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March 2003

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Phosphorus loads to the Krka River, Slovenia, are estimated, concluding that agriculture and wastewater both contribute around half of present total loads. Implementation of sewage treatment and agricultural management measures could reduce P loads by 40%, with wastewater then only contributing around one third of overall loads.

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Michigan, USA p10 Nitrogen addition increases stream periphyton growth

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A study of the Wensum river, Norfolk, South-East England, looks at the impact on nutrient concentrations and on aquatic plants of introducing sewage works nutrient removal.

European Union Workshop p13 **Defining eutrophication criteria**

The EU Water Framework Directive requires Member States to achieve "good ecological quality" in (most) surface waters by 2015. This EU Workshop began to define what this means with respect to eutrophication. The definition will also be relevant for the Urban Waste Water and the Nitrates Directives, and for OSPAR.

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Germany, Sweden

National objectives for P-recovery announced in Germany and Sweden

Both Germany and Sweden have announced national objectives for phosphorus recovery for recycling from sewage. Sweden's action plan centres on recycling P to land through sewage sludge use in farming, whereas the German Federal Environment Ministry (UBA) suggests recovery for recycling in sewage works.

The German Federal Environment Ministry (Umwelbundesamt UBA) announced in March 2003 the objective of developing phosphorus recovery for recycling from sewage and other wastes. The press release followed the organisation of a symposium (Berlin, 6-7 Feb. 2003) which brought together around one hundred German experts, regulators and water industry operators to discuss P-recovery from sewage and wastes. It also followed a call be the Baden Württemberg Land environment Minister in February to ban sewage sludge spreading on farmland.

UBA suggests that existing taxes on waste water could be used to support the technical development of phosphorus recycling.

Sweden has also announced the objective of developing phosphorus recycling, but the Swedish EPA (Environmental Protection Agency) action plan published in December 2002 proposes to achieve 60% P-recycling by 2015 largely by re-use in agricultural by sewage sludge spreading. The Agency estimates that at present 46% of sewage phosphorus is already effectively recycled through agricultural sludge application. Sweden hopes to move back to agricultural sludge spreading following severe restrictions imposed by farmers over the last few years, because of concerns about health or pollution contamination risks, with the introduction of new EU sludge spreading quality criteria which are expected to be proposed soon by the EU Commission (see below).

Both the Swedish and German authorities recognise that phosphorus can be recovered for recycling by various process including recovery from wastewaters in sewage works or from sewage sludge incineration ashes. German Environment Ministry press release (in German): http://www.umweltbundesamt.de/uba-info-presse/presseinformationen/pd01903.htm

Translation shortly available at: http://www.nhm.ac.uk/mineralogy/P-recovery/

Swedish EPA press release (in English): http://www.internat.naturvardsverket.se/index.php3?main=/docu ments/press/2002/p021216.htm

EU Commission (DG Environment) proposed new rules concerning agricultural spreading of sewage sludges: http://europa.eu.int/comm/environment/waste/sludge/index.htm

Water treatment

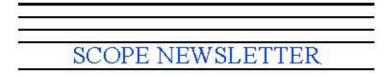
Sewage sludge management in Europe

Large quantities of Europe's sewage sludge production are currently recycled by agricultural spreading, effectively allowing both economic disposal and recycling of the nutrients (phosphate and nitrogen) and organic contents¹. However, this route is under significant pressure because of public concerns – objectively justified or otherwise – concerning risks of heavy metal, pharmaceutical pathogen or chemicals contamination of soils and/or of agricultural products (food). There is also concern about risks of run-off of such contaminants to ground and surface waters (drinking water supplies).

1: approximately 36.4% of European sewage sludge is spread on land, according to Rebecca Renner in *"Sewage Sludge, Pros and Cons"*, Environmental Science & Technology vol. 34 - I.19 1, October 2000, text at: *www.mindfully.org/Pesticide/Sewage-Sludge-Pros-Cons.htm*

These concerns have led in some countries (eg. UK) to agreements between farmers organisations, water companies and supermarkets to limit levels of contaminants and to ensure pre-treatment of sewage sludges before spreading, or in other countries (eg. Sweden, Switzerland) to farmers organisations recommending or legal implementation of bans on agricultural sludge use.

