydolyses to orthophosphates.

Magnesium and potassium

Sodium and calcium were not significantly eluted during the different experiments, whereasmagnesium and potassium are released.

The ratios of release of these elements to to phosphorus release were (water at 40°C):

DMg/DP = 0.19 mol/mol
DK/DP = 0.19 mol/mol

Implications of iron addition

The authors then made a tentative release test on ash produced in a full-scale biological P-removal sewage plant. Phosphorus elution was insignificant. The ash was coloured redish because of the presence of iron. It was therefore decided to test the implications of the presence of iron in the sludge on P elution from the sludge incineration ash.

This was done by adding ferric chloride solution to the laboratory bio-P plant sludge, before incinceration, to give iron contents in the sludge of zero, 0.75 and 3 % Fe dry weight.

The 3% iron in the sludge was equivalent to a sludge molar Fe:P ratio of less than 0.25.

The ash from the 0.75% iron sludge slowed slightly reduced P elution at 85°C, whereas the 3% iron sludge ash showed very low P elution.

The authors suggest, given the molar ratios present, that this may be due to the **formation of heterogenous iron polyphosphate complexes** during incineration.

========= Incineration Temperature =========

Under incineration at 1000°C (instead of 650°C) the laboratory bio-P plant sludge was vitrified. P elution was reduced in this case by around half (using water at 40°C).

"Release of Phosphorus from ash produced by incinerating waste activated sludge from Enhanced Biological Phosphorus Removal", Wat. Sci. Tech., vol.34 n° 1-2, pages 407-415, 1996.

Y. Matsuo, Dept. Civil Engineering, Faculty of Science and Engineering, Chuo University, Kasuga, 1-13-27, Bunkyo-ku, Tokyo 1121, Japan.

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - Sewage Sludge

Citric acid P-extraction

This paper presents experimental work carried out to assess the feasibility of extraction of heavy metals from sewage sludges, in order to facilitate appropriate re-use, for example in composting. Results show that 80–90% of sludge phosphorus is also extracted using citric acid at pH 3-4.

Lab scale experiments used sewage sludge from the Almere municipal sewage treatment works, Holland. This is a low-loaded activated sludge plant producing secondary sludge which is dewatered in decanting centrifuges after addition of inorganic flocculants.

This dewatered sludge contains 7.9 g/kg iron, 21.5 g/kg aluminium and 22.3 g/kg phosphorus (of dry matter). The heavy metal concentrations exceed legal standards (for fertilisers) for cadmium (2 mg/kg), copper (472 mg/kg) and zinc (425 mg/kg), with a total metal content of 1.96 mol/kg dry matter (heavy metals and competing metals).

Elution experiments were performed by diluting sludge to 5g/l in 500 ml containers. Extraction was measured after five time periods from 0.04 to 11 days.

======== Organic acids ========

Two different organic acids were tested (citric and oxalic) as well as nitric acid (in order to distinguish pH effects from complexing effects).

Citric and oxalic acid both proved more effective at eluting metals at relatively mild pH’s than nitric acid. Oxalic acid, however, tended to be removed by precipitation of calcium oxalate, resulting in a lower effectiveness than for citric acid.

The extraction of different metals by citric acid at different pH’s was studied over varying temperatures and reaction times. Results are presented for elution of copper, zinc, calcium and iron.

The authors conclude that a pH < 4 is necessary in order to avoid degradation of citric acid (so that the elution acid can be reused several times). 50% of citric acid is degraded after 30 days at pH 3 but after only 8 days at pH 6.

========= 80–90% extraction of phosphorus =========

The authors indicated that 80–90 % of total phosphorus in the sludge is also eluted out at the same time as metals (the exact conditions for these figures are not given).

They conclude that ***“extraction with citric acid could be an attractive option to recover the economic cost of phosphate”.***

Following elution, metals and phosphorus would need to be removed from the extracting liquid, both to avoid accumulation of metals in the elution process, and to permit phosphorus recovery. The authors suggest this would be possible by chemical sulphide precipitation for the metals or ion exchange.

Because citric acid is readily biodegradable under aerobic and anaerobic conditions, traces remaining in the sludge are not a problem for further processing or agricultural recycling.

"Removal of heavy metals from sewage sludge by extraction with organic acids". Wat. Sci. Tech. Vol. 40 n° 1 pages 129-136, 1999.

A. Veeken, H. Hamelers, Dept. Agricultural Env. and Systems Technology, Wageningen Agricultural University, PO Box 8129, 6700 EV Wageningen, Holland.

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - Japan

P-recovery as calcium phosphates

Laboratory experiments used calcium silicate hydrate seeds in a 50–250 ml/hour fixed and expanded bed reactors to precipitate calcium phosphates from secondary effluents and sidestreams of different sewage works. Around 70% P-recovery efficiency was achieved at a pH of 8 without prior decarbonation, producing a recovered phosphate material with a 17% phosphorus content.

The seed material used was produced by mixing siliceous and calcareous raw materials, followed by autoclaving. This produced, under suitable conditions, nearly spherical calcium silicate hydrate (tobermorite) particles with card-house or needle shaped crystal growths on the surfaces. For the experimental work, 1.7–2.4 mm diameter seed particles were used. The shape of the surface tobermorite crystals did not appear to affect calcium phosphate precipitation efficiency.

========= Experiments with secondary effluent =========

Initial experiments used a 50 ml/h reactor consisting of a sidearm test tube, and sand-filtered sewage works secondary effluent. The reactor was tested with both a fixed bed and a 25% expanded bed using an upstream circulator. The 50 ml/hour flow rate gave a reactor residence time of around one hour. Several runs of up to 400 days duration were carried out.

A variety of calcium ion sources were tested, including calcium chloride and seawater, to give a calcium ion concentration of 40–80 mg/l. Seawater proved a less effective calcium ion source (at comparable calcium concentrations), possibly because of sodium inhibition of phosphate precipitation.

Removal of soluble phosphate from the effluent treated varied from 80% at pH 9 to 70% at pH 8.5.

The authors suggest that optimal operating conditions would be around pH 8.5, allowing reliable soluble phosphate removal from 2 mg/l down to 0.6 mg/l, with a reactor residence time of 30–40 minutes.

======== P-rich sludge sidestreams ========

Further experiments then used sludge treatment sidestreams with soluble phosphate contents of 10–50 mg/l in expanded bed reactors of 250 ml/h flow rate. The bed was expanded 12.5% by an upstream circulator. Bed size was 250 mg of seed crystal, giving once again a reactor residence time of around one hour. In certain runs, calcium chloride was added to dose calcium ion concentrations to 80 mg/l in the reactor (higher calcium concentrations did not improve performance) and sodium hydroxide to control pH at different levels in the range pH8–pH9. In other runs, hydrated lime addition was used.

Several runs of up to four months in different conditions were carried out.

For these higher effluent phosphate concentrations, soluble phosphate removal rates of 80% were achieved at a pH of 8, considered by the authors to be the optimal operating pH for treating such effluents. In this case, around 60% of the total phosphorus in the treated effluent was trapped on the bed crystals.

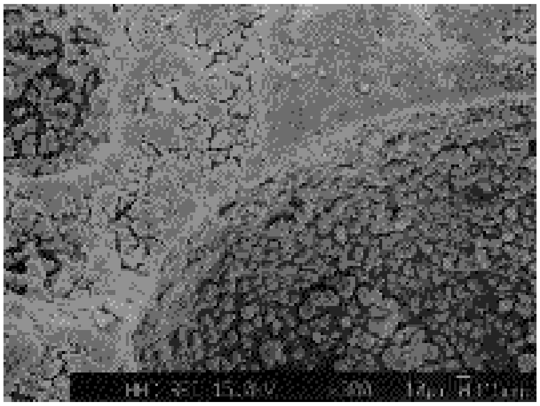
======== Quality of recovered phosphate product ========

The citrate solubility of the precipitated phosphates were assessed. Complete solubility in 2% citric acid indicated that these are partially formed hydroxyapatite crystals, and that the recovered material could be used as a slow release fertiliser. When 50 mg soluble phosphate concentration effluents are treated with a one hour reactor residence time, the phosphorus content of the bed material reached around 16% after six months' operation, approaching that expected of commercial mixed phosphate fertilisers.

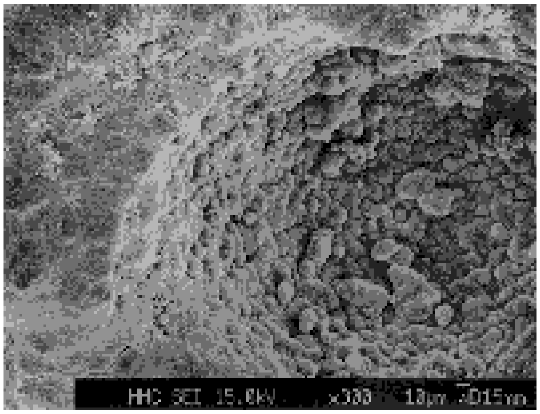
In addition, the heavy metal content of the recovered phosphate material is relatively low (after 126 days) : 3.4 mg/kg arsenic, 0.5 mg/kg cadmium (both around half the level in the initial seed material) and 0.021 mg/kg mercury (the same as in the initial seed material). These levels are one to two orders lower than recommended maximum values for use in fertilisers in Japan.

======== Crystallisation process and reliability ========

The authors suggest, on the basis of surface analysis, that the seed material is first covered with a calcium-excess calcium phosphate of unknown structure, then by poorly-crystallised hydroxyapatite and finally by fine granular hydroxyapatite crystal layers.



SEM after 1 day of operation



SEM after 7 days of operation

The authors indicate no problems with seed material deterioration even after several month long runs, and no problems with biofilms or slime, even in the presence of significant concentrations of organic matter in the effluents (200–400 mg/l COD in the sidestream effluent treated).

"Phosphorus removal with calcium silicate hydrates as seeding crystals in sidestreams". Proceedings of the 54th Annual Conference of the Japan Society of Civil Engineers (part 7), pages 336-339, 1999 (in Japanese).

K. Moriyama, Kyushu Kyoritsu University, Faculty of Engineering – Civil Engineering Section, MN807-8585, 1–8 Jiyugaoka, Yahata Nishi-Ku, Kitakyushu City, Japan. Email : moriyama@kyukyo-u.ac.jp). Seed crystal materails are produced by Mitsubishi Materials Corporation - Email : to-kojma@mmc.co.jp.

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - Wastewater chemistry

Struvite precipitation kinetics

Nucleation of struvite (magnesium ammonium phosphate) was studied using pure solutions in the laboratory and precipitation onto different surfaces under varying mixing conditions was then studied in thesupernatent of storage lagoons of anaerobically digested sludge at the Sacramento Regional Wastewater Treatment Plant (685,000 m^3/day), Northern California.

This work follows a previous paper in which a solubility constant for struvite was experimentally determined and confirmed in the sewage sludge supernatents.

========= Nucleation times =========

Struvite nucleation was studied using pure reagent solutions with different equimolar concentrations of struvite constituents in Pyrex beakers in the lab. Supersaturation was varied by adjusting the pH in the range 6.3-7.9. Mixing energy was altered by adjusting stir speeds. Nucleation was detected by light scintillation.

Struvite nucleation was found to be reaction controlled, with nucleation times strongly dependent on struvite supersaturation and mixing energy having only a minor effect.

========= Struvite precipitation =========

Struvite accumulation was studied in the sewage works (anaerobically digested) sludge supernatent by suspending duplicated or triplicated surfaces in three selected locations in the lagoons : an undisturbed zone, a moderately mixed zone near a brush aerator operating 12 hours/day, and a high energy zone covered by splashing from the brush aerator when in operation.

To measure struvite growth rates, stainless steel flat surfaces of 2250 mm^2 were used. PVC and acrylic plastic surfaces were used to examine the effects of surface roughness on struvite accumulation rates.

Struvite accumulation occurred in all three zones in the sludge supernatent, but accumulation rates and crystal habit varied significantly according to the location. The struvite in the undisturbed zone formed long crystals, whereas that in the high energy zone was less elongated and more tightly packed.

Growth rates for the three zones were 1.8 g/m^2/day in the undisturbed zone, 4 g/m^2/day in the medium energy area and 22.4 g/m2/day in the high energy zone. After an initial induction period, in which a first layer of struvite crystals was established on the surface, constant growth rates were observed for each zone.

The pH and total inorganic carbon content of the supernatent were measured at the three different zones. Carbonate concentration was around one order of magnitude higher than for equilibrium with atmospheric CO_2 because of biological CO_2 production in the sludge digesters and in the lagoon. The splashing of supernatent into the air above the aerator may have caused CO_2 release and thus a higher pH (confirmed by measurements) in the supernatent in the mixed and splash zones.

Calculated theoretical struvite growth rate differences between the three zones (+3.3% between undisturbed and moderately mixed zones ; +4.2% between moderately mixed and splash zones) were very significantly lower than actual growth differences (+125%, +460%)

========= Different surfaces =========

Experiments in the lagoon supernatents showed that acrylic surfaces had a lower accumulation rate than PVC, and PVC in turn significantly lower than stainless steel. On the two plastic surfaces, most of the accumulation was not on the smooth surfaces, but in fact on rough surface edges where the surface samples had been sawn. However, even when only these rough edge surfaces were taken into account, the struvite accumulation rate/mm2 was still lower on the plastics than on stainless steel.

In a further experiment, roughened stainless steels surfaces were compared with unmodified surfaces. The roughened surfaces had higher initial struvite accumulation rates, but rates were similar once an initial struvite coating had covered both surfaces.

========= Concentration or kinetic parameters ? =========

The authors conclude that **struvite nucleation and the initial deposit of a first struvite layer on a new surface (induction) are mainly reaction-controlled (dependent upon supersaturation and thus pH),** with only a small transport influence. Induction is strongly influenced by the relative surface roughness of different materials.

Struvite crystal growth is essentially transport-controlled and is primarily influenced by mixing energy intensities, with a low sensitivity to temperature variation. At higher mixing intensities, control shifts to surface integration processes, and becomes more temperature sensitive.

========= Solubility constant =========

In previous work, the solubility constant of struvite had been measured using laboratory formation and dissolution equilibrium experiments, then confirmed in the same sludge supernatents used for the above work.

Formation experiments were carried out using solutions of $MgSO_4.7H_2O$ and $(NH_4)H_2PO_4$ in duplicated, pH adjusted with sodium hydroxide, in sealed 400 ml glass beakers at 25°C which were opened at 38 and 105 days. pH was measured on opening. The filtered precipitate was dried at 40°C in order to avoid loss of water of crystallisation (which occurs at 60°C according to Ando et al., 1968).

Dissolution experiments were carried out using struvite manufactured in the laboratory using the above method, and struvite collected from deposits formed during operation of the Sacramento sewage works (after identification of the material as struvite using powder X-ray diffraction analysis). The experimental conditions (time, temperature, equipment) were the same as those of the formation experiments.

Formation equilibrium was shown at pH 6.25-6.34 for phosphate concentrations of 20.6-21.6 mmol/l, or pH 7-7.12 for phosphate concentrations of 6.46-7.1 mmol/l. Dissolution equilibrium was shown at pH 8.06-8.34 for phosphate concentrations of 1.65 –1.94 mmol/l.

A solubility constant for struvite of pKSO = 13.26 was established, comparable to 13.15 proposed by Taylor et al. 1963 and 13.12 by Burns and Finlayson 1982.

The authors conclude that the solubility of struvite is lowest at pH 10.5-11, decreasing nearly linearly from pH 5 up to around pH 9. In particular, the authors predict significantly lower solubility at pH's 7-10 than do previous authors (Snoeyink and Jenkins curve, 1980).

A number of samples of sewage works sludge supernatents and digester supernatents were collected. Their conditional struvite solubility product was calculated and compared with the predicted curves. **The authors' curve correctly predicted struvite precipitation problems in the sludge lagoon supernatents** (whereas these were not predicted by the Snoeyink and Jenkins curve), corresponding to field observations of scaling on pipes and equipment in these lagoons.

"Kinetics effects on preferential struvite accumulation in wastewater", Journal of Env. Engineering, August 1999, pages 730-737. "Predicting struvite formation in digestion", Wat. Res., vol. 32 n° 12 pages 3607-3614, 1998.

K. Ohlinger, Civil and Environmental Engineering, University of Albama, Tuscaloosa, AL 35487–0205. T. Young, E. Schroeder, Civil and Env. Engineering, University of California, Davis One Shields Avenue, Davis, CA 95616, USA.

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - European Union

Phosphorus discharges dropping

"Environment in the European Union at the turn of the Century" is the latest report from Europe's green watchdog, the European Environmental Agency. This report, published in June 1999, indicates that cleaner rivers due to the application of waste water treatment legislation, and in particular reduced point phosphorus discharges, are one of the few environmental success stories.

This is against a background of **general environmental deterioration resulting from increased energy use and growth in transports.** Problems particularly emphasised are **the "snail-like" progress of nature protection measures,** waste, increased production and use of chemicals, noise, pollution and landscape fragmentation.

The report particularly underlines the continuing pressure on the environment from greenhouse emissions and increasing chemicals and waste. Considerable uncertainties are identified regarding areas where data is inadequate (soil loss, biodiversity, pesticides) or where issues are currently emerging (human health related questions such as hazardous substances or genetically modified organisms).

The report does identify some environmental success stories, in particular acid rain, ozone depletion substances and reduced pollution of water by organic and nutrient pollution from point sources.

========= Marked reductions in phosphorus from sewage works =========

The number of heavily polluted rivers has been reduced significantly, mainly as **a result of improved waste water treatment** (industries and sewage). The proportion of heavily polluted rivers in Western Europe has fallen from around 25% in 1975–80 to around 5% in 1992–98, in particular as a result of application of the urban waste water treatment Directive.

Over the past 15 years, many northern European countries have achieved 50-80% reductions in organic matter discharges and **60-80% reductions in phosphorus discharges from urban waste water treatment plants.**

Full implementation of the urban waste water treatment Directive 91/271 should **further reduce phosphorus discharges from sewage by 21% across Europe in the near future.**

======== Sources of phosphorus ========

The report indicates the proportion of phosphorus reaching surface waters from various sources : **agriculture is indicated to contribute 43% in the UK, 46% in Germany, 50% in Switzerland and 38% in Denmark.** In Norway, fish farms alone contribute around one half of the phosphorus discharged.

Over the North Sea catchment area, total phosphorus discharge to surface waters is estimated at 2.7 kg/hectare, with roughly half coming from sewage, somewhat more than a third from agriculture and the remainder from industrial and background sources.

======== Phosphorus levels declining in rivers and lakes ========

The phosphorus concentration in European Union rivers has been decreasing since the mid-1980's, with roughly a 25% reduction over a decade. The reductions have been most pronounced in the most polluted rivers. Similar improvements have been achieved in lakes, although the water quality in may cases is still poor and below that of good ecological status.

Regarding nitrates, on the other hand, the report emphasises the extent of nitrate contamination problems in drinking water extractions (although data across Europe and comparisons of changes over time are not available) and indicates that nitrate levels in surface waters have not decreased, despite the reduced application of nitrogen fertilisers.

Overall, regarding the effectiveness of policies for water quality, the report suggests that control of discharges has been relatively effective for point sources (treatment of urban and industrial waste waters), although there is room for improvement in most Member States.

Construction and upgrading of sewage works in Accession Countries would result in considerable reductions in pollutant discharges. The application of the urban waste water treatment Directive 91/271 in these countries would reduce phosphorus and nitrogen loadings to the Baltic and Black Seas by 15–30%.

"Environment in the European Union at the turn of the Century", European Environmental Agency 1999. ISBN 92-828-6888-5.

Available from EEA Information Centre, Kongens Nytorv 6, 1050 Copenhagen K, Denmark. Available in several languages. Price 21 Euros.

Email: information.centre@eaa.eu.int

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - Lower Rhine river

Silicate limitation of algal development

The production of phytoplankton was analysed in the three main branches and sedimentation areas of the lower Rhine river in Holland. A model based on carbon and silicate metabolism derived from sampling programme data which followed the water flow as it moved downstream.

Data were based on samples taken on five dates in 1988, one each month from April to August. Water was collected from the surface of the river at several points across its width. **The same body of water was sampled over a 96 hour period,** as it moved down the three branches of the river, the speed of movement being calculated on the basis of the average flow rate. The samples were analysed for photosysnthesis (carbon absorption at different light intensities), for dry weight of suspended matter and chlorophyll-a. Sky irradiance was obtained from local weather stations and the vertical light attenuation of the water was measured at the sampling stations.

======== Phytoplankton development model ========

A **plug-flow model of phytoplankton development** was constructed on the basis of :

- photosynthetic production and silicate uptake
- loss factors of algal biomass : respiration, grazing and sedimentation

The photosynthetic production was modelled on the basis of the sample data (measured photosynthetic rate of samples, sky irradiance data) and by application of reduction factors related to light attenuation in the water column (for all algal species) and to silicate limitation (applied to diatoms only).

======== Silicate limitation ========

It was assumed that phytoplankton growth was not limited by nitrogen or phosphorus, as average concentrations of soluble nitrogen and phosphorus in the lower Rhine were 5 mgN/l and 0.3 mgP/l respectively (1988), **whereas silicate in the river water was sometimes depleted in summer.**

The dissolved silicate concentration was modelled as affecting diatom growth, algal silicate uptake and algal cellular Si/C ratio (standard Si/C ratio = 0.6 mgSi/mgC, minimum 0.3).

The fraction of diatoms in the algal population was derived from cell counts taken on the five sampling dates, varying from 53–86% diatoms at the most upstream point and changing little as the water moved downstream.

Silicate was assumed to be not released from algae except after settling to the river bed, and a literature derived estimate of 10 mgSi/m2/h was used for release from the sediment.

Dissolved silicate concentrations at the upstream sampling point were observed to be lower during algal blooms (May, July and August) and to decrease as the water moved down the Rhine.

========= Algal grazing and biomass loss =========

Respiration losses, as a function of water temperature, were based on literature values from Janse and Aldenberg 1990 and Westlake 1980.

Settling rates, again based on literature values fro shallow lakes from Janse and Aldenberg 1990, were taken to be 3% per day for 5m deep water, which may be an underestimation for the sedimentation areas of the lower Rhine.

For zooplankton grazing of algae, the Janse and Aldenberg lake-derived functions were also applied, despite the fact that in **much of the lower Rhine rotifers are the dominant grazer with crustaceans reaching substantial numbers in the lowest reaches.**

======== Modelling results and conclusions ========

In periods without algal blooms (April, June), chlorophyll-a concentrations increased linearly as the water moved down the river. For the other months, **an initial increase was followed by a substantial decrease further downstream, thought to be the result of accelerated zooplankton grazing** (cf. Ruyter van Steveninck et al 1990).

The model correctly predicted significant phytoplankton losses due to zooplankton grazing during algal bloom conditions. Simulated zooplankton densities were in the range of 0.1–0.2 mgC/l, not far removed from the maximum zooplankton densities observed in the Rhine of 0.3 mgC/l (van Zanten and de Ruyter van Steveninck 1991).

The model predicted changes in dissolved silicate concentrations along the river matching with observations and diurnal variations agreeing with literature data.

The model indicates that the daily photosynthetic production rate can reach 50% of the algal biomass, enabling significant algal production even within the relatively short residence times resulting from river flow.

The model suggests that silicate limitation can decrease this algal production rate by a factor of 0.4–0.5, a reduction factor comparable to that observed in dilute plankton systems such as in Narragansett Bay (Kremer and Nixon, 1978). This is in agreement with certain field observations, such as the halving of phytoplankton photosynthetic capacity after dissolved silicate depletion in the Rhine (de Ruyter van Steveninck et al. 1992), or the observation of dead or poor condition diatoms at stations with low silicate concentrations (Bijkerk, in de Ruyter van Steveninck et al. as above).

"A model of phytoplankton production in the lower Rhine verified be observed changes in silicate concentration". Journal of Plankton Research, vol. 15, n° 6, pp 659-682, 1993.

W. Admiraal, Aquatic Ecotoxicity Section, University of Amsterdam, Kruislaan 320, 1098 SM, Amsterdam. S. Mylius, Inst. Theoretical Biology, Leiden University, PO Box 9516, 2300 RA, Leiden. E. de Ruyter van Steveninck, IHE – Aquatic Ecology, PO Box 3015, 2601 DA, Delft. D. Tubbing, National Inst. of Public Health and Environmental Protection, PO Box 1, 3720 BA, Bilthoven, Holland.

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - Lake Ecology

Dissolved Organic Carbon and nutrient response

The term dystrophic was first used for lakes with high Dissolved Organic Carbon (DOC) by Theinemann in 1921. This overview paper presents the different ways in which varying DOC levels modify lake response to many environmental and anthropogenic factors. The authors suggest that the widely used lake nutrient level - algal productivity paradigm should be extended to take into account DOC concentrations.

Although DOC varies considerably in forms and properties, its overall ecosystem significance can be approximated by measuring light absorption, which varies as a function of coloured DOC. The authors suggest using light absorption at a wavelength of 320 nm which is a reasonably good approximator, even if the 320 nm absorption / DOC ratio can vary over an order of magnitude.

The use of this “proxy” for the real quantities and properties of DOC is comparable to the widespread use of “total phosphorus” concentrations as a proxy indicator of eutrophication status (chlorophyll concentration). Both these proxies **show a clear statistical relationship but do not reflect the varying characteristics of any given waterbody**.

========= Importance of DOC =========

Variations between the concentration and forms of DOC in different lakes will very significantly modify response to factors such as nutrient loadings, organic toxins, metals, acid precipitation, increased UV radiation (resulting from deterioration of the ozone layer) or climate change. **The authors group these effects into four areas :**

Processes influenced by DOC in fresh water :

1. Attenuation of solar radiation

- reduces primary productivity
- attenuates damaging UVR radiation
- decreases mixing in small lakes

- alters depth distribution of algae and grazers
- alters water colour

2. Indicator of watershed characteristics and of local and global processes :

- reflects watershed drainage, morphology, vegetation
- drought decreases DOC
- forest fires increase DOC
- acidification decreases DOC
- global warming modifies DOC

3. Modification of response to toxicants and to nutrients

- increases acidity but reduces impact of acidity on biota
- reduces metal toxicity, binds pethylmercury
- reduces toxicity or bio-availability of organic toxins
- alters availability of P; Fe and modifies carbon cycle, thus modifying nutrient response

4. Problem for drinking water supply

- reduces effectiveness of disinfectants
- generates toxic chemicals with chlorine or ozone disinfectants

======== DOC and nutrient response ========

Lake response to nutrients is modified by DOC both directly, through reduced availability of phosphorus (Stewart and Wetzel 1982, Francko 1986) and iron (Jackson and Hecky 1980), but also, to a large degree, indirectly through effects on primary production, water temperature, mixing …

Carpenter et al. 1998 estimated that increasing refractory DOC from 5 to 17 mg/l will **reduce primary production and chlorophyll concentrations** (because of reduced light penetration) to an extent comparable to a reduction in phosphorus loading from 5 to 0.5 mgP/l. Field evidence of this is derived from work by Christensen et al. 1996, where Long Lake, Wisconsin, USA, was artificially divided to separate sources of organic carbon. DOC in the East Basin almost doubled from 7.5 to 14.1 mg/l over 2 years, suppressing increases in primary production even when the lake was enriched with N and P.

======== Evidence from Alaskan glacial lakes ========

The pronounced deglaciation chronosequence has left behind in Glacier Bay, Alaska, a series of lakes varying in age from 10 to over 1,000 years, in a pristine environment with low lake productivity. The younger lakes have only sparse vegetation in their watersheds, are fed by groundwater and have extremely low DOC.

As the lakes become older, vegetation, and then peat, develop in the watershed, often leading to high levels of DOC in the older lakes. Consequently, the depth penetration of 320 nm light decreases with lake age. Phosphorus concentrations, on the other hand, remain relatively constant.

Light and UVR penetration data from a subset of 32 of these lakes show pronounced directional changes in coloured DOC, indicative that the low DOC levels in the younger lakes make them very vulnerable to environmental modifications.

To summarise, the authors indicate that **higher DOC levels render lake ecosystems significantly more capable of adjusting to changes in environmental factors**, to anthropogenic stressors or to nutrient loadings. DOC also provides a valuable indication of how lakes interact with their watershed and local climate.

The authors conclude that **the reinstatement of a DOC axis in the nutrient – productivity paradigm will provide a more reliable conceptual framework for understanding lake ecology** and for addressing lake management.

"Dissolved organic carbon and nutrients as regulators of lake ecosystems : resurrection of a more integrated paradigm". Limnol. Oceanogr. 44 (3, part 2), 1999, pages 795-803.

C. Williamson, D. Morris, O. Olson, Dept. Earth and Env. Sciences, Lehigh University, Bethlehem, Pennsylvania 18015-3188, USA. M. Pace, Institute of Ecosystem Studies, Cary Arboretum, Box AB, Millbrook, New York 12545, USA.

SCOPE NEWSLETTER

SCOPE N°36 - 03/2000 - Texas Reservoirs

Nutrient limitation of algal growth

Nutrient limited algal growth in two Texas reservoirs was studied by a combination of nutrient addition experiments and statistical modelling. Algal growth proved frequently and strongly nutrient limited, with N being more often stimulatory than P. Half saturation constants for nitrogen were in the range 20–200 µg/l, relatively high compared to literature values.

The two reservoirs studied were Eagle Mountain Lake (32°52’ N) and Cedar Creek Lake (32°14’ N). Their areas are respectively 3,638 and 13,950 ha ; mean depths both 6.1m ; residence times 198 and 275 days. Their dissolved inorganic N:P ratios were respectively 3.33 and 2.62 by weight ; and total N (excluding dissolved organic N) : total P loading ratios 5.04 and 4.29.

On eighteen separate dates in January - June 1994, samples were collected from several sites in the two reservoirs and mixed together to make a composite sample for each reservoir.

======== Bottle bioassay experiments ========

In order to permit development under non-crowded conditions, the algal population concentrations in the samples were “diluted” by a factor of 9 by adding 0.2µm filtered sample water. Development of algal density was measured (using chlorophyll concentration) over 4 days, following addition of 0, 10, 100, 200 and 1000 µg/l of soluble P or soluble N, trace elements only, or 1000 µg/l of both P and N plus trace elements (3 duplicates for each test). Light and temperature were maintained at conditions typical of the mixed layers of the reservoir at the relevant time of year.

"Dissolved organic carbon and nutrients as regulators of lake ecosystems : resurrection of a more integrated paradigm". Limnol. Oceanogr. 44 (3, part 2), 1999, pages 795-803.

C. Williamson, D. Morris, O. Olson, Dept. Earth and Env. Sciences, Lehigh University, Bethlehem, Pennsylvania 18015-3188, USA. M. Pace, Institute of Ecosystem Studies, Cary Arboretum, Box AB, Millbrook, New York 12545, USA.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Nitrogen - Phosphorus ratios

Variations in nutrient-chlorophyll relations

Data on total nitrogen, total phosphorus and chlorophyll-a concentrations from 133 lakes were analysed to test predictions of nutrient limitation and nutrient-chlorophyll regression theories. Results were confirmed with independent data from other lakes.

Ordinary regression analysis of Chl-a, total P (TP) and total N (TN) gave the following equations :

$$\log_{10}\text{Chl-}a = -0.39 + 0.874 \log_{10}\text{TP} \ (r^2 = 0.69)$$
$$\log_{10}\text{Chl-}a = -3.131 + 1.445 \log_{10}\text{TN} \ (r^2 = 0.69)$$
$$\log_{10}\text{Chl-}a = -2.213 + 0.517 \log_{10}\text{TP} + 0.838 \log_{10}\text{TN} \ (r^2 = 0.81)$$

The best fit LOWESS regression curves suggest that there is a concentration of TP (around 100-125 µgP/l) above which increases in TP have nearly no effect and increases of TN a reduced effect (unlike for TP, there is no asymptotic value for TN). Low values of TN also have little effect.

========= No higher Chl-*a* values related to high TP =========

It is often widely suggested that **high TP concentrations (above the asymptotic value) are not related to increased Chl-*a* values** because of light limitation. However, the continuing (if slower) increase in Chl-*a* values related to higher TN concentrations suggests that this cannot be the correct explanation.

It has already been indicated by other authors that TN is nearly as closely related to Chl-*a* as is TP (Forsberg and Ryding 1980) or better related (Canfield 1983). In the data analysed, **TN had the same predictive power as TP but with a steeper slope.** Nonetheless, most work on freshwaters looks at TP - Chl-*a* relations with little or no concern for TN - Chl-*a* relations.

========= TN : TP ratios =========

It is to be noted that TN and TP ratios are log-log significantly correlated for the data analysed (r=0.71).

Analysis of the TN:TP ratios shows that **there is a clear region (23 < TN:TP ratio < 28, by weight) for which Chl-*a* values vary considerably with changes in nutrient concentrations** (TP and/or TN). At low (TN:TP < 15) and high (TN:TP > 35) ratios, Chl-*a* values are scarcely related to nutrient concentrations.

As might be expected from nutrient limitation theory, in lakes with very high TN:TP ratios (> 50), TP does indeed become more closely related to Chl-*a* concentrations than TN.

======== Variations in TN: Chl-*a* and TP:Chl-*a* relations ========

Various authors have previously underlined the **substantial variability in nutrient:Chl-*a* relations (eg. Smith and Shapiro, 1981) : regression coefficients vary to the extent of giving several fold differences** for predictions for individual lakes.

Various previous authors have also demonstrated that multiple regression analyses of other biological and physical factors do not explain much of the residual uncertainty.

The authors data analysis shows that the TN:Chl-*a* and TP:Chl-*a* regressions vary consistently with TN:TP ratios. **The authors indicate that these results show that the use of constant slope nutrient:chlorophyll models is inappropriate.**

They also indicate that, because of the nonlinearity of slopes, **it would be "very difficult at best" to develop a single multiple regression models to account for the widely changing behaviour of phytoplankton biomass and nutrient levels at different TN:TP ratios.**

An explanation of this variability is offered : **variation in phytoplankton species composition.** The TN:TP ratio at which Chl-*a* values vary most with nutrient concentrations (23-28 by weight) is close to the average cellular N:P ratio of algae (30 by weight, Shuter, 1978). Thus varying response could result from changes in phytoplankton species composition between species best adapted to differing TN:TP ratios.

"Unifying nutrient – chlorophyll relationships in lakes". Canadian Journal of Fisheries and Aquatic Sciences, vol. 46, number 7, 1989. Pages 1176-1182.

Y. Prairie, C. Duarte, J. Kalff. C. Duarte. Dr Carlos Duarte, Instituto Mediterraneo de Estudios Avanzados CSIC, carretera de Valldemossa km 7.5, 07171 Palma de Mallorca (Islas Baleares), Spain.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Florida

Assessing factors limiting algal growth

Spring/summer samples from a number of sites in three Shallow Florida lakes and along 46 km of a low-flow river were analysed for different forms of phosphorus and nitrogen (total, dissolved, biologically available), for chlorophyll-a and Secchi disc transparency, and using nutrient enrichment bioassays.

The "Redfield ratio" of 106:16:16:1 (by atoms) for carbon: nitrogen : silicon : phosphorus is derived from the largely constant ratio found in marine particulate matter by Redfield *et al.* 1963. This ratio is generally thought to be applicable to freshwater algal systems, except for the silicon requirements of diatoms which are approximately twice those of marine organisms. By extension, freshwater literature often considers that TN:TP ratios (measured total nitrogen: total phosphorus) > 16:1 indicate that phosphorus is the limiting nutrient for algal growth. To test this hypothesis, samples from four Florida surface waters were studied :

- **Lake Apopka,** 124 km 2 : hypereutrophic, mean TP 203 µg/l, mean TN 5110µg/l, TN:TP = 56:1.
- **Lake Okeechobee,** 1732 km 2 : five distinct ecological zones sampled mean TP 58-127µg/l, TN 1180-1342 µg/l TN:TP from 23 – 52.
- **Lower Saint Johns River,** 46 km reach, residence time 3 - 8 weeks : mean TP 75 µg/l, mean TN 1200 µg/l, TN:TP = 35
- **Anderson-Cue Lake,** oligotrophic : nutrient levels similar to rainwater.

======== TN:TP ratios wrongly predict P limitation ========

Use of the TN:TP ratios for these waters suggest that they are phosphorus limited, but this proves not to be the case.

Nutrient enrichment bioassays indicate that Lake Apopka, Lake Okeechobee and the lower Saint Johns River are in fact limited by nitrogen and/or light. The generation of algal growth in Anderson-Cue Lake requires not only the addition on both nutrients, but also trace metals.

Comparison of dissolved available nutrients (DIN Dissolved Inorganic Nitrogen : Soluble Reactive

Phosphorus SRP) ratios predict that Lake Apopka, Lake Okeechobee and the lower Saint Johns River are nitrogen limited, thus proving to provide better indicators than TN:TP ratios.

The authors note however that SRP measurements do not take into account stored cellular phosphorus, which can often be accumulated by algae in sufficient quantities to support several cell divisions. **DIN:SRP ratios >16 can thus also give a false indication of P limitation.** Nitrogen can also be stored in cells, but storage is limited and quantitively less significant than P storage (Reynolds, 1984).

The authors suggest that the comparison of biologically available nitrogen (essentially DIN plus urea) to BAP biologically available phosphorus (SRP plus cellular phosphates, which can be hydrolysed by enzymes – Newman *et al.* 1994) would provide a better indication of nutrient limitation. For comparison, concentrations of the various forms of phosphorus (different availability) in Lake Okeechobee are given :

µg/l	***SRP***	***BAP***	***TP***	***TN:TP ratio***	***BAN:BAP ratio***
Lake Okeechobee					
Zone 1	*46*	*114*	*127*	*23*	*17*
Zone 2	*27*	*34*	*94*	*28*	*11*
Zone 3	*15*	*20*	*68*	*44*	*9*
Zone 4	*12*	*21*	*58*	*52*	*9*

========= Wollenweider model =========

The accuracy of total phosphorus concentrations for predicting chlorophyll-a levels were tested. Relatively low predictability was shown ($R^2 = 0.59$). **A better fit was found for the regression of chlorophyll-a on total nitrogen** ($R^2 = 0.77$), similar to that found using both TP and TN ($R^2 = 0.81$).

