SCOPE NEWSLETTER

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WATER POLICY

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.

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.

ECOSYSTEM BALANCE AND EUTROPHICATION

Estuary nutrient balance

Nitrogen, phosphorus and dissolved silicon can each control algal growth in estuaries in certain situations. Reductions in both nitrogen and phosphorus inputs are probably necessary for effective water management.

Nutrient impacts and management

Nutrient limitation, the role of wastewater treatment in successful eutrophication management, and possible implications of cultural eutrophication for climate change.

Ariel view of the three + one artifical wetland lagoons, with behind them the sewage works, the Muga river and the Empuriabrava holiday complex: See: Costa Brava Spain, page3.

ANALYTICAL METHODS

Harmonising analysis methods for phosphorus in sediments

An EU programme involving 15 laboratories in 11 Member States has assessed different methodologies for sequential extraction of different phosphorus forms from freshwater sediments and proposes a reference protocol.

PHOSPHORUS RECOVERY AND RECYCLING

Phosphorus and nitrogen recovery from urine

Struvite production is shown to be an effective route for recovering phosphorus from urine-separative toilets

An economic and environmental evaluation of P-recovery

The opportunities are examined for using struvite recovered from waste waters in existing UK fertiliser markets and the environmental and economic feasibility are assessed.

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

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Centre Européen d'Etudes des Polyphosphates

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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.

R. Foy, Agricultural and Environmental Sciences Division, and S. Lennox, Biometrics Division, Dept. of Agriculture and Rural Development for Northern Ireland, Newforge Lane, Belfast BT9 5PX, Northern Ireland. Email : **Bob.Foy@dani.gov.uk**

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".

Lluís Sala. Consorci de la Costa Brava. Plaça Josep Pla, 4, 3rd. E-17001 Girona, Spain. E-mail: **ccblsala@grn.es** and Rafael Mujeriego, Department of Hydraulic, Coastal and Environmental Engineering, Universidad Politécnica de Cataluña, Gran Capitán, s/n, E-08034 Barcelona, Spain. E-mail: **rafael.mujeriego@upc.es**

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.

D. Conley, Dept. Marine Biology and Microbiology, National Environment Research Institute, PO Box 358, DK4000 Roskilde, Denmark. Email : **dco@dmu.dk**

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.

V. Smith, Dept. Ecology, University of Kansas, Lawrence, KS 66045, USA. G. Tilman, Dept, Ecology, University of Minnesota, Saint Paul, MN 55108, USA. J. Nekola, Natural and Applied Sciences, University of Wisconsin, Green Bay, WI 54311, USA. **Email : valsmith@falcon.cc.ukans.edu**

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 Willams 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.

B-B. Lind, Swedish Geotechnical Institute, Chalmers Vasa, Building 5, SE-41296 Göteborg, Sweden and Z. Ban, S. Bydén, Environmental Sciences, Göteborg University, Box 464, SE-40530 Göteborg, Sweden.
Email : **bo.lind@swedgeo.se**

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..

M. Gaterell, Environmental Change Institute, University of Oxford, 1a Mansfield Road, Oxford OX1 3SZ, UK. R. Gay, J. Lester, TH Huxley School of the Environment, Earth Sciences and Engineering, Imperial College of Science Technology and Medicine, London, SW7 2BP, UK Email : J.lester@ic.ac.uk. R. Wilson, 36 Lombard Court, Old Portsmouth, Hampshire, PO1 2HU, UK.
Email : j.lester@ic.ac.uk

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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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avenue E. Van Nieuwenhuyse 4, bte 2, B1160, Bruxelles - Belgium.
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