This EU report analyses the different options for sewage sludge disposal and concludes that agricultural use is the best environmental and economic solution. The development of the agricultural spreading route requires the improvement of both sludge qualities and of public confidence. **Sludge quality guarantee and labelling systems** will be a key tool to improve this, but with a



significant cost to water companies. Research into sludge quality, pollutants and their fate in the environment and in food, and the publication of this research will be important in facilitating public acceptance.

Proposed tighter regulations

In order to develop public confidence, the EU is proposing a significant tightening of regulations concerning biosolids spreading (currently covered by *EU Directive 86*/278), to require fuller sludge pretreatment before spreading, to lower soil and sludge limits for heavy metals, and to introduce limits for certain organic contaminants.

The report estimates that this will have little impact in countries where national sludge spreading regulations are already much more stringent than the existing EU Directive requirements (Denmark, Finland, Sweden, Netherlands. **Implementation costs will however be significant** in countries where existing national regulations are only somewhat more stringent (Austria, Belgium, France, Germany, Poland) or are similar (Greece, Ireland, Italy, Luxembourg, Portugal, Spain, UK, Estonia, Latvia) to the current EU Directive.

Who will bear the costs ?

The total cost implied by the proposed Directive tightening for the 15 EU Member States is estimated at almost **1 billion Euros/year**, with a large proportion of this cost being born by four EU states who currently recycle to agriculture large volumes of sludge (Germany 29% of total cost, UK 26%, France 16%, Spain 11%).

As a European average, sewage sludge disposal costs are estimated at 318 \notin tonne dry matter (DM), that is at $0.12 \notin m^3$ of drinking water supplied, compared to total sewage costs of $0.87 \notin m^3$, that is 14%. Total drinking water service costs (production and treatment) are estimated at 2.2 $\notin m^3$. Average sludge disposal costs are estimated to vary from 263 – 344 \notin tonne DM. Landspreading of solid/semi-solid sludge is estimated to cost 110-160 \notin tonne DM, of which 10-30% of the cost is covered by the fertiliser value of the sludge.

The report estimates that implementation of the proposed sludge spreading Directive tightening would result in 67% (short term) rising to 83% (long term) of sewage sludge failing limit values for heavy metals or organic pollutants in the absence

of an effective "pollution prevention" policy to reduce the input of such contaminants to raw sewage. Such a policy could reduce the proportion of sludge failing limit values to around 25%. Despite this, the total cost to all stakeholders (water companies, farmers, industry, public / consumers, local authorities) of the new Directive *with* the pollution prevention policy could be around 15% higher than *without* such a policy.

A key difference is that *without* the pollution prevention policy, 60% of the costs are born by local authorities (ending up on the public's water bill), 20% by farmers and 16% by the general public (environmental and health impacts), whereas *with* the policy 60% of the costs are born by the pollution producing industries (discharge pollution prevention costs).

"Disposal and recycling routes for sewage sludge", report for the EU Commission – DG Environment – B/2, SEDE/ Arthur Andersen, January 2002. Available at: http://europa.eu.int/comm/environment/sludge/sludge_disposal.htm

Phosphorus recovery

Germany Struvite shows to be good fertiliser

Struvite precipitation was tested in a pilot animal slurry treatment plant in Northrhine-Westfalia, Germany, sponsored by a farmers' cooperative. The recovered struvite was then tested for fertiliser potential (nutrient availability to plants) using randomised pot experiments with four replicates and oats (*Avena sativa*) and ryegrass (*Lolium multiflorum*).

The pot trials used luvisol (pH-CaCL₂ 6.5) and a 1:1 brown earth / quartz-sand mix (pH-CaCL₂ 5.5) for the phosphorus availability experiments, and brown earth (pH-CaCL₂ 5.5) for the magnesium and nitrogen availability experiments.