The authors emphasise that **using total nutrient level regressions to model chlorophyll levels is based on correlated not causal factors** and that many lakes do not fit the predicted patterns.

In the case of the Florida waters, assessment of nutrient limitation is confused by rooted macrophytes which compete with phytoplankton for available nutrients. Water depth, light limitation and wind induced water column mixing (which can suspend benthic algae and sediment nutrients) also render the assessment of trophic status more difficult.

The authors conclude that they have shown that **TN:TP ratios give false predictions of limiting nutrient status.** However, measurements of biologically available nutrients or nutrient limitation bioassays, which provide information on current nutrient limitation, must also be interpreted in a historical perspective. Managers must evaluate and use many sources of information to define policies to control and prevent undesirable algal and macrophyte problems.

"Assessing nutrient limitation and trophic state in Florida lakes". In Phosphorus Biogeochemistry in Subtroipical Ecosystems, CRC/Lewis Publishers 1999, pages 321-339.

K. Reddy, G. O'Connor, C. Schelske. Contact : Prof. Claire Schelske, Water Resources, Inst. Of Food and Agricultural Sciences, Florida University, 7622 NW 71st Street, Gainesville, FL 32653-3071, USA.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Belgium, River Meuse

Grazers can sometimes control algae in rivers

There is a certain amount of experimental evidence of zooplankton control of algal development in lakes, where grazing can lead to clear water phases even in eutrophic lakes and can modify phytoplankton species composition. Such grazing is particularly associated with larger zooplankton species, which are generally absent from rivers (because of short residence times). This study shows, however, that zooplankton control of algae can nonetheless also occur in rivers.

The site studied, La Plante in Belgium, is situated 537 km from the source of the Meuse river and 348 km from confluence of the Meuse and the lower Rhine. Phytoplankton, zooplankton and grazing measurements, as well as physical (flow, temperature, light) and chemical parameters (water nutrient concentrations) were measured during the spring and summer over a three year period (1994-1996).

At the point studied, the Meuse is on average 100m wide and 3.95m deep, with alkaline, nutrient rich waters. **Total phosphorus varied during the three years studied from 27 – 428 µgP/l with annual averages of 133 – 226 µg/l.** Total nitrogen varied from 2.3 – 16;3 mgN/l, with annual averages of 3.6 – 4.3 mgN/l.

Flow varies from up to 500 m^3/s down to below 50 m^3/s with low flows of below 100 m^3/s occurring in spring and summer.

======== Variations is phytoplankton and zooplankton populations ========

The study provides considerable data on algal and grazer species variation, populations and seasonal variations. Changes in algal biomass and species composition observed each spring were probably influenced mainly be decreasing flow and increasing light and temperature. The spring development of zooplankton appeared to depend on weather conditions, probably occurring in response to downstream transport resulting from flow and to temperature variations.

The most abundant spring zooplankton were *Brachionus calyciflorus* and *B. angularis*, rotifers widely considered to be generalists.

Maximum daily filtration rates of 113%/day were achieved when rotifer densities reached several thousand per litre. **Such high filtration rates have rarely been reported from rivers.**

Grazing rates during the spring algal bloom ranged from 0.5 – 2.15 gC/m^2/day. In most cases, **this was sufficient to reduce algal biomass by a factor of 10 within two weeks** and approached or even surpassed the algal net production rate.

Even higher grazing rates were noted in summer, at the same time as a shift towards larger species of algae and a decline in algal biomass. These changes occurred after increases in grazer biomass and species diversity, and probably resulting from selective grazing of the smaller algal species.

The **zooplankton grazing effectiveness was very size specific,** depending on the relative size composition of both the algal and grazer communities, rendering simple model simulation of grazing impossible.

The authors suggest that **the algal community composition in large rivers can, at times, be effectively controlled by grazers,** but that this occurs when physical restraints are reduced (low flow, high temperature) and when availability of edible algae allows high grazer biomass.

"Can a community of small-bodies grazers control phytoplankton in rivers". Freshwater Biology n° 39, pages 9-24, 1998.

V. Gosselain, L. Viroux, J-P. Descy, Freshwater Ecology Unit, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, 5000 Namur, Belgium.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Lake Mendota, Wisconsin

Factors affecting summer algal density

Lake Mendota is a eutrophic 24m deep lake in Winsconsin with a 604 km^2 rural watershed. The principal phosphorus loading is from agricultural run-off in the main tributary rivers.

Over the period 1976 – 1995, data were collected for summer water clarity (Secchi disk depth visibility), indicative of algal development ; phosphorus loadings ; spring in-lake phosphorus concentration ; daphnia species distribution, size, density and biomass ; lake mixing index (Schmidt stability – indicative of temperatures and wind). Lake water mixing is lower during high spring and summer temperatures.

Total phosphorus in the lake water in spring varied during the twenty years from 70 – 160 µg/l with no definite long-term trend.

The deep water in the lake is generally anoxic by early July, so zooplankton counts through a vertical net sweep were corrected to give densities in oxygenated water zones only.

========= Daphnia densities =========

The main zooplankton grazer species present in the lake were almost always *Daphnia pulicaria* and *Daphnia galeata mendotae*. *Daphnia* biomass was generally greater in years when *D. pulicaria* dominated. *D. g. mendotae* dominated most spring clear water periods, probably because of relatively high predation by fish (cisco, yellow perch, white bass). *D. pulicaria* dominated in years with lower fish predation.

Over the study period, *Daphnia* biomass varied from near zero to 487 µg/l, with averages of 236µg/l in June in *D. pulicaria* dominated years and 127 µg/l in *D g. mendotae* years, falling respectively to 66 and 14 µg/l in August..

20 cm Secchi disk depths fell to an average of 1.92m in August in *D. pulicaria* years and 1.44m in August in D. g. mendoatae years.

========= Modeling algal growth =========

The different factors tested as predictor variables for algal development were phosphorus loadings, April in-lake phosphorus concentrations, *Daphnia* biomasses and lake stability. These factors varied considerably, but independently (non significant correlation coefficients).

Significant relationships were found between July - August mean Secchi disk depth (indicator of water clarity, and so of algal development) and April in-lake phosphorus concentration, midsummer *Daphnia*, lake mixing.

June Secchi depth is, however, governed mostly by May and June *Daphnia* biomass. Loss of water clarity occurred in only two years, and was probably the result of high fish zooplankton predation in one year and of an unusual spring (inedible) blue-green algal bloom *(Aphanizomenon flos-aquae)* in the other year.

In years with early spring warming, water clarity can occur early (in May rather than June), leading to declines in Daphnia populations and subsequent algal development in summer.

External phosphorus loadings were not a very effective annual predictor variables, because much of the lake's phosphorus availability in any one year comes from internal loading, which is related to mixing.

The authors conclude that summer water clarity is essentially governed by in-lake phosphorus concentrations, related mainly to lake mixing, and *Daphnia* grazing.

"Summer water clarity responses to phosphorus, Daphia grazing and internal mixing in Lake Mendota". Limnol. Oceanogr. 44(1), pages 137-146, 1999.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - China

Health impacts of water pollution

China faces a range of serious water quality problems, with significant health impacts.

Widespread contamination of surface and drinking waters by pesticides and nitrates results in regional diseases such as gastric illnesses and cancers in areas with intensive irrigated agriculture.

The discharge of **30 billion tons/year of sewage - 97.3% of which is untreated** - results in 1.5 million cases of acute schistosome infections/year, as well as the common occurrence of hepatitis A, diarrhea, para-cholera and typhoid.

The rapid development of small industries in rural areas (Town and Village Industries = TVIs) is accentuating industrial pollution problems, as these installations generally operate without any waste water treatment.

Pollutants generated include heavy metals, cyanide and phenol.

======== Nitrates and pesticides ========

China currently feeds some 1.2 billion people from only 133 million ha of arable land. This has led to a rapid intensification of agriculture, with considerable use of mineral fertilisers and a wide range of pesticides.

The average rate of application of mineral fertiliser nitrogen application in China (Sun 1995) was 191.6 kg/ha, which is around 3.55 x the world average. The P:N ratio for mineral fertiliser application was however roughly half the world average.

90% of rural populations rely on shallow water tables (0.2 - 10m depth). The quality of these resources has deteriorated rapidly. **There are a number of reported cases of groundwater nitrate levels well above the WHO guideline** for drinking water (10 mg/l NO_3-N) : Yuanmingyuan, Tai-hu lake, Matan - Lanzhou City (291 mg NO_3-N), Ganshu, Beijing, Fujian, Zhejiang.

One survey found nitrates in excess of norm levels in 37 out of 69 groundwater resources tested.

Pesticides are applied at an average of 2.82 kg/ha active ingredient. As a result, significant concentrations occur in rivers and lakes, and even offshore. Concentrations of up to 80 µg/l of HCH have been reported, with, for example, 3.89 µg/l in Tai-hu Lake.

Concentrations of **DDT, HCH, Alachlor, Dimehypo, Delachlor, Aldicarb, Aldicarb sulfoxide, and Aldicarb sufone** have also been found in groundwater, leading in some cases to the closure of drinking water wells.

One study looking at the use of Pentachlorophenolate to eradicate the snail *Oncomelania* (intermediate host of shcistosomiasis) showed concentrations of up to 6.8mg/g in foods, 7.3 g/l in milk and 257 mg/g in human body fat in areas using the pesticide. The rate of cancer mortality in these areas was 2 - 3 times higher than control areas, although this may have been influenced by other factors.

Eutrophication of rivers and lakes is also a widespread problem, with numerous cases of toxic algal blooms. These can result in health problems, including a risk of liver cancer. Eutrophication in China is a consequence of excessive use of fertilisers, discharge of untreated sewage, animal manures and industrial waste waters.

========= 2.7% of sewage treated =========

Almost all monitored urban river sections in China in 1994 failed to meet designated quality standards (131 out of 135). Moreover, 52 of these urban 135 river sections failed even to meet the lowest quality standard.

Most urban pollution is linked to organic loads. In 1995, only 100 sewage works were operational across China. **Only 2.7% of China’s 30 billion tons/year of urban sewage are treated before discharge.**

The result is significant health risks, with only 6 of China’s 27 largest cities providing drinking water which meets government standards. 1.5 million people contract schistosome infections annually, and the incidence of typhoid fever is 10.6/100,000.

Pollution from sewage is compounded by intensive cultivation of vegetable plots and small-scale poultry and other animal rearing installations in cities.

Even larger quantities of industrial waste waters are produced (approx. 15 x sewage volumes), and these are also largely untreated. Small rural industries (Town and Village Industries) pose a particular problem, with a rapid increase in industrial production and virtually no waste water treatment. Specific problem industries include paper and pulp mills, chemical industries, metal treatment, dyeing and leather tanning plants.

"Agricultural diffuse pollution from fertilisers and pesticides in China". Wat. Sci. Tech. Vol. 39, n° 3, pages 25-32, 1999.

Yong Li, Dept. Environmental Science, Institute of Soil Science, CAS, Nanjing 210008, China. Jiabao Zhang, Dept. Soil Physics, Institute of Soil Science, as above.

World Resources Institute dossier "Water pollution and human health in China" : http://www.wri.org/health/prcwater.htm.

C. Maurer, C. Wu, World Resoureces Institute, Washington DC, USA. Y. Wang, Chinese Academy of Sciences, Bejing. S. Xue, School of Public Health, Shanghai Medical University, China.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Baltic Rivers

Underestimation of diffuse sources

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Baltic Lakes

Phosphorus forms in sediments and release mechanisms

This study compared the chemical form and vertical distribution of bound phosphorus in sediments from two Baltic lakes, one oligotrophic and one eutrophic. Conclusions were drawn regarding phosphorus release mechanisms from sediments and regarding mechanisms for long-term P burial in the different lakes.

The lakes studied are in the Northern German lowland Baltic lakes region. **Lake Stechlin** is one of the last oligotrophic lakes in this region, with an area of 4.25 km^2 and a maximum depth of nearly 70m. The whole water body has permanently oxic conditions.

Lake Feldberger Haussee (1.3 km^2, max. depth 12m), on the other hand, was originally slightly eutrophic and was then heavily polluted by sewage inflow. Following sewage diversion in 1980, quality has gradually improved, but total phosphorus concentrations are still over 100 μgP/l and oxygen depletion often occurs in the deeper waters.

========= Similar sediments despite differing trophic states =========

Sediment cores were taken from depths of 32m in Lake Stechlin and 8.5m in Lake Haussee, in spring and summer. Samples of the sediment cores from different depths were separated and analysed for organic matter, $CaCO_3$, Fe, Al, Mn, Ca and different forms of phosphorus, in the interstitial water and in the sediment particles. Differently bound phosphorus forms were assessed as soluble reactive phosphorus (SRP) and total phosphorus (TP), by using a progressive sequence of extractions with 1M NH_4Cl, 0.11M $Na_2S_2O_6$, 1M NaOH, 0.5M HCl and $K_2S_2O_8$.

The overall composition of the sediment, and in particular the proportion of organic matter, proved relatively similar in the two lakes. The soluble P concentration in the interstitial water was however significantly higher in the eutrophic Lake Haussee.

========= Importance of Fe- and Mn- bound phosphorus in

oligotrophic conditions ========

The proportion of NH_4Cl extractable P in both lakes decreased in deeper sediments, where the pH was lower. During the NH_4Cl extraction, relatively large amounts of Ca were mobilised, suggesting that a significant proportion of the NH_4Cl extractable P is **loosely adsorbed to calcite.** The proportion of such loosely adsorbed P in Lake Haussee (4-8% of total P) was higher than in Lake Stechlin (1-3%).

Reductant soluble ($Na_2S_2O_6$ extracted) P was considerably higher in Lake Stechlin than in Lake Haussee (1.29 gP/kg n the top 1cm of sediment, compared to 0.32 gP/kg in Lake Haussee). The amounts of Fe and Mn extracted were also higher in Lake Stechlin. $Na_2S_2O_6$ extracted P levels were higher near the sediment surface and made up 54% of total P in the top centimetre of Lake Stechlin sediment. This is related to the oxic conditions occurring at the sediment surface in this oligotrophic lake.

It is suggested that **burial of Fe- and Mn- bound P, involving moving into anoxic conditions, is the main mechanism for phosphorus release in the sediments of Lake Stechlin.**

NaOH extractable P was higher in Lake Haussee, as were the amounts of extracted Al. This corresponds to higher levels of Al- and Fe- bound phosphorus in the eutrophic lake.

======== Importance of $CaCO_3$- bound phosphorus in eutrophic conditions ========

In the Lake Haussee sediment, some 32% of total phosphorus is bound to calcium carbonate ($CaCO_3$), compared to only around 14% in Lake Stechlin, despite similar $CaCO_3$ levels in the sediments. **This suggests that co-precipitation of phosphorus with autochthonous calcite precipitation increases the P-binding capacity of the sediments.**

In Lake Haussee, the level of labile organic phosphorus at the sediment surface decreased rapidly with depth.

======== Differing phosphorus mobilisation between the two lakes ========

The authors conclude that whilst the quantities of dissolved, loosely adsorbed, metal oxide- and calcium carbonate- bound phosphorus are higher in the sediments of the eutrophic lake, the Fe- and Mn- bound (reactant soluble) fraction was considerably higher in the oligotrophic lake.

The mobilisation of recently deposed labile organically bound phosphorus is the driving mechanism for sediment phosphorus release in eutrophic conditions, whereas release from Fe and

Mn (due to burial leading to anoxic conditions) is the main mechanism in oligotrophic conditions.

Co-precipitation of phosphorus with calcite is an important mechanism in both conditions. Since this process takes place faster in eutrophic conditions, it can be a significant self-cleaning mechanism, thereby permitting long-term removal of phosphorus from the lake water.

"Phosphorus binding forms in the sediment of an oligortophic and an eutrophic hardwater lake of the Baltic Lake district (Germany)". Wat. Sci. Tech. Vol. 37, n° 3, pages 51-58, 1998.

T. Gonsiorczyk, P. Casper, R. Koschel. Institute of Freshwater Ecology and Inland Fisheries, Dept. Limnology and Stratified Lakes, Alte Fischerhütte 2, D16775 Neuglobsow, Germany.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Surface Water Management

Phosphorus in sediments

This paper provides an overview of current knowledge regarding phosphorus cycling mechanisms within sediments and discussions the implications for surface water management and for global environmental cycles.

For a number of lakes, it has been shown that **internal P loading by release from sediments can equal or exceed external nutrient inputs.** The retention of phosphorus in surface waters, by immobilisation, burial and infiltration to deep sediments, has a major impact both on the quality of the surface water and ultimately on the transport of phosphorus into the sea. It is generally recognised that it is phosphorus availability which limits marine productivity over geological time scales.

======== Sediment retention mechanisms ========

Sediment nutrient retention results mainly from the **deposition of particles on the sediments** as dead or decaying phytoplankton (primary production). In some waters, however, the deposit of inorganic phosphorus precipitants can be of significant importance (deposit of calcium carbonate particles, adsorbtion on ferric (oxi)hydroxide surfaces).

Within the sediment, a number of **microbiologically and chemically induced transformations** take place as well as in-sediment transport through sediment mixing and accumulation and water percolation. Over the long term, the accumulation of nutrients in the sediments will be equal to the net sediment accumulation rate (m/year) multiplied by the average nutrient content. Over the shorter term, high P loadings result in the binding on iron in the sediments, and this phosphorus can readily be released back into the water when P loading is reduced or with changes of redox state in the sediment.

Long term retention of phosphorus in the sediments therefore depends on three mechanisms : net deposit of particulate P, early diagenetic cycling and transformation of reactive P compounds in the sediment surface layer, burial of non mobilisable P compounds in deeper sediment layers.

======== Case studies ========

The paper examines four cases where phosphorus sediment mechanisms have been studied, each related to

nutrient inputs from the river Rhine :

- Lake Veluwemeer, Holland
- Ijsselmeer, Holland
- The Western Dutch Wadden Sea
- The German Bight in the North Sea.

The authors note that **average P concentrations in the Rhine have been reduced from around 30µg/l in the late 1970's to 5 µg/l today.**

In **lake Veluwemeer,** sediment P retention occurs in the deeper part of the lake and is mainly associated with calcium compounds (50-60%) or iron and aluminium compounds (10-20%). Around 70% of the downward transport of P results from infiltration of dissolved P, and the remaining 30% from burial. Roughly 50% of the P in the sediment is not susceptible to reduction. When phosphorus loadings to the lake were reduced in 1979-1980, accompanied by increased flushing with water rich in nitrate and carbonate, the P concentration in the lake dropped rapidly and this was not offset by significant sediment release.

However, in **lake Ijsselmeer a rapid roughly 60% reduction in P loadings from 1982 resulted in only slight decreases in water P concentrations** until 1988 when they fell sharply. The relatively high sediment P retention in Ijsselmeer, despite low sediment iron concentrations, is thought to be related to sedimentation of the input river particle load and to continuous delivery of new sorption surface by the river Ijssel.

In the **Wadden Sea,** particulate organic matter is imported with the tides and deposited near the main land where it is mineralised during the summer when the temperature is higher.

In the German Bight, nutrients are transported to and deposited in the Skagerrak as a result of currents. Because this transport takes around a year, only aged organic materials are deposited and most are mineralised before arrival. Large amounts of P are released from the Skagerrak sediments in summer, when oxygen penetration to the sediment is near zero, by the reductive dissolution of iron : pore water concentrations of phosphorus can reach 700 µg/l.

======== Agricultural sources and lake management ========

The authors note that there is now considerable knowledge available concerning the mechanisms and dynamics of sediment nutrient retention and release. The number of scientific papers on this subject, particularly the **number of papers relating to lake restoration being published, is decreasing,** indicating that we now "know enough".

The authors note, however, that the considerable research over the last two decades has not resulted in new approaches to lake restoration. There have been few applications of sediment restoration techniques. The knowledge developed has, though, led to **more realistic expectations of lake restoration programmes.**

The authors indicate that it is increasingly recognised that **most of the nutrients of anthropogenic origin entering lakes and coastal waters originate from agriculture.** Management policies therefore need to be defined at the whole watershed level and take into account the transformations undergone by agricultural phosphorus inputs as they move through surface waters to the sea.

For the future, there is considerable interest developing into the **long term role of phosphorus in global productivity cycles.** Van Cappellen and Ingall (1996), for example, demonstrate that the redox dependent burial of phosphorus in ocean sediments provides a powerful forcing mechanism for balancing production and consumption of atmospheric oxygen over geological time scales.

The authors indicate the need for studies of **how phosphorus cycling affects the atmospheric carbon dioxide balance, and thus the greenhouse effect.**

"Phosphorus retention is sediments". Wat. Sci. Tech., vol. 37, n° 3, pages 31-39, 1998.

P. Boers, D. van der Molen, Institute for Inland Water Management and Waste Water Treatment (RIZA), PO Box 17, 8200 AA Leystad, Holland. W. van Raaphorst, Netherlands Institute for Sea Research (NIOZ), PO Box 59, 1790 AB Den Burg, Holland.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Grassland

Phosphorus leaching from farmland

Large monolith lysimeters (135 cm deep, 80 cm square) were used to measure reactive and organic phosphorus concentrations in leachate underneath farm grassland under natural rainfall conditions.

Four replicate lysimeters were used in each of four different soil types (silty clay, well drained clay-loam, sandy loam over chalk, sandy soil), with intact soil blocks installed in a field site at the Institute of Grassland and Environmental Research, North Wyke, Devon, UK.

They were managed as typical cut grassland with application of NPK fertiliser in accordance with UK Ministry of Environment guidelines. 25 kg/year/ha of phosphorus was applied as Triple Super Phosphate mineral fertiliser.

Natural rainfall was around 1100 mm/year and leachates were collected between November 1997 and June 1998.

======== Most leached phosphorus biologically available ========

The average total phosphorus concentrations in the different soils' leachates at 1.35m depth ranged from 61 - 152 µgP/l; high enough to present a significant threat to surface waters, and remained consistently high throughout the drainage year.

The percentage of total phosphorus present in leachate in an immediately biologically available form (molybdenum reactive P) varied from 68 - 86% between the different soil types.

The authors underline, however, that the "unreactive" fraction of total phosphorus is generally organic, and is thought to be potentially bioavailable after enzyme metabolism in surface waters. Further research is necessary to quantify the bioavailability of the organic fractions of leached phosphorus from grasslands.

The authors also measured the "Olsen-P" status of the soil ($NaHCO_3$ extractable phosphorus), which is generally used as an index of soil phosphorus status. There was no apparent correlation between Olsen-P in the soil and the concentration of phosphorus being leached.

========= Grassland P-leaching : a significant risk of surface water pollution =========

Farmed grasslands cover large areas of land in the UK and the authors conclude that, in contrast to traditional perceptions, phosphorus leaching from them can pose a significant risk to surface water.

Most past evidence regarding phosphorus leaching from agricultural land comes from plot-scale studies where sub-surface leaching has rarely been measured. The authors' direct measurements from large monolith lysimeters suggests phosphorus leaching of 51 - 152 µg/l, mainly in inorganic bioavailable form.

"Phosphorus leaching under cut grassland". Wat. Sci. Tech vol.39, n° 12; pages 63-67, 1999. B. Turner, Dept. Geography, Royal Holloway, University of

London, Egham, Surrey TW20 0EX, UK. P. Haygarth, IGER Soil Science Group, North Wyke, Oakhampton, Devon EX20 2SB, UK.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Baltic Sea nutrient reductions

Cost-effectiveness of wetland management

This study establishes a model for calculating the costs of nutrient reductions (N, P) in the 14 drainage basins (9 countries) surrounding the Baltic Sea, based on sources of atmospheric deposition and run-off, and on mechanisms for nutrient retention. Cost-effective routes are identified for achieving the 50% reductions in N and P set as objectives by HELCOM.

The nine countries surrounding the Baltic Sea are Finland, Estonia, Latvia, Lithuania, Russia, Poland, Germany, Denmark and Sweden, with a drainage area of 1.4 million km 2 and 75 million inhabitants. These countries signed in 1974 the Helsinki Convention, to monitor and protect the ecological quality of the Baltic Sea and a **Ministerial agreement to reduce nutrient loads to the Baltic (N, P) by 50%.**

This action is seen as necessary because of ecological damages resulting from eutrophication, including toxic algae and oxygen depletion near the sea bed. The ultimate effect is reduced cod stock and areas of sea bed without biological life (Wulff et al., 1990).

======== Data collection difficulties ========

The authors underline the difficulties met in obtaining data concerning nutrient leaching and retention for many of the 14 catchment basins of the Baltic Sea. Estimates were therefore made of the basis of data available, mainly from Sweden.

The estimated total anthropogenic nutrient load to the Baltic Sea is estimated as **728,000 tons/year N** from within the Sea’s catchment, plus around 22,000 tons/year N atmospheric deposition from outside this basin; and **37,000 tons/year P.** These estimates fall within the range of other published figures.

Agricultural sources account for more than a half of nitrogen load and a third of phosphorus load. Sewage (from households and industry) accounts for nearly a third of nitrogen load and two thirds of phosphorus load.

Poland has the highest nutrient emissions, with a third of total nitrogen and a half of total phosphorus load.

======== Source reduction, land use and nutrient retention ========

To assess cost-effectiveness of nutrient reduction measures, these were divided into three different types of action :

- **source reductions,** including improved sewage treatment, catalysts in cars and ships, scrubbers at point sources, reductions in deposition of fertilisers and agricultural manures
- **land use measures,** including better manure spreading, changes in crops, tree planting
- **retention measures : restoration of wetlands as nutrient sinks.**

Wetland retention of nutrients is estimated at between 10% and 50% depending on type and location (Janson, 1994). **Restoration of natural wetlands is significantly more effective than creation of artificial wetlands.**

======== Sewage treatment and wetland restoration ========

The authors main conclusions are that improving sewage treatment and wetland restoration are the most cost-effective nutrient reduction measures.

To achieve 50% reductions, **costs for reducing nitrogen loads are roughly five times higher than those for reducing phosphorus loads. This is largely the** consequence of low marginal costs for phosphorus removal in sewage works.

At the 50% reduction level, for the most cost-effective hypothesis, roughly one third of the nitrogen load reductions come respectively from sewage treatment, agricultural measures and wetland restoration. Again for a 50% reduction, **around two-thirds of the phosphorus reduction come from sewage treatment** and about one fifth from wetland restoration.

If wetland nutrient retention capacity is reduced by 25% (for example by drainage and wetland destruction), the costs for achieving the 50% nutrient reductions increase by 35%.

======== Much higher costs for nitrogen reduction ========

Annual costs to achieve a 50% reduction in total nutrient emissions from the Baltic Sea catchment are estimated at 1,400 million Euro and 340 million Euro for nitrogen and phosphorus respectively.

If a 60% reduction from the Baltic catchment area is required, which would be necessary to achieve an overall 50% reduction for the Baltic Sea (because of inputs from areas outside the catchment), total costs would be multiplied by nearly three times.

If the objective of a 50% reduction from the Sea’s catchment area is achieved by obliging each country to reduce its loads by 50% (rather than achieving a 50% total reduction distributed between different countries in the most cost-effective way), then total costs will by multiplied by around four times.

"Cost-effective nutrient reductions to the Baltic Sea". Environmental and Resource Economics n° 10, pages 341-362, 1997.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Wetlands

Long-term phosphorus assimilation capacity

Wetlands' phosphorus assimilation capacity and long-term response to phosphorus loadings are estimated from analysis of a North American wetland data base and of Everglades test sites.

Phosphorus inflow and outflow levels from the 126 wetlands in the North American data base indicate **low phosphorus outflow concentrations (35 – 50 µgP/l) for inflow loadings below a change point ranging from 0.4 to 1.4 mgP/m^2** (95% confidence limits).

These results were compared with observations of ecosystem changes in Everglades test sites along a 10 km P-loading gradient. Inflow was 2.7 mgP/m^2 annual average around the Hillsboro canal discharge, descending to the natural background level of 0.3 mgP/m^2 10 km downstream. Phosphorus metabolism and ecosystem condition were characterised by calculating phosphorus loadings and measuring water phosphorus concentrations, soil phosphorus accretion rates, phosphatase activity in water, N:P ratios in plants, changes in plant community structure, plant productivity and macroinvertebrate diversity.

========= Ecosystem differences above 1 mgP/m^2/year =========

Surface water phosphorus concentrations and soil P accretion rates are highly correlated and both decrease exponentially with distance from the nutrient inflow.

Water phosphorus concentrations were up to 100 µgP/l near the nutrient inflow, and above 60 µ mg/l in areas with a phosphorus loading of more than around 1 mgP/m^2/year : that is higher than the average baseline concentration of 43µg/l. in North American marshes, calculated from the data base Two biochemical indices, phosphatase activity in the surface water and N:P ratios in sawgrass *(Cladium jamaicense)* indicated that the **marsh vegetation was in effect phosphorus limited only where phosphorus loadings were below 1 mgP/m^2/year** (the Everglades wetlands are naturally P-limited).

Detailed measurements of community structure showed significant changes resulting from what is now nearly 30 years of nutrient input from agricultural run-off : the dominant vegetation varied from dense cattail grass *(Typha domingensis)* in the phosphorus impacted zone through mixed grasses to dominant slough and sawgrass in the unenriched areas. However, **the plant community changed little past the point 5.1 km downstream from the nutrient-rich inflow, beyond which phosphorus loadings were below the 1 mgP/m^2/year level.**

Sawgrass plant productivity was nearly double in the areas with loadings higher than 1 mgP/m 2 /year, but plant 1 mgP/m^2/year had maintained 18 out of 19 native macrophyte and slough species.

Macroinvertebrate densities and diversities were higher in nutrient loaded areas but were reduced to natural levels where phosphorus loadings were less than 1 mgP/m^2/year.

The authors conclude that a phosphorus loading of 1 mgP/m^2/year can be taken as a threshold which North American wetlands are generally able to tolerate over the long-term without significant ecosystem modifications and without loss of their phosphorus retention capacity.

======== Even P-limited wetlands can sustainably assimilate phosphorus ========

At loadings above this, wetlands will lose native species and become phosphorus saturated over a number of years. On the other hand, **even phosphorus limited wetlands seem able to sustainably retain phosphorus at loadings below around 1 mgP/m^2/year** without significant changes in ecosytem structure and function.

The actual long-term phosphorus assimilation capacity figure may vary from one site to another, perhaps within the range 0.4 - 1.4 mgP/m^2/year and this requires further investigation at other sites.

"Long-term phosphorus assimilative capacity in freshwater wetlands : a new paradigm for sustaining ecosystem structure and function" Environmental Science and Technology, vol.33, n° 10, 1999; pages 1545-1551.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Italy

Phosphate recovery without chemical addition

This paper reports experiments carried out using a 9 cm diameter, 1m high, sand-seeded fluidised bed reactor used to precipitate a mixture of struvite and calcium phosphate.

Full-scale phosphate precipitation installation at Treviso, Italy.

Since writing of this paper, a full-scale installation has been constructed, due for commissioning this summer, after further testing using a 9 cm diameter/3m high pilot plant (carried out at Ancona, Italy). The full-scale installation will treat a third to a half of the digester liquors from the new Treviso biological nutrient removal (BNR) sewage works (100.000 pe.), near Venice, Italy, using the same air stripping process presented in this paper. The Treviso waste water plant uses an original system where sorted organic household refuse is mixed with BNR sewage sludge for fermentation/ digestion both to produce methane (approx. 2,000 m^3/day) and to provide fatty acids necessary to "feed" the biological nutrient removal process.

This paper presents experiments using a 1m high pilot fed with anaerobic digester centrifuge liquors from a biological nutrient removal wwtp at Ancona, Italy. **This pilot plant work follows laboratory studies already reported (see SCOPE Newsletter n° 33).** Phosphate precipitation was initiated by a **pH increase generated only by CO_2 stripping (by intensive aeration), without the addition of any chemicals.**

The feed liquors had the following average characteristics (mg/l) :

pH	***7.7***
SCOD	*1320*
PO_4	*139*
NH_4	*914*
Ca	*153*

Mg	*24*
HCO_3	*3550*

The fluidised bed column was filled with 3.3 kg of quartz sand (0.21 - 0.35 mm), giving a compressed bed height of 0.4m and an expanded height of 1m. Two reactor vessels ahead of the fluidised bed column (in the fluid recycling loop) ensured aeration and a return to equilibrium of excess dissolved air. The aeration rate was up to 50l/m and the liquor recycle rate was 0.23 m^3/h (approx. 4 x the reactor volume hourly). Injection into the fluidised bed used a heavy gravel layer in the base of the bed to disperse and mix the flow, rather than a system of nozzles or injectors.

The pH, ion concentrations and recycling rate (reactor contact time) were modified to assess the impact of these different parameters of phosphate removal efficiency and precipitation.

========= Struvite and calcium phosphate =========

Experiments were carried out using artificially increased concentrations of Ca and Mg in the digester liquors to study the balance **between struvite (magnesium ammonium phosphate MAP) and calcium phosphate (CP) precipitation.** The MAP/CP ratio in the precipitated phosphates, using real sludge digester liquors only, was around 2:3 and relatively constant on the sand granules from the bottom to the top of the reactor bed. Calcium enriched liquors produced 80-100% CP and magnesium enrichment 80-100% MAP. The authors conclude that the two crystallisations occur without competition.

========= 96.5 % P-removal =========

The mass balance of phosphorus was monitored by comparing total input P to total and dissolved P in the outflow fluids and estimates of P precipitated on the seed crystals. The mass balance could be account for all input P with an error of under 10%.

Phosphorus removal efficiency (total output P / total input P) was high, reaching 96.5%.

The loss of "fines" from the reactor was very low (crystallised phosphates not agglomerated to seed sand granules and leaving the reactor suspended in fluid) : an average of 1.7% of total input P, with a maximum of only 3.5%. This meant that a filter step was not necessary on the reactor outflow.Fines were measured as the difference between outflow total and soluble P.

========= Phosphate precipitation efficiency =========

The precipitation efficiency of the reactor (proportion of input total P fixed onto sand seed crystals) was relatively good, nearly always at least 70% (14 out of 17 runs).

This **efficiency was strongly pH dependent,** varying from 58.2% at pH 7.4 to 86.7% at pH 8.55. The percentage of fines did not, however, increase significantly with higher pH. A pH of around 8.2 was considered adequate for optimal operation.

Phosphate precipitation efficiency was also strongly related to contact time, which was calculated from the fluid recycling rate through the reactor, from fluid velocities within the reactor and from the mass/surface area of seed crystals present.

Mathematical equations were developed to predict efficiency as a function of pH and contact time (the latter estimated by the fluid recycling ratio through the reactor).

========= Recovered phosphates =========

The mass balance of the seed grains in the reactor, after 24 days operation, showed **11.9 – 12.6% PO_4 by weight (approx. 4% P),** around 5.3% Ca, 1.2% Mg and 0.9%NH_4 .

"Phosphate removal in real anaerobic supernatants: modelling and performance of a fluidized bed reactor". Wat.Sci. Tech. vol 38, n° 1, 1998.

P. Battistoni, Institute of Hydraulics, Engineering Faculty, Unviersity of Ancona, 60131 Ancona. P. Pavan, University of Venice, Dept. Env. Sciences, Dorsodura 2137, Venice. F. Cecchi, Dept. Chemistry, University of L'Aquila, L'Aquila. J. Mata-Alvarez, Dept. Chemistry and Engineering, University of Barcelona, c. Marti i Franque 1/6, 08028, Barcelona, Spain.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Holland

Conclusions and futures for P-removal

The waste water treatment group of the Dutch National Water Association (NVA) organised a symposium on the policy, technologies and sustainability aspects of phosphorus removal in Amersfoort on 2nd July 1999.

It is now five years since large-scale phosphorus removal in sewage works was introduced in Holland, and this conference aimed to draw conclusions from this experience. **A phosphorus removal level of 75% is required in Holland,** as a result of national implementation of agreements between Rhine and North Sea countries (OSPARCOM). Dutch phosphorus discharge limits are more stringent than those in much of Europe, as they are based on ten-day moving average concentrations, rather than annual averages.

The phosphorus reduction objective set by OSPARCOM in 1987 was 50%, this has been more than achieved with a 60% reduction in phosphorus flowing into Holland in the Rhine as well as a 60% reduction in Dutch point source emissions.

========= Chemical or biological P-removal ? =========

Technical and economic presentations were made of chemical P-stripping and biological nutrient removal by Ir. P. de Jong **(Witteveen & Bos).** He considered the operating costs of biological phosphorus removal to be somewhat lower and indicated that 40% of operators now prefer biological systems, partly on grounds of sustainability.

Ir. M. Bentwelsen (Hoogheemraadschap van Delfland) indicated that in 1996 around 80% of phosphorus removal was by chemical precipitation and 20% by biological nutrient removal. He stated that chemical P-removal increases sewage sludge production by 15% and increases the iron content of sludge solids from 8% to 20%. Costs of metal salts have fallen in recent years, so that the chemical P-removal costs are now around 6.1 Euros/ kgP. He nonetheless concludes that, because of sludge generation and of salt discharges, chemical P-removal will be phased out over the coming 20-30 years and be replaced with biological systems.

Other speakers also indicated that biological nutrient removal was gaining ground. **Ing. H. Ellenbroek (Waterschap Regge en Dinkel)** indicated phosphorus removal costs of 2.4 Euros/kgP removed by biological treatment, 3.5 Euros/kgP for combined biological + chemical removal.

======== Sustainability and phosphorus recycling ========

Dr. Ir. Klapwijk (Wageningen Agricultural University) presented Life Cycle Analysis work carried out for the Dutch water research board STOWA. This suggests that, if nutrient removal requirements are satisfied, sewage treatment represents a minor contribution to most environmental issues. Only 4.4 % of Dutch nutrient releases to the environment will come from sewage following the implementation of phosphorus and iron discharge limits.