Performance of struvite was compared with that of raw phosphate and dicacalcium phosphate (DCP), all at 0.6 g $P_2O_5/9$ kg pot; with NH_4NO_3 + CaSO₄ at 0.4 gN/ 9 kg pot ; and with MgSO₄ (KS) at 1 mg Mg/9 kg pot. Phosphorus uptake by

oats was significantly higher (2.5-3x) for each of the three P applications (struvite, raw phosphate, DCP, compared to the no P addition control), but slightly lower with raw phosphate than for struvite and for DCP (soil pH 5.5).

Ryegrass also showed considerably higher P uptakes for the three P treatments, but with P uptake in the raw phosphate treatment significantly lower than for struvite and DCP (soil pH 6.5).

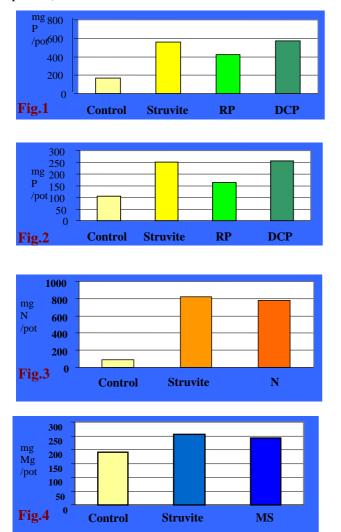


Fig.1: P uptake of ryegrass, soil pH 5.5, **Fig.2:** P uptake of ryegrass, soil pH 6.5 **Fig.3:** N uptake of ryegrass, soil pH 5.5

Fig.4: Mg uptake of ryegrass, soil pH 5.5

This suggests that struvite P availability is as good as commercial fertiliser at soil pH 5.5 and 6.5 (whereas raw phosphate effectively showed a lower P availability at the higher soil pH).

Nitrogen uptake was significantly better with struvite than with ammonium nitrate for oats (both at soil pH 5.5), with both being considerably higher (6-9x) than for the control.

Magnesium uptake also marginally better from struvite (oats, soil pH 5.5) than with KS, with both being somewhat higher than the control (1.3-1.4x).

Struvite precipitation was tested in a pilot animal slurry treatment plant in Northrhine-Westfalia, Germany, sponsored by a farmers' cooperative. The recovered struvite was then tested for fertiliser potential (nutrient availability to plants) using randomised pot experiments with four replicates and oats (*Avena sativa*) and ryegrass (*Lolium multiflorum*).

The authors conclude that nutrient availability in struvite is at least comparable to that of commercial fertilisers, even on near neutral soils, and that struvite precipitation is thus a useful tool for separating phosphorus and nitrogen from animal slurry in a form which can be used as a fertiliser.

"Plant availability of phosphorus, nitrogen and magnesium applied with magnesium-ammoniumphosphate (struvite) derived from animal slurry". Poster presented at the IWA/NVA Conference "From nutrient removal to nutrient recovery", Amsterdam, 2-4 October 2002. Poster summary available at http://www.nhm.ac.uk/mineralogy/P-recovery/

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Piggery wastes Struvite formation for N-removal

The authors studied the results of adding a struvite (magnesium ammonium phosphate, MAP) formation pre-treatment step to a 5 / 10 litre laboratory scale installation treating scrapper-type piggery waste waters. The water treated had a relatively low carbon/nitrogen ratio because most solids are separated out and not discharged in the liquid: COD around 4,300 mg/l, total nitrogen around 1,700 mgN/l, NH3-N around 1,600 mgN/l.

The pilot treatment plant used a 5.4 litre upflow anaerobic sludge bed reactor (AUBF) with a hydraulic residence time of 2.7 days followed by a 10 litre aerobic reactor with a hydraulic residence of 5 days, with sludge recycling. When the system was operated without the struvite formation pre-treatment step, the effluent nitrogen concentration ranged from 500-1,000 mg/l.

Struvite formation was induced by adding phosphate and magnesium ions to the influent before it entered the AUBF reactor, to concentrations equivalent to 1:1 ratio to 1,000 mgNH₃-N/l (0.71 molar), and increasing pH to 8.5. This caused ammonium to be precipitated as struvite, increasing the inflow carbon/nitrogen ratio from 2.8 to 6.0.