He considers that biological phosphorus removal is more sustainable than chemical treatment. Sustainability can be further improved by reductions in energy consumption, stricter discharge limits (effluent polishing) and the recovery of phosphates for recycling as calcium phosphates or struvite.

Ir. Gaastra (Hoogheemraadschap Uitwatrende Sluizen) presented operational experience of phosphorus recovery as calcium phosphates at the Geestmerambacht sewage works. The recovered phosphates are now being recycled in the phosphate industry. He estimates costs as 4.5 - 5.5 Euros/kgP removed.

The symposium was concluded with a general discussion as to the relative costs of biological and chemical phosphorus removal and regarding possibilities for phosphorus recycling. **It was noted that the phosphate industry is actively supporting recovery for re-use.**

Source : H_2O, Tijdschrift voor watervoorziening en waterbeheer. 16 July 1999, No. 14/15 (32), pages 40/41 (in Dutch).

Symposium proceedings available (in Dutch) from Mr. Bommele, NVA bommele@vewin.nl

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Berlin area

Full P-removal from sewage key to surface water restoration

This paper summarises measures taken to reduce eutrophication of surface waters in the Berlin area. This is important because these waters are used to replenish groundwater supplies and provide drinking water through bank filtration systems. The water bodies themselves are used intensively for navigation, commercial fisheries, leisure activities.

Berlin is located in a lowland area with many rivers and lakes covering approximately 6% of land surface. Average rainfall is around 600 mm/year and the natural groundwater recharge of around 200 mm/year is not sufficient to maintain groundwater levels.

Drinking water is extracted from underground as the area's sandy soil is efficient in eliminating bacteria and viruses. Wells at depths of 70 - 170 m extract water that has filtered through the ground for around 2 months, either from natural groundwater or from artificial groundwater refilling.

This **bank filtration of surface water** has been shown to eliminate or degrade many contaminants, the best safeguard against the passage of undesirable substances is to provide high quality surface water. The organic substances present in eutrophic surface waters can impair the quality of bank filtered water, in particular due to volatile substances produced by algae.

========= Ambitious nutrient reduction strategy =========

This has led the Berlin area to **implement an ambitious strategy aimed at achieving low nutrient concentrations in surface waters.**

Targets of 0.07 - 0.08 mgP/l in rivers (Havel, Spree) and around 0.04 - 0.06 mgP/l total P for the major Berlin lakes (Tegel, Schlachtensee, Krumme) are considered necessary to avoid nuisance levels of algae.

The author indicates that the achievement of these targets in the rivers will require not only management of sewage works discharges, urban stormwater and industrial discharges, but also limitation of diffuse agricultural sources. The latter would necessitate buffer strips along rivers, reducing fertiliser use and reducing tile drainage - but these are sensitive political issues.

========= The need for advanced phosphorus removal from sewage =========

The achievement of nutrient reduction objectives for the Berlin lakes necessitate advanced phosphorus removal installations in sewage works, as well as ensuring full connection of households to sewage networks, avoiding sewage works overflow (ensure adequate capacity) and optimal management of urban stormwaters.

Berlin Wasserbetriebe's investments in improved sewage treatment since the reunification of Germany will total around 12 billion DM (1992 - 2004).

The Wassmansdorf sewage treatment plant was commissioned in 1994 and treats sewage from 1 million person equivalents achieving 0.05 mg/l phosphorus discharge by biological methods only.

========= P-stripping of lake inflow =========

For Lake Tegel, one of the city's larger lakes (4 km^2, surrounded by wells extracting a mixture of groundwater and bank filtered water to supply 700,000 people), a water treatment installation has been built on the lake's inflow. This plant treats 100 million m^3/year, flushing the lake approximately three times per year with treated surface water. The plant reduces phosphorus input concentrations from around 5 mg/l to below 0.02 mg/l using a four step chemical P-stripping process : precipitation - coagulation - flocculation, sedimentation, post-precipitation and flocculation - filtration.

This has enabled a concentration of 0.02 mg/l total P to be achieved in the lake's water.

Berlin's strategy is to improve surface water, to enable quality drinking water to be reliably and ecologically supplied by filtration through soil. **This necessitates action on diffuse nutrient sources, stormwater management, prevention of combined sewer overflow, full connection of households to sewage works and efficient nutrient removal in sewage works.**

"Improvement of the surface water quality in the Berlin area". Wat. Sci. Res. vol. 38 n° 6 pages 191-200, 1998.

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SCIENTIFIC
COMMITTEE
ON PHOSPHATES

SCOPE NEWSLETTER

IN EUROPE

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IMPLEMENTATION OF THE 1991 EU URBAN WASTE WATER TREATMENT DIRECTIVE AND ITS ROLE IN REDUCING PHOSPHATE DISCHARGES

(Summary of Report)

The deadline fixed by EU legislation for phosphorus removal in sewage works was 31 December 1998. This report assesses to what extent this objective is being achieved.

Waßmannsdorf sewage works, Berlin. Phosphorus removal achieving discharge levels of 0.6 mgP/l (objective 2000 0.5 mg/l) using biological processes only (enhanced biological nutrient removal EBNR). 1 million pe. Commissioned 1997. Berlin Wasser Betriebe.

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EXECUTIVE SUMMARY

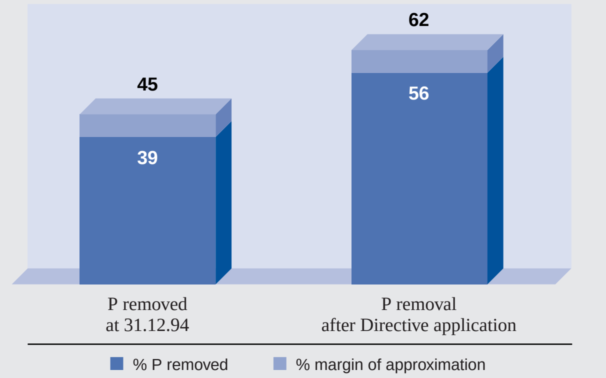
INTRODUCTION

Phosphate pollution in surface waters may lead to eutrophication problems - excessive growth of algae and higher plants with adverse effects on ecosystems and amenity. A number of policy initiatives exist to overcome this problem, at international, national and local levels. The most important of these within the European Union is the urban waste water treatment Directive 91/271. This report outlines the way that the Directive tackles the problem of phosphate discharges from waste water, the degree to which it has, so far, been implemented in Member States and considers potential future developments.

PHOSPHATE POLLUTION

There has been a decline recently in the quantities of phosphate discharges (both point and diffuse sources) to the surface waters of Europe. However, phosphate concentrations in surface waters are still, across much of Europe, very much higher than would be the case without human influence and in places severe eutrophication problems continue to occur.

Estimated % removal of phosphates from sewage for ten EU states



Sources of phosphate pollution vary considerably in different European countries. They principally include agriculture, sewage and industry. In some cases one source may predominate and in others combinations of sources are significant. However, generally approximately one third of phosphate sources to surface waters are derived from sewage.

Phosphates from sewage can be controlled in a number of ways in waste water treatment works. Secondary treatment may remove about 30-40% of phosphate present. However, more stringent control is provided by tertiary treatment, either biological (70-85% removal depending on conditions), chemical (up to 95% removal), or some combination of the two.

THE URBAN WASTE WATER TREATMENT DIRECTIVE AND ITS IMPLEMENTATION

The EU urban waste water treatment Directive 91/271/EEC is an important tool in dealing with some of the major sources of phosphate pollution. *Inter alia*, regarding nutrient discharges from sewage works, the Directive requires that phosphates and nitrates must be removed (to specified limits) wherever discharges are into ‘sensitive areas’, defined as being ‘eutrophic or which in the near future may become eutrophic’. However, its specific action on phosphates is limited to waste water treatment works serving conurbations above 10,000 pe., or to overall reductions of 75%, although “appropriate” treatment is also required for smaller villages. Other pressures (eg international conventions or national priorities) may result in additional action.

Even though the urban waste water treatment Directive was adopted eight years ago, it is not yet clear the extent to which it has been implemented in Member States. The complexity of the Directive and the range and flexibility of measures contained within it make assessment difficult.

TABLE 1

	Phosphate production prior to treatment (ktP/a)	Nutrient discharge 31-12-94 (ktP/a)	Percentage P removal due to treatment at 31-12-94	Nutrient discharge after implementation of the Directive (ktP/a)	Reduction in phosphate discharge required	Percentage phosphate removal after implementation
Phosphorus discharge	375	208-227	39-45%	143-164	27-31%	56-62%

Estimated phosphate discharge from waste water treatment plants at present level of waste water treatment for the ten EU Member States[1] and as expected after full implementation of urban waste water treatment Directive (EEA, unpublished).

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[1] France, Finland, Germany, Greece, Italy, Luxembourg, Netherlands, Portugal, Spain, United Kingdom.

The most recent implementation report (COM (98)775) is incomplete and does not address the issue of nutrient removal. The following conclusions can nonetheless be highlighted:

1. Transposition of the Directive is satisfactory in most Member States as is implementation of requirements regarding collection and secondary treatment of sewage, with the notable exceptions of Belgium and Italy.
2. A range of approaches has been adopted for the designation of sensitive areas under the Directive and designation is still not complete.
3. This report could not address the likelihood of compliance with the end of 1998 deadline for nutrient removal in sensitive areas.
4. It is likely that most Member States will have met the treatment requirements for sensitive areas by the end of 1998. Exceptions will include France and Spain (where implementation will be incomplete), the UK (which designated more sensitive areas in 1998 and will meet requirements for these at a later date) and Greece and Italy (for which sensitive area designation is lacking or uncertain).
5. The Commission has indicated that it will examine compliance for both designation and treatment closely. This may place further pressure on Member States to designate further sensitive areas.
6. It is estimated that currently in ten EU Member States, containing 90% of the EU population, about 375,000 tonnes of phosphorus is produced in domestic waste water each year. In 1994 39-45% of this was removed in waste water treatment works.

FUTURE IMPLEMENTATION OF THE DIRECTIVE

Following full implementation of the urban waste water treatment Directive, it is estimated that phosphate removal will have increased in ten Member States (discharging 375 kt of phosphate per year prior to treatment) to between 56 and 62%, with total discharges after treatment ranging from 143-164 kt phosphate per year, as illustrated in Table 1.

The remaining Member States also generally exhibit high levels of phosphate removal. Three of these Member States (Austria, Denmark and Sweden) had 14.2 pe of their total 21.8 pe with nutrient removal on waste water treatment at the end of 1994. This represents at least a further 9,900 tonnes of phosphate removed from a total of 15,300 tonnes produced.

It is, however, unlikely that implementation will meet the timetable in the Directive and that any future timetable will largely depend on domestic and Commission pressure on individual Member States. Indeed a European Court of Auditor's report of 18 June 1998 stated that 'most of the Member States were finding [meeting the requirements for sensitive areas] difficult to achieve...within the specified time frame'. The Commission's response was hardline, stating that it 'considers the deadlines for achieving the objectives ... sufficient, and does not at present consider proposing any changes in the deadlines'. The Commission also noted that no Member State had requested changes to the deadlines.

It is expected that the urban waste water treatment Directive will result in the following treatment conditions across the EU:

- The population not connected to sewers will be halved.
- No untreated waste water should be discharged.
- Most waste water will be subject to, at least, secondary treatment.
- 45% of municipal sewage will be subject to tertiary treatment (nutrient removal).
- Secondary treatment will predominate in Belgium, Ireland, Italy, Portugal, Spain and the UK.
- Secondary treatment with nutrient removal will predominate in Austria, Denmark, Finland, France, Germany, Luxembourg, the Netherlands, and Sweden.

FUTURE TRENDS

At this time it is impossible to be precise about the future of phosphate removal from urban waste water. The deadline for meeting discharge requirements for sensitive areas under the urban waste water treatment Directive was the end of 1998. However, it will be some time before it is known precisely whether some Member States have complied for those areas designated and whether the correct areas have been designated. It can already be concluded that many northern EU Member States will have complied with the Directive's requirements, while for many southern Member States, compliance will be only partial. Any additional action has been entirely a matter for national policies, which have diverged significantly, although even the UK, which has had, until recently, little phosphate removal, has identified national priorities for which action beyond that in the Directive may be necessary.

Future developments must also take account of the general thrust of policy development on water in the EU demonstrated by the proposed water framework Directive. As currently proposed, this leaves standing the existing Directive's requirements, but focuses on a more holistic management of river basins, which should result in Member States identifying which of all phosphate sources is the most cost-effective to tackle. This may, or may not, include further action on urban waste water. It is certainly likely to highlight agricultural sources as the next pollution problem to address.

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1 INTRODUCTION TO PHOSPHATE POLLUTION AND ITS CONTROL

2 THE EU URBAN WASTE WATER TREATMENT DIRECTIVE AND ITS IMPLEMENTATION IN MEMBER STATES

3 LOOKING TO THE FUTURE AND CONCLUSIONS

1. INTRODUCTION TO PHOSPHATE POLLUTION AND ITS CONTROL

1.1 PHOSPHATE POLLUTION IN EUROPEAN SURFACE WATERS

The pollution of surface waters by phosphates from a wide variety of sources is a serious problem in many parts of Europe. Phosphorus is a plant nutrient and excess quantities of it, together with an excess of the other main plant nutrient, nitrogen, can lead to extensive growth of phytoplankton, macroalgae and higher plants. In some cases, and along with other factors such as reduced flow rates resulting from dams or weirs or changes in the balance of food webs, this can adversely affect invertebrate and fish populations and even result in the production of toxic substances from algal blooms (Farmer, 1997).

Etymologically, eutrophication simply means high concentrations of plant nutrients, but the word is often in fact used to refer to the adverse response of an ecosystem to excess nutrients (Harper, 1991) and the problems mentioned above.

Plants require both phosphorus and nitrogen to grow and one or other of these nutrients is usually the limiting factor preventing excess growth. In freshwaters this tends to be phosphorus, while in many marine waters nitrogen is often limiting. Thus prevention of eutrophication symptoms in freshwaters usually emphasises targeted action against phosphorus and, for marine waters, action against nitrogen. However, there are instances where this pattern is different and action may often need to be targeted at both pollutants.

In natural, unimpacted freshwaters total phosphorus concentrations are usually below 25 mgP/l, although some natural minerals may cause locally elevated levels. Unless otherwise demonstrated, it is generally assumed that concentrations above 50 mgP/l are the result of anthropogenic influences. A survey of rivers across Europe (EEA, 1998) found that a large proportion of 1000 monitoring stations had levels of total phosphate exceeding 50 mgP/l, many by a considerable margin. Indeed only about 10% of

TABLE 1.1

MEMBER STATE	EXTENT OF EUTROPHICATION
Austria	Some localised eutrophication.
Belgium	Widespread eutrophication in rivers, canals, lakes and coastal waters. Most of the surface waters in Flanders are classified as eutrophic.
Denmark	Extensive eutrophication of rivers and lakes.
Finland	Eutrophication limited to a few localised areas.
France	Eutrophication localised to particular river basins, lakes and reservoirs, especially the Loire and Meuse.
Germany	Serious eutrophication, especially lakes in southern Germany, the Baltic Sea and Schleswig-Holstein.
Greece	Highly localised eutrophication, but important.
Ireland	Highly localised eutrophication, but important.
Italy	Serious eutrophication problem affecting lakes, rivers and reservoirs. Discharges to the Adriatic Sea cause acute problems.
Luxembourg	Significant eutrophication.
Netherlands	Widespread eutrophication in most surface water bodies.
Portugal	Eutrophication rarely a problem.
Spain	Eutrophication is localised, but an increasing problem.
Sweden	Eutrophication localised in the south, but generally of decreasing significance.
United Kingdom	Eutrophication localised, but of high significance in a number of rivers, canals, lakes and reservoirs.

Extent of eutrophication in EU Member States.

the monitoring stations reported mean total phosphorus concentrations below 50 mgP/l. Table 1.1 provides a brief summary of the types of problems found in different EU Member States. It can be seen that in some cases eutrophication problems are widespread, in other cases localised. This is reflected in the choice of approach in different Member States to the designation of sensitive areas (areas where a reduction in nutrient discharges is required) under the 1991 urban waste water treatment Directive, the principle EU legislative initiative to, *inter alia*, reduce impacts of eutrophication (see chapter 2).

Phosphates in surface waters can sometimes be of natural origin (bedrock), but are often the result of soil erosion, agricultural run-off and discharges of municipal and industrial waste waters. Sewage contains phosphates from human sources (about 2g P/person/day), detergents, food waste, food additives and other products.

There are marked trends in phosphate concentrations in surface fresh waters across Europe (EEA, 1994, EEA, 1998). The lowest concentrations of phosphate are found in the streams and rivers of the Nordic countries. Here 91% of the monitoring stations report mean concentrations below 30 mgP/l and 50% below 4 mgP/l. This pattern results from a generally very low human population and the presence of a slow-weathering and nutrient-poor bedrock. Higher phosphorus concentrations are found in a band stretching across central Europe, from southern England to Romania. While some monitoring sites in southern Europe also report high phosphate levels, the general pattern is for lower concentrations than central and eastern Europe, often because much of the waste water produced is discharged directly to the sea.

A similar pattern of phosphate levels in lakes can also be found, with low concentrations in the Nordic and Alpine regions. However, in many parts of Europe lakes can be severely affected by phosphate eutrophication. This can be a particularly difficult problem to address as phosphates may accumulate in lake sediments. Even when the phosphate pollution source is controlled these accumulated phosphates may be released (eg by climatic events or the action of fish) into the water column and maintain a eutrophic condition. Overcoming this problem requires expensive manipulation of the sediments and lake biota.

Phosphate levels have shown a general decline across Europe between 1987 and 1996. This trend occurs for annual average concentrations for both total and dissolved phosphorus, but it appears that high peak concentrations still occur even where improvements are being made. Improvements have been found in most regions and much of this is due to increased treatment of urban and industrial waste water and some decline in agricultural fertiliser use.

There has also been an improvement in lake water phosphate concentrations, although many lakes are still seriously affected.

Phosphate concentrations in the marine environment are more variable. However, high levels are found in the North Sea, Mediterranean, Baltic and Black Seas. Phosphate discharges have continued to increase in, for example, the North Sea, and, in other areas have largely remained stable.

1.2 SOURCES OF PHOSPHATE

Phosphate pollution arises from a number of sources (Table 1.2). Point sources (eg from waste water treatment plants, industry and some agricultural) account for more than half of the phosphates discharged in Europe. The principle sources of phosphate in municipal waste water coming from human waste and, in some countries, from the use of detergents.

Emissions of phosphates from sewage into surface waters, across Europe, have typically fallen by about 30-60% since the mid-1980s (EEA, 1998). However, this decline has varied considerably across the continent. For example, declines in emissions from the Netherlands and Denmark have been of the order of 70-90%, largely as a result of highly improved waste water treatment.

Table 1.2 indicates the main phosphorus sources in each EU Member State. The data are based partly on phosphate input information (eg on detergents) and partly on *de-novo* calculations. The calculation for human phosphate production assumes that each person in the EU produces 0.7 kgP each year and that 50% of this is available. It is important to note, therefore, that it provides data on the generation of phosphate waste from each sector, not discharge, ie it does not take account of the degree of phosphate treatment of waste water once produced (except possibly for a generalised average removal rate of 50%). The relative importance of each sector to *in situ* eutrophication will depend on waste water treatment and other pollution control measures.

The amount of phosphate discharged from waste water treatment plants has been declining for two reasons:

1. There has been a steady decline in the quantity of phosphate produced by each person in many EU Member States, leading to a reduction in the concentration of phosphate in the receiving waters of treatment plants. This has largely been due to a reduction in the use of phosphates in detergents. For example, in Denmark the production of phosphate in the 1980s was about 1.2-1.6 kg/year pe, while in the 1990s this has declined to about 1.0 kg/year pe.

2. There has been an increase in the number of waste water treatment plants providing some form of phosphorus removal. Some of this is the result of increased secondary treatment, which removes some phosphate, while in many instances high rates of phosphate removal occur.

Overall in the 1980s typical average values for phosphorus discharges were about 0.7-0.8 kgP/year pe, while at present they are around 0.05-0.2 kgP/year pe in those Member States with high levels of phosphorus removal. Table 1.3 provides an example of this trend from Denmark However, given problems in calculating the contribution of different sources of phosphate input, most recent figures from the European Environment Agency (unpublished, 1998) still estimate an overall discharge from waste water treatment (human, detergent and industry) of 208-227,000 tonnes per year from the EU (excluding Austria, Belgium, Denmark, Ireland and Sweden). Data from Morse *et al* (1993) above suggest that these sources would contribute around 200,000 tonnes per year. It is evident that clearer summary information is required, specifically indicating how such data are obtained and calculated.

1.3 POLICIES TO CONTROL PHOSPHATE POLLUTION

Policies (legislation, conventions, etc) to control phosphate pollution or eutrophication more generally can be found at many levels in Europe. Of most interest in this study are those at the EU and national level. Principally these include the urban waste water treatment Directive and national programmes to implement this. It is also worth stressing that there is also a significant role for local policy initiatives in some cases. This may include formal implementation in federal states such as Germany. However, general eutrophication strategies are often developed at a catchment or river basin level (eg in France or the UK) taking account of different pollutant sources (eg waste water and agriculture) and seek local solutions albeit within a national policy framework. Again examples of these will be considered in the Member State specific chapters.

Finally, there are also the impacts of international agreements or conventions. These are important in taking a broader view than is currently undertaken within EU legislation and some can be briefly summarised here.

1.4 INTERNATIONAL CONVENTIONS

It is important to note that some pressure for action on the discharge of pollutants to surface waters comes also from international conventions to protect marine environments. These include:

- The Helsinki Convention (HELCOM) to protect the Baltic Sea.
- The Paris and Olso Conventions (OSPAR) to protect the North Sea and Atlantic.
- The Barcelona Convention to protect the Mediterranean Sea.

Much of the action required under these conventions has focused on the reduction in emissions of dangerous substances (from industrial and urban waste water). However, there has also been agreement for action in relation to the discharge of nutrients (both nitrogen and phosphorus). It is not possible here to examine all of the developments in detail, but some key points can be illustrated by examination of HELCOM and OSPAR.

Photo: Chevalier/F38300 Bourgoin

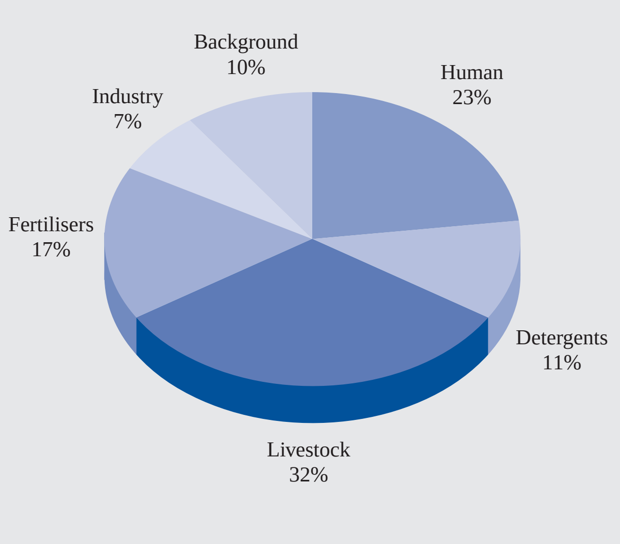
Photo: Thornton/CEEP

Agriculture is the source of around 50% of phosphorus input to surface waters (see table 1.2), particularly inadequately stored and treated animal wastes from intensive livestock production and runoff resulting from soil erosion or inappropriate fertiliser use.

TABLE 1.2

Member State	Human	Detergents	Livestock	Fertilisers	Industry	Background	Total (t/a)
Austria	20	10	36	16	6	12	13
Belgium	26	11	43	7	8	5	13
Denmark	12	11	55	11	5	6	15
Finland	18	9	17	15	3	38	9
France	18	15	31	19	6	11	106
Germany	28	3	44	12	6	7	97
Greece	21	7	18	34	5	15	17
Ireland	9	7	49	24	2	9	15
Italy	35	2	26	18	8	11	56
Netherlands	23	3	57	9	5	3	24
Portugal	24	14	27	16	7	12	15
Spain	19	16	18	26	7	14	72
Sweden	21	10	15	14	7	33	14
UK	24	19	29	14	8	6	82
EU total *(excluding Luxembourg)*	**23**	**11**	**32**	**17**	**7**	**10**	**548**

Phosphate sources in Europe in 1992 (percentage from each source and total) (source Morse et al, 1993).



1.4.1 HELCOM

This Convention has probably focused more on the effects of nutrients than other Conventions. In particular it is clear that eutrophication in the Baltic Sea is driven by discharges of both nitrogen and phosphorus and action is needed to reduce both in order to reduce the problem. However, the recent huge improvement in phosphate removal from discharges in Sweden has begun to highlight nitrogen reduction as a leading priority. The Baltic Sea is also interesting in that the countries bordering its shores are characterised by two contrasting groups:

- EU Member States that have taken extensive action to reduce nutrient, including phosphorus emissions from urban waste water discharges, eg Sweden.
- Eastern European Countries which have very poor levels of waste water treatment, especially in relation to phosphate removal, eg Poland.

TABLE 1.3

	1984	1989	1990	1991	1992	1993	1994	1995
Concentration (kgP/year pe)	0.67	0.48	0.43	0.30	0.26	0.19	0.19	0.14

Concentration of phosphorus in outflow water from waste water treatment plants in Denmark 1984-1995.
(Danish Environmental Protection Agency, 1995; EEA, unpublished)

It is also important to note that much improvement is taking place due to a decline in the use of fertilisers by agriculture. This is largely due to the collapse of intensive collective agriculture since the end of the Communist governments and its subsequent poor performance as an economic sector. In Estonia, for example, the use of phosphorus-based fertlisers fell from 60,000 tonnes to 10,000 tonnes per year between 1988 and 1994.

1.4.2 OSPAR

OSPAR has also focused on the need to reduce discharges of pollutants to marine waters. This includes actions to reduce nutrient inputs, both nitrogen and phosphorus, eg for an overall input of all pollutants by 50% between 1990 and 1995, which was achieved in some cases, though not for phosphates. Eutrophication areas were identified on the coasts of Belgium, Denmark, Germany, France, the Netherlands, Norway and Sweden. Although the UK also identified three estuaries, these have undergone further studies and the problem, where accepted, is considered to result from nitrogen pollution.

Action to reduce nutrient inputs has focused on discharges to those eutrophication areas identified, ie from the states listed above and from Switzerland which discharges upstream on the Rhine. The UK argues that no action beyond that in the urban waste water treatment Directive is required because it does not consider that its discharges affect eutrophication on the eastern side of the North Sea. Action is identified in five areas for phosphate emissions:

- Municipal waste water treatment
- Detergents
- Agriculture
- Fish farming
- Industry

1.4.3 Phosphate discharges

The particular action taken by different countries is outlined in other sections of this review. However, it can be seen from Table 1.4 and Table 1.5 that action of discharge of phosphates to marine areas under these two conventions has limited success and that mostly in the Baltic Sea. The apparent increase in discharges from Sweden is largely a problem of earlier reporting of riverine inputs in 1991. Significant increases from the Netherlands is probably largely agricultural. It is uncertain what the future impact of the urban waste water treatment Directive will be. This is because only proportions of some countries (eg Germany and France) discharge to the North Sea and nutrient removal is (and will remain) limited in a number of countries (eg Portugal, Spain and the UK). Given also the fact that the most important source is agricultural, the potential impact of the Directive may be limited.

TABLE 1.4

COUNTRY	1991	1995
Belgium*	2.0	4.0/5.0
Belgian Coast	2.0	1.8
Denmark	2.3	2.0
France	No data	No data
Germany	11.6	11.5
Ireland	6.3	7.3
Netherlands	17.0	34.1
Norway	3.3	3.9
Portugal	3.1	3.1
Sweden	0.2	1.3
United Kingdom*	39/40	36

Annual discharges of total phosphorus (1000 tonnes/year) to the North Sea and north-east Atlantic Ocean. Source EEA (1998).

* (low/high estimate)

TABLE 1.5

COUNTRY	1990	1995
Denmark	5.3	2.3
Estonia	2.8	1.3
Finland	3.4	3.6
Germany	1.2	0.6
Latvia	3.2	2.2
Lithuania	1.7	1.4
Poland	15.0	14.2
Russia	9.5	7.1
Sweden	4.0	4.7

Annual discharges of total phosphorus (1000 tonnes/year) to the Baltic Sea. Source EEA (1998).

1.5 TREATMENT PROCESSES TO REMOVE PHOSPHATES FROM WASTE WATER

Two basic types of process are available to remove phosphates from waste water. These are chemical and biological treatment (Horan *et al*., 1994; Brett *et al*., 1997).

Chemical phosphate removal involves the stripping of phosphate by the addition of metal salts, of which the metal phosphate is insoluble. Common salts used include aluminium or iron chloride or sulphate, and in some cases calcium hydroxide (lime) The phosphate present precipitates as iron or aluminium phosphate. Not all phosphate present in waste water is present as soluble orthophosphate (and so able to react with the added salts). However, the organic phosphate that may be present may also be adsorbed onto the preciptate and thus enhance phosphate removal. The precipitate can be removed by mechanical methods.

Biological phosphate removal involves the removal of phosphates by the action of bacteria. The bacteria use the energy contained in the organic matter contained in waste water (or also sometimes, where necessary, with added organic substrate) to incorporate the phosphate into their own biomass.

It is beyond the scope of this review to examine the details of each type of process, with their particular advantages and disadvantages. However, it is important to summarise a number of key points about each process type as these may affect the possible adoption of particular systems by countries or individual companies required to reduce phosphate discharges and the costs of these options.

Key points relating to chemical phosphate removal include:

- The process may operate at any phosphate concentration and at any temperature. It is not, therefore, too dependent on the quality of the waste water received or the climate.
- The chemical reactions can remove phosphate down to very low concentrations, sufficient to meet the most stringent regulatory discharge limits.
- Chemical phosphate removal can result in the production of significant additional volumes of sewage sludge due to the quantities of precipitate produced. This may be a disdvantage if sludge disposal is a problem.
- Chemical treatment systems do increase the quantities of chloride or sulphate discharged into the receiving waters and these may change their quality. The implications of this depend on the character of the receving waters and its undesirability is open to significant debate.
- The investment costs of chemical treatment plants are lower than biological treatment plants, but the annual running costs are significantly higher. The implications for choice of installation depends, therefore, on the particular short or long-term financial strategy of the private or public operator involved.

Key points relating to biological phosphate removal include:

- The efficiency of phosphate removal increases with increasing phosphate concentration and is better when waste water contains at least 5-10 mg/l. This is important where waste water may be regularly or occassionally diluted (eg with rain water in combined sewer systems) or where domestic waste water may have lower phosphate concentrations (eg where phosphates in detergents have been reduced or prohibited).
- The activity of the bacteria requires the presence of readily assimilable organic molecules for the biological phosphate removal process. This means that the COD/P ratio should be at least 35 or the BOD/P ratio is above 20. Where organic matter concentrations are low, or the proportion of appropriate molecules (short chain fatty acids) is insufficient, organic substrates may be added as part of the treatment process (eg acetone, methanol, biological fermentation liquors).
- It is usually very difficult to meet some of the strictest phosphate discharge consent levels found in the EU, eg 1 mg/l, as biological treatment often only removes between 40 and 70% of the phosphate present (or exceptionally 80-85%). Where severe restrictions exist biological treatment has to be combined with an additional chemical precipitation.
- The activity of the bacteria is temperature dependent. The optimum temperature is 30°C, but it can operate down to 5°C. If removal of phosphates can be seasonal (eg to prevent spring and summer algal blooms in rivers) then reduction or even cessation of activity in winter may not be a problem. However, if continuous removal is necessary (eg to prevent phosphate build-up in sediments) biological removal may prove ineffective in cold climates.
- Biological treatment systems are able to be installed more readily in smaller treatment works.

Table 1.6 summarises the relative phosphate removal efficiencies of different stages and options in waste water treatment. Both biological and chemical processes produce sludge. In pure biological removal the sludge is formed by accumlation of cellular polyphosphates, producing around 3.4 kg of suspended solids per kilogramme of phosphorus. Chemical processes produce a precipate of phosphate with iron (or other added cation) producing around 5-7 kg of suspended solids per kilogramme of phosphorus. Combined processes varying in their relative contribution of different sludge types and quantities depending on the details of operation.

TABLE 1.6

Treatment option	Phosphate removal
Primary	5-10% (P removed is that combined to organic particulates)
Secondary	20-40% (Due to bacterial metabolic action)
Tertiary: biological	40-85% (Heavily dependent on a range of conditions)
Tertiary: chemical	95% (or more) (Degree of removal dependent on quantity of salts added to reach a desired endpoint)

Phosphate removal rates for different waste water treatment options.

A further method of waste water removal is the septic tank. The use of septic tanks varies across Europe, but is particular common in remote or rural areas where the costs of connection to sewerage collection systems are too high to be practical. Septic tanks are of various designs and may allow more or less significant ingress of phosphates into the soil. Provided this is not close to water courses, the phosphate released is usually trapped onto the soil particles.

It is also important to note that the construction of artifical reed beds is becoming more widespread in Europe as a means to treat waste water. The use of the common reed takes advantage of a number of characters of such beds. They actively aerate the sediment, which aids in nitrogen removal by the nitrification of ammonia. The sediments also act as a filter for ammonia. The usually high iron content also helps to remove phosphate. A recent survey (Haycock, 1996) of the efficiency of 285 European reed-beds for pollution control has shown that while they are good at controlling organic pollution, they are more variable at the removal of phosphate (average reduction of 65%). The survey found that the ability of reed-beds to remove phosphate was a function of the way that they are constructed. Reed-beds only begin to control nutrients after the biological oxygen demand has been reduced significantly, but this requires reed-beds of a large size. For good phosphate removal a reed-bed may need to be about six times the size of one required to control BOD alone. Many such reed-beds are recent constructions and it is uncertain how they will perform over many years, as their efficiency declines. It is evident, therefore, that reed-beds are not an option for treatment of large quantities of discharge (for phosphate removal the area of reed-bed required to treat waste water from one person is about 20-30 m^2) and they do not meet the high rates of removal required by the urban waste water treatment Directive.

Biological phosphorus removal is achieved by subjecting sewage sludge micro-organisms to a controlled series of anoxic/anaerobic and aerobic phases in specifically engineered tanks. The process is often combined with biological denitrification. 70 - 80% removal of phosphorus can generally be achieved, but some modern installations reliably achieve 90% removal or better. Biological phosphorus removal and denitrification at Hofkirchen sewage works, Austria (Phostrip process).

Photo: Posch and Partners Consulting Engineers, Innsbruck, Austria.

Chemical phosphorus removal is achieved by adding precipitation chemicals, usually iron or aluminium salts. Near 100% of phosphorus in sewage can be removed. Installations for storing and dosing chemicals for phosphorus precipitation, Darmstadt sewage works, Germany.

Photo: Posch and Partners Consulting Engineers, Innsbruck, Austria.

However, for small sources they may be a valuable additional tool to reduce the overall phosphate load to surface waters, along with having the additional benefit of providing some useful wildlife habitat.

1.6 CURRENT USE OF CHEMICAL AND BIOLOGICAL PHOSPHATE REMOVAL SYSTEMS TO TREAT WASTE WATER IN SELECTED EU COUNTRIES

Chemical removal systems have been in existence in Europe for many years longer than biological systems and this certainly affects the current distribution of systems adopted in the EU, ie in those countries that took action to remove phosphates at an early stage. The current situation in a selection of Member States is as follows:

Denmark

Denmark requires very strict phosphate discharge limits and has low concentrations of phosphate in receiving waters. Older plants are based on chemical treatment. However, in recent years there has been a greater concentration on biological systems, usually with combined chemical precipitation.

France

France has adopted the use of both simple biological (very rarely enhanced biological) and chemical removal systems. However, they are limited in number (see chapter 5). It is important to note that many of the biological systems operate at low efficiency. In 1997 only 11% of the 210 treatment plants studied had an efficiency of 80% removal or more. Another important particularity in France is that many waste water treatment works are small, 85% serving agglomerations of 5,000 pe or less.

Germany

Germany has about 900 treatment plants with phosphate removal. Only about 13% of these involve biological treatment. This is partly because of some very strict discharge limits and some areas with older plants. However, future systems may favour a higher proportion of biological removal.

Italy

Phosphate removal is not widespread in Italy currently, but almost all existing plants are based on chemical treatment systems.

The Netherlands

The Netherlands is similar to Denmark in its strict limits and early relial on chemical treatment and recent developments in biological systems

Sweden

Sweden has very strict phosphate discharge limits and it was an early country to require extensive phosphate removal. Thus most systems are chemical treatment plants and those with biological systems have combined chemical treatment.

United Kingdom

Until the advent of the urban waste water treatment Directive, the UK had installed very few phosphate removal processes. By 1997 23 removal systems were operating, only 3 based on biological treatment. By the end of 1999 this will have increased to 50, all new systems being chemical. While the receiving waste water has sufficiently high phosphate concentrations to operate biological removal, the BOD levels are often lower than required for efficient operation.

1.7 CONCLUSIONS

There has been a decline recently in the quantities of phosphate discharges (both point and diffuse sources) to the surface waters of Europe. However, phosphate concentrations in surface waters are still, across much of Europe, very much higher than would be the case without human influence and chronic and severe eutrophication problems continue to occur.

Sources of phosphate pollution vary considerably in different European countries. They principally include agriculture, human and food wastes, detergents and industry. In some cases one source may predominate and in others combinations of sources are significant. It is important to note that discharges from each of these sources is changing rapidly, both spatially and over time. Any analysis of policy responses does, therefore, have to take this into account in seeking to identify cost-effective solutions to eutrophication problems and that variable policy responses are needed to ensure that the most effective action is taken in the most appropriate location.

Policy responses exist in a number of frameworks, at local, national, EU and international level. Each has an important role to play, as will be explored later in this study.

There are a variety of methods available to reduce phosphate concentrations in waste water prior to discharge. The type of method chosen depends on a range of factors including:

- cost
- practicalities of location
- type of sewage collection systems
- size
- relationship to the eutrophication problem
- national experience
- climate
- policy requirements (national or EU).

Finally, general EU policy is itself still developing, both in relation to central and eastern Europe and towards a more holistic, catchment-based approach to pollution control.

2. THE EU URBAN WASTE WATER TREATMENT DIRECTIVE AND ITS IMPLEMENTATION IN MEMBER STATES

2.1 INTRODUCTION

Eight years ago Directive 91/271/EEC on the treatment of urban waste water was adopted. The Directive sets a number of emission standards for urban waste water discharge and requires the step-wise introduction of comprehensive treatment facilities.

This analysis is based on all reports of Member States which have so far been submitted to the Commission according to the provisions of Article 17 of the Directive2 and the implementation report published by the European Commission in December 1998. These reports are mostly based on data from 31 December 1992. Therefore, an effort was made to contact all competent authorities of the Member States to up-date the information and discuss special questions of interest. Specific details relating to some individual Member States are contained in subsequent chapters.

2.2 SITUATION OF SEWAGE TREATMENT IN EUROPE PRIOR TO THE DIRECTIVE

In this section the situation of sewage treatment in the European Community during the 1980s is outlined. This information serves as a baseline against which the success of the urban waste water treatment Directive can be measured.

At the end of the 1980s the provisions for collection and treatment facilities within Europe were, and continue to be, very unequal (Table 2.1). While in the former West Germany 84 % of the total treatment capacity was tertiary, in Portugal most of the waste water (about 89 %) discharged was untreated. The situation in Belgium resembled the situation in Portugal - about 70 % of the sewage reached the receiving waters untreated. In the UK, while almost all sewage was subject to treatment (84 %), waste water discharged into the sea received no proper treatment at all and sewage sludge was dumped at sea.

The data presented in Table 2.1 should be interpreted with care. The data are drawn form different information sources (IKSR, WHO, EC) and data do not exist for all the Member States. Nevertheless, the table indicates vast differences in treatment standards among the Member States. A study undertaken for the Community also highlighted the need for regulating sewage treatment. In 1984, only 45 % of the total organic load was undergoing any treatment (COM(89) 518 final).

Hence, in 1989 the European Commission proposed a Directive on the treatment of urban waste water. The intention of this Directive was to establish a comparable standard and to guarantee a high level of treatment for the whole territory of the European Community.

TABLE 2.1

	TOTAL CONNECTION RATE: SEWERAGE AND TREATMENT IN SEWAGE WORKS	MECHANICAL TREATMENT ONLY
Belgium	no data	no data
Denmark	98%	8%
Germany	90%	2%
Greece	no data	1% (1985)
Spain	29% (1985)	13% (1985)
France	50%	no data
Ireland	no data	no data
Italy	60%	no data
Luxembourg	91%	14% (1985)
The Netherlands	89%	7%
Portugal	11%	4%
Great Britain	84%	6%

Urban Waste Water Treatment in EU Member States (in 1987). Source: Dörr (1998).

[2] By Mid 1998 ten Member States had submitted reports: Denmark, Germany, France, United Kingdom, Ireland, the Netherlands, Austria, Sweden, Spain and Portugal.

2.3 THE EU DIRECTIVE ON URBAN WASTE WATER TREATMENT (91/271)

The principle measure taken to control, *inter alia*, phosphate pollution from urban waste water has been the 1991 urban waste water treatment Directive. This has set significant requirements for a range of issues relating to waste water treatment across the EU (NRA, 1995) and because of the costs of compliance is one of the more difficult elements of EU environmental legislation for central and eastern European countries to comply with in preparation for EU accession (see chapter 7). Some Member States do undertake measures additional to the requirements of the Directive and these will be considered in the following chapters.

The purpose of the Directive is to stimulate the Member States to invest in the collection and treatment of urban waste water. Different requirements and deadlines apply to the different areas of discharge (‘sensitive’, ‘normal’, and `less-sensitive’ areas). The Directive leaves the Member States much freedom in its implementation, such as a choice between limit values for treatment plant effluents and percentage reduction goals and a choice between reducing phosphorus and nitrogen discharges.

2.4 FORMAL AND TECHNICAL COMPLIANCE REQUIREMENTS

Particular for the Directive is the strict timetable for fulfilling the formal and technical obligations. The formal compliance date of 30 June 1993, until when Member States had to transpose the Directive into national laws, regulations and administrative provisions, was, in fact, hardly met by any Member State.

The last deadline for the technical compliance is to be met by the year 2005. According to the type of area and size of agglomeration, the Directive sets minimum standards for the collection, treatment and discharge of urban waste water. Table 2.2 supplies an overview of these requirements and the respective deadlines. The data in the cells refer to the size of the agglomeration (stated as sewage load in population equivalents (p.e.)) and the type of area (less sensitive, normal and sensitive areas).

Urban waste water that is collected is to be subject to treatment, which generally becomes more stringent the larger the agglomeration. The treatment levels required also depend on whether the receiving waters are coastal, estuarine or freshwater and whether discharges are to sensitive, normal or less sensitive areas. In general, agglomerations with a population equivalent (p.e.) greater than 2,000 p.e. are to be subject to a minimum of secondary treatment (biological treatment with a secondary settlement). For agglomerations greater than 15,000 p.e. secondary treatment must be in operation by 31 December 2000, while the deadline for smaller towns is in general five years later. All agglomerations greater than 10,000 p.e. discharging into sensitive areas required more stringent (tertiary) treatment (ie nutrient removal) by the end of 1998.

All agglomerations with a population equivalent (p.e.) greater than 2,000 are obliged to have collection systems by the end of either the year 1998, 2000 or 2005, depending on their size and the type of area they are discharging to (Article 3).

2.5 THE DESIGNATION OF AREAS

In Article 5 and 6 of the Directive the Member States are asked to designate ‘sensitive’ (Article 5) and ‘less sensitive’ (Article 6) areas according to Annex II A and B. An area is to be classified sensitive, in which case significant reductions of nitrogen and/or phosphorus are required. This is necessary:

- either when the receiving water is ‘eutrophic or which in the near future may become eutrophic if protective action is not taken’ (as defined by the list of criteria in the Annex);

TABLE 2.2

	12/1998	12/2000	12/2005
sewerage collection	> 10,000 p.e. in sensitive areas	> 10,000 p.e. in normal and less sensitive areas	> 2,000 p.e. in all areas
primary or secondary treatment		> 15,000 p.e in less sensitive areas[1]	>10,000p.e in less sensitive areas[1]
secondary treatment		> 15,000 p.e in normal areas	> 2,000 p.e. in normal and sensitive areas[2]
more advanced treatment	> 10,000 p.e. in sensitive areas		
if the sewerage is collected in agglomerations < 2,000 p.e., appropriate treatment should be applied			

Technical Compliance Deadlines for Collection and Treatment Requirements from Directive 91/271

- or if the water is used for drinking water abstraction;
- or if the water requires a more stringent than a secondary treatment in order to meet other EU Directives.

A Member State has the possibility to designate its entire territory as a sensitive area under Article 5 para.8. In areas, where sewage is discharged into the sea, without any adverse effects on the environment, coastal and estuarial waters may be designated to be less sensitive. Here, standards for treatment are lower. A minimum of primary treatment (a physical and/or chemical process involving the settlement of suspended organic solids which produces a specified reduction in biological oxygen demand (BOD) is required. For such 'less sensitive areas' secondary treatment is not required for agglomerations smaller than 150,000 p.e. discharging into coastal waters and for agglomerations between 2,000 and 10,000 p.e. that discharge into estuaries.

2.6 REQUIREMENTS FOR MORE ADVANCED TREATMENT

In sensitive areas adequate collection and 'more stringent than secondary' (i.e. tertiary) treatment systems had to be installed by 31 December 1998 for all discharges from agglomerations of more than 10,000 population equivalents.

Article 5 para.2 states that:
"[...] urban waste water entering collection systems shall before discharge into sensitive areas be subject to more stringent treatment than that described in Article 4 [...]"

Member States are basically free to choose among five approaches of how to apply "more stringent treatment" in sensitive areas (i.e. how to remove nutrients): four options according to Article 5 para.3 and one option according to Article 5 para.4. These options comprise of phosphorus reductions, nitrogen removal or a combination of both.

The four options according to Article 5 para.3 are listed in Annex I, table 2 of the Directive. If one chooses option 1 or 2, the effluent of the treatment plants in sensitive areas must meet emission limit values for either phosphorus (P) or nitrogen (N). The limit values for P are 2 mg/l in agglomerations of between 10,000 and 100,000 population equivalents and 1 mg/l in larger agglomerations (measured as P). The limit values for N are 15 mg/l for agglomerations of between 10,000 and 100,000 population equivalents and 10 mg/l in larger agglomerations (measured as N). Alternatively to the use of limit values, phosphorus may be reduced by 80 % or nitrogen by 70 - 80% (options 3 and 4). The following Table 2.3 summarises this information.

The 5th option is based on Article 5 para.4 of the Directive that states that the above requirements need not apply in sensitive areas for which it can be shown that the minimum percentage of reduction of the overall load entering all urban waste water treatment plants in that area is at least 75 % for total phosphorus and total nitrogen. With the wording 'overall load entering all urban waste water treatments plants in that area', this Article clearly opens the possibility for emissions trading within an 'emissions bubble'[3]. However, it also could establish restrictions. Notably, the 'bubble area' must be a 'sensitive area' within the definitions of the Directive, the reduction must be achieved over all urban waste water treatment plants and not only in the larger installations, and the reduction probably must be attained for both phosphorus and nitrogen simultaneously. The weight of these restrictions is not clear but unlikely to present serious obstacles to a pragmatic implementation of an emissions trading regime.

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[3] 'Bubble' usually refers to the total amount of emission that is allowed within a specific area. The competent authorities are free to chose how the reduction goal is met - it is only of importance that the reduction goal is met in total. In the context of the Urban Waste Water Treatment Directive this means for example, to reach a reduction goal of 50 % one treatment facility may eliminate all emissions whereas another facility does not reduce its emissions at all. "Emission trading" therefore may occur in the sense, that treatment facilities negotiate their respective reduction targets among each other. Facilities with low standards are thereby enabled to buy emission rights from facilities which overcomply with the Directive.

TABLE 2.3

PARAMETERS	CONCENTRATION	MINIMUM PERCENTAGE OF REDUCTION[1]
Total Phosphorus	**Option 1** 2 mg/l P (10,000 - 100,000 p.e) 1 mg/l P (more than 100,000 p.e)	**Option 3** 80%
Total Nitrogen	**Option 2** 15 mg/l N (10,000 - 100,000 p.e) 10 mg/l N (more than 100,000 p.e)	**Option 4** 70-80%

Requirements for Discharge from Urban Waste Water Treatment Plants to Sensitive Areas. Source: Council Directive 91/271/EEC concerning Urban Waste Water Treatment. Annex I, table 2.

[1] Reduction in relation to the load of influent.

None of the EC Member States so far appear to have used the possibility of establishing emissions trading in sensitive area bubbles, and it does not appear to have been discussed among the national experts in the Technical Committee established by the Directive. The general lack of interest may be regrettable as a potentially important source of economies in pollution abatement costs remains untapped, in spite of the wide-spread concerns about the financial implications of the Directive.

Some Member States like the Netherlands and Luxembourg make use of the provision of Article 5 para 4. These Member States regard their whole territory as a sensitive area. However, to our knowledge, no trading of emission rights has occurred among the different treatment facilities. This might be due to the ownership structure of the waste water treatment plants in these countries.

2.7 ADDITIONAL PROVISIONS

According to Article 14, sewage sludge should be reused if possible and resulting effects on the environment should be limited to a minimum. The disposal of sludge is to be subject to general rules, registration or authorisation by 31 December 1998. The same deadline applies for the ending of dumping of sewage sludge from municipal sewage treatment at sea or other surface waters.

The Member States are obliged to publish situation reports every two years on the disposal of urban waste water and sludge and send them to the Commission (Article 16). According to the European Commission no Member States has yet submitted such a situation report. Likewise, programmes for the implementation of the Directive according to a ‘format’, set out in the Council Decision 93/481 (OJ L 226, 7.9.1993), had to be submitted to the Commission by 30 January 1994 (Article 17). The implementation programmes consist of a set of tables including information on the state of sewage collection and treatment at the end of 1992 and scheduled plans for the implementation of the requirements set by the Directive. By mid 1998 only ten Member States had submitted their implementation programmes to the Commission.

Emission limit values and minimum percentage reductions that systems of secondary and tertiary treatment must meet, as well as the reference methods for monitoring and evaluating the results, are set out in Annex I of the Directive. It also sets emission limits for nitrogen and phosphorus discharges from treatment plants to designated sensitive areas.

Those smaller towns or villages which are not obliged by the Directive to install secondary treatment systems are nevertheless required to provide ‘appropriate’ treatment, sufficient to ensure compliance with quality objectives or the requirements of other relevant Community legislation.

Derogations and exceptions to these general rules are possible when the installation of sewerage systems involves ‘excessive costs’ and alternative systems giving the same degree of environmental protection can be used. Under Article 8, Member States may apply to the Commission for derogations from the requirement to install secondary treatment for larger towns over 150,000 p.e., if it can be justified on the basis of technical reasons and be for a geographically-defined population. The compliance deadline can then be postponed to the end of 2005.

Article 11 regulates industrial waste water that is discharged into municipal collection systems and treatment plants. Such discharges are to be subject to prior regulation and/or authorisation and subject to pre-treatment until 31 December 1993. Conditions to be met by the waste water are specified in Annex I(c). These include health security for the personnel working in the sewerage services, the protection of sewerage installations from corrosive substances and the provision that the resulting sludge can be disposed safely in an environmentally acceptable manner. Bio-degradable industrial waste water from specified sectors of the food and beverage industry listed in Annex III, which is not discharged into municipal treatment plants is also to be subject to prior regulation/authorisation by 31 December 2000 (Article 13).

A Committee of representatives of Member States and the Commission is established to consider future changes in the standards set in the Directive.

2.8 IMPLEMENTATION OF THE URBAN WASTE WATER TREATMENT DIRECTIVE

2.8.1 Level of Implementation

The following information is based on the national implementation programs which had to be submitted by the Member States according to the Commission Decision 93/481/EEC and with the data contained in the Commission’s own 1998 implementation report. Due to this decision the format of the presentation of the data is standardised. However, this does not mean that the data are directly comparable. Data on sewage collection and treatment are collected differently in the Member States. The discussion about the comparability of data on urban waste water remains quite controversial (for a thorough discussion compare EWPCA 1995).

The Directive uses a number of colloquial expressions like “agglomeration”, “heavy rain” or “unusual situation”. These terms are not adequately defined, which makes it difficult to apply the provisions of the Directive consistently in all Member States.

TABLE 2.4

(g/DAY)	A	DK	F	D	GR	IRL	I	L	P	E	NL	UK
BOD_5	60	60	57	60	50-60	60	54-60	60	54- 60	60	54	60
N	12	-	15	11	10-14	-	12	11	-	-	-	-
P	2	-	4	2,5	2-2,5	-	2-3	2,5	-			

Definitions of Populations Equivalents (p.e.) in Member States. Source: Jacobsen et al. (1997).

TABLE 2.5

MEMBER STATE	TRANSPOSITION	DESIGNATION OF SENSITIVE AREAS	IMPLEMENTATION PROGRAMME REPORT
Austria	Not in conformity	Yes (none)	Yes
Belgium	Yes	Yes	Not in conformity
Denmark	Yes	Yes (Article 5.8)	Yes
Finland	Yes	Yes (Article 5.8)	Yes
France	Yes	Yes	Yes
Germany	Yes	Yes	Yes
Greece	Not in conformity	No	Yes
Ireland	Yes	Yes	Yes
Italy	No	No	No
Luxembourg	Yes	Yes (Article 5.8)	Yes
Netherlands	Yes	Yes (Article 5.8)	Yes
Portugal	Yes	Yes	Yes
Spain	Yes	Yes	Yes
Sweden	Yes	Yes (Article 5.8)	Yes
United Kingdom	Yes	Yes	Yes

Implementation of the urban waste water treatment Directive in Member States according to requirements relevant to nutrient control and its reporting according to the European Commission (COM(98)775).

TABLE 2.6

	CATEGORY I	CATEGORY II	CATEGORY III
Areas of Discharge	only sensitive areas	sensitive/normal areas	sensitive, normal and less sensitive areas
Member States	Denmark The Netherlands Sweden Ireland	Austria[1] France Germany	Portugal United Kingdom Spain

Overview of the different Areas of Discharge in the Member States
1 The whole territory of Austria is treated as normal area

Additionally, in cases where the Directive requires the use of certain parameters, Member States still apply different criteria as in the case of the BOD parameter. According to the Directive, one population equivalent (1 pe) should be measured as biological oxygen demand of 60 g per day. In most cases it cannot be determined which definitions are applied in the national implementation reports. Nevertheless, Table 2.4 presents the variety of definitions of population equivalent used in the Member States. However, these are very similar, except for the somewhat higher phosphate definition in France.

According to the 1998 implementation report of the Directive, most Member States have undertaken the basic legal requirements which would lead to regulatory action to remove phosphate from urban waste water discharges where necessary (Table 2.5). However, legal transposition is lacking or is incomplete in some cases, particular Italy, and Greece and neither has yet designated sensitive areas (although some data for Greece do relate to areas that may be designated). Of the other Member States only Austria considers that no sensitive area designations are required. All Member States have reported on the early stages of implementation of the Directive, except Italy. However, no Member States will have reported yet in relation to the 31 December 1998 deadline for compliance with discharge requirements in sensitive areas.

2.8.2 Sensitive areas

The designation of sensitive areas remains incomplete across the EU (Table 2.4). The deadline for compliance with discharge limits for sensitive areas was 31 December 1998, but as stated above some Member States (eg Greece and Italy) have still not adopted domestic legislation to formalise the designation process. It will also be some time before Member States have reported on implementation of this requirement. Designation is important in that, in most cases, it will drive the installation of nutrient removal, although this is less important in Member States where phosphate removal has been a domestic environmental objective for some time.

As can be seen from Table 2.6 Member States can be categorised into three groups, according to the identification of sensitive areas. Denmark, Sweden and the Netherlands fall into category 1. These Member States regard their whole territory as sensitive area. The second category comprises Member States, in which normal areas also exist, like France, Germany, Ireland and Austria. However, Austria is an exception in the sense that it regards its whole territory as normal area. This was done primarily to gain time, as Austria still aims to meet the requirements for sensitive areas in their whole territory without being bound to the strict deadlines for sensitive areas. The third Category consists of Portugal, the United Kingdom and Spain. Besides having sensitive areas, these Member States have also designated less sensitive areas. Most of the territory in these countries is regarded as a normal area. The following table gives an overview of these results.

2.8.3 Discharges and agglomerations

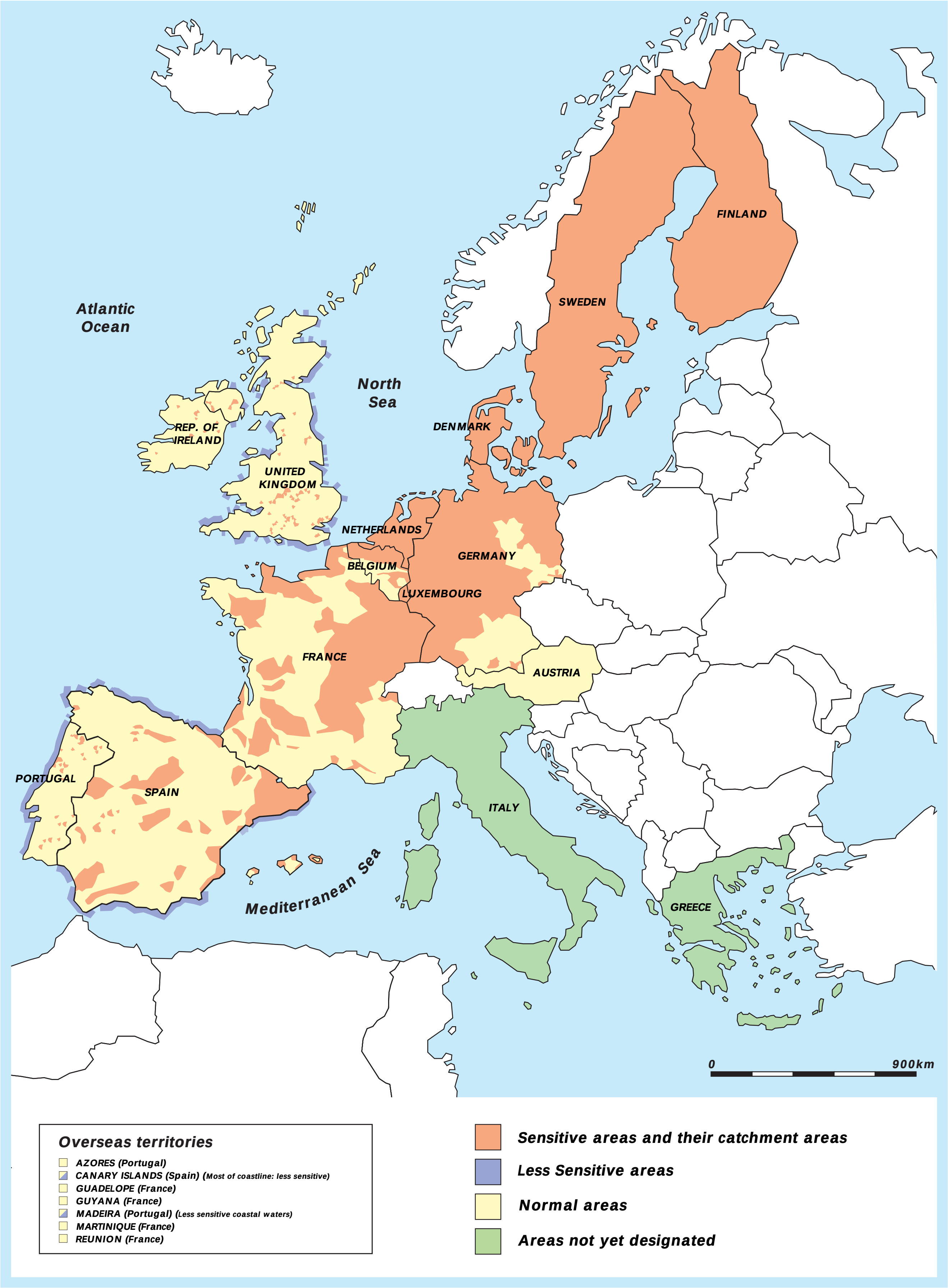
The organic load discharged to normal, sensitive and less sensitive areas and the number of agglomerations within each area are shown in Table 2.7. Table 2.7 requires interpretation. The population data are, of course, not the same as population equivalents (see above), which is why the total population equivalent in the final column is different to the Member State population. It is also important to note that the data are based on agglomerations of 2,000 pe or above. Thus small populations (eg in rural areas) are not included. This also means that the number of agglomerations and the population equivalent in sensitive areas is not the same as that required to adopt tertiary treatment under the Directive. This requirement only applies to agglomerations of 10,000 pe or more. Thus although 37% of the organic load (population equivalent) in the EU is discharged within sensitive areas, this would not all require nutrient removal.

2.8.4 Capacity of collection systems and treatment facilities

Table 2.8 indicates the capacity of the collection systems as a percentage of the respective load in the area of discharge and how the capacity is predicted to change by 2005. Table 2.9 provides a similar analysis of the capacity of treatment facilities. For example 89.2% for Austria (first cell in Table 2.8, column 2) means that the capacity of collection systems ‘deemed to be in compliance‘, is able to carry 89.2% of the load in normal areas.

While considering the percentage of the capacity of treatment and collection systems, as given in Table 2.8 (collection systems) and 2.9 (treatment plants), it has to be noted that “100% capacity” does not indicate an ideal capacity adequately to treat 100% of the generated sewage. This would only be possible if at all places and at all times the respective treatment or collecting capacity matched the amount of waste water discharged. It is however more likely that some agglomerations have an overcapacity of treatment or collection systems whereas other agglomerations face a lack of capacity. Therefore, a total capacity of 120% is regarded as sufficient to collect and treat all waste water discharges to facilities that are deemed to be in compliance with the Directive.

The *collection systems* ‘deemed to be in compliance’ of the Member States in category I (Table 2.6) show a remarkable overcapacity. Sweden has the highest overcapacity with 174%, followed by Denmark (144.6%) and the Netherlands (126.5%). At a first glance, the data do not seem to reflect the situation in Sweden adequately.



Extent of "sensitive areas" and "less sensitive areas" across Europe.

TABLE 2.7

Member State	Population (1000 inhabitants)	Normal areas		Sensitive areas		Less sensitive areas		Total	
		Agglomerations	1000 pe	Agglomerations	1000 pe	Agglomerations	1000 pe	Agglomerations	1000 pe
Austria	8,040	703	18,569	0	0	0	0	703	18,569
Belgium	10,131	119	1,775	245	7,389	0	0	364	9,164
Denmark	5,216	0	0	382	8,393	0	0	382	8,393
Finland	5,099	0	0	201	4,007	0	0	201	4,007
France	58,027	2,359	49,927	1,137	20,583	0	0	3,496	70,510
Germany	81,533	1,179	27,397	3,658	101,406	0	0	4,837	128,803
Greece	10,442	169	6,189	60	2,101	86	1,913	315	10,203
Ireland	3,577	137	3,748	9	170	0	0	146	3,918
Luxembourg	407	0	0	42	914	0	0	42	914
Netherlands	15,423	0	0	414	17,218	0	0	414	17,218
Portugal	9,912	598	12,651	114	1,814	34	1,806	746	16,271
Spain	39,170	2,611	47,263	253	4,659	356	22,517	3,220	74,439
Sweden	8,816	0	0	454	7,496	0	0	454	7,496
UK	58,276	1,764	61,816	127	4,187	155	10,523	2,046	76,526
Total	314,069	9,632	229,335	7,088	158,073	631	36,759	17,351	424,361

The population equivalent and number of agglomerations of greater than 2,000 pe in normal, sensitive and less sensitive areas in each Member State (excluding Italy) according to the 1998 European Commission Implementation Report (updated for Germany)

However, according to the Swedish Environmental Agency this overcapacity is due to an inaccurate prognosis of the population and economic development. Within category II Austria and Germany have a collecting capacity of approximately 90%, France of 79% and Ireland about 24%. The collection capacity for the United Kingdom seems to be calculated on the basis of the sewage generated, as it reaches exactly 100%. In Portugal and Spain the relative share of the collection systems 'deemed to be in compliance' lies around 50%.

A different picture of the status of implementation is drawn, if one regards the capacity of *treatment plants* 'deemed to be in compliance'. Within category I Denmark is an exception: the percentage of 70.9% of treatment plants 'deemed to be in compliance' indicates that work remains to be done here. The Netherlands with 124.3%, show slight overcapacities, Sweden again has remarkable overcapacities at its disposal (173.9%). Similar to the performance of collection systems, there are large differences in the capacity of treatment plants within category II. Germany nearly hits the 100% mark with a capacity of 98.5% of treatment plants in compliance in sensitive areas. More investments need to be made in normal areas, as treatment plants in compliance can only handle 56.7% of the load in these areas. In total Germany has a capacity of 90% for treatment plants 'deemed to be in compliance' - this capacity is comparable to the German capacity of collection systems. In Austria, the treatment capacity 'deemed to be in compliance' of 77% shows that improvements can be made. France faces a relatively high necessity for further investment in the treatment sector.

Currently only 57.2% of the waste water load can be treated in facilities that are deemed to be in compliance with the Directive. In Ireland the number of treatment facilities that are deemed to be in compliance with the Directive seems to be quite low. According to the Irish implementation report only 12.3% of the waste water is treated in compliant facilities. However, these data might have to be qualified, taking into account the low population density in Ireland. In Portugal, Spain and the United Kingdom (category III) the capacity of the treatment systems 'deemed to be in compliance' only allows for the treatment of a third of the waste water discharge.

TABLE 2.8

Member State	1992 (1000 pe)	% capacity in compliance	2005	Increase (1000 pe)	Increase (percentage)
Austria	16,571	89.2	19,467	2,896	17
Belgium	1,721	18.8	2,201	480	28
Denmark	12,133	144.6	12,133	0	0
Finland	3,395	84.7	3,576	181	5
France	55,780	79.1	70,508	14,728	26
Germany	114,107	88.6	127,055	12,948	11
Greece	7,278	71.3	8,708	1,430	20
Ireland	878	22.4	3,918	3,040	346
Luxembourg	914	100.0	969	55	6
Netherlands	21,780	126.5	21,780	0	0
Portugal	9,367	57.6	16,462	7,095	76
Spain	35,001	47.0	74,439	39,438	113
Sweden	13,044	174.0	13,044	0	0
United Kingdom	76,526	100.0	75,604	-922	-1
Total	368,472	86.8	449,864	81,392	22

The capacity of waste water collection systems (in population equivalents) in Member States as reported for 1992 and as predicted for 2005 from the Commission implementation report (updated for Germany). The percentage capacity in compliance is calculated by comparing the collection capacity with the total discharge in each Member State for agglomerations greater than 2,000 pe in Table 2.7, page 20.

The latest OECD Environmental Performance Review of Belgium points at particular serious delays in implementing the Directive. Water management presents a key challenge according to the report. The country’s high population density, strong industrialisation and very intensive agriculture result in a strong pressure on water resources. According to the report the introduction of modern waste water treatment in Belgium is “among the lowest in the OECD”. The implementation of the Urban Waste Water Treatment Directive therefore remains a political and financial challenge in Belgium.

There are limited sources of more up to date comparative data on EU Member States. The status of treatment in ten EU Member States in 1994 (population of 334 million or 535 million population equivalents, ie 90% of the EU total), together with the expected requirements following implementation of the Directive are shown in Table 2.10. The data are from unpublished work of the European Environment Agency and the total population equivalents used are different from that given in the Commission’s implementation report of the Directive. Note also that the tables consider levels of treatment from waste water treatment works (not total waste water production) and, therefore, the population equivalents will change as connection rates to sewerage systems increase. It can be seen that it is estimated that after implementation 48% of waste water from treatment plants will be subject to tertiary nutrient removal. If one adds in the estimate for the remaining part of the population which will be unconnected to sewerage systems (29.2 million pe), the proportion of the overall population with nutrient removal is 45%.

The data show significant differences to Table 2.9. Some of levels of treatment are significantly higher. However, this may be in part that the analysis is not limited to agglomerations greater than 2,000 pe. It is also important to note that different forms of tertiary treatment (nutrient removal and disinfection are not distinguished).

TABLE 2.9

Member State	1992 (1000 pe)	% capacity in compliance	2005 (1000 pe)	Increase (1000 pe)	Increase (percentage)
Austria	14,413	77.6	19,467	5,054	35
Belgium	5,499	60.0	9,919	4,420	80
Denmark	5,950	70.9	9,246	3,296	55
Finland	3,598	89.8	3,935	337	9
France	40,333	57.2	69,378	29,045	72
Germany	115,436	89.6	143,831	28,395	25
Greece	2,058	20.2	8,637	6,579	320
Ireland	483	12.3	3,810	3,327	689
Luxembourg	777	85.0	969	192	25
Netherlands	21,396	124.3	22,053	657	3
Portugal	5,731	35.2	16,387	10,656	186
Spain	23,872	32.1	73,754	49,882	209
Sweden	13,038	173.9	13,038	0	0
United Kingdom	29,335	38.3	75,323	45,988	157
Total	277,939	65.5	469,747	191,808	69

The capacity of waste water treatment facilities (in population equivalents) in Member States as reported for 1992 and as predicted for 2005 from the Commission implementation report (updated for Germany). The percentage capacity in compliance is calculated by comparing the collection capacity with the total discharge in each Member State for agglomerations greater than 2,000 pe in Table 2.7, page 20.

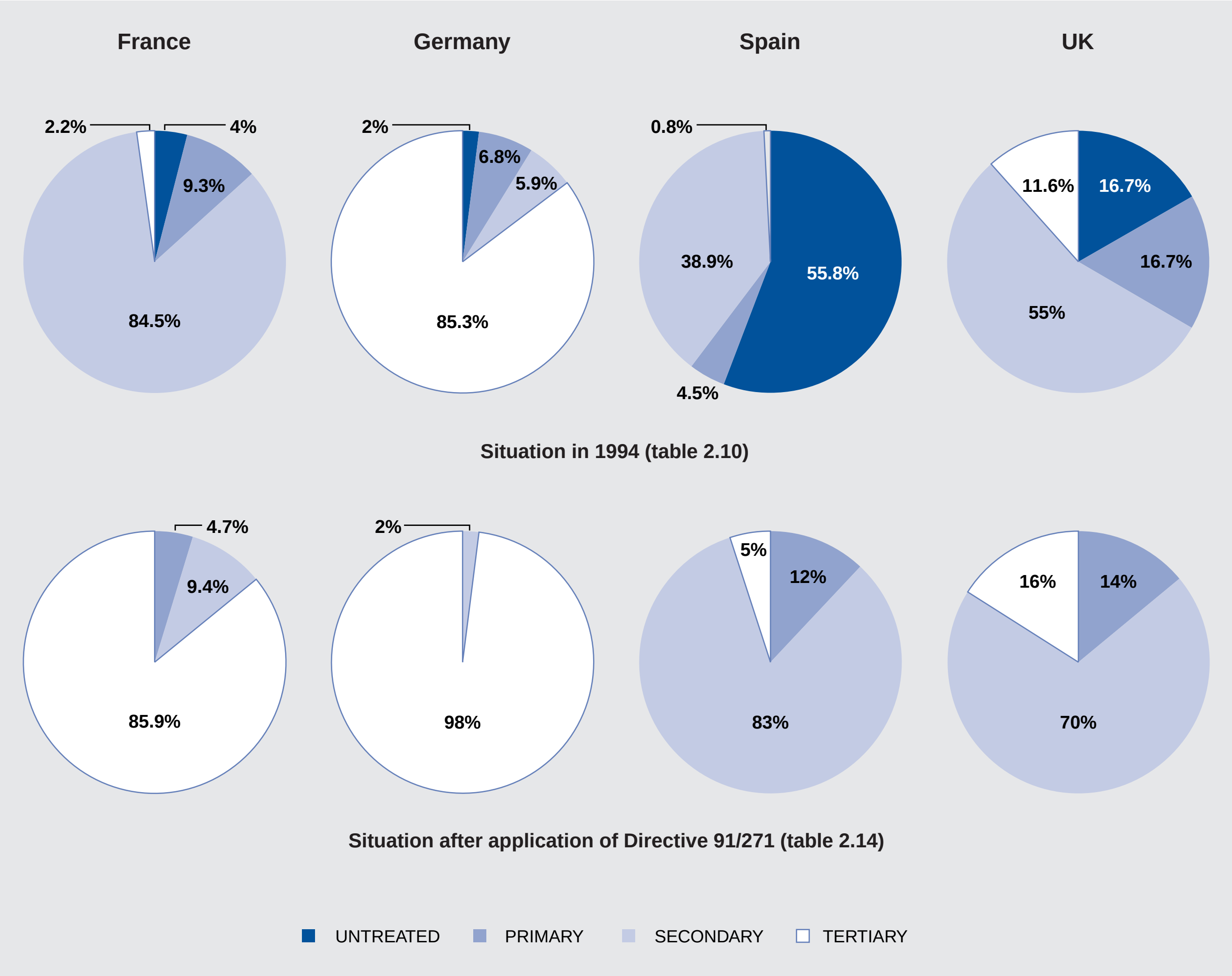
2.8.5 Discharge limits for phosphate in EU Member States

The Table 2.11 compares the discharge standards for phosphorus within the 1991 urban waste water treatment Directive with those of a selection of Member States. It can be seen that the requirements in some Member States (eg France and the UK) are exactly those indicated in the Directive. However, other Member States (most notably Sweden) have significantly stricter discharge standards. The effect of varying standards is to affect the type (and thus cost) of the phosphate removal processes adopted in the Member States and, possibly, the extent to which eutrophication is overcome in particular circumstances. It is important to note that where some Member States have discharge limits following, or similar to, the Directive, they may also adopt stricter limits for especially sensitive environments.

2.8.6 Tertiary treatment

Information contained in the Member States implementation reports provides only limited information on tertiary treatment provision in some Member States for the end of 1992. The data available are given in Table 2.12. A more up to date picture is given in Table 2.10 above.

A direct comparison of the data on nutrient elimination is not possible, although Table 2.13 does give an overview of the capacity of treatment works for different Member States according to the level of treatment. As explained above the Member States can chose from a variety of options to reduce nutrients. According to the different approaches the Member States supplied different information in their national implementation programmes. Again, Sweden reports an overcapacity of treatment plants equipped with tertiary treatment. The Netherlands have, for nearly their whole territory, tertiary treatment at their disposal. In Denmark, nearly half of the waste water load can be treated with tertiary treatment. In Germany, the majority of treatment plants allow for tertiary treatment, which in Germany mainly means phosphorus elimination. This is also true for Ireland, where eutrophication can be addressed most efficiently by phosphorus elimination. Large scale phosphorus reduction facilities already existed in Ireland. Ireland tries to go well beyond the requirements



Levels of waste water treatment in four EU Member States

TABLE 2.10

Member State	Untreated	Primary	Secondary	Tertiary	Total
Finland	0.0	700	0.0	4,800	5,500
France	2,000	4,500	41,000	1,000	48,500
Germany	2,500	8,300	7,300	104.6	122.7
Greece	2,700	2,700	700	1,800	7,900
Italy	28,800	7,000	53,000	6,000	94,800
Luxembourg	60	30	480	50	620
Netherlands	100	200	5,700	18,000	24,000
Portugal	7,400	1,000	2,00	200	10,900
Spain	43,600	3,500	30,400	700	78,200
United Kingdom	13,000	13,000	43,000	9,000	78,000

Levels of waste water treatment (in 1000 population equivalents) in selected EU Member States in 1994. (Source: EEA unpublished).

TABLE 2.11

SOURCE OF STANDARDS	COMMENTS	DISCHARGE LIMITS
Austria		2 mg/l (< 5,000 pe) 1 mg/l (> 5,000 pe) 0.5 mg/l (>10,000 pe in the catchments of lakes)
Denmark	To North Sea (annual average) Small rivers.	1.5 mg/l 0.3 mg/l
France	As total P, annual average. Required for discharges to designated sensitive areas. Alternatively a treatment plant may operate to reduce total P by 80%.	2 mg/l (10,000-100,000 pe) 1 mg/l (>100,000)
Germany	Standards apply to short-term sampling (variable) and 80% of samples each day must comply.	2 mg/l (>10,000-100,000 pe) 1 mg/l (>100,000 pe)
The Netherlands		2 mg/l (< 100,000 pe) 1 mg/l (>100,000)
Sweden		0.5 mg/l (< 50,000 pe) 0.3 mg/l (> 50,000 pe or for discharges to sensitive waters)
United Kingdom	As total P, annual average. Required for discharges to designated sensitive areas. Alternatively a treatment plant may operate to reduce total P by 80%.	2 mg/l (10,000-100,000 pe) 1 mg/l (>100,000)

Phosphate discharge limits (mg/l) from selected Member States.

TABLE 2.12

MEMBER STATE	CAPACITY OF TREATMENT WORKS			NUMBER OF TREATMENT WORKS		
	Tertiary treatment	**Phosphorus removal**	**Nitrogen removal**	**Tertiary treatment**	**Phosphorus removal**	**Nitrogen removal**
Austria		5,379			206	
Denmark	4,627			67		
France	6,152			164		
Germany	23,602	21,812	8,519	312	374	172
Portugal	30			1		
Spain	471			9		
Sweden		11,561			191	
United Kingdom	248			10		

Capacity and number of treatment works with tertiary waste water treatment (1992) according to Member State implementation reports.

of the Directive by installing phosphorus reduction also in agglomerations under 2,000 p.e. In Luxembourg, 90% percent of the treatment facilities are biological. Some of the biggest treatment plants do not remove nitrogen. In 1991 a nitrogen removal programme was set-up. However, it will be difficult for Luxembourg to meet the 1998 deadline for sensitive areas. The phosphorus removal seems to be considerably advanced and therefore there are no problems with regard to phosphorus. The United Kingdom and Spain hardly have any treatment plants equipped with tertiary treatment in the implementation reports.

Further examination of the status in individual Member States (see chapters 3-6) indicates that France is unlikely to comply with the requirements for sensitive areas for some years. Germany will meet outstanding requirements in the east by 2005. Spain, however, has only recently undertaken designations and appears to place nutrient removal as a lower priority to other waste water treatment requirements. In contrast, the requirements for existing designations in the UK should have been met by the end of 1998. Implementation and future trends are, therefore, highly variable.

2.9 FUTURE IMPLEMENTATION OF THE DIRECTIVE

It is difficult to predict future implementation of the urban waste water treatment Directive. It is certainly unlikely that timetables contained within the Directive will be met, as they have not been followed up to this point. Any future timetable will largely depend on domestic and Commission pressure on individual Member States. Indeed, some Member States are still designating sensitive areas. These remain to be confirmed in Greece, identified in Italy and the UK has just announced a major expansion in the number of designations. Such changes make predictions uncertain. It is also important to stress the point made at the outset that implementation of the Directive allows significant flexibility to Member States and, therefore, the particular action taken will reflect practical, political and economic considerations as decisions are made. The Commission may, in the future, put pressure on individual Member States to designate further areas as it begins to examine the basis for the existing designations. The Commission may take a more objective view of which sites suffer from adverse eutrophication, based on the definition in the Annex to the Directive.

However, the European Environment Agency has commissioned some work to consider future implementation in ten Member States. Table 2.14 summarises the likely levels of treatment in each Member State following full implementation of the Directive. In a number of Member States the current pattern of treatment is much as currently exists, eg high levels of tertiary treatment in the Netherlands, relatively low levels in Spain and the UK (albeit it with improvements). The largest predicted change is for France, which, in order to meet this, would also require significant investment in phosphate removal outside sensitive areas. This is further elaborated in Table 2.15.

From Table 2.14 it is possible to estimate the amount of phosphate that will be removed from waste water. Table 2.16 provides an estimate of the quantity of phosphate produced in the receiving waters of the waste water treatment plants in the ten Member States described in Table 2.16, an estimate of removal rates in 1994 and of the removal rate following implementation of the urban waste water treatment Directive.

For four of the Member States these data may be broken down as shown in Table 2.19. It should be noted that the estimate given for the likely levels of treatment that will be applied in France in Table 2.14 is considerable more stringent than might be assessed from examination of current requirements for sensitive areas. This would suggest that resulting tertiary and secondary treatment would remove about 55% of the phosphate produced. Only a completion of studies on the appropriateness of current designations in France will resolve this discrepancy.

Overall the effect of the treatment facilities required would be to remove between 56 and 62% of the domestic phosphate produced in the ten Member States. The remaining Member States also generally exhibit high levels of phosphate removal. Three of these Member States (Austria, Denmark and Sweden) had 14.2 pe of their total 21.8 pe with nutrient removal on waste water treatment at the end of 1994 (Table 2.10). This represents at least a further 9,900 tonnes of phosphate removed from a total of 15,300 tonnes produced.

2.10 SEWAGE SLUDGE PRODUCTION

Many of the issues relating to sludge production and disposal are outwith the scope of this study. However, of relevance to waste water treatment (as sludge production varies with choice of treatment) is the cost of sludge disposal. This varies significantly and some comments are made in subsequent chapters. However, Table 2.19 provides an overview of current and predicted levels of sludge production and its likely use in agricultural spreading.

Within the United Kingdom, Spain and Ireland part of the sewage sludge was discharged into the sea. This is now prohibited under the urban waste water treatment Directive. However, Spain has indicated that it will continue to dispose of around 57,000 tonnes of sludge in this way. In general, the discharge of sewage sludge is handled quite heterogeneously in the Member States. Germany produces the largest amount of sewage sludge. In Denmark, the largest amount of sewage is reused in agriculture, a practise that is politically controversial.

TABLE 2.13

	Sensitive Areas	Collection systems[1]	Treatment Plants[1]	Tertiary Treatment
	%	%	%	%
Denmark	100	144.6	70.9	~ 50
The Netherlands	100	126.5	124.3	~ 100
Sweden	100	174	169.8	~ 160
France	29.2	79.1	57.2	~ 10
Germany	78.7	88.6	89.6	~ 90
Ireland	6.3	22.4	12.3	no data available
Austria	0	89.2	77.6	~ 25
Portugal	12.2	56.9	34.8	~ low
United Kingdom	5.2	100	38.7	~ low
Spain	4.3	47	32.1	~ low

Comparative overview of the treatment capacity in Member States according to levels of waste water treatment (1992). The column "sensitive areas" states the percentage of the sensitive areas in relation to the total territory (given in p.e.). The column "collection systems" indicates how much of the total waste water load for the country ideally can be handled by collection systems 'deemed to be in compliance'. The third column "treatment plants" deemed to be in compliance gives the same information with regard to the treatment facilities. 'Tertiary Treatments' refers to phosphorus elimination, denitrification or both. The capacities of treatment plants equipped with tertiary treatment are set into relation to the total capacity of treatment plants.

[1] Facilities that are deemed to be in compliance with the Directive

TABLE 2.14

Member State	Untreated	Primary	Secondary	Tertiary	Total
Finland	0.0	0.0	0.0	5.5	5.5
France	0.0	3.0	6.0	54.5	63.5
Germany	0.0	0.0	2.5	121.0	123.5
Greece	0.0	0.1	1.3	8.6	10.0
Italy	0.0	4.2	87.0	10.6	101.8
Luxembourg	0.0	0.03	0.1	0.48	0.61
Netherlands	0.0	0.0	0.2	24.0	24.2
Portugal	0.0	2.1	10.9	1.2	14.2
Spain	0.0	10.2	70.3	4.2	84.7
United Kingdom	0.0	11.0	55.0	13.0	79.0
Total	0.0	30.6	233.3	243.1	507.0
Percentage EU10	0.0	6.0	46.0	48.0	100.0

Waste water treatment after implementation of the urban waste water treatment Directive (in million population equivalents) (EEA, unpublished).

2.11 COSTS

Assessing the costs of implementation of the Directive across the EU is difficult. A detailed analysis is outwith the scope of this study. However, some brief comments can be made which are important in considering future developments. The 1998 implementation report estimates that the overall investments required for upgraded waste water collection systems between 1993 and 2005 will be 68.53 billion ECU. The upgrading required for treatment systems over this period is given in Table 2.19.

Unfortunately no detailed figures are available on the expected costs of upgrading nutrient removal across the EU as the result of implementation of the Directive. Many of the investments indicated in Table 2.17 will, in practice, largely be costs of installation of secondary treatment. According to these data, Germany will spend by far the largest amount of money on the implementation of the Directive. However, these data are hard to interpret, as it is impossible to see which data refer to general investments in the waste water sector and which data refer to costs induced by the urban waste water Directive.

TABLE 2.15

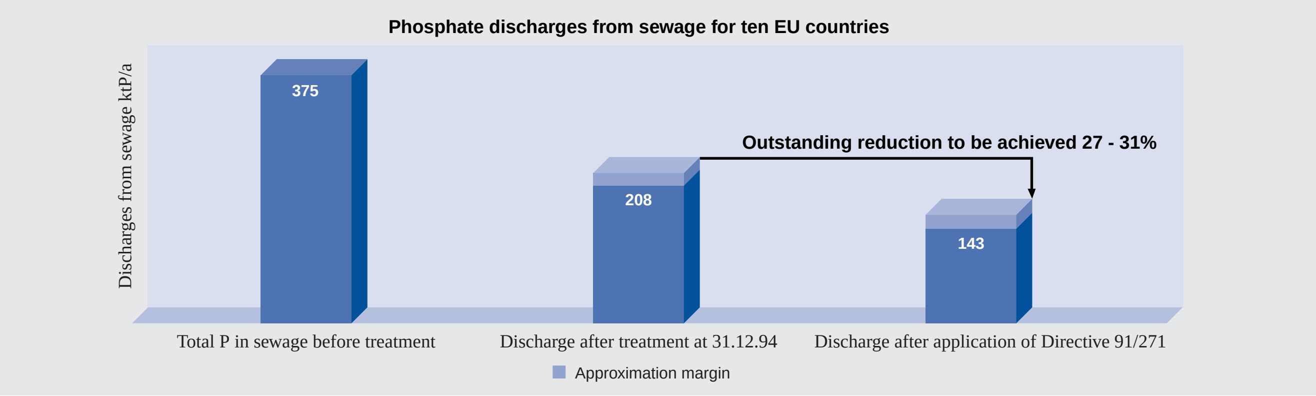
MEMBER STATE	UNTREATED	PRIMARY	SECONDARY	TERTIARY
Finland	0	-13	0	13
France	-4	-4	-76	84
Germany	-2	-7	-4	13
Greece	-34	-33	4	63
Italy	-30	-3	28	4
Luxembourg	-10	0	-61	71
Netherlands	0	-1	-23	24
Portugal	-68	6	56	4
Spain	-17	-3	15	4
United Kingdom	-17	-3	15	4

Changes in levels of waste water treatment in different Member States following implementation of the urban waste water treatment Directive and the situation in 1994 (Tables 2.10 and 2.14). The table presents predicted percentage increases or decreases in the proportion of each level of treatment.

TABLE 2.16

	Phosphate production prior to treatment (ktP/a)	Nutrient discharge 31-12-94 (ktP/a)	Percentage P removal due to treatment at 31-12-94	Nutrient discharge after implementation of the Directive (ktP/a)	Reduction in phosphate discharge required
Phosphorus discharge	375	208-227	39-45%	143-164	27-31%

Estimated phosphate discharge from waste water treatment plants at present level of waste water treatment for the EU10 given in Table 1.7 and as expected after full implementation of urban waste water treatment Directive (EEA, unpublished).



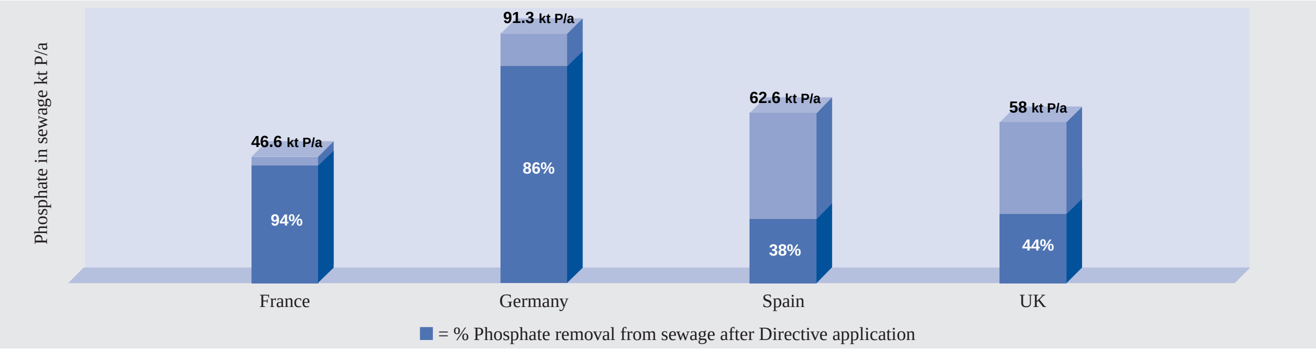


TABLE 2.17

	France	Germany	Spain	United Kingdom
Phosphate production prior to treatment	46.6 kt P/a	91.3 kt P/a	62.6 kt P/a	58.0 kt P/a
Estimated phosphate removal after full impementation of the Directive	40.1 kt P/a	85.7 kt P/a	23.7 kt P/a	25.3 kt P/a
Percentage of phosphate removed after full implementation of the Directive	94 %	86 %	38 %	44 %

Estimates of phosphate removal in four Member States based on the unpublished EEA data (Table 2.15), assuming 95% removal from tertiary treatment and 40% removal from secondary treatment.

It is also important to note that investment in waste water collection and treatment may be supported in some cases by EU funding through a range of financing initiatives. For example, the Cohesion Fund supports investments in infrastructure in the four poorer countries of the EU (Greece, Ireland, Portugal and Spain). Between 1993 and 1996 over 1.5 billion ECU were spent on waste water collection and treatment projects in the four countries from various EU sources. In 1998 the European Court of Auditors published a report (opinion 2/98) critical of the management of many of these projects. The Court examined 67 projects representing a total investment of 467 million ECU (292 million ECU supported by the EU under a variety of programmes). The Court found:

- A number of projects were designed so far in advance that at construction they were outdated (eg were an insufficient size or technical capacity)
- Projects did not adequately take account of issues such as storm water.
- Many projects provided inaccurate estimates of costs prior to construction.
- Some projects were delayed leading to increased costs.
- Treatment plants were constructed which did not meet the basic requirements of the urban waste water treatment Directive, so necessitating further investment to ensure compliance.
- Some plants built to the correct standards were not functioning due to lack of finance for running costs.

It is, therefore, clear that in some cases additional investments will be required and that estimates of costs for implementation of the Directive may contain inaccuracies.

TABLE 2.19

Member State	Investment
Austria	2.12
Belgium	2.14
Denmark	1.7
Finland	0.55
France	4.02
Germany	28.87
Greece	0.73
Ireland	1.14
Luxembourg	0.27
Netherlands	1.83
Portugal	0.94
Spain	6.15
Sweden	1.50
United Kingdom	9.74
Total	61.70

Forecasts of investments in treatment systems between 1993-2005 to implement the urban waste water treatment Directive. Data are in billions of ECU at 1994-5 prices (1996-7 for UK). Data for Greece are limited to 1993-2000.

2.12 DEVELOPMENTS IN INDIVIDUAL COUNTRIES

2.12.1 Introduction

As stated earlier, policies developed at a national level to tackle the problem of phosphate discharges from waste water treatment plants will take account of developments at an EU level and also of national priorities. This section provides a brief overview of the status of such policies in four contrasting EU Member States (France, Germany, Spain and the United Kingdom), which have had historically different levels of tertiary treatment and have taken different approaches to the designation of sensitive areas. Given the current focus on the enlargement of the EU in central and eastern Europe, this section also concludes with some comments on the likely future responses of this region to the phosphate removal provisions in the Directive.

2.12.2 France

France has designated a significant proportion of its territory (just over a quarter in terms of population equivalent) as sensitive areas under the urban waste water treatment Directive. However, the Water Agencies have elsewhere indicated other sites which may be at risk from eutrophication which are not currently designated. For example, the Rhône-Méditerrannée-Corse Water Agency indicates that ‘not a majority of eutrophic rivers...but selectively identified rivers marked by a very important and chronic eutrophication problem’ are designated as sensitive areas. Over 50 stretches of river identified by this Agency as showing symptoms of eutrophication (regular and important vegetal growth) are outside designated sensitive areas, including most of the Ain and Durance river basins. For the Artois-Picardie basin, where currently <10% of the basin is designated a “sensitive area”, The SDAGE (official water management plan, June 1997) states that “*Given the variety and intensity of problems present, the whole of the Artois-Picardie water agency area has a vocation to figure as a sensitive area*”.

However, in conformity with the spirit of Europe in 1996 only 38% of the treatment works serving >10,000 pe in sensitive areas, representing only 13% of the population equivalent, removed phosphate to 80% efficiency or greater. It is not known what upgrading will have been completed by the Directive’s implemen-tation deadline for sensitive areas of 31 December 1998, but it is certain that significant further investment is still needed to meet its requirements.

It is also apparent that the pattern of nutrient removal in France is not obviously connected to the requirements of the Directive. There are many more agglomerations with nitrogen removal systems than there are for phosphate removal. While nitrogen is an important nutrient contributing to marine eutrophication, the distribution of nitrogen removal from waste water in France is not targeted at protection of the coastal zone. Phosphate removal itself also does not seem to be targeted at the requirements of designated sensitive areas. Of treatment works with >80% phosphate removal, only around a third discharge in sensitive areas, amounting to about half of the population equivalent served with phosphate treatment. Most sensitive areas still contain large waste water point sources with poor phosphate removal. In contrast there are some undesignated areas with provision of phosphate removal systems. This probably reflects the consequences of some early investment in nutrient removal systems prior to designation. With full implementation of the Directive, tertiary treatment should be applied to discharges from at least a population equivalent of 15.5 million (from a country total of 70 million pe).

There is little prospect of France complying with the requirements for sensitive areas in the near future. Ultimately action from the European Commission could free-up financial sources for investment that are not being made available today. It must be remembered that France still has to make significant investments in sewage collection and basic treatment. For Lyon and Marseille (France’s second and third largest conurbations), currently 85% and 83% only of the sewage is, respectively, collected, with 56% and 31% only removal of organic matter. If the Directive requirements were fully implemented, then France would remove more phosphate from waste water than is necessary under the Directive, given the current presence of phosphate removal outside sensitive areas. Phosphate removal rates of greater than 80% currently apply to discharges of about 2.5 million population equivalent outside of sensitive areas. Overall this would result in high level phosphate treatment for at least 25% of waste water discharges in France. Together with extensive installation of secondary treatment, this would mean that approximately 55% of the phosphates in waste water would be removed. This is significantly lower than suggested in the EEA (unpublished) estimate for France (see above).

2.12.3 Germany

The new *Länder* in Germany, in particular, have considerable problems in their inheritance of an old infrastructure and in huge costs of upgrading their waste water treatment systems, although this general upgrading would have resulted even without the existence of the urban waste water treatment Directive due to the existing strict German environmental legislation.

Most of the territory of Germany is designated as sensitive. Only three of the *Länder* have not designated the whole of their territory as sensitive, although the main reason for this widespread designation has been to reduce nutrient inputs into the Baltic and North Seas as much as protection of inland surface waters. Germany has installed extensive phosphate reduction in waste water treatment plans across the *old Länder*. Many of these installations are on smaller treatment works. Germany is, therefore, expected to remove very high levels of phosphate produced in human waste. Sludge re-use will be just under 50% of that produced, so that much of this phosphate recovered may be utilised. Given the size of the Germany population in relation to the EU, and that by 2005 the country is still expected to produce a third of the sludge within the Union and that the four other largest EU Member States (France, Italy, Spain and the UK) will not approach phosphate removal rates of Germany, it seems that Germany will retain its position as the major source of phosphate removal (or recovery for re-use) in the EU.

2.12.4 Spain

The situation of waste water treatment in Spain required a major effort in order to achieve compliance with the obligations and periods established by the urban waste water treatment Directive. As a result, priority has been assigned to the construction of waste water treatment plants in large urban population centres.

Spain has tended to declare the smallest number possible of sensitive areas and population centres required by the Directive. In contrast, special attention has been paid to waste water treatment in less sensitive areas (much of the coast except for closed bays and estuaries and some areas with major urban population centres). In these less sensitive zones the protection established in the Directive has been increased, with secondary treatment proposed for most municipalities of 150,000 pe or less. This is because many coastal areas are bathing areas, so secondary waster water treatment has been considered necessary for the purpose of satisfying the quality sections of the bathing waters Directive and conserving the competitiveness of Spanish coasts in the tourism market.

Actions planned for waste water treatment are not being carried out at an optimal rate for achieving compliance with the Directive and its deadlines, although a major effort is underway to ensure the highest level of compliance possible. Within this general framework, compliance with the time lines established by the urban waste water treatment Directive for waster water treatment in sensitive areas has not been considered a priority.

2.12.5 United Kingdom

The structure of the water services in England and Wales is unlike that in other Member States in being based on a private system. The near monopoly status of water service provision also means that an unusual regulatory system has been adopted with an investment/price regulator and an environmental regulator.

The urban waste water treatment Directive has proved to be one of the most expensive EU environmental Directives to have been implemented in the UK. This is not just because of any requirement for tertiary treatment in sensitive areas, but also because of the extensive requirement for primary, secondary and, now, tertiary (disinfection) treatment in coastal areas, together with the effects of ceasing the dumping of sewage sludge at sea.

Phosphate pollution occurs throughout the UK, though it is not ubiquitous. As a result the UK has taken the approach of designating individual sensitive areas under the Directive. The government has recently extended considerably the number of designated sensitive areas. This will result in additional requirements for phosphate removal. It is uncertain whether there will be any further pressure to extend the number of designations still further, although any such development would not occur in the near future.

A new investment/price review is currently being undertaken in England and Wales and will not be complete until the end of 1999. There are a number of contrasting opinions. However, it is clear that the government is expecting significant additional action on environmental improvements, including phosphate control. However, this is also to be balanced against pressure for cuts in prices, but also the need for a range of other important environmental objectives, such as compliance with bathing water standards, controlling lead in drinking water, etc. Whatever the balanced reached, the capital investment costs for 2000-2005 will be significant (around £8.5 billion).

2.12.6 Central and eastern Europe

Ten central and eastern European states are currently in the process of transposing and implementing EU legislation in preparation for future membership of the EU. It is clear that the urban waste water treatment Directive will be one of the most expensive items of EU legislation requiring approximation.

Many central and eastern European states have inherited poor waste water collection and treatment systems. However, there is significant variation between individual states. Almost no provision had previously been made for nutrient removal. Improvements are already being made. However, the domestic priority is to collection systems and primary and secondary treatment requirements in the Directive. Indeed, as no sensitive areas are designated it is unknown what levels of tertiary treatment will be required.

Some investment in phosphate removal has taken place. This has mostly been due to bilateral aid from Scandinavian countries in the Baltic States and Poland as part of a general programme to protect the Baltic Sea. The European Commissions' best estimates for capital investments for waste water treatment are 27,794 MECU without nutrient removal and an additional 5,407 MECU with nutrient removal. These levels of investment are beyond the short-term financial ability of central and eastern European states. Implementation of the provisions of the Directive will either require extensive foreign assistance or a long implementation period.

3. LOOKING TO THE FUTURE AND CONCLUSIONS

3.1 INTRODUCTION

It can be seen from the preceding chapters that while significant action is being taken to tackle the problems of phosphate pollution from waste water discharges, a lot more remains to be done before the problems of eutrophication can be controlled. This chapter will examine briefly some potential future developments at the level of the EU and what other action might be taken to reduce phosphate pollution.

3.2 EUROPEAN UNION ACTION

3.2.1 Future action on the urban waste water treatment Directive

The European Commission is currently involved in a number of actions to ensure that the current provisions of the urban waste water treatment Directive are enforced. Indeed it is clear that even basic measures to ensure its implementation have been lacking in some instances. Current Commission action includes:

- Follow-up to the 1998 European Court of Auditors and Commission reports on financing and implementation of the Directive. This will include closer examination of schemes and also of general implementing measures such as the designation of sensitive areas and levels of waste water treatment therein.
- Application (December 1998) to the European Court of Justice against Italy for failure to transpose legislation to give effect to the Directive. Italy is currently responding by drafting such legislation. It is also likely that action will also be taken against Italy for its failure to ensure that discharges of urban waste water from Milan have been adequately treated to prevent severe pollution of the River Po and the Adriatic Sea.
- A Reasoned Opinion (December 1998) against Greece for adopting legislation in 1997 that does not fully comply with the provisions of the Directive, eg in identifying sensitive areas.
- A Reasoned Opinion (December 1998) against Belgium concerning its implementation programme. This relates to the city of Brussels, which will not have the required collection and treatment systems in place until 2004 (six years after the Directive deadline of 31 December 1998).

It can be seen that the Commission is having to examine basic issues relating to transposition and implementation. These types of problems can be analysed relatively easily. Similarly, failure to install phosphate removal in sensitive areas could also be readily determined. However, far more difficult is an assessment of whether the right surface waters in a Member State have been correctly designated as sensitive areas. The pressure within a Member State may lead to it failing to designate particular waters due to the economic costs of investment in treatment facilities. The only way to assess compliance is to review all data on surface water quality to determine which waters should be designated as sensitive, also bearing in mind that the Directive specifies that this includes waters which ‘may become’ eutrophic in the future. This is complicated further by the urban waste water treatment Directive providing no clear criteria for defining a eutrophic water body and that more detailed criteria have been developed within each Member State. Currently the Commission has also begun this task. It has funded a study to examine sensitive area designation in France and the United Kingdom. While this study will be complete at the beginning of 1999, results will not be announced until studies of all remaining Member States (which have not chosen the option of designating the whole of their territory) are completed. The Commission also issued proposals in May 1999 for a new study on the state of compliance of Member States with the designation of sensitive areas and discharge requirements. These studies will be particularly important in determining whether any further extension to phosphate removal will be required to implement the provisions of this Directive.

It is also important to note that the European Commission is taking increasingly tough action on other measures to reduce eutrophication from other sources. For example, in July 1999 it has made an application to the European Court of Justice against Germany and Luxembourg and notified a Reasoned Opinion against France, Belgium and the Netherlands concerning the implementation of the nitrates Directive. Problems have arisen due to adequate designations and the way that farm action programmes have been implemented.

3.2.3 The proposed water framework Directive

The proposed water framework Directive (COM(97)64, COM(97)614 and COM(1998)76) is currently under intense debate within the legislative processes of the EU. It provides the basis for an overall management framework for surface (including estuarine and coastal) waters and groundwaters. This is a major new development for EU water legislation, which has, until now, largely been issue-specific. It also provides a second important development in that environmental objectives are not only determined by chemical criteria, but also by ecological criteria. This latter development has not before appeared in EU water legislation (except in so far that ecological assessments are necessary in maintaining the conservation status of sites designated under the birds and habitats Directives).

The purpose of the Directive (Article 1):

'to establish, for the protection of surface fresh water, estuaries, coastal waters and groundwater in the Community, a framework which:

a) prevents further deterioration and protects and enhances the status of aquatic ecosystems and, with regard to their water needs, terrestrial ecosystems..'

The key elements of the proposal are:

- Establishment of River Basin Districts: integrated management
- Characterisation of River Basin Districts by ecology, geology, hydromorphology, demography, land use, economic activities, etc.
- Identification of historical trends in water quality and use.
- Assessment of water quality, quantity, status and monitoring.
- Identification of point and diffuse sources of pollution and other anthropogenic influences.
- Meeting the requirements of Protected Areas.
- Undertaking economic analyses of water use.
- Full cost recovery of water use by sector: industry, households, agriculture.
- Developing a programme of measures to achieve objectives in each River Basin District.

The environmental objectives and the way that they are to be met are outlined in Article 4:

'Member States shall draw up and make operational within a comprehensive River Basin Management Plan the programmes of measures envisaged as necessary, in order to:

a) prevent deterioration of ecological quality and pollution of surface waters and restore polluted surface waters, in order to achieve good surface water status in all surface waters by 31 December 2010...'

The key criterion for judging performance is thus the achievement of 'good ecological status'.

Waters will be classified into five classes, being 'high', 'good', 'fair', 'poor' and 'bad'. 'Ecological status' is itself assessed by the worst performance of three separate assessments of biological, chemical and hydromorphological status. The proposal contains a number of definitions of different aspects of ecological status and also provides a detailed set of parameters (Annex V) to assess high, good and fair biological, chemical and hydromorphological status for lakes, rivers, estuaries and coastal waters. It is difficult to summarise these here, especially as there have been extensive proposals for changes to these, especially from the Environment Council, so that the final wording of the detailed definitions in any final adopted text is uncertain. However, it is worth highlighting some from the original proposal:

PROPOSED WATER FRAMEWORK DIRECTIVE ANNEX V. NORMATIVE DEFINITIONS FOR GOOD ECOLOGICAL STATUS:

Rivers and lakes (similar for estuaries and coastal waters):

'General: detectable but low-level impacts on biological communities, and the physicochemical and physical environment. The biota shows signs of disturbance but deviates in terms of survival, reproduction and development only slightly from that normally associated with the ecotype under undisturbed conditions.

Phytoplankton: no accelerated growth of algae and higher forms of plant life such as to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned.

Macrophytes and phytobenthos: Only slight changes in species composition and abundance compared to type-specific conditions. No significant changes (increase or decrease) in macrophyte and phytobenthic biomass due to anthropogenic activities (eg nutrients).

Chemical: concentrations/levels not exceeding standards established so as to ensure the functioning of the ecosystem and the occurrence of the biological community specified above.'

Note the definition of good status follows that used for defining eutrophication in the urban waste water treatment Directive (Article 2.11):

"eutrophication" means the enrichment of water by nutrients, especially compounds of nitrogen and/or phosphorus, causing accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned.'

The urban waste water treatment Directive (Article 5) requires that Member States identify sensitive areas according to the criteria laid down in Annex II. However, this only provides general guidance to determine the threat from eutrophication. A number of parameters may be used to judge this, which might most easily be chemical (nitrogen or phosphorus concentrations). The proposed water framework Directive, however, stresses the importance of biological characters in assessing ecological quality and it will be necessary to determine the biological response (eg phytoplankton and macrophytes) to eutrophication in evaluating water status.

However, the links between the definitions in the urban waste water treatment Directive and the proposed water framework Directive are deliberate and suggests, therefore, that there is no stricter classification of eutrophic waters intended by the proposal.

The basic management unit to meet the requirements of the proposed Directive is that of the River Basin District (Article 3). Each River Basin District is to produce a River Basin Management Plan. These plans are required to provide a range of information for the District (Articles 5-11). The following are relevant to this discussion:

- Geographical and geological characteristics
- Hydrological characteristics
- Demographic information
- Land-use and economic activity
- Point sources of pollution
- Diffuse sources of pollution
- Other anthropogenic influences
- Economic information (values, prices, costs, including historical trends, investments and forecasts divided by households, industry and agriculture) for collection and discharge of waste water.
- Register of protected areas (EC, national and local designations), covering sensitive waters (e.g. nitrates, bathing waters, etc.) or nature conservation.
- Details of monitoring regimes for ecological and chemical characteristics and for protected areas.

Some of these characteristics are already covered by existing Directives (eg identification of protected areas). However, it is the linking together of a wide range of environmental issues with economic activity to provide an integrated management plan which is the radical departure for this Directive.

The proposed water framework Directive incorporates (and repeals) a number of existing items of EU water legislation. However, the urban waste water treatment Directive is not one of these. Indeed the implementation of the proposed water framework Directive must take special account of the provisions of the urban waste water treatment Directive, especially sensitive areas. This is understandable as any potential change in the provisions of the urban waste water treatment Directive would create further delays to the implementation of its objectives. It is, however, also not entirely efficient. Under the proposed water framework Directive surface waters which are eutrophic would be classified as below ‘good status’ and it would be up to Member States to identify the most efficient (least cost) route to improving water quality. If part of the discharge of nutrients is from waste water treatment works serving an agglomeration > 10,000 pe, then the Member State may have no option but to install tertiary treatment, even if other controls may be less costly (eg reducing agricultural inputs). However, the proposal may result in the need to take action to reduce phosphate pollution from small waste water treatment works in order to achieve good ecological status.

3.3 FUTURE CHOICE OF PHOSPHATE REMOVAL SYSTEMS IN EU MEMBER STATES

It is unlikely that there will be any radical change in the types of systems prefered within Member States. The strict standards required by the urban waste water treatment Directive tend to lead to the use of chemical phosphate removal (or combined biological/chemical removal). However, there is also a significant historical factor, whereby Member States tend to prefer systems with which they are already familiar.

Phosphate removal is also undertaken on smaller treatment plants than the 10,000 pe threshold of the Directive. Again such systems follow the same national patterns (eg chemical removal in Sweden). The use of reed-beds is also becoming more common for some small sources.

The adoption of more holistic policies towards phosphate pollution (both the 75% general reduction allowed under article 5.4 in the urban waste water treatment Directive and river basin management in the proposed water framework Directive) should enable a greater mix of treatment systems to come into operation.

3.4 OTHER DEVELOPMENTS IN REDUCING PHOSPHATE POLLUTION OF SURFACE WATERS

It is beyond the scope of this study to provide a detailed examination of the efforts to reduce eutrophication problems by controls of phosphate pollution sources other than from human waste. Such sources may include:
- agriculture;
- industry;
- detergents;
- fish farming.

The relative importance of each of these is highly variable, particularly at a local level. The earlier chapters detailing policy responses in different Member States illustrate that catchment-based or similar approaches to pollution control (including those of phosphates in sewage) may result in a range of local policy conclusions regarding different pollution sources.

It is important to note that sources of phosphate pollution exist other than sewage and that policies are under development to control them. This is part of the context for any future development of policies relating to urban waste water and is consistent with the approach advocated by the proposed water framework Directive.

3.5 CONCLUSIONS

At this time it is impossible to be precise about the future of phosphate removal from urban waste water. The deadline for meeting discharge requirements for sensitive areas under the urban waste water treatment Directive was the end of 1998. However, it is already certain that some Member States will not have complied for those areas already designated, it is not clear when compliance will be achieved and it will probably even longer before the results of the review of the designations themselves is published. Any additional action has been entirely a matter for national policies, which have diverged significantly, although even the UK, which has had, until recently, little phosphate removal, has identified national priorities for which action beyond that in the Directive may be necessary.

Future developments must also take account of the general thrust of policy development on water in the EU and this is towards a more holistic management of river basins, which should result in Member States identifying which of all phosphate sources is the most cost-effective to tackle. This may, or may not, include further action on urban waste water. It is certainly likely to highlight agricultural sources as the next pollution problem to address.

Finally, EU policy is also expanding in the sense of its potential implementation in ten central and eastern European countries. It is clear that significant phosphate removal will be necessary in these states. However, the extent of the requirement is unknown as no sensitive areas are identified to date. Moreover, implementation of the urban waste water treatment Directive is so costly in these Accession States, that it is likely that some derogations will be applied. This may mean that it is some years before widespread investment (except for particular foreign-supported construction) is available for tertiary treatment.

Bological phosphorus removal at Laon sewage works (North East France), Lyonnaise des Eaux. Capacity 40,000 pe.

Photo: Lyonnaise des Eaux

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The full report is available at:
http://www.ceep-phosphates.org

The text of the urban waste water Directive is also available at:
http://europa.eu.int/eur-lex/en/lif/dat/1991/en___391L0271.html

The SCOPE Newsletter is a regular publication (5-6 issues per year) which presents summaries of recent published articles and other scientific information concerning phosphates in the environment: environmental fate of phosphates, eutrophication and surface water management, phosphate recovery from wastes for recycling.

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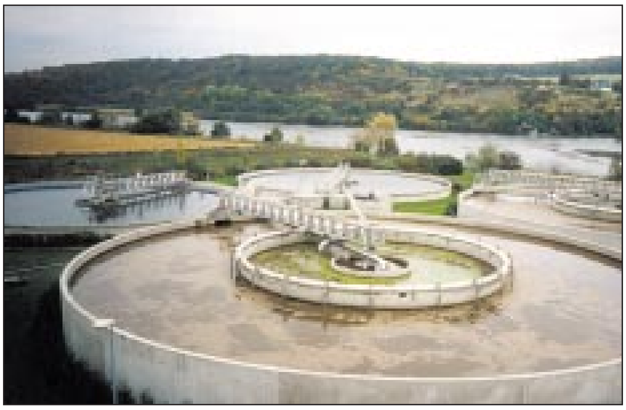

Bological phosphorus removal at Vernon sewage works (Western Paris area), Lyonnaise des Eaux. Capacity 60,000 pe.
Photo: Lyonnaise des Eaux

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Australia

Most river P from soil erosion

The Australian National Eutrophication Management Programme (NEMP) has published a statement representing the agreed scientific consensus on sources and transport of phosphorus to inland surface waters. The aim was to provide managers with generally accepted guidelines for identifying action priorities. This statement is summarised below.

The statement was the conclusion of a joint workshop convened by NEMP (National Eutrophication Management Programme) and Environment Australia. The findings of the workshop have recently been published as an "occasional paper" by the Land and Water Research and Development Corporation.

The scientists at the workshop concluded that although phosphorus is a natural element in water, and essential for animal and plant life, levels currently reaching many rivers are too high.

Agricultural fertilisers and agricultural effluent have for a long time been considered the main sources of phosphates in rural environments, typical of many Australian rivers. Point sources such as sewage, intensive livestock production, irrigation and stormwater collection systems can be the major source in urban areas. Overall, **diffuse sources of phosphorus are the dominant component in most Australian catchments.**

======== Soil erosion main source ========

However, only in certain local circumstances (intensive agriculture, urban areas, poorly adsorbing sands) are the above sources the main input to rivers: **most phosphorus in Australian catchments derives from soil erosion, in particular caused by water.**

Transport of phosphorus from diffuse landscape sources can occur in both dissolved and particulate form.

Storms are the cause of most of the transport of phosphorus from land to rivers, when soil is eroded from hill-slopes, from the beds and banks of gullies and streams. Heavily grazed lands, irrigated areas, intensive livestock farms and horticultural areas are particularly at risk.

In the Murray Darling Basin, for example, gullies are widespread. The phosphorus associated with soil particles in these gullies is generally from natural sources and not from fertiliser use. Although much of the soil erosion which caused gully formation occurred several decades ago, active gullies continue to input phosphorus to rivers.

In river systems such as the Murray- Darling Basin, most of the diffuse-source phosphorus input comes from gully erosion and stream bank collapse of readily dispersible soils. **It is very likely that most of the phosphorus is "native" phosphorus coming from subsoils as a result of weathering of naturally occurring phosphorus containing rocks.**

The message to river managers is that the priority must be to reduce soil erosion, and in particular to stabilise gullies and stream banks. Gully stabilisation can often be combined with farm land improvement. Stream bank stabilisation can be achieved by physical management, by riparian vegetation and by limiting livestock access to stream banks. Other management practices, such as reduced or contour tilling or buffer strips can also slow down soil erosion towards rivers.

Nonetheless, fertiliser run off should not be overlooked in some cases, such as coastal plains and irrigated field areas. Fertiliser phosphates are soluble and so more readily available to algae than phosphorus bound to soil erosion particles.

The "occasional paper" explains phosphorus transport mechanisms in different soil types and summarises case studies from a number of Australian catchments. The paper concludes that **management practices developed for phosphorus control in the Northern Hemisphere will have only limited success in Australia, because of the high proportion of surface water phosphorus which comes from soil erosion, soil macropore and sub-soil transport in gullies.**

LWRRDC (Land and Water Resource Research and Development Corporation) Occasional Paper 16/98 "Phosphorus in the landscape: diffuse sources to surface waters", published following the NEMP May 1997 workshop; and LWRRDC "Rivers for the future" magazine, n° 8, summer 1999.

LWRRDC, GPO Box 2182, Canberra ACT 2601, Australia. http://www.lwrrdc.gov.au

SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Lot River, France

Nutrients, sewage treatment, algal growth

For 57 reaches (total 297 km) of the lower Lot river (from Entraygues to the Garonne river confluence), data was collected and behaviour modelled for flow, light, temperature, nutrient concentrations and inputs (point and diffuse), phytoplankton biomass and zooplankton grazing. The model established was then used to assess the impact on algal biomass of scenarios for sewage treatment.

The portion of the Lot considered has 10 affluents and 66 sills, constructed to facilitate navigation, many with lateral canal systems and hydroelectric installations. The river can be considered to be of the Mediterranean type, with heavy autumn and winter precipitation and a hot dry summer. The August flow often naturally falls below 10 m^3/s compared to an annual mean of 150 m^3/s. Dams built above Entraygues are intended to maintain summer flow above 16 m^3/s. However, the series of sills in the lower river generate high residence times and low flow rates in certain reaches, leading to algal growth problems. Chlorophyll levels can reach 60 µg/l and cyanobacterial blooms *(Microcystis*) occur.

A **model of algal growth** was developed on the basis of water monitoring from July – October 1991 and 1992, and from available river board data (Agence de l’Eau Adour Garonne). Monitoring was carried out with two samples taken a few kilometres apart in order to "frame" a water mass, and then repeated as it moved along the river (movement calculated from flow rate data and morphology).

========= Nutrient inputs =========

The model developed also takes into account:

- sedimentation, estimated as a function of water velocity and depth
- release of nutrients from sediments light (meteorological data)
- water temperature
- light extinction, estimated as a function of depth and of chlorophyll concentration
- phytoplankton, calculated as overall biovolume, ignoring species variations
- internal nutrient storage in phytoplankton and nutrient excretion
- nutrient concentrations: P-PO 4 , N-NH 4 , N-NO 3

- dead organic matter
- nutrient inputs - point loads: estimated by multiplying the shore population of each reach by average P, N and BOD values, adding industrial sources, and weighting by estimated sewage treatment efficiency (presence or absence of treatment plants, % connection, % removal of P, N, BOD)
- nutrient inputs – diffuse sources: estimated for each reach from ground use and nutrient export coefficients (Pallo, 1993)
- loss of phytoplankton through sinking, considered as related to turbulence and estimated by water velocity
- zooplankton grazing, estimated by a constant predation factor applied to reaches with high grazer densities

========= Loss of biomass in deep reservoirs =========

The model simulates changes in summer algal biomass and nutrient levels ($P\text{-}PO_4$, $N\text{-}NH_4$, $N\text{-}NO_3$) along the stretch of river studied (57 reaches). After calibration, the model simulations correctly reproduce evolution of these variables for a broad range of low river flow rates (9 – 94 m^3/s).

Maximum biomass is reached in the middle reaches studied. The biomass produced upstream is proportional to available nutrients. Downstream, on the other hand, in deeper reservoir reaches, light does not penetrate into much of the water column and so algal respiration exceeds production. The reduction of phytoplankton biomass in lower reaches is accentuated by sinking (due to lower water velocities) and by zooplankton grazing.

Nutrient concentrations are low in the middle and lower reaches, due to consumption by algae, despite sources in the lower reaches. Comparison of predicted and measured nutrient levels suggest that **point source inputs entered in the model are probably underestimated.** This may be explained by tourist numbers increasing summertime populations and sewage outflows well above the annual average levels.

========= Sewage treatment scenarios =========

The model developed was used to assess different scenarios for sewage treatment and nutrient inputs:

0: average **current situation**
1: improved sewage treatment – **application of the EC Urban Waste Water Treatment Directive 91/271**

    1.1 – to conurbations > 10,000 pe.
    1.2 – extension to conurbations > 5,000 pe.
    1.3 – extension to conurbations > 2,000 pe.

2: **malfunction** of existing sewage treatment
3: **doubled N and P inputs** in lower reaches and stratification of deep reaches

The EC Directive 91/271 requires (in sensitive areas) that the population of conurbations > 10,000 pe. be connected to sewage treatment with at least 70% nitrogen and 80% phosphorus removal. This should be compared with the present situation of only one third connection to sewage works and mean sewage works efficiencies of 36% for nitrogen and 20% for phosphorus removal.

The **application of the EC Directive** to conurbations > 10,000 pe. (scenario 1.1, affecting five sewage works) brings a **considerable decrease in algal biomass** in reaches below Toirac (reach 13), perceptible as far as Fumel (reach 50). Scenarios 1.2 and 1.3 (conurbations of > 5,000 and > 2,000 pe.) affect respectively one sewage works and one further effluent but do not bring significant further improvements.

Scenario 2, malfunction of existing sewage works, makes practically no difference compared to the present situation, probably because of the very low current connection to and efficiency of waste water treatment.

The third scenario (3) attempts to reflect nutrient levels which proved higher in observed data than those predicted by be model: it assumes bursts of nutrient release from sediments resulting from stratification in the river, as well as higher point inputs. This scenario predicts algal peaks in two lower reaches (Le Temple, reach 54, and Villeneuve, reach 55) which may explain blooms noted in later years (but not in 1991 or 1992 which were relatively rainy summers with higher than average flow rates).

"A model of phytoplankton development in the Lot river (France). Simulations of scenarios." Wat. Res. vol. 33, n° 4 1999. Pages 1065-1079.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Mediterranean

Nutrient transport in the Rhône river

The nutrient input (nitrogen, phosphorus, silicate) of the Rhône river to the Mediterranean Sea was assessed for the year June 1994 – May 1995 using a combination of nutrient concentration measurements and flow data.

The Rhône is the main river flowing into the western basin of the Mediterranean, with an average annual flow rate of 1690 m^3/second, compared, for example, to 200 m^3/s for the Ebro or 234 m^3/s for the Tiber.

The Rhône's input thus has a direct influence on primary production in the Golfe du Lion where 50% of primary production can be attributed to river inflow and associated land runoff.

Total nitrogen input from the Rhône is calculated by the authors as 115,000 – 127,000 tonnes N/year with:

- 92 - 96,000 tonnes N as nitrate (around 80%)
- 1,300 - 1,500 tonnes N as nitrite
- 6,300 - 6,700 tonnes N as ammonium
- 9,700 - 9,800 tonnes N as dissolved organic N
- 5,300 - 12,700 tonnes N as particulate N

Total phosphorus input to the Mediterranean from the Rhône is calculated as 6,500 – 12,200 tonnes P, of which only 25 – 45% is soluble, the remainder being particulate.

SCOPE editor's note: It is interesting to compare this figure with an estimate of total phosphorus in sewage in the Rhône catchment. We assume 0.7 kg/year/habitant P from human sources (published figure) and 0.35 kg/year/h P in detergents (1996 consumption, France only). The population of the Rhône catchment in France is 9 million (Agence de l'Eau) and approximately 3 million in Switzerland. ***Total sewage phosphorus load (before sewage treatment) would thus be approximately 11,500 tonnes.*** *(By comparison with estimated soluble in the Rhône), this suggests that 60-80% of sewage P load is removed either in water treatment and/or in river sedimentation.*

The particulate P in the Rhône was found to be:

- 5 - 34% iron bound
- 43 - 56% calcium bound
- 6 - 28% acid soluble organic
- 11 - 13% NaOH soluble organic

The high particulate fraction of the phosphorus input leads to a significant variation in results between the different calculation techniques (evaluation of total water flow rate or solid flow rate).

Total silicate input is calculated as 135,000 – 139,000 tonnes Si / year.

The authors estimate that the Rhône's mean annual nitrate concentration has increased by around 50% over the last two decades.

They estimate that the Rhône represents around 10 – 20% of the total N and **2 – 6% of total P input to the Mediterranean Sea** and that this nutrient load is significant with regard to the Mediterranean's nutrient balance and primary production.

"The input of nutrients by the Rhône river into the Mediterranean Sea: recent observations and comparison with earlier data". Hydrobiologia 373/374, 1998, pages 237-246.

T. Moutin, P Raimbault, H. Golterman, B. Coste, Laboratoire d'Océanographie et de Biogéochimie, Centre d'Océanologie de Marseille, Campus de Luminy, case 901, F 13288 Marseille Cédex 9, France.

SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - USA

Ecosystem ascendancy and nutrient dynamics

Ecosystem ascendancy dynamics were employed to look at flows of carbon, nitrogen and phosphorus between the different compartments of the Chesapeake Bay ecosystem. Amongst other conclusions, it appeared that in summer the overall ecosystem was N limited, but that the nekton were nonetheless P limited. In winter and spring, limitation was mainly related to cycling of both N and P between bacteria, microflagellates and dissolved organic P. In autumn, no clear pattern appeared.

It is now generally recognised that different compartments of an ecosystem can be limited by different factors or combinations of factors. Thus, **where primary production may be limited at a given time and context by one particular nutrient, other compartments of the ecosystem may be limited by other factors.** Network ascendancy, developed from information theory, involves examining the dynamic exchanges of different factors between different ecosystem compartments, as well as sources and sinks.

This paper reports results of a decade long study of the Chesapeake Bay, USA. The authors evaluated the magnitude of exchanges of N, P and C along 122 pathways (between 36 ecosystem compartments), as well as 55 exogenous flows of carbon and external nutrient inputs.

========= Carbon and nutrient cycles =========

Relatively separated carbon cycles were found within on the one hand the planktonic compartments, and on the other the benthic and nektonic compartments. Transfer between these cycles was mainly through sessile and nektonic filtering organisms. The "microbial loop" for carbon proved non-existent, **bacteria acting essentially as sinks transferring carbon out of the system.**

Nutrient pathways were evaluated by assuming that net production from a given compartment has a fixed nutrient:C ratio characteristic of the donor species.

Nitrogen was found to be much more actively cycled within the system than carbon. Some 50,000 simple nitrogen cycles were enumerated, compared to only 61 for carbon. Bacteria were very active in cycling nitrogen, to some extent returning it to available forms in the water, but mostly cycling it within sediments.

======== Nitrogen limitation ========

It can be shown that the element available to a given ecosystem component at the lowest levels, compared to stoichiometric needs, will be the element which moves slowest through this component.

Marine systems, such as the one studied, are generally thought to be "nitrogen limited". **The phytoplankton and benthic algae in Chesapeake Bay do indeed appear to be nitrogen limited over the year, but this is not the case for the heteroptrophic ecosystem compartments.**

One noticeable feature, is that **all the nekton compartments prove to be P limited, as are the two planktonic bacterial compartments.** This property may be due to the large relative needs of vertebrates for phosphorus for bones, and of bacteria for ATP/ADP. Sediment bacteria, close to abundant P supplies, tend however to be nitrogen limited, as reduced N is in short supply in the sediments.

Other findings are more difficult to explain, for example P limitation of meiofauna and crustacean deposit feeders, or carbon limitation of the blue crab.

======== Seasonal variation ========

These overall patterns persist throughout the seasons, with some variations. In autumn, the phytoplankton, ctenophores and oysters become carbon limited, which corresponds to the reduction in light available for photosynthesis.

However, despite the relative stability of specific pathway limitations throughout the year, the overall network limiting flows of the ecosystem change considerably between seasons.

In summer, nitrogen is indeed the general controlling factor and overall limitation of the ecosystem can be traced back to the rate of cycling of nitrogen between particulate nitrogen in the sediments and fixed bacteria. Although NH_4 may be plentiful in the sediments, organisms may still be limited by the availability or reduced nitrogen.

In winter and spring, the key controlling mechanism seems to be the "microbial loop". As indicated above, carbon is not cycled, but nitrogen and phosphorus are, between dissolved organic phosphorus (DOP), free bacteria and heterotrophic microflagellates. The DOP pool is most sensitive to microcflagellate excretion and the bacteria are mainly P limited; the microflagellates, on the other hand, are N limited and receive most of their nitrogen from the free bacteria. The phosphorus ingested by the microflagellates is somewhat in excess of their needs and is excreted, effectively fertilising the growth of the P-limited bacteria, their prey. The overall ecosystem limitation thus depends on this bacteria –

microflagellates co-dependency, which itself is limited by both N and P.

In autumn, it is not possible to identify a cycle which defines overall ecosystem limitation. Phytoplankton become carbon (photosynthesis) limited and benthic primary production becomes sensitive to external N inputs. Much of the rest of the ecosystem is essentially sensitive to external P inputs. **Thus in autumn, the system compartments are each differently dependent on external inputs (light, nutrients): all metabolic demands are declining, and the system is in collapse rather than control.**

The authors conclude that the assessment of the role of chemical nutrients in ecosystems requires adequate quantification of the whole system status. **They underline the importance of the dual nutrient feedback control mechanisms** identified in Chesapeake Bay. These internal control systems enable the whole ecosystem metabolism to be maintained and stabilised.

"Nutrient controls on ecosystem dynamics: the Chesapeake mesohaline community. Journal of Marine Systems 19, 1999. Pages 159-172.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Nutrients, zooplankton and algae

Top-down or bottom-up control ?

Algal response to increases in nutrients and in zooplankton populations were tested in 20l carboys suspended in the oligotrophic Flathead Lake, Montana, USA. Algal growth was stimulated by addition of N and P, in some cases by addition of N only, but not by addition of P only. Addition of zooplankton at ambient (oligotrophic) nutrient concentrations did not reduce chlorophyll production, but restoration of natural zooplantkon population concentrations did prevent increased algal development at increased nutrient levels.

The experiments reported were carried out to assess the implications of decreases in zooplankton abundance in the lake resulting from introduction of the invertebrate zooplankton predator *Mysis relicta*. Twenty litre carboys filled with natural ambient lake water and phytoplankton/zooplankton communities were used for four triplicated 5-day experiments in July and October 1987 and in May and August 1988. Zooplankton populations were unchanged or adjusted to around 50% of current lake densities, or to 4x or 7x these densities using a 280 µm sieve to remove or catch and add zooplankton. The authors indicate that these increased **densities are comparable to those found in the lake before the introduction of *Mysis relicta.***

The phytoplankton community was dominated by grazable species (diatoms, small flagellates, chlorophytes, chrysophutes, small monocellular coccal cyanobacteria). Zooplankton mortality was low (never exceeding 15% over the duration of the experiments), so that there were no obstacles to grazing effects.

======== N and N+P response ========

The ambient nutrient concentrations in the lake water used for the experiments varied as follows:

- P (soluble reactive P): non detectable - 0.5 µgP/l
- N (NH_4+): non detectable - 4.9 µgN/l
- N (NO_3-): non detectable - 5.8 µgN/l

Simultaneous addition of N and P (to 140 µgN/l and 60 µgP/l) caused significantly increased chlorophyll production (algal development) in all four series of experiments. Addition of only N caused statistically significant algal development in the October experiments, whereas **there was no significant response to the addition of P only in any of the experiments.**

======== Zooplankton control of algal growth ========

Changing zooplankton population densities in the ambient nutrient level carboys had no significant effect on **production to be held below the "control" level** (ie. no nutrient addition, ambient zooplankton densities). In this latter case, chlorophyll concentrations after 5 days were brought down to around 2.5 µg/l compared to 3 µg/l in the "control" and around 4 µg/l for the carboys with nutrient addition and without increased zooplankton.

Initial ambient zooplankton densities varied as follows:

Individuals per litre:

- Caloid copepods 3 - 11.9
- Cyclopoid copepods 3.6 - 5.2
- *Daphnia thorata* 0.1 - 4
- *Bosmina longirostris* 1 - 2.3

The authors conclude that, at current ambient lake nutrient levels (oligotrophic), zooplankton densities make little difference to algal development, probably because densities are so low that grazing pressure is not a major influencing factor. The authors therefore suggest that current management practice of Flathead Lake should concentrate on nutrient abatement (bottom-up control).

In the case of higher nutrient levels (eutrophic waters), top-down controls become more important. In particular, **the experiments show that increasing zooplankton densities can enable control of algal development despite nutrient enrichment with densities of zooplankton comparable to those found in natural ecosystems** (where predation or other factors have not reduced zooplankton populations).

"Role of nutrients and zooplankton in regulation of phytoplankton in flathead Lake (Montana, USA), a large oligotrophic lake." Hydrobiologia 373/374, 1995. Pages 755-763.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Freshwater ecology

Phytoplankton control at high nutrient levels

This paper examines both literature field data and mesocosm experimental results regarding daphnia control of edible phytoplankton. Stable control of phytoplankton at high nutrient levels is generally observed, whereas standard arithmetical predator-prey models would predict large population fluctuations.

Several hypotheses are suggested as possible explanations of this difference between model predictions and real ecosystem behaviour.

McCauley and Murdoch (1990), reviewing field data, concluded that **daphnia and algal populations are generally stable** (with low amplitude cycles) at both low and high nutrient concentrations. Populations are stable up to an algal carrying capacity (K) of at least 3 mgC/l (this is defined as the maximum potential biomass of edible algae in summer, in the absence of competitors and grazers, and is used as an indicator of nutrient levels).

Watson *et al.* (1992), analysing data from >100 northern temperate lakes, showed furthermore that the **populations of edible algae increase by only 1.8x for a 10-fold increase in phosphorus levels.** Inedible algae populations, on the other hand, increase six-fold over the same range (ie. inedible algae increase from 0.05 to 0.3 mgC/l as K increases from 0.3 to 1.2 mgC/l. 20-25% of algae in these lakes are estimated to be edible.)

========= Predator-prey models =========

The authors model calculations are based on field data from four natural lake environments, calculated values for a fifth, and data from a series of experimental tanks at Santa Barbara and Calgary.

- the four lakes were: Lake Maarsseveen (Koning and Dorgelo, 1982), Hall Lake (Taylor, 1981), Lake Constance (Lampert and Schober, 1978) and Lake Washington (Edmondson and Litt, 1982)
- calculated values concerned Eglwys Nynydd Reservoir (based on George and Edwards, 1974)
- the Santa Barbara tanks contained a single edible alga species *Chlamydomonas reinhardii* and the zooplankton grazer *Daphnia pulex* in nutrient rich water (K > 3 mgC/l). In these systems, tanks

without Daphnia moved to become a "pea soup" of edible algae.
- b the Calgary tanks contained a mixture of edible and inedible algae with *Daphnia pule*x.

======== Modelling and algal population stability ========

Basic models of predator-prey population dynamics predict extreme instability in a nutrient rich environment where predation suppresses prey populations below carrying capacity. This is known as the **"Paradox of Enrichment"** and large amplitude cycles are predicted as the prey is periodically suppressed by predation, "escapes" to carrying capacity, is caught up and suppressed again. **This does not, however, appear to actually occur in many ecosystems, and in particular for daphnia / edible algae in nutrient enriched waters.**

Evidence from mesocosms containing only one species of algae and of Daphnia suggests that the stability is inherent to the predator-prey relationship, and is not the result of other factors (competition between species, predation of Daphnia by fish, refuges for algae …)

======== Stable algae control by Daphnia ========

In the natural and experimental systems studied **Daphnia proved able to suppress edible algal populations to well below the limits set by nutrient resources, even in nutrient rich systems.** In the Santa Barbara tanks, for example, the biomass in tanks containing Daphnia are around 1% of that reached in the absence of Daphnia.

Also, Daphnia is strongly food-limited. Daphnia egg clutches in cultures can reach 20 – 30 eggs, but in both the natural and experimental systems, the average clutch is < 1 egg, and even in recruitment drives reaches < 2 eggs.

The authors test four hypotheses for mechanisms which could explain this **stable limitation of algal populations:**

- increased abundance of inedible algae interfere with Daphnia grazing
- Daphnia death rate increases with nutrient enrichment
- Daphnia death rate increases with Daphnia density
- Daphnia grazing rate varies with Daphnia density

All of these hypotheses are rejected, because models using them would predict much higher algal biomass than observed at high nutrient levels. Observations also show that Daphnia death rates do not increase with Daphnia density or nutrient levels.

The authors suggest three other mechanisms which could contribute to stability and merit further investigation:

- inedible algae absorb nutrients reducing their availability to edible species
- limited spatial movement of algae enhances stability through a combined effect of many local populations (meta-populations)
- variation between the Daphnia individuals present contribute to overall stability

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"Plankton abundance and dynamics across nutrient levels: tests of hypotheses", Ecology 79(4), 1998. Pages 1339-1356.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Nutrient cycling

Algal response to nutrients dependent on grazer N:P:C stoichiometry

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This comprehensive paper brings together conclusions from a number of recent papers concerning how differences in nutrient element stoichiometry (N:P:C) between algae and grazers in pelagic ecosytems affect consumer nutrient recycling (rate and ratio of elements cycled).

A.C. Redfield *et al.* in 1963 first demonstrated a characteristic elemental ratio between N, P and C in marine phytoplankton, showing that this left a "fingerprint" on the cycling of the major elements 0, N, P and C throughout oceanic and indeed biosphere food webs. This ratio was then shown to be relatively reliable in marine waters, whereas **algal nutrient ratios in fact vary widely in fresh waters.** Since then, there has also been considerable work indicating that the nutrient stoichiometry of grazers is often very divergent from the typical "Refield ratio". Ratios for three typical crustacean grazers are given as illustrations:

- *Acanthodiaptomus pacificus* 240C: 48N: 1P
- *Bosmina longirostris* 151C: 26N: 1P
- *Daphnia similis* 80C: 14N: 1P.

Equally, many studies have looked at grazer nutrient recycling, generally for N in marine waters and for P in freshwaters, but rarely were both nutrients taken into account or their relative recycling rates looked at.

======== Grazer community changes nutrient limitation of algae ========

In the 1980's, papers began to appear suggesting differing cycling rates between N and P and indicating that the grazers *Daphnia* had a much lower P cycling rate when algal P:C ratios were low. In 1988 Elser *et al.* showed that the nutrient limiting algal growth shifted from P to N when the dominant grazer changed from *Daphnia* to copepods, as a result of fish population modifications. Three years later, data was published showing that *Daphnia* have a 2-3 times lower body N:P ratio than copepods.

========= Stoichiometry modelling =========

The authors review models of N:P and C:P stoichiometry effects on nutrient cycling and pelagic ecosystem balance.

Sterner (1990) developed a model to predict the N:P ratio of cycled nutrients as a function of algal N:P, grazer N:P and grazers' ability to retain a growth limiting nutrient. This model illustrated how **grazer N:P ratios affect the relative rate of release of these nutrients back into the water** by the grazers, thus in turn influencing the nutrient regime experiences by algae. **response to nutrients dependent**

Another set of models looks at C:P ratios. Starting with Osten and Ostgaard (1985), these models suggested that the rate of P recycling by grazers would fall with increasing C:P ratios. Olsen *et al.* indeed concluded from experimental data and the model that **for a C:P ratio > 370 *Daphnia* no longer cycle soluble P back into the water.** Urabe and Watanabe (1992) further indicated that P limitation of *Daphnia* development is likely in the natural environment. Elser and Hassett (1994) indicated that algal P:C ratios in many natural fresh waters systems will be lower than P:C ratios for most grazer species. This would significantly limit P cycling, and thus P availability for algae.

========= Dynamic modelling and algal state switches =========

Andersen (1997) extended the static models to look at the dynamic feedback effect that changing nutrient cycling would have on algal nutrient ratio, and thus again on grazer ratios and cycling. **In the case of algal P:N ratios below grazer needs, this will result in relatively lower P cycling, reducing P availability for algae, and thus further reducing algal N:P ratios.**

He concluded that **ecosystems could move between two distinct stable states,** either the different food web levels can adapt with nutrient elements being cycled indefinitely in a limit cycle, or one nutrient can become progressively scarcer, increasing pressure on grazers until they are driven to extinction. Movement between these states depends on given properties of the ecosystem's trophic dynamics (grazing, ingestion and assimilation rates).

When Andresen extended his model to include nutrients held in particles, detritus and bacteria caused the model to predict dynamic chaos The capacity of grazers to differentiate between such particles and algae will significantly affect the real behaviour of ecosystems.

========= Experimental evidence =========

The authors present a literature review and analysis of experimental evidence of differential release of nutrients by zooplankton. Firstly, evidence shows that grazers maintain nearly constant body nutrient ratios despite variations in food ratios. Secondly, other experiments reviewed show that **grazer nutrient release ratios are not constant,** but vary considerably in relation to food nutrient ratios. Statistical analysis of the different published experimental results also shows that zooplankton with relatively higher body ratios tend to cycle less P, resulting in lower P:N ratios in water.

======== Effects on algal growth and blue greens ========

Some evidence shows that **differential nutrient cycling can indeed affect algal growth,** but this would appear to be affected by other factors. In Castle Lake, California, for example, Elser *et al.* showed that the relative severity of N to P limitation of algae was correlated to estimated grazer N:P ratios in two out of three study years.

One interesting application of grazer stoichiometry effects may be on blue-green algae. Grazing by *Daphnia* or other high P:N ratio grazers, which cycle nitrogen relatively faster than P, may be to counter risks of blue-green development by decreasing relatively availability of P.

"The stoiciometry of consumer-driven nutrient recycling: theory, observations and consequences". Ecology n° 80(3), 1999. Pages 735-751.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Anaerobic liquors

CO_2 stripping with air for struvite recovery

Experiments were carried out to examine phosphate precipitation rates and forms from the supernatent of anaerobically digested biological nutrient removal sewage sludge. Precipitation was assessed during natural ageing of the supernatent and the inhibiting effects of Mg and bicarbonate ions were studied. Phosphorus recovery as struvite was then demonstrated using CO_2 stripping by aeration to increase pH only (no chemical addition) in a bench-scale batch fluidised bed reactor.

Sludge handling and digestion can pose problems in biological nutrient removal (BNR) water treatment plants, firstly because of struvite (magnesium ammonium phosphate) deposits, and secondly because of uncontrolled release of phosphates into supernatent (which is then recirculated to the BNR system, decreasing nutrient removal performance). This paper studies the phenomenon of phosphate precipitation in the digester supernatent and the **possibility of utilising struvite precipitation to recover phosphates for recycling,** thus resolving these two operating problems.

========= Supernatent parameters =========

The liquid from the dewatering section (belt press) of a 100,000 pe biological nitrification - denitrification sewage treatment works was used, with phosphate concentrations adjusted in some cases to simulate higher P levels in bio-P sludge lines. The supernatent had an initial pH of 7.3 and the following ion concentrations (mg/l):

PO_4 : 18
Mg: 53
Ca: 184

Experimental phosphate concentrations were adjusted to 18 - 180 mg/l.

========= Natural ageing =========

A first series of experiments were run to examine the precipitation of phosphates from digester supernatents over three days of natural ageing.

An increase in pH (to 8.3 - 8.5) and a decrease in phosphate concentration was observed. **Phosphate removal was 81%** from an initial concentration of 164 mg/l and 53% from 18 mg/l. Around 1/3 of the phosphate removal occurred during the first few hours, with levels then declining progressively.

This phosphate removal was thought to result from the increase in pH due to progressive CO_2 loss from the supernatent: CO_2 partial pressure changed progressively over the ageing time from an initial 30-40% (biogas) to 0.035% (air).

The molar depletion of different ions over the ageing period indicated that phosphate removal was due to struvite formation.

======== Supersaturation curves for calcium phosphates and struvite ========

Supersaturation curves for the different starting concentrations of phosphates were established by adding alkali and by air stripping of CO_2.

This demonstrated that the supernatent supersaturation curve existed at a lower pH than for struvite and at a higher pH than for calcium phosphates.

It was concluded that bicarbonate and magnesium ions are inhibiting calcium phosphate (hydroxyapatite) formation.

======== Fluidised bed struvite recovery reactor ========

On the basis of these experimental results, a bench-scale fluidised bed batch reactor was constructed to investigate **struvite precipitation by air stripping only** from supernatents with a phosphate concentration < 50 mg/l.

The reactor had an internal diameter of 58 mm and an expanded bed height of 300 mm. Upflow rates of 1.8 - 5 l/min were tested.

Air stripping for 56% of the time proved to be insufficient for effective phosphate precipitation, whereas continuous aeration (15 l/min) enabled phosphate removal of up to 80% (pH increase to 8.3-8.6) in 120 - 150 minutes.

Quarz sand (0.21-0.35 mm) was used as a seed crystal. Total phosphorus and soluble phosphorus concentrations in the reactor effluent were very similar, showing that **nearly all of the phosphates removed from solution were being precipitated in the reactor and not "lost" as fines** in the effluent. Also, there were no deposits formed on the reactor structure itself, showing that precipitation was only occurring within the solution on the seed crystals.

Ion balance analysis showed that all the phosphates precipitated were in the form of struvites.

========= Feasibility of P-recovery without chemical addition =========

The authors conclude that CO_2 stripping by aeration can be sufficient – without the addition of chemicals - to **enable effective phosphate removal and recovery as struvite from bio-P sewage works digester or sludge treatment supernatents.**

"Phosphate removal in anaerobic liquors by struvite crystallization without addition of chemicals: preliminary results", Wat. Res. vol. 31, n° 11, 1997. Pages 2929-2929.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - France

Comité Environnement Détergents

The French "Comité Environnement Détergents" officially presented, in Paris on 24th June 1999, the results of several years of research into the potential risk to the environment of detergents. The Committee's research programme was the result of an agreement between the French Environment and Research Ministries and the detergent industry and has involved over 50 experts and scientists and a steering committee grouping industry, regulators, environmental and consumer associations.

The Comité Environnement Détergents research programme has included:

- measuring the removal rate achieved for different detergent components in six sewage works of different configurations and types
- examining the feasibility of a "eutrophication test" using algal growth
- comparing concentrations of different detergent components likely to be found in rivers (using a detailed model of 800 river reaches) with concentrations liable to have an environmental impact (taking into account removal in existing sewage works)

========= Phosphorus removal in sewage works =========

A detailed study of the performance of six different sewage works was carried out in order to assess the removal rate for different detergent components (Cemagref, Groupement d'Anthony, report dated October 1996). The results for phosphorus removal are as follows:

Sewage Works	*Type*	*Load pe*	*Inflow P mg/l*	*Removal of P (%)*
Corbeil-Essonnes	*activated sludge + trickling filter*	*70,000*	*11.5*	*52% removal*
Nîmes	*bacterial bed + trickling filter*	*40,000*	*11.8*	*25% removal*
Vauciennes	*natural lagoon*	*620*	*19.1*	*65% removal*

Villeneuve Saint-Denis	*intensely aerated activated sludge*	*660*	*9.6*	*84% removal*
St-Thibaul-des-Vignes	*trickling filter*	*150,000*	*13.6*	*53% removal*
Bormes-les-Mimosas	*chemical*	*variable (seasonal)*	*10.4*	*87% removal*

The two sewage works using activated sludge treatment thus both achieved over 50% phosphorus removal. The study indicates that nearly 75% of French sewage treatment (% capacity pe.) currently uses activated sludge systems.

The study shows that removal of surfactants in activated sludge sewage works is generally excellent (95% or higher). Removal rates for EDTA and NTA are very variable (these substances are used in P-free detergents in some countries, but not in France, where can nonetheless be present in small quantities from other sources). Borate is not removed at all in sewage works.

========= Environmental exposure =========

The main body of studies presented in Paris involved a comparison between model-predicted concentrations of various detergent components in 800 river reaches (within risk of environmental impact. **The model took into account the exact situation in each river reach regarding population (and thus detergent use, based on national averages) and sewage treatment (connection rate, type of sewage works, operating efficiency).**

The components studied were: LAS surfactants, ethoxylate surfactants, soap, **zeolite, cellulose polymers, acrylic polymers (these three substances are used in P-free detergents),** phosphates, phosphonates, perborate, perborate activator TAED, propylene glycol (solvent used in liquid detergents) and optical enhancers.

For each component, PEC (Predicted Environmental Concentrations) were compared with calculated PNEC (Probable No Effect Concentrations), the latter being estimated from the best available experimental toxicity data with a safety factor being incorporated.

The work so far was entirely based on modelling. Field samples should now be taken in river reaches to confirm the calculated results.

The only products for which the PEC exceeded the PNEC (ie. releases from detergents were **susceptible to have an effect on the environment) in average flow conditions were LAS surfactants, ethoxylate surfactants, soap and TAED activator.** These were also the main components susceptible to reach PNEC concentrations in more than a quarter of hydrological zones in very dry weather conditions.

Wherever PNEC concentrations are exceeded, the Committee concludes that this is **the result of inadequate connection to sewage treatment or exceptionally inadequate design or operation of**

sewage works. A very significant proportion of all components reaching rivers comes from sewage which is not reaching sewage works (populations not connected) or sewage works by-passes (resulting from under capacity or inadequate storm-water retention).

======== Eutrophication "test" ? ========

After consideration, the expert sub-committee of the Comité Environnement Détergents decided that **"with the current state of scientific knowledge, it is not possible to establish a PNEC for eutrophication effects".**

This is coherent with the European Union decision to reject the concept of a "CDV (critical dilution volume) eutrophication" in the EU laundry and dishwasher EcoLabel schemes (both of which authorise phosphate containing detergents).

The Comité Environnement Détergents had work carried out by Cemagref (Groupement de Bordeaux n° 8, report dated December 1995) into the feasibility of designing a standard bioassay test using freshwater planktonic algae to test substances' eutrophication potential. This report concluded that **any such test would have to use algae which had previously been phosphorus starved** or they would not react coherently to phosphate input. Such conditions could not be considered to reflect the situation in a freshwater ecosystem.

The Comité Environnement Détergents report indicates that, in very low flow river conditions, detergent phosphate would currently result in river concentrations above 50 µgP/l in 28% of reaches studied (the Committee indicates that this concentration is given in literature as indicative of rivers' potential trophic level). In these cases, the Committee indicates, **phosphorus reaching the river is the result of untreated sewage or of sewage works not adequately removing phosphorus.** The Committee states that to confirm such results would require constructing **"a model which includes all other sources of phosphorus and the positive implications of the progressive implementation of the urban waste water treatment Directive, and to verify results with field sampling".**

======== Lake Geneva and the Redon ========

The figures presented by the Comité Environnement Détergents complete those previously obtained by the French Environment Ministry Phosphorus Working Group (report dated 17th April 1986) and referred to in the Comité Environnement Détergents' Paris presentation. This report, looking at phosphorus inputs into Lake Geneva and into a small tributary of the lake, the river Redon, concluded that, at the time, **detergents contributed only 7% of total phosphorus inputs to Lake Geneva.** This assumed that 50% of municipal and industrial waste water phosphorus came from detergents, which would correspond to universal use of very high P detergents: the proportion of phosphorus coming from detergents would be significantly lower today.

This study also underlined the **importance of phosphorus release from lake sediments:** the potential quantity being comparable to the lake's total anthropogenic phosphorus load. Lake sediment phosphorus is related to past phosphorus loads and ecosystem functioning.

A very detailed study was carried out of all the point sources along the Redon river. This study suggested that for this tributary of Lake Geneva, 16 – 20% of phosphorus in the river outflow came from detergents. This was considered to be unrepresentatively high because only one fifth of the Redon catchment's population were connected to sewage treatment at the time.

This study concluded that **a change in use to P-free detergents in the basin would not lead to measurable differences in phosphorus concentrations flowing from the river into Lake Geneva.**

Report of the ***Comité Environnement Détergents*** *"A contribution to the evaluation of the environmental risks of different domestic laundry detergent components" dated 24th June 1999. Available from: AISD (Association des Industries des Savons et des Détergents), 118 avenue Achille Peretti, 92200 Neuilly sur Seine, France.*

Report of the French Environment Ministry ***"Phosphorus"*** ***Working Group, sub-group "Redon"****, 17th April 1986 "Studies of the Redon river and of phosphorus enrichment of Lake Geneva". Available on request from CEEP.*

SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - France - Vilaine River

Detergents contribute < 3% of surface water P

Total nitrogen and total phosphorus loads, from natural and anthropogenic sources, to the upper Vilaine river (above Rennes) were compared with export in the river water over a one year period 1994-5.

The section of river studied is 90 km long with a catchment of 902 km2. 78% of the land surface is agricultural. The area is one of France's main cattle production centres (1.93 heads/ha in 1988), with land use being predominantly grass, both temporary and permanent (the latter making up more than 40% of agricultural land use) and maze maze (around 30%), with some wheat (<7%).

The population is 60,000 persons, mainly in 40 small towns (the biggest, Vitré, has a population of 15,000). There are 20 municipal and 4 industrial sewage works.

River water was sampled for flow rate and nutrient concentrations at 20 different sampling sites on the Vilaine and on tributaries within the upper Vilaine catchment, enabling the contribution of subcatchments to be studied. Sampling was carried out every 2 weeks during periods of low flow, and more frequently during high flows. The river is typical of this area of France, with low flows during summer and autumn, and a relatively short period of high discharge (70% of the annual flow) from December to March.

Nutrient loads were calculated using data from point sources and estimates based on agricultural statistics and land use. Export from each subcatchment and from the whole catchment was calculated using measured concentrations and flow rates.

======== Nitrogen sources ========

Nitrates accounted for more than 86% of total nitrogen load. Sewage works were a significant source with the Vitré waste water treatment plant alone accounting for 1.5% of total catchment nitrogen.

The nitrogen export rate from land varied considerably between subcatchments, from 25.1 to 64.9 kg total N/ha/year. The highest export subcatchment showed the highest density of cattle and the highest % area of permanent grassland. Some nitrogen was retained in ponds and reservoirs: for example, 140 tonnes total N in the Haute Vilaine reservoir (7 million m3) over the year studied. 15% of total nitrate load was retained in the water bodies of the catchment.

Overall, non point sources contributed 95% of total nitrogen over the whole catchment.

========= Phosphorus sources =========

One of the main features of phosphorus movements was the large amount retained in the Haute Vilaine reservoir (28% of input load retained). **Overall, 15% of the total catchment phosphorus load was retained in the different reservoirs.**

Vitré appeared to have a more significant impact on total P than on total N. However, the quantity of total P input from the town’s industrial and municipal sewage plants was calculated (1.8 tonnes/year) as insufficient to account for the load measured, so that other local point sources may be occurring.

Overall, total P export from the whole catchment was around 100 tonnes over the year studied. As for total N, most of this export occurred during the high flow period (December – March).

P loss from land varied from 1.15 to 1.3 kg total P/ha/year.

Similarly to nitrogen, non point sources (agriculture) were highly dominant for phosphorus loadings: 90% of total P inputs.

SCOPE Newsletter editor's note: On this basis, taking detergent phosphates in France as 27% of sewage phosphates (IFEN "L’Environnement en France" 1999), it can be concluded that detergents represent less than 3% of the total P load to this surface water system (27% x 10%).

The total P outflow from the catchment for the 12 month period studied was 103 tonnes P.

SCOPE Newsletter editor’s note: This can be compared with detergent phosphate consumption for the catchment population, which can be estimated as (population = 60,000) x 0.348 kg/year (per person consumption of detergent phosphate as P, France 1996) = 21 tonnes. This corresponds to roughly 20% of total P outflow, so that only a small proportion of the expected detergent phosphates actually appear as surface water load, the remainder presumably being removed in sewage treatment or not reaching the lower river waters (adsorption to soils after septic tanks, transfer to sediments …).

The authors note that this study shows the significant buffer effect on nutrient loadings of stagnant waters, and the need for a better understanding of the exchanges of nutrients between sediments and water.

"Seasonal and spatial trends of nitrogen and phosphorus loads to the upper catchment of the river Vilaine (Brittany): relationships with land use". Hydrobiologia 373/374, 1998.

S. Moreau, G. Bertru, Laboratoire d'Evolution des systèmes Naturels et Modifiés, Université de Rennes I, France. C. Buson, Institut Scientifique et Technique de l'Environnement.

SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - Catchment management

Phosphorus loss from agricultural soils

Measurements of P losses from small subcatchments around the Rosemaund agricultural station in the River Lugg catchment area, UK, indicate significant variations between different land uses and drainage systems. The authors offer an overview of current research into agricultural P loss and emphasise the need for small-scale models which take into account P transfer mechanisms as well as export coefficient estimates.

The areas studied were the Belmont catchment (150 ha), two subcatchments within this (Jubilee 31 ha and Moorfield 6.3 ha) and a drained arable field area within Jubilee (Foxbridge 5.9 ha). All the Foxbridge measurements were taken in the field drain, thus indicating subsurface P runoff only.

Total phosphorus runoff to surface water was assessed for each catchment using a combination of measured values (P concentration and outflow volumes) and estimates (based on literature values for runoff related to different land uses). **Total P export varied from 1.06 to 2.64 kg/ha/year between the different catchments**, with a molybdate reactive fraction of around 1/4 (higher for Belmont, which was influenced by the farm yard and a small sewage works serving the farm buildings and workers' houses).

========= Subsurface runoff =========

Foxfield showed a **loss of total P, in the subsurface drain, of 1.64 kg/ha/year, indicating the significance this type of runoff**. The low soluble fraction in this runoff (15% MRP) corresponds to subsurface transport of P adsorbed to suspended clay and silt particles.

P loss from the Jubilee subcatchment was the highest, despite having 30% grassland (near zero for Moorfield). This was thought to be related to differing seasonal runoff patterns : the duration of runoff flow at Moorfield was December – march only, compared to all year for Jubilee.

Total P runoff figures are compared to literature values given as (kg/ha/year):

- **arable land 3, but up to 30 in undrained clay-rich soils**
- **grassland 0.5**

- **woodland 0.02**

======== Scale of modelling ========

The authors offer an overview of soil phosphorus loss processes and of current research, underlining that both **soluble and particulate P loss to surface waters eventually become bioavailable in aquatic systems**, contributing to nutrient enrichment.

Phosphorus can be lost from soils to surface waters either attached to soil particles in subsurface drainage or surface runoff (erosion) or in a soluble form when soil P-adsorbtion capacities are saturated with intensive use of fertilisers or manure. Exchanges occur between surface, shallow subsurface and deep subsurface flow of phosphorus, depending upon soil P-saturation, slope of soil and permeability.

Surface P runoff in the UK is particularly related to soil erosion and downhill sediment transport during prolonged, intense rainfall events. The quantities of phosphorus transported by this pathway to surface waters depend on soil surface characteristics, soil properties and steepness of slope near water courses.

Subsurface drainage of grassland and arable farmland also provides a very effective pathway for the transport of phosphorus to surface waters. Where the upper layer of the soil’s P-adsorption capacity has been exceeded by fertiliser or manure application, or where downward movement is accelerated by macropore flow, subsurface drains can intercept vertical leaching of soluble phosphorus, bypassing existing soil adsorption capacities.

The long term agricultural application of phosphorus in excess to crop requirements leads to a **progressive saturation of soil P-adsorption capacities** along soil horizons. This also occurs downslope as P is continually transported from soils upslope. Although this process may be very localised, with saturation occurring along preferential P-transport channels (relating to water flow or soil structure), it still has a major influence on the quantities of phosphorus reaching surface waters, because of the transport of phosphorus along these preferential pathways.

Particulate phosphorus can also be transported below the surface of the soil by eluviation of fine soil particles. Selective adsorption of soluble P to fine soil particles can lead to a P-rich layer accumulating below the root zone or to lateral transport of colloidal P-rich material along rapid flow pathways through the soil, providing a further mechanism for transfer to surface waters.

Such conceptual models of P export provide useful understanding, but most experimental work has been carried out at the plot scale, under site specific conditions. These plot scale experiments, with careful hydrological isolation and drainage, allow accurate estimations of P transport along specific pathways.

To complete plot scale studies and conceptual models, the authors identify a clear need for research at the small catchment level (1 – 10 km2) to enable accurate estimations of P export from given land use and management systems.

"Phosphorus loss from agricultural catchments: pathways and implications for management". Soil Use and Management, 1998 – 14.

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SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - South Africa

P-reduction fails to bring benefits

The effects of a 1 mg/l ortho-P standard for sewage works releasing into the Vaal river, near Johannesburg South Africa, are assessed by comparing the 10 years prior to the decision with the 10 years after it. Although 40% of sewage works were not complying, average ortho-P emissions from works were reduced over 50%.

The Vaal rivers system studied flows into the 64 km long Vaal River Barrage, used by Rand Water for drinking water extraction. **The river system's water quality is heavily dependent on sewage treatment**, as it is fed by the Vaal river (releases from an upstream dam, 65% of flow), along with two rivers, the Klip (31%) and the Suikerbosrant (7%) which both flow through greater Johannesburg. In the case of the Kip river, 87% of flow is made up of sewage works outflow. Catchment land use is dominated by industrial, gold mining and domestic development.

Ortho-P emission values from the sewage works within the river system were collated over the 20 year period, as were ortho-P and chlorophyll concentrations in the upstream dam release water, the Kip and Suikerbosrant rivers and at the water extraction point in the Val River Barrage. Algal species composition was also monitored at the water extraction point.

======== Reduction in reservoir ortho-P but not chlorophyll ========

Compliance with the 1 mg/l ortho-P emission limit increased from 6-13% to 52-60% of sewage works, and mean **ortho-P levels in sewage works emissions decreased from 8.63 to 3.49 mg/l along the Suikerbosrant, and from 4.37 to 1.98 mlg/l along the Kip river**. This decrease in emissions resulted in **very significant decreases in aquatic ortho-P concentrations:**

- **35%** in the Kip river
- **52 to –54%** in the Suikerbosrant and Vaal rivers
- **37%** at the water extraction point in the Vaal River Barrage.

These decreases in aquatic ortho-P did not, however, result in significant reductions in chlorophyll

concentrations at the water extraction point: median levels were unchanged and mean levels actually increased from 22.6 (SD = 24) to 25 µg/l (SD = 28).

The relative frequency of occurrences of chlorophyll > 30 µg/l decreased very slightly from 72 to 69% (this level is considered by Rand Water as the maximum possible for drinking water treatment).

======== N:P ratios and blue-green algal blooms ========

The reduction in aquatic ortho-P was accompanied by a very **considerable increase in the N(ammonium+nitrate): P(ortho-P) ratio**, from 2.5:1 to 13:1 at the Vaal River Barrage water extraction point. This was probably a result not only of ortho-P emission reductions, but also of increased nitrogen emissions due to increased sewage works outflows, inadequate maintenance and overloaded sewage works.

The algal species composition also changed: **Cyanophyceae (*Anabaena* and *Oscillatoria*) increased in dominance ten-fold** and Chlorophyceae (*Scenedesmus* and *Chlamydomonas*) doubled. This resulted in increased incidence of taste and odour problems, with concomitant possible toxic algal blooms.

======== Phosphorus not limiting ========

The authors conclude that phosphorus is not limiting in the system, that efforts should be made to continue to reduce the sewage works P-loadings (by achieving 100% compliance with the 1 mg/l discharge limit, and possibly by further tightening this limit) as well as **reducing nitrogen loads.**

"The implications of point source phosphorus management to potable water treatment". Water Science technology, vol. 37 n° 2, 1998.

R. Heath, M. Steynberg, R. Guglielmi, A. Maritz, Scientific Service, Rand Water, PO Box 54, Vereeniging 1930, South Africa.

SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - Gulf of Mexico

Estuarine algae and N+P co-stimulation

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18 litre microcosms filled with water from three sites in the Perdido Bay (Alabama – Florida, Gulf of Mexico) were used to assess the response of native phytoplankton assemblages to addition of nitrogen, phosphorus and the two nutrients together.

Experiments were carried out monthly, for a year (May 1990 – April 1991) at each site (12 x 3 experiments). Each experiment involved four treatments, each triplicated (12 microcosms): control, phosphate 10 µM above ambient, nitrate 50 µM above ambient, and finally combined phosphate and nitrate at these levels above ambient.

The three sites sampled were selected to represent a variation in estuarine conditions: upper, middle and lower bay areas. Perdido Bay has a total area of 130 km2 and an average depth of 2m. Exchange with the sea is limited by a narrow estuary mouth (Perdido Pass) so that the estuary tends to be stratified. The main sources of fresh water are the humic-rich Perdido river and Eleven Mile Creek (which carries paper mill wastes), both flowing into the upper bay.

Salinity at the three sampling sites showed a clear geographical gradient, varying from 0.2% (May) – 1.7% (October) in the upper bay, intermediate in the middle bay, and 0.3 – 1.4% higher than these values in the lower bay.

Surface water temperatures were similar between the three sites, varying from 28-31°C in June – September to 10°C in December.

The 18 litre microcosms were filled with bay water, filtered to remove zooplankton but not microheterotrophs (63µm mesh) and maintained in an outdoor water bath at temperatures similar to those of the bay water at the different seasons.

10% of the water volume of each mesocosm was replaced daily with new temperature adjusted water from the same site. Nutrient addition was carried out on day zero.

======== Response to simultaneous P and N addition ========

Phytoplankton response to nutrient addition, measured by chlorophyll-a concentration, fell into two main categories: primary N or P stimulation (ie. some growth with the addition of only one nutrient, enhanced growth with addition of both) and N+P co-stimulation (addition of both nutrients required to obtain a growth response).

Exclusive P stimulation occurred only once in the 36 experiments (ie. no additional growth with N+P compared with only P). Exclusive N stimulation was not detected.

As an overall pattern, primary P stimulation tended to occur during the cool season and at low salinity, whereas primary N stimulation occurred during the warmer months and at higher salinity.

As would be expected, primary P stimulation was generally associated with high ratios of dissolved organic nitrogen (DIN) to dissolved organic phosphorus (DIP): ratio range 18 – 288. Primary N stimulation was associated with DIN:DIP ratios in the range 8 – 46.

======== Frequent conditions near N+P co-stimulation ========

Examination of ambient nutrient and chlorophyll ratios produced contradictory and unclear indications. Whilst DIN and DIP concentrations and ratios suggested that P would be limiting most of the year, particulate organic nitrogen (PON): **particulate organic phosphorus (POP) ratios suggest N limitation.** PON: chl-a ratios, on the other hand, suggest N sufficiency.

The authors conclude that the Perdido Bay phytoplankton assemblages may often be poised near a condition of joint N and P co-stimulation.

They suggest that DIN and DIP may be coupled to algal biomass production, whereas ambient PON and POP may be more influenced by the net effects of grazing by microheterotrophs and zooplankton, mineralisation and detritus.

"Seasonal growth stimulation of sub-temperate estuarine phytoplankton to nitrogen and phosphorus: an outdoor mesocosm experiment". Estuaries, vol. 21 n° 1, 1998.

D. Flemer, US Environmental Protection Agency, National Health and Environmental Effects Laboratory – Gulf Ecology Division, Gulf Breeze, Florida 32561 – 5299, USA. R. Livingston, S. McGlynn, Center for Aquatic Research, Florida State University, Tallahassee, Florida 32306, USA

SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - Holland

Sediment P and lake recovery

Lake Veluwe, Holland, was created in 1956, by the formation of polders. The lake received heavy nutrient loading resulting in eutrophication until 1979. At this time, P-removal was introduced at the local sewage plant in conjunction with a programme of winter flushing of the lake with low-nutrient polder water. This study looks at the recovery of the lake and the response of sediment P levels.

The lake has very particular hydrology. It was created between existing "old" land and newly recovered polder farmland (lying some 5m below sea level) in order to limit groundwater losses from the "old" land. The lake has a shallow, sandy-bottomed area bordering the "old" land (<1m depth), fed by an inflow of streams and infiltration of underground water, and a deeper area (1 – 3 m depth) with a silty base, from which water seeps out of the lake towards the polder.

In the first years after the creation of the lake in 1956 the water was clear with a rich animal and community. Macrophytes were dominated by Characeae.

The high nutrient loading began to effect the water quality in the 1960's. By 1970, the water had become turbid (Secchi depth < 20 cm), submerged macrophytes had disappeared and algae were dominated by cyanobacterai, in particular Oscillatoria agardhii.

A monitoring and restoration programme was launched in the 1970's and in 1979 P-removal was installed at the sewage works discharging into the lake and regular winter flushing with polder water (low in nutrients and in algae) was introduced.

Phosphorus loading to the lake was thus reduced from 3 to 1 gP/m^2/year and the average hydraulic residence time decreased from 0.45 to 0.2 years. Additional flushing from 1985 onwards further decreased the residence time to 0.15 years.

======== Immediate nutrient and chlorophyll response but ecological recovery only after a decade ========

Phosphorus and chlorophyll-a concentrations in the lake responded within a year, but the lake remained turbid.

Only in the early 1990's, more than 10 years after the reduction in nutrient loading, was the beginning of ecological recovery observed. Macrophytes reappeared, macrofauna and fish densities began to change and the water became transparent in much of the lake.

This **hysterisis effect**, whereby a shallow lake does not rapidly respond (in terms of ecological recovery) to reductions in nutrient loading, is thought to be related

to release of accumulated sediment phosphorus. The sediment P levels were modelled for Lake Veluwe and compared with measurements.

========= Sediment phosphorus and lake ecology =========

Phosphorus concentrations in the deeper lake sediment around 1979 were of the order of 0.5 – 0.6 gP/kg dry weight. Those in the shallower lake sediment were around 0.08 gP/kg.

Changes in the deeper lake sediment P can be related to changes in the lake's ecological condition. Initial levels are estimated to have been around 0.3 gP/kg. Modelling of sediment P levels suggest that the change from clear to turbid lake water took place when deeper lake sediment P reached 0.44gP/kg and that the change back from turbid to clear water occurred at 0.38 gP/kg.

The relatively rapid recovery of Lake Veluwe in response to nutrient loading reductions is probably the result of the particular hydrology: infiltration of "old" land groundwater into the lake through the shallow area sediment and seepage out of the lake through the deeper area sediment. This situation means that phosphorus build up in the shallow area sediment was limited during initial high nutrient loads, and that phosphorus tends to be moved towards the deeper area sediments. This latter effect is significantly reduced with the development of macrophytes in the shallow area following lake recovery.

The paper models sediment phosphorus changes as a function of infiltration, seepage, burial of suspended matter, precipitation of calcium phosphates and hydrology.

The model suggests that sediment P concentrations will return to the initial levels (as at the lake's creation) only in 2006. At this time, a balance will be reached between supply of P to the sediments and the P removal rate.

"Changes in sediment phosphorus as a result of eutrophication and oligotrophication in Lake Veluwe, the Netherlands". Wat. Res. vol. 12 n° 11 1998.

D. Van der Molen, R. Portlielje, P. Boers, Institute for Inland Water Management, PO Box 17, 8200 AA Lelystad, Holland. L. Lijklema, Ketsheuvel 33, 6871 EB Renkum, Holland.

SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - Shallow lakes

P storage in a prochlorophyte

The summer phytoplankton community of many shallow Dutch eutrophic lakes is dominated by large filamentous cyanobacteria such as *Anabaena, Aphanizomenon* and *Oscillatoria*. The Loosdrecht lake system, a series of shallow, hypertrophic lakes in the centre of Holland, is generally dominated in summer by another prokaryote, the prochlorophyte *Prochlorothrix hollandica.*

This species differs from cyanobacteria in its photosynthetic apparatus, which lacks the phycobilisomes present in cyanobacteria and contains chlorophyll-b.

The total P concentration in the Loosdrecht lakes' water is high, but summer concentrations of soluble reactive P can be very low. Phosphorus can be released from the sediment as distinct pulses by wind action. In this context, it was decided to compare the P uptake and storage capacities of *Prochlorothrix hollandica* (isolated from the Loosdrecht lakes) with those of a cycanobacterium (*Planktothrix agardhii*, formerly named *Oscillatoria agardhii*; originally isolated from Lake Veluwemeer, Holland).

Growth conditions were studied in 2 litre culture vessels at around 20°C with artificial light (approx. 40 µmol/m2/s photon irradiance).

Phosphorus concentrations were adjusted to 200 µgP/l to represent low P levels. Pulses of phosphorus were generated by adding 300 µgP/l at hourly intervals for several hours until the algal cells became P saturated.

The literature indicates that *Prochlorothrix* has a lower growth rate than *Planktothrix* (0.025 and 0.036 / hour, respectively).

The studies showed that *Prochlorothrix* has a significantly higher maximum P uptake rate. For both species, the P uptake rate decreases linearly as a function of cellular

P content, but this rate of decrease was slower in *Prochlorothrix*. Not only was the maximum cellular P content of *Prochlorthrix* much higher (11% of dry weight, compared to 4.2% for *Planktothrix*), the minimum cellular P content of *Prochlorthrix* was also lower, so that this species can accumulate much more cell phosphorus.

From the experimental results and modelling, it was calculated that in a steady state *Prochlorothrix* would develop with slightly lower cellular P levels (0.27% d.w. predicted, 0.31% observed, compared to 0.37% / 0.38% for *Planktothrix*), bringing the residual P concentration in the surrounding water (R*) down to 0.01 µgP/l, compared to 0.067, µgP/l for *Planktothrix.*

This value for *Prochlorothrix* is one of the lowest R* values ever reported for a phytoplankton species. Given the species' high P storage capacity, *Prochlorothrix* would appear to be amongst the best P competitors of freshwater phytoplankton. This is demonstrated by competition experiments between the two species studied, where *Prochlorothrix* dominated *Planktothrix* in steady state low P conditions, and less effectively in conditions with pulsed P additions. Models were developed to predict competition between the two species: the Droop model proved relatively good, whereas the Monod model, which does not take resource storage into account, did not provide useful predictions.

The question raised is therefore not so much "Why does *Prochlorothrix* dominate in the Loosdrecht lakes?" but rather "Why does it not dominate in most shallow lakes?".

The authors suggest that *Prochlorothrix* may have disadvantages for ecological factors other than P limitation. These may include grazing, sedimentation losses or competition for nitrogen.

"Competition between a prochlorophyte and a cyanobacterium under various phosphorus regimes : comparison with the droop model". J. Phycol. 34, 1998.

H. Debecou, J. Huisman, L. Mur, Lab. Microbiology ARISE, Univ. Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam. R. Jonker, AquaSense, PO Box 95125, 1090 HC Amsterdam, Holland.

SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - Wastewater strategy

WWTP upgrading best option for the Danube

A study of 9* countries of the Danube basin compares the cost and environmental effectiveness of different investment scenarios for improving sewerage collection and urban waste water treatment.

> ** Austria, Bulgaria, Czech Republic, Hungary, Moldova, Romania, Slovakia, Slovenia, Ukraine. Because of the political situation, data from Bosnia-Herzegovia, Croatia and Yugoslavia were not available.*

The study was based on evaluations of emissions, water quality and waste water management costs assessed for the "Nutrient Balances for the Danube Countries" in the framework of the Environmental Programme for the Danube River Basin by experts from seven Danube countries.

The area of the Danube basin under consideration has a population of 58 million, 52% of whom live in conurbations of more than 10,000 people.

Within these, 75% of the population is connected to sewerage in, but only 20% outside them. An estimated 14 million p.e. of raw wastewater is discharged by industries not connected to urban sewerage (but this figure is probably underestimated).

Of the wastewater collected by sewerage, 33% is discharged either untreated or with only mechanical treatment. Only 20% of the wastewater collected undergoes some kind of tertiary treatment.

50% of the WWTP's (urban waste water treatment plants) are overloaded and 60% more than 15 years old.

In total, 75% of capacity will require reconstruction within the next 10 years.

======== Extension of sewerage? ========

Two scenarios were considered for investments in sewerage networks:

A. no construction of new sewerage (no extensions of networks); costs limited to maintenance and replacement of faulty and leaky sewerage (an estimated 10% of existing sewerage will require reconstruction by 2005).
B. realistic extension of sewerage networks, according to national legal requirements or development plans.

For each of these two sewerage system scenarios, four waste water treatment investment scenarios were considered:

(0) no improvement of sewage treatment; investments limited to operation and reconstruction where necessary of existing plants

(1) EC requirements for non-sensitive areas: ie. biological treatment (90% BOD, 75% COD removal) for all collected sewage

(2) EC requirements for sensitive areas: ie. as (1) plus nutrient removal (80%P, 70%N) for treatment plants serving more than 10,000 pe.

(3) treatment requirements defined as a function of water quality requirements (as regards BOD and NH4N – oxygen regime)

(4) scenario (3) enhanced to add **P-removal for all sewage works**

======== Economic burden of maintenance ========

The authors underline the very high cost faced by the Danube countries studied simply to maintain and replace as necessary existing sewerage and sewage treatment installations. The scenario "A0" (no extension of sewerage networks, no improvement of treatment works) alone implies a total cost of around 2 billion Euros/year.

The second conclusion is the very high cost of extension of sewerage networks: the scenario "B0" (development of sewerage according to existing plans) is 80% more costly than "A0", for a proportion of the population connected increased from around 50% to only 58%.

The costs for the most extensive improvement scenario for waste water treatment ("A2") are very similar to costs for developing sewerage ("B0"). However, **the effort on water treatment significantly decreases emissions to surface waters (overall 80% reduction in BOD from sewage works discharges, 20% reduction in total phosphorus emissions from all sources), whereas the development of sewerage ("B0") actually increases discharges to surface waters** (though infiltration to underground waters should be reduced).

======== 20 – 23% reduction in total P loading to surface waters ========

Removal of phosphorus at all sewage works (not only those serving >10,000 pe.) accentuates the achieved reduction in total P loading to surface waters: -20% for "B2", -23% for "B4" (reduction of all sources of P to surface waters).

Overall, P-removal is not one of the more costly investment decisions: P-removal at all sewage works compared to at no sewage works ("B4" vs. "B3") only increases total sewerage and sewage treatment costs by 4-6%.

On the basis of no P-removal at sewage works, the authors suggest that **the use of P-free detergents would reduce phosphate loadings by 8-10 %, compared to the 23% reduction achievable by sewage works P-removal.** Furthermore, the reduction offered by P-free detergents would be much smaller in a scenario where P-removal was introduced in a significant number of sewage works.

======== Necessity for nitrogen removal ========

The authors estimate that installing secondary biological treatment only in sewage works would not suffice to prevent increases in emissions to surface waters if sewerage collection is developed (scenario "B1"). Because of the low dilution in much of the basin, **advanced nitrification treatment will be necessary in many cases to ensure "good ambient quality water"** taken by the authors to be BOD < 9 mg/l and NH4-N < 1.5 mg/l).

The application of EC requirements for sewage treatment (scenario "B2": nutrient removal in works serving > 10,000 pe.) would reduce total nitrogen load to surface waters by around 15% (compared to the reduction of –20% achieved for P loadings).

The additional costs for nitrogen removal are 10 – 15% of total costs (compared to 4 – 6% for P-removal).

"Wastewater management in the Danube basin". Water Science Technology vol. 38, n° 11, 1998.

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SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - Biological nutrient removal

Upgrading of existing sewage works for bio- N and P removal

Upgrading of the 54,000 pe. Holten sewage works (Holland) was carried out in order to meet effluent requirements of <10 mg total N/l, <1 mg P/l and <10 mg suspended solids/l, whilst minimising investments, running costs (energy, chemicals) and maintaining a good sludge volume index. The method developed was then applied to other sewage works (6 presented).

The Holten WWTP originally consisted of two parallel aerated plug-flow activated sludge tanks. To upgrade to biological nutrient removal, these were put in series and compartmentalised into anaerobic (anoxic) and aerobic zones. A plug-flow anaerobic reactor compartment was added in front of the two tanks to prevent the introduction of nitrates into their anaerobic compartments.

After this anaerobic reactor, which acts as a selector as well as facilitating the hydrolysis of particulate COD, some hydrolysis products remain. Compartmentalisation of the anoxic zone is therefore necessary to achieve a good sludge volume index (SVI). At Holten, this compartmentalisation enabled SVI to be reduced from 150 to 80 mg/l.

======== Sludge retention time ========

In order to optimise nitrification and availability of CED for denitrification, sludge retention time (SRT) was maximised (up to 50 days). This tends to deteriorate bio-P removal effectiveness which is optimal with high sludge productions and low SRT.

In order to improve bio-P removal, sludge is recycled through anaerobic and anoxic conditions, with presettling of influent before the anaerobic reactor (minimising accumulation of inerts and heterotrophs). Chemical P-removal in the sludge line is applied (addition of iron in the sludge digester).

The presettling stage produces a primary sludge which, when mixed with the secondary sludge, improves digestion, thus increasing methane energy production and decreasing sludge generation. Bypassing the presettler and inputting raw sewage to the anaerobic reactor improved bio-P removal (increased COD substrate) and also increased N removal (the nitrogen, however, was not denitrified, but simply transferred to the increased sludge volume produced). After assessment, it was decided to maintain the presettler: the lower nutrient removal efficiency (with presettler) was considered less important than the decreased energy and increased sludge production.

======== In-line P-stripper ========

The operation with a long sludge retention time limits the phosphorus being removed to sludge, so that some chemical P-stripping was necessary to ensure that P effluent levels remained below discharge consents. Addition of P-stripping chemicals in the main reactor tanks would result in accumulation of precipitants in the sludge, reducing nitrification activity. It was nonetheless wished to avoid construction of a new and separate P-stripping tank. As a solution, **baffles were added in part of the anaerobic zone, creating a settling area from where a P-rich clear liquor can be decanted.** This liquor (on average 10% of through-flow) is then transferred to the sludge digester where P-striping chemicals are dosed.

This specific combination of in-line bio-P removal and off-line P-precipitation minimises new investments and is denoted the BCFS© process (Biologische Chemishe Fosfatt Stikstof verwijdering).

Process control is very important for the biological nitrogen and P removal, and to adjust chemical P-stripping. This is ensured by redox probes in the anoxic and anaerobic zones which control the recycling of mixed liquors and withdrawal of P-rich liquor from the in-line settling area.

"Upgrading of waste water treatment processes for integrated nutrient removal – the BCFS© process". Water Science Tech. Vol. 37 n°9, 1998.

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SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - Sewage sludge digestion

Differing availability of phosphorus and metals

Extraction and speciation methods for phosphorus and different metals (Fe, Ca, Mg, Cu, Zn, Mn, Cr, Ni) were tested on model compounds then applied to anaerobic digesters fed with high-P sludge from plants operating chemical (iron precipitation) and biological phosphorus removal.

As an initial experiment, extraction of the different metals from carbonate, sulphate and phosphate model compounds was tested using the Stover et al method (1976). Phosphate extraction from calcium phosphate, magnesium phosphate and iron phosphate was tested using different extractants and the Uhlmann et al method (1990).

As a second stage, availability of phosphorus and of the different metals was tested in anaerobic digesters treating high-phosphate content sewage sludge:

A. sludge from a plant operating chemical P-removal (CPR) using iron precipitation: 37.9 g total P/kg dried sludge
B. sludge from this plant during shutdown of the P-precipitation process: 13.3 gP/kg
C. sludge from a plant operating biological P-removal (BPR) on a part of works throughflow: 11.0 gP/kg
D. sludge from a plant without P-removal: 9.1 gP/kg

======== Low P-availability after chemical P-stripping ========

Total phosphorus was divided into soluble, water extractable, NaOH total P extractable (organic), NaOH phosphate extractable (inorganic), HCl extractable and aqua regia digestion P (residual).

Not surprisingly, phosphorus was significantly less readily available in the digester treating CPR sludge, with only 3.2% soluble or water-available P (compared to 22.5% and 16.8% in digesters B and C).

The proportion of organic phosphorus in the different reactors, at around a quarter of total P present, was very similar.

========= Struvite precipitation =========

Reactors B and C had higher HCl extractable P levels (24% and 23%) suggesting that, in the absence of iron and in the presence of hard water (Ca, Mg) the alkaline earth metals render insoluble a significant proportion of total P.

It could have been expected that the low redox conditions in the anaerobic digesters would cause an increase in soluble phosphates in digester A (CPR) by reduction of the ferric precipitate ion. This did not occur, the authors suggest because of re-precipitation in the form of Fe3(PO4)2 = vivianite (cf. Singer 1972, Thomas 1966).

In the absence of sufficient ferrous ions, re-precipitation as struvite (magnesium ammonium phosphate or magnesium potassium phosphate) is probable and the formation of struvite in sludge digesters downstream of biological P-removal plants has been widely reported (Borgerding 1972, Rabonowitz and Barnard 1995). The P-extraction results are compatible with this hypothesis, with a high NaOH inorganic fraction in reactor A (fraction in which vivianite should be found) and a high HCl and residual fractions in B and C (fractions in which struvite should be found).

Jardin and Popel (1994), for example, concluded that **nearly all the magnesium and 54% of the P released during digestion of BPR sludge precipitated as struvite.**

========= Release of organic polyphosphates from BPR sludge =========

Polyphosphates intracellularly accumulated during BPR processes are known to be released under anaerobic conditions. Also, it is known that BPR micro-organisms fix phosphates on the cell surface in high concentrations and that these phosphates can be released by washing in water (Steichan and Schon 1991).

These phenomena could explain the relatively higher soluble and water available P in reactor B. However, these fractions are not great enough to account for all released polyphosphates.

BPR phosphate uptake is known to be accompanied by uptake of Mg and K and their release to be accompany polyphosphate release. **The authors suggest that this mechanism could facilitate struvite precipitation** in reactor B.

========= Availability of metals in CPR sludge =========

Comparisons of metal extractability show that the different metals are somewhat more easily available in the CPR sludge digester (A). Residual and nitric acid extractable metal fractions dominate for chromium and nickel in reactors B and C, whereas these metals are mainly Na4P2O7 or KF extractable in reactor A.

Residual fractions for Fe, Mg, Cu, Zn and Mn are also higher in reactors B and C.

The authors suggest that **increased chromium availability in reactor A** may be the result of the association of chromium with the organic fraction of sludge as a result of flocculation during P-precipitation.

"Metal and phosphate speciation during anaerobic digestion of phosphorus rich sludge". Wat. Sci. Tech. vol. 36 n° 6-7, 1997.

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SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - Ecological nutrient removal

Using fish and periphyton for P and N removal

Tanks containing periphyton and algal-grazing fish were tested as ecological systems for nutrient removal, enabling recovery of the nutrients for recycling: in the mucous-bound fish feces which accumulate in collectable sediment and in the production of harvestable fish biomass.

Various authors have demonstrated the potential of periphyton as an ecological nutrient removal system. Periphyton can take up both N and P from wastewaters at a very high rate, they naturally adjust growth and nutrient uptake rates to nutrient concentrations, and they are well adapted to high water through-flow rates. However, the periphyton communities have to be harvested in some way in order to effectively remove the fixed nutrients, otherwise they tend to senesce or slough off, returning nutrients to the water. Effective and clean methods for harvesting the periphyton are often not economically viable: rotating discs, vacuum systems, harvesting by hand... **This paper presents experiments testing the use of algal-grazing fish as a simple nutrient harvesting system.**

The principal experiment reported involved a four month outdoor (Spring – early Summer) run with 24 cascading mesocosm tanks (influent flowing through the tanks in series), each with around 35,000 cm2 of 0.64 cm mesh plastic screen acting as a substrate for periphyton growth. **The tanks contained two algal-grazing fish:** the cichlid *Tilapia mossambica* and the minnow stoneroller *Campostoma anomalum*. Altogether (for the 24 tanks), 712 fish were stocked (average fish wet mass/tank 250 g).

Artificially polluted water was made by adding agricultural fertilisers to reservoir water to bring nutrients up to concentrations typical of domestic sewage: average 0.39 mg TP/l and 1.09 mg TN/l.

After a period of system stabilisation, nutrient removal rates of over 50% were achieved, with outflow TP concentrations generally below 0.15 mg/l and TN below 1 mg/l.

Total phosphorus removal rates by fish growth (transfer of P into fish biomass) were around 27 mg/day/m2 mesocosm water surface area, and removal by sedimentation of feces around 21 mg/day/m2.

The periphyton biomass at the end of the experiment was mainly filamentous green algae (in particular *Cladophora glomerata*) as well as association diatoms such as *Cyclotella meneghiniana, Gomophoneam* *subtile and Nitzschia amphibia.*

The authors conclude that such fish/periphyton systems could provide a useful ecological method for removing nutrients from wastewaters, with the fish being a valuable product either for consumption or river restocking. The fish would, however, tend to assimilate toxicants present in the wastewaters: this could provide a useful quality indicator, but would limit their value for consumtion.

The authors consider that the nutrrient remvoal rates can be improved (for example by better feces drainage) but point out that, even if efficiency is doubled, removal of 1 mg P/l from an effluent volume of 1,000 m3/day would require a water surface area of 10,000 m2.

"Ecologica water treatment system for removal phosphorus and nitrogen from polluted water". Ecological Applications 7(2) 1997 (Ecological Society of America).

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SCOPE NEWSLETTER

SCOPE N°32 - 05/1999 - Scandinavia

Zeolites increase sewage sludge and deteriorate filterability

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A study by Tampere University Finland and the Swedish Royal Institute of Technology assesses the effects of detergent zeolites on sewage sludge characteristics.

Zeolites are the most widely used partial substitute for phosphates in laundry detergents. The effects of two zeolites (Doucil-P and Doucil-A24) in concentrations of 10 – 30 mg/l were tested in sludge from a full scale sewage plant, sludge from a pilot unit fed with synthetic waste water, and in the nitrification-denitrification system of a pilot plant fed with synthetic waste water.

The paper reports estimates of **zeolite concentrations in European sewage plant influent** varying from 10 mg/l (Hopping 1978) to 60 mg/l in hard water areas of Germany (Fischer *et al.* 1978).

======== Increased sludge filtration times ========

Sludge filtration time was on average 40% longer with zeolite addition. This is thought to be the result of negative effects on flow structure, either by complexing metal ions or because of the amporphousness of zeolite. Longer contact times (24h) or higher zeolite concentrations (up to 3g/l) caused even longer filtration times (5 – 9 x longer).

======== Increased sludge solids ========

Zeolite also caused an **increase in sludge solids: a 25 – 30% increase in mixed liquor suspended solids**, although this did result in improved sludge settling. Fischer *et al*. (1978) had previously reported increases in sludge suspended solids of up to 33%. Unlike Fischer *et al*., however, the authors found no improvement in treatment efficiencies of COD, P and N as a result of zeolite addition.

Zeolite addition caused a **significant increase in sludge aluminium content**, from 5 mg/l (mixed liquor suspended solids) to 10 – 13 mg/g. This increase is not as high as would be expected given the 15% (approx.) aluminium content of zeolite. This difference was not expected by the authors.

"Effects of detergent zeolite in a nitrogen removal activated sludge process", Water Science Technology vol. 38 n° 2, 1998.

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - United Kingdom

Eutrophication management strategy

The UK Environment Agency has issued a consultative report entitled "Aquatic eutrophication in England and Wales" which describes the causes and impacts of eutrophication, outlines a proposed strategy for assessing and managing eutrophication and seeks the views of interested parties on the proposed approach.

The Environment Agency defines eutrophication as: *"the enrichment of waters by inorganic plant nutrients which results in the stimulation of an array of symptomatic changes. These include the increased production of algae and/or other aquatic plants, affecting the quality of the water and disturbing the balance of organisms present within it. Such changes may be undesirable and interfere with water uses."*

========= Phosphorus sources =========

The report indicates the % contribution of the main sources of phosphorus entering surface waters in the UK:

- agricultural 43%
- human and domestic wastes in sewage 24%
- detergents 19%

The report estimates that 70% of total nitrogen input to inland surface waters is from diffuse sources (agriculture, precipitation and urban run-off, in order of decreasing magnitude).

The report underlines the magnitude of nutrient inputs to surface waters in the UK, related to high population density and agricultural activity: the UK has the third highest phosphorus loading to surface waters of the EU/EFTA nations.

========= Measuring eutrophication =========

The UK Environment Agency uses six "viewpoints" for measuring the state of the environment:

- land use and resources
- biological populations, biodiversity
- compliance with standards and targets
- "health" of environmental resources
- changes at long term reference sites
- aesthetic environmental quality

The report underlines the importance of assessing changes in water bodies’ states over time (ie. measurements of changes from a baseline state estimated by "hindcasting").

For rivers, where a well established network of monitoring sites exists, trends in nutrient concentrations and loads can be established and relationships between dissolved oxygen concentrations and algal and plant growth indicate the impacts of eutrophication.

========= Catchment approach to management =========

The Environment Agency proposes a management strategy based on partnership and consultation of the different sectors involved in water management and use, and on a catchment approach.

Within each catchment area, the establishment of a Local Environment Agency Plan (LEAP) will include defining whether or not eutrophication is identified as a local priority. Where this is the case, a local Eutrophication Control Action Plan (ECAP) will define **actions regarding point sources and solutions to deal with diffuse sources such as changes in farming and forestry practices.**

========= Phosphorus standards =========

Ecological targets, taking into account a "reference" condition and corresponding to the **optimal chemical and biological quality that could be expected in a given water body**, are considered to be the long term tool for assessing eutrophication status. This approach will be a requirement of the EC Water Framework Directive.

Pending the development of such target systems, the Environment Agency proposes **interim standards for phosphorus in standing and running fresh waters:**

	Standing µg/l total P[1]	**Running µg/l SRP[2]**
oligotrophic	8	20
mesotrophic	25	60

meso-eutrophic	-	100
eutrophic	85	200

1 – annual geometric mean total phosphorus
2 – annual mean soluble reactive phosphorus

The report indicates, however, that **such national standards should be applied with caution and should not prevail over site-specific standards** derived from scientific understanding of a particular water body. In particular, the attainment of phosphorus targets is likely to bring ecological benefits only in cases where phosphorus is limiting. The use of "hindcasting" techniques may assist in defining achievable targets for given sites but need to be studied carefully.

The above standards can be used for screening out actions which are unlikely to provide benefits. If the full range of available nutrient control techniques is not capable of bringing concentrations down to levels close to the adopted standard, then such control actions are unlikely to be justified.

Environmental Issues Series – Aquatic eutrophication in England and Wales. UK Environment Agency Consultative Report, December 1998.

UK Environment Agency, Rio House, Waterside Drive, Aztec West, Almondsbury, Bristol BS 32 4 UD, England.

Document available at:
http://www.environment-agency.gov.uk

SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - River management

Nutrient targets to control algae

The State of Montana wished to obtain indications relating aquatic dissolved nutrients (DIN, SRP) to algal densities. The State also wished to know whether total nitrogen and phosphorus would provide better management indicators, to obtain indications regarding management options for upstream nutrient point sources and to assess effects on *Cladophora* algae.

The Clark Fork River drains around 57,000 km2 of western Montana. The study concerns the upper river, which has nine major tributaries and nine towns. Land use is mainly forest, agriculture and rangeland. **Benthic chlorophyll-a levels in parts of this basin routinely exceed 100 mg/m2 (considered undesirable for water quality) and growths of the nuisance filamentous green alga *Cladophora* are occasionally abundant** in nitrogen limited upper sections.

======== 200 site model ========

A series of eutrophication models were derived from analysis of a data base from over 200 river sites from North America, Europe and New Zealand. Total nitrogen and phosphorus (TN, TP), dissolved inorganic nitrogen (DIN), soluble reactive phosphorus (SRP), their ratios, latitude, temperature, stream gradients and light were related to benthic chlorophyll-a (seasonal mean, maximum). Macrophyte development was not addressed.

Percentages of cases where chlorophyll-a levels exceeded 50, 100, 150 and 200 mg/m2 were calculated for different nutrient ranges.

======== Total nitrogen levels best indicator ========

Total nitrogen and total phosphorus were found to offer the best correlation with chlorophyll-a.

Relations between season mean values of dissolved nutrients (DIN, SRP) and benthic chlorophyll are characterised by an extremely high variance, so that **dissolved nutrient levels explain only a very low proportion of observed chlorophyll-a variations** (although a closer relationship was shown for the Clark Fork River data than for the general data base).

Regression model results on the general data base showed that control to 275 µg/l of total nitrogen would generally yield acceptable chlorophyll-a levels (mean 100 mg/m2, maximum 150 mg/m2). If TP is taken as the variable, similar results would be obtained with TP up to 35 µg/l and TN at 252 µg/l.

A probablistic method suggests that both seasonal mean and maximum chlorophyll-a levels will be below 100 mg/m2 if total nitrogen is below 200 µg/l or TP below 50 µg/l. **The plots confirm that there is a clearer relationship between TN and chlorophyll-a than for TP.**

Finally, a reference station approach was used, looking at nutrient levels at six sampling stations in the Clark Ford River basin where acceptable levels of benthic algae are found. Target nutrient levels were then calculated as the mean summer TN and TP concentrations from five years sampling at these sites. This gave values of 318 and 20.5 µg/l respectively for TN and TP.

To conclude, the authors suggest that maintaining mainstream total N and total P levels below 350 and 30 µg/l respectively should correspond to benthic algal chlorophyll-a density below nuisance levels of 100 mg/m2 in most streams.

The authors underline that these targets may not be applicable in all river systems and that targets should always be fixed on the basis of objective local criteria.

The use of TN and TP targets (rather than DIN and SRP) offers the advantage of easier linking with land use practices (for which nutrient input to water is generally measured as TN and TP), thus facilitating efforts to control non point sources.

======== Management control options ========

The authors were unable to develop models to provide management scenarios likely to both lower algal biomass and also reduce *Cladophera* dominance. This is because the low total nitrogen levels considered necessary for chlorophyll-a limitation imply nitrogen limitation, which can correspond to *Cladophera* development.

Regarding nutrient point source management, under normal summer baseline flow conditions, 100% removal of nutrient inputs from one source and a 7 mg/l total nitrogen (TN) limit at another less important source further upstream would suffice to ensure TN levels lower than 350 µg/l throughout the basin. **Further nitrogen loading requirements would be necessary** if target TN levels are to be achieved during critical summer low flows. The authors indicate that the management strategy could also include actions to increase flows during periods of low flow to increase dilution.

"Developing nutrient targets to control benthic chlorophyll levels in streams: a case study of the Clark Fork River", Wat. Res. vol. 31 n° 7, 1997.

W. Dodds, Division of Biology, Kansas State University, Manhattan, KS 66506. V. Smith, Env. Studies Program/ Dept. Systematics & Ecology, University of Kansas, Lawrence, KS 66405. B. Zander, US Environmental Protection Agency (EPA), Region 8, Suite 500, 999 18th Street, Denver, CO 80202, USA.

SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Agriculture

Phosphorus loss from fields by leaching

This paper offers a summary of available literature concerning phosphorus leaching and sub-surface run-off in agricultural soils, particularly in agricultural drainage systems. Current research shows that in a number of cases, phosphorus levels in drainage water exceed surface water phosphorus targets.

The realisation that transport of phosphorus from agricultural soils to surface waters is of significant environmental concern dates from the early 1970's (Ryden *et al*.). Despite considerable research into this area, **non point source pollution of surface waters by agriculture remains a major problem today** (Foy and Withers, 1995; USEPA, 1994; Sharpley *et al*., 1994).

Systems have been put forward to identify agricultural fields which are most vulnerable to P loss (Phosphorus Index : Lemunyon and Gilbert, 1993; Sharpley, 1995) and models developed to simulate the effects of changing soil and crop management (Sugiharto *et al*., 1994). **Most of this work, however, has only concentrated on P transport by surface erosion and surface run-off.**

Phosphorus, from mineral fertilisers, manure, sewage sludge and other soil amendments, tends to **accumulate in agricultural top-soil by binding to the more erodible soil components:** clays, organic matter, oxides of iron and aluminium. This paper examines how phosphorus is lost from soils by leaching and sub-surface run-off (movement in shallow, perched, ground water towards nearby streams) and shows that this phenomenon can be significant in certain circumstances, particularly where artificial drainage is accelerating water movements.

Ryden *et al*. indicated (1973) that *"losses of P to subsurface and ground water run-off, although of little significance from an agricultural standpoint, may under certain conditions constitute* ***a significant loss of P from agricultural watersheds in terms of the P enrichments of surface waters…*** *losses of P in subsurface run-off can be similar or even greater than those in surface run-off"*. Ryden *et al.* cited eight studies in which dissolved inorganic P in subsurface run-off in drainage systems exceeded 0.01 – 0.05 mg/l.

======== Certain soils liable to P leaching ========

As early as 1933, Bryan, working with deep, sandy soils in Florida, showed that available P 90 cm down in soil under heavily fertilised citrus groves was 48 mg/kg, compared to 6 mg/kg in virgin soil.

Humphreys and Pritchett, 1971, showed that 6-10 years after applying superphosphate fertiliser for the production of slash pine *(Pinus elliottii)*, the fertiliser had leached down to at least 50 cm in very sandy soils. This leaching was reduced in finer-textured soils and soils with higher aluminium concentrations.

Fox and Kamprath (1971) showed that phosphorus leaching also occurs in course mineral soils with high organic content and in organic soils, presumably because of low soil concentrations of the constituents mainly responsible for P retention: clays, oxides of iron and aluminium, carbonates. **Leaching losses from organic soils was shown to depend on sesquioxide content** (20% P leaching in high sesquioxide conditions, and up to 80% leaching where sesquioxides were below 850 mg/kg).

P leaching has also been shown to occur where phosphorus fertilisers are continuously applied in excess of crop requirements (Schwab and Kulyingyong, 1989; Knudsen and Beagle, 1996).

======== P leaching and manure application ========

The above studies show that P leaching can occur in certain types of soils (deep sandy soils, organic soils) or after long-term over-application of mineral fertilisers. **The most common cause of P leaching is probably, however, the continuous application of organic wastes (manures, sewage sludge).** This is, in particular, the result of basing manure application levels on crop nitrogen needs, which generates significant over-application of phosphorus.

Studies cited indicate the possibility of P leaching related to long-term application of poultry litter, cattle manure an pig wastes.

Sommers *et al.* studied the effects of 11 years of **application of municipal wastewaters** on two soils and noted significant leaching in a sandy loam but only limited downward movement of P in a clay loam.

In one study in Holland (Breeuswma *et al.*, 1995), more than 40% of areas sampled had total P concentrations in groundwater of > 1 mg/l. This was ssociated with intensive spreading of dairy, pig and poultry wastes as well as high mineral fertiliser use. Breeuswma *et al.* estimated that leaching losses of P > 0.43 kg/ha would cause groundwater to exceed 0.15 mg/l total P.

======== Agricultural drainage accelerates P leaching ========

The paper summarises 25 studies relating concentra-tions of P in drain run-off to fertilisation and soil type.

Soluble phosphorus in subsurface drains reached levels of 0.2 mg/l in several cases. In one study (Culley and Bolton, Ontario, 1983) 25% of watershed total P and 50% of ortho-P were estimated to come from subsurface drainage.

In general, the studies summarised show that the highest levels of P are found in drainage ditches fed both by subsurface and surface run-off.

Three recent research projects in Delaware, Indiana and Quebec are reviewed. These studies each look at the effects of long term intensive animal manure application combined with agricultural drainage.

Most of **Delaware's** 270 million broiler chickens are produced in Sussex County, which has around 100,000 ha of cropland. P levels in soils in this area are now rated as optimal (29%) or excessive (53%). Sallade and Sims (1997) found dissolved P levels in drainage ditches ranging from <0.01 – 0.82 mg/l.

======== Winter P release ========

Various studies in Delaware have shown that P solubility tends to increase during saturated soil conditions, generally occurring in the winter and spring. This will increase the potential for P transport at these periods.

Indiana counts around 4.3 million farmed pigs in increasingly intensive operations. Research by Provin *et al.* (1995) has aimed at examining the link between soil P tests (Bray P1) and leaching potential. Cumulative water soluble P in soils correlated well with Bray1 so this test gives a reasonable indication of likely losses to drainage waters. The prediction ability can be further improved by taking into account other measurable soil properties such as exchangeable Ca.

Recent research at 27 sites in the **Saint Lawrence lowlands, Quebec**, showed total P concentrations in subsurface drains from 0.01 – 1.17 mg/l. The research has shown that leached P concentrations are often much higher during rain occurring after a long dry period, and can be related to conditions facilitating rapid penetration of water (soil crevices or pores), thereby emphasising the importance of P mineralisation. Highest levels were recorded after autumn applications of pig manure.

======== Further research ========

The authors identify four areas for further research:

- how to identify fields and watersheds where subsurface P run-off is likely to be significant?
- how to improve soil testing to improve subsurface run-off management?
- how to improve understanding of the hydrologic pathways of subsurface run-off and P leaching?
- what actions can reduce subsurface run-off and how will they impact agriculture?

"Phosphorus loss in agricultural drainage: historical perspective and current research", J. Environ. Qual. 27, 1998.

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Measurement techniques

Soluble Reactive Phosphorus greatly overestimates ortho-P

Soluble Reactive Phosphorus (SRP) is often equated with the free ortho-Phosphate ion. The author shows, however, that the standard molybdenum method used to measure SRP can both hydrolyse organic phosphate compounds and displace phosphates from colloids. Analysis of lake water samples showed that the free ortho-P ions actually represent only a small fraction of the SRP concentration measured.

SRP is generally determined using molybdenum in acid conditions (pH<2) to produce phosmolybdic acid, which is then reacted with vanadium, ascorbic acid or SnCl2 to produce molybdenum blue. The acidity and the presence of transition metal ions can potentially contribute to the hydrolysis of organic phosphorus compounds.

The author used weak ion exchange chromatography to estimate **the extent to which certain organic P species are susceptible to hydrolysis under the conditions of the standard SRP test.** The study examined both commercially available organic phosphorus compounds (representative of those found in the environment) and native P species isolated from an eutrophic lake water sample.

======== Varying susceptibility to hydrolysis ========

Certain compounds (tripolyphosphate, DNA, RNA, inositol hexaphosphate) were resistant to hydrolysis (<2% hydrolysis under the SRP test conditions). Others were hydrolysed to a limited but significant extent (7 – 37%): c-AMP, myo-inositol 2-monophosphate, phosphorylchlorine chloride). 5’-AMP, finally, underwent near 100% hydrolysis.

======== Very little of the SRP in lake water samples was in fact free Ortho-P ========

Natural water samples were collected from Ryan’s 2 Billabong, a shallow eutrophic oxbow lake near Albury, Australia. P species fractions were separated using weak ion chromatography.

Overall, very little of the measured SRP in these samples proved to be free ortho-P.

Somewhat less than half the SRP measured was the result of hydrolysis of (unidentified) organic P species, whilst the majority of the measured SRP was associated with a fraction which adhered strongly to ion-exchange resin and could only be eluted at very high pH.

The author suggests that this latter fraction may consist of labile P compounds associated with small organic or inorganic colloids.

Although the eutrophic billabong water samples studied may represent an extreme case, the author concludes that SRP cannot be equated with free ortho-phosphate.

"Reactive organic phosphorus revisited", Wat. Res. vol. 32 n° 8, 1998.

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - France

Variation in sediment phosphorus bioavailability

Physical and chemical properties and bioavailalability of phosphorus associated with sediment particles were measured in different flow conditions and at different places in the 33 km2 watershed of the Redon river, which flows into the French side of Lake Geneva.

This watershed is mainly made up of glacial rock formations, so that its sediments have relatively similar mineral properties. The watershed is mountainous upstream, rising to 1540m, flowing down into an area of gentle slopes covered mainly by pasture land, and urbanised near its exit into Lake Geneva. Particulate phosphorus runs off into the upstream watershed from cultivated land and forests, and soluble phosphorus enters the river from sewage discharges downstream.

Samples were collected from a variety of sites in the watershed, including river bottom sediment, ditches draining forested areas, ditches in intensively cultivated areas, inlet and outlet of a marshland receiving agricultural run-off and parent watershed soils.

The characteristics of the phosphorus associated with particles from these different sites were assessed using different chemical extraction methods, using a bioassay method to evaluate bioavailability, and using an isotopic tracer to determine the ability of the sediment particles to fix and exchange phosphorus with water.

======== Increasing bioavailability and decreasing fixation ========

Sediment total P increased towards the river outflow, from 393 mg/Kg upstream, through 562 – 700 in agricultural drainage networks, to 680 – 741 mg/kg in the lower river. **Bioavailability of phosphorus in particles increased significantly more, however, being 1.5 – 2 x higher at the river outflow.** Similarly, the P fixing ability of the - ediments decreases significantly.

The total phosphorus content of the particles was thus not a good indicator of phosphorus bioavailability.

Total phosphorus in the agricultural soils (800 – 830 mg/Kg) was considerably higher than that found in the river sediments.

========= Positive effects of marshland =========

The total and organic phosphorus levels in particles upstream and downstream of an area of marshland were shown to be similar (total phosphorus 708 mg/Kg upstream and 781 mg/Kg downstream). However, **the bioavailable phosphorus dropped significantly with the passage through the marshland and the phosphorus fixing capacity increased considerably** (reaching the highest level of all sample sites). This was probably a result of increased calcium carbonate, iron and organic matter levels in the sediment particles.

========= Modification of particles during transport =========

The authors suggest that the properties of sediment associated phosphorus, and in particular its bioavailability, depend not only on the sediment particle origin, but strongly on changes occurring during transport through the watershed. In particular, during periods of low flow, **interactions occur with sources of soluble phosphorus (eg. from sewage).** This means that spates following low flows will cause sediments to release soluble phosphorus.

For the Redon river, such releases of phosphorus are important: **storm spates following dry periods (mainly summer storms) contribute 40% of exported particulate phosphorus.** The authors suggest that this phosphorus is likely to be relatively bioavailable, further increasing the impact of these releases. They also note that these often occur in the spring and summer when the receiving lake is susceptible to algal development.

"Physico-chemical properties and bioavailability of particulate phosphorus of various origin in a watershed of Lake Geneva", Wat. Res. Vol 32 n° 2, 1998.

J. Dorioz, J. Pelletier, Institut de Limnologie, INRA, BP 511, F74203 Thonon, and P. Benoit, Laboratoire des Sols, INRA Grignan, F78850 Thiverval-Grignan, France.

SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - C/P stoichiometry

Food chain production is phosphorus dependent

Large indoor mesocosms containing algae, microbes and herbivores were used to study food chain response to increased energy input (light). Although the mesocosms with more light showed increased algal growth, this was not transmitted up the food chain and herbivore populations actually showed decreased development.

Two large stainless steel indoor mesocosms (11m high, 0.86m diameter) were used for two runs, with the assignment of the mesocosms being inversed for the second run. Temperature was controlled at 20°C in the upper 2.5m and 10°C below that. Light was supplied with high wattage, near daylight spectrum lamps with constant 24 hour illumination. Incident light levels were 60 and 400 µE/m2/s.

The experiments were started by filling the mesocosms with 5µm filtered water from a Minnesota lake, so that **the water contained the natural microbial community.**

Initial phosphorus levels in the experiments were 0.72 and 0.5 µgP/l, corresponding to the state of the lake's water. Nitrogen was increased artificially by fertilisation (using NH4NO3) to 500 µgN/l to avoid nitrogen limitation.

Phosphorus limited cultured algae *Scenedesmus acutus* were added on day zero and zooplankton herbivores *Daphnia hyalina* on day 4. Initial algal and zooplankton densities are not indicated in the paper. Runs lasted 26 days. Throughout the runs samples of seston, bacterial population, algae and zooplankton were taken to assess biomass/numbers and particulate carbon and phosphorus were also measured.

======== Increased seston carbon and algae, but decreased zooplankton ========

Increased seston carbon and **decreased zooplankton biomass** in the high-light mesocosms were both statistically significant. **Increased algal biovolume** was apparent at a statistically nearly significant level (p=0.08). Total seston carbon closely matched algal biomass, but bacterial biomass and heterotrophic bacterial numbers showed no significant relationship to increased light. **The main seston chemistry**

effect of the increased light was to increase algal carbon.

The decrease in zooplankton was statistically significant both in terms of numbers (individuals/litre) and biomass. Assuming low mortality (since there were no predators present), this indicates that the increased seston carbon and algal development was not passed on to secondary production.

This experiment alone cannot exclude the possibility that the lower Daphnia growth may be a direct result of increased light on grazing behaviour or efficiency, but previous experiments has shown that light does not affect grazing (Buikema 1973).

========= High carbon/phosphorus ratios and lower secondary production =========

It is known that the chemical make up of consumer species varies less than that of primary producers, and in particular that consumers often have a higher nutrient/carbon ratio. Thus ecosystems with low carbon/phosphorus ratios are well balanced to the needs of secondary producers. This is true both for terrestrial and aquatic food chains.

In particular, it has been shown that **algae with high carbon/phosphorus ratios provide a poor quality food for herbivores** such as Daphnia (Sterner 1993).

These mesocosm experiments demonstrate that this can result in a higher energy input to a phosphorus limited system not being transferred up the food chain, or indeed resulting in lower secondary production.

The authors indicate that such phenomena could prove important in the context of global warming and increasing atmospheric CO2. Anticipated increases in primary pro-duction may not result in increases in secondary production.

"Carbon: phosphorus stoichiometry and food chain production", Ecology Letters 1 - 1998.

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Estuaries

Nutrients and grazing

Macroalgal development in coastal ecosystems can be limited by bottom up processes, such as nutrient loading (in particular, anthropogenic nitrogen) and by top-down processes (zooplankton grazing either reducing algal biomass or changing community composition).

This study compared algal and zooplankton populations (composition, number, changes), primary production and zooplankton grazing rates, and nutrient loading, in three estuarine subwatersheds of the Waquoit Bay, Cape Cod, Massachusetts:

Estuary:	**Child's River**	**Quashnet River**	**Sage Lot Pond**
Nitrogen load kgN/ha/year	HIGH 624	MEDIUM 520	LOW 64
Open water area (ha)	13	19	13
Residence time (days)	1.1	0.3	2.2
Depth (m)	1.1	0.5	0.9

Evaluations of macrophyte biomass, macroalgae and zooplankton were carried out from spring through to autumn of 1994 and 1995. Field grazing experiments were carried out in floating field cages during the summer and early autumn of 1993 and 1994.

======== Field measurement of grazing rates ========

For these grazing experiments the macroalga *Cladophora vagabunda* was used, because of its abundance in all three estuaries and because previous experiments had shown it to be a preferred food of several zooplankton species. The zooplankton amphipods *Microdeutous gryllotalpa* and *Cymadusa compta* and the isopod *Idotea baltica* were studied: *M gryllotalpa* because it was the most abundant grazer in all three estuaries, the other two species to compare larger zooplankdon (up to 15 and 20mm respectively).

Grazing rates were measured using 9 x 9 x 9 cm 500µm mesh cages, with four cages suspended in each estuary, each with 500 mg (rinsed wet weight) of Cladophera vagabunda and with different initial grazer populations (control = no grazers, 15 *Microdeutopus gryllotalpa*, 10 *Cymadusa compta*, 5 *Idotea baltica*). Seven such experiments were each run for four days.

======== Algal growth and nitrogen load ========

C. vagabunda grew in almost all of the control cages (except early autumn runs and one case in the low nitrogen estuary) and **growth rates were clearly related to the estuary nitrogen loads:** around 0.1%/day in the low nitrogen water to around 5.4%/day in the high nitrogen water.

The average % nitrogen in the dry weight of the algae at the end of the experiment also varied between the estuaries : it was around 1% higher in the high nitrogen water than the low nitrogen water. This is consistent with other studies in these estuaries which indicate 3.9% nitrogen in *C. vagabunda* collected from the high nitrogen estuary compared to 3.1% in the low nitrogen estuary.

Algal carbon content, on the other hand, did not vary significantly.

The high nitrogen-content algae would be expected to provide a better food source for zooplankton (high N:C ratio). Other studies had already shown that algae from the high nitrogen estuary were a preferred food and/or were grazed faster by different species than those from the low nitrogen estuary.

======== Grazing rates and eutrophication ========

The field experiments showed that grazing rates increased with grazer size, reaching an average of 7.3 mg/individual/day for *I. baltica*. For the two larger grazer species, grazing rate was significantly higher with higher water nitrogen levels (roughly 2x higher), presumably because of the improved food quality of the algae (high N:C ratio, as indicated above). The grazing rate of *Microdeutupus gryllotalpa*, however, did not vary significantly between the three estuaries.

Overall, the increase in grazing rates with higher nitrogen were exceeded by the greater increase in *C. vagabunda* growth rates, so that experimental end weights of algae were consistently higher in the cages in estuaries with higher nitrogen loading.

In most of the experiments, however, *C. vagabunda* was effectively controlled by the densities of zooplankton in the cages. Whilst algal weight generally increased in the control (no zooplankton) cages (with the exceptions indicated above), it generally decreased in cages with zooplankton. An exception was the grazer *M. gryllotalpa* in the high nitrogen estuary which was unable to control algal growth (increases in C. vagabunda weight of up to 10%).

========= Estimating primary production and predicting grazer impact =========

As a second stage, the study makes estimations of total *C. vagabunda* production and total grazing, on the basis of total biomass and growth rate estimations, in the three estuaries. These estimates are based on observations of the algal canopy biomass and thickness (light limitation slows or prevents growth), on field measurements of zooplankton species density and on experimental measurements of grazing rates for different zooplankton.

These estimations suggest that there is a potentially significant mid-summer impact of grazers on macro-algae in estuaries subject to lower nitrogen loads.

It was noted that there were only half as many grazers in the medium nitrogen estuary than in the low nitrogen water, and only a half as many again in the high nitrogen estuary. This is thought to be the consequence of hypoxic events and to the change in macroalgal canopy strcture: in dense canopies, only the upper 6-10 cm are available habitat for grazers as the canopy becomes anoxic below this depth. Changes in algal community (substitution of macroalgae for eelgrass in high nitrogen conditions) may also deteriorate food quality and make zooplankton more vulnerable to predation.

Grazer abundance increased in all three estuaries through to a July-August peak, corresponding to the period when algal abundance would be expected to be at its highest. In fact, however, biomass surveys indicated no net increase in macroalgal biomass in the summers of 1991, 1992, and net decreases in the summers of 1994, 1995.

========= Conclusions =========

The authors indicate that, for these estuaries, higher nitrogen loadings result in increased macroalgal biomass (3x), loss of eelgrass *(Zostera marina)* and a decrease in zooplankton herbivore abundance (4x lower).

They suggest that grazers (copepods and amphipods) at densities above 4 individuals/litre can play a significant role in controlling macroalgal development.

In the estuaries studied, the comparison of total production and grazing suggests that zooplankton do indeed control macroalgae in the low nitrogen estuary, causing summer algal biomass levels to be stable or even decrease.

In the high nitrogen loaded estuary, however, algal biomass and growth rates are too high, along with significantly reduced grazer populations. The consequence is that grazing is no longer capable of controlling algal biomass.

"Relative importance of grazing and nutrient controls of macroalgal biomass in three temperate shallow estuaries", Estuaries vol 21, n° 2, June 1998.

J. Hauxwell, J. McClelland, P. Behr, I. Valiela, Boston University Marine Program, Marine Biological Lab., woods Hole, Massachusetts 02543, USA.

SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Scotland

Limits to sewage sludge disposal

139,000 ha of land around Edinburgh, Scotland, were studied to determine the area potentially suitable for sewage sludge spreading: agricultural land with limited slope, suitable soil properties including heavy metal retention, and without risk of water pollution. The resulting area was compared with a projected 70% increase in sludge quantities produced by the Edinburgh area's waste water treatment plants.

Sludge quantities produced by the 750,000 population of the Edinburgh area is expected to reach 21,800 tonnes dry solids/year by the end of the year 2000.

========= Sewage sludge increases =========

As a result of application of the Urban Waste Water Treatment Directive 91/271, sewage sludge production is expected to increase by 2005 by an average of 50% over the EC as a whole and over the UK, Furthermore, marine disposal of sewage sludges is no longer possible as from the end of 1998.

Sewage sludge is a valuable organic manure, providing recycling of nitrogen and (where sewage treatment processes leave it in an agriculturally available form) of phosphorus. It improves soil physical properties, in particular water retention capacity and structural stability.

However, these benefits of agricultural spreading have to be balanced against **potential long-term risks due to the addition of heavy metals and organic compounds such as polynuclear organic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).** These substance persist in soils so that any addition above "natural" levels must be carefully monitored.

========= Defining potential spreading soils =========

Edinburgh is situated on the South shore of the Firth of Forth and the study examined an area of 139,000 ha situated to the South, East and West of the city.

Data were collected over this area concerning soil types (soil properties, morphology, analytical data) from existing soil maps and soil inventory points. Data were also assembled regarding the slope of land (calculated from altitude contours) and land use.

From these different data, the different areas physically suited for sewage sludge spreading were mapped according to the following criteria:

- slope < 15 degrees
- land use of arable or improved agricultural grassland
- not rocky
- reasonable soil depth, drainage and organic surface horizons.

On the basis of these physical parameters, 57.6% of the land area was potentially suitable for sludge spreading.

Risk of water pollution was then assessed, on the basis of soil hydrology types (which model water movement in the soil, soil properties and hydrology, including depth to aquifer). **Only 4.5% of the total area offered a low risk of both ground and surface water pollution.**

As a final selection criterion, the metal-binding capacity of soils was assessed, on the basis of pH, texture, clay content, organic matter and colour (a surrogate for oxide content). It was concluded that this property was closely dependent on pH. Current regulations suggest that sludge amended soils should be tested for pH only every 20 years, but the changes possible over this time could considerably alter binding capacities for many metals.

Comparison of soil baseline metal concentrations and EC recommended soil metal limits, for zinc, copper, nickel, lead and chromium suggest that sludge applications could not exceed around 25 – 30 years.

========= High land requirement =========

On the basis of predictions for sewage sludge production, the study estimates that sludge would need to be applied to 5.9% of potentially suitable land every year (application of 5 tonnes dry solids of sludge/ha/year).

This figure exceeds the area of land not at risk of polluting water.

In addition, sludge spreading has never before been implemented on such a large proportion of available land in the UK. Severn Trent Water, for example, currently use only 1% of suitable land each year.

"Sewage sludge recycling to agricultural land: the environmental scientist’s perspective", J. Ciwem n° 11 April 1997.

W. Towers, P. Horne, Macauley Land Use Research Institute, Aberdeen, UK.

SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Switzerland

Biologically induced phosphate precipitation

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12 experiments were carried out to assess the kinetics of phosphate precipitation at different pH's (in the range 7 – 8.1) in mixed liquor taken from the aerobic phase of an enhanced biological phosphorus removal sewage plant.

Biological activity was inhibited using formaldehyde and pH was adjusted using sodium hydroxide and hydrochloric acid. Initial soluble phosphate concentrations ranged from 0.68 – 1.46 mole/m3 and soluble calcium concentrations from 1.58 – 2.1 mole/m3. Magnesium concentrations, at around 0.6 mole/m3, varied from 0.19 – 0.56 x those of phosphates. Temperatures were held constant at various levels from 9.5 – 22.6 °C.

========= Effects of formaldehyde =========

After the inactivation using formaldehyde, no aerobic respiration could be detected. Liquor then left for 24 hours showed a clear decrease in soluble calcium concentrations, an increase in potassium, a slight increase in phosphates and no change in magnesium concentrations. It is concluded that the formaldehyde was having a destructive effect on the sludge flocs or micro-organisms, but that polyphosphates were not being hydrolysed (constant magnesium concentrations). Calcium ions were probably being immobilised by carbonate precipitation or other processes, such as absorption onto detergent zeolites.

========= pH and phosphate precipitation =========

pH was adjusted in the different experiments in the range 7 – 8.1, with both rapid increases/decreases and progressive changes being tested. The effects of pH changes on soluble calcium, phosphate and magnesium concentrations were studied.

In all experiments, the soluble phosphate concentration decreased with increasing pH and vice versa. Soluble calcium concentrations showed a strong positive correlation to changes in phosphate concentrations, whereas magnesium concentrations remained nearly constant. **It was thus concluded that soluble phosphorus removal was the result of calcium phosphate precipitation only** (not struvite = magnesium ammonium phosphate precipitation).

No data is given for ammonium concentrations in the liquor used (taken from the aerobic phase of a pilot biological phosphorus removal plant, JHB mode with separate denitrification of return sludge). This is regrettable, as this parameter would influence the precipitation of struvite. Other literature sources report significant struvite precipitation from waste waters (eg. page 8, Scope Newsletter n° 30).

========= HDP and HAP =========

The removal of soluble phosphates was shown to be strongly dependent on pH and partly reversible. The ratio of change in soluble calcium concentration to change in phosphate concentration was clearly different between experiments with rapid changes in pH and those with slow, progressive pH changes (2.2 compared to 1.6 mole Ca/mole P).

The authors suggest that this may be explained by a two step precipitation of calcium phosphates:

- **formation of a surface complex of HDP hydroxydi-calcium phosphate $Ca_2HPO_4(OH)_2$, occurring with rapid pH changes;**
- formation of HAP hydroxyapatite $Ca_5(PO_4)_3OH$, occurring through transformation of HDP with progressive pH changes and at higher pH’s where the solubility product of HDP is exceeded.

The formation of HDP was reversible if the pH returns to a lower value, whereas that of HAP was not reversible under the experimental conditions.

It is also noted that whereas the HDP complex was more easily formed at higher temperatures, HAP was more easily formed at lower temperatures.

========= Crystallisation conditions =========

A dynamic model was established for the crystallisation conditions for the two forms of calcium phosphates, HDP and HAP. Most parameters in this model could be accurately estimated, except the temperature dependence of HAP formation.

Regarding the formation of HDP, an exceptionally high solubility product was found ($10^{-22.6}$ M^5), significantly higher than literature values. Also HDP formation was shown to be exothermic. These results indicate that it was not a pure compound being formed, but **an amorphous mixed crystal.** The authors suggest that this may be related to the presence of inhibiting magnesium and carbonate ions.

One of the implications of this is that, in typical waste water conditions (concentrations of soluble calcium 1 – 2 mole/m^3, pH 7 – 7.7), precipitation of the HDP complex will only occur at relatively high soluble phosphate levels: for example, around 25 mole P/m^3 at pH 7.6 and 10°C or at pH 7.4 and 20°C.

Such high soluble phosphate concentrations are typically encountered after the anaerobic release phase of biological P removal.

========= Up to 40% partly reversible phosphate removal =========

Phosphate precipitation gave soluble phosphorus removal rates of up to 40%. For example, in experiment B1, phosphate concentration was reduced from around 1.1 to 0.7 mole/m3 after 4 hours by progressively increasing the pH up to 8.1 at a temperature of 15.8°C.

This phosphate removal was however partly reversible. For example, in experiment A2, phosphate concentrations were reduced from nearly 0.8 to around 0.65 mole/m^3 during two abrupt pH increase phases to 7.7, but returned to around 0.77 mole/m^3 when pH was returned to around 7 (total experiment time 7 hours).

The authors conclude that, when the solubility product for the HDP complex is exceeded, phosphates are irreversibly fixed as HAP calcium phosphates at a rate of 0.5 mole P per day.

"Kinetics of biologically induced phosphorus precipitation in waste water treatment" Wat. Res. vol. 33 n° 2 – 1999.

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