The struvite formation caused inflow organic carbon to be reduced by only 13% (average influent TCOD reduced from 4,750 to 4,140 mg/l). The struvite pre-treatment however reduced the process effluent total nitrogen concentration from 790 - 1,605 mgN/l (43% nitrogen removal only) to 350 mg total N/l (80% nitrogen removal).

The authors conclude that struvite precipitation (by phosphate and magnesium addition) can be an effective process for improving nitrogen removal from piggery waste waters with low carbon/nitrogen ratios. They suggest that the struvite could be recovered and recycled as a fertiliser.

"Struvite formation and subsequent biological process for nitrogen removal in the piggery wastewater". Paper at the IWA/NVA Conference "From nutrient removal to nutrient recovery", Amsterdam, 2-4 October 2002.

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Japan

P-recovery from piggery wastewaters

Aeration followed by settling was tested as a phosphate precipitation process for screened (1.5 mm mesh) swinery wastewaters from the Japan National Institute of Livestock and Grassland Science (NILGS) piggery, Ibaraki, Japan.

Initial batch experiments were carried out to assess feasibility and operating parametes, then a continuous-mode pilot plant (0.6m diameter, 2.43m high) was tested over a 50-day run. The swine wastewater used was relatively variable, depending on washing of the installations, with average soluble concentrations of P-PO₄ = 5.2 mmol (161 mgP/l), N-NH₄ = 39 mmol (543 mgN/l), magnesium 4.9 mmol (119 mg/l) and calcium 3.4 mmol (136 mg/l).

The initial batch mode experiments used 30 litres of screened piggery wastewater. This was first aerated in a 21cm diameter column, using a ceramic diffuser for aeration, for up to 3 hours. An optimal aeration rate of around 13 m³air/m²/hour was found, enabling the wastewater pH to be raised from 7.0 to 8.0 in half an hour, and up to pH 8.5 after 3 hours. This pH increase corresponded to a considerably decrease in I-C concentration in the wastewater, indicative of dissolved CO₂. An aeration rate of half this level was found insufficient to raise pH (no phosphate precipitation) whereas a doubled aeration rate allowed a slightly higher pH increase (pH 8.7) but without bringing a significant change in phosphate precipitation.

2 hours aeration was found to be adequate to reduce both soluble phosphate and magnesium from around 5 mmol to below 1 mmol, with continuing aeration on to 3 hours resulting in only a very small further reduction. The changes in concentrations of soluble/insoluble phosphate, magnesium, ammonium and calcium led to the conclusion that a mixture of struvite (magnesium ammonium phosphate) and calcium phosphate crystals were being formed.

To test the settling of the precipitated phosphates, half of the batch aeration solutions (15 litres) was poured into a vertical 10cm diameter cylinder (190cm depth), with sampling ports along its sides, and allowed to settle for one hour. Samples were taken from ports 40 and 90 cm above the cylinder bottom

after 15, 30, 45 and 60 minutes, and from the bottom of the cylinder at the end of the hour settling.

Sampling showed that after 15 minutes, the phosphate crystals had almost entirely settled below the port 90cm above the cylinder bottom, but that 30 minutes were required to reach low levels 40cm above the bottom. After one hour, for different batches, 90-92% of the precipitated phosphates (calculated from changes in soluble concentrations during aeration) were recovered in the settled solids on the cylinder bottom.

Continuous pilot plant

On the basis of the information gathered from the batch experiments, a **pilot reactor** was constructed an aeration zone (central 0.3m diameter column) surrounded by a settling zone (2.43m high, 0.6m diameter outer cylinder). The aeration rate was set at 26 m³air/m²/hour, higher than the optimum derived from the batch experiments, to allow for scale-up efficiency loss. Total residence time in the whole reactor was 22 hours (inflow/outflow rate = $0.024m^{3}$ /hour of wastewater), with an upflow velocity of 0.11 m/h in the settling zone.

This installation achieved a pH of 8.0 in the aeration zone, but this decreased to 7.6 at the reactor outlet (at the top of the settling zone), probably because the wastewaters were becoming anaerobic in the unmixed settling zone.

The plant, over a 50-day run, achieved average removal rates of 65% for soluble phosphate, 51% for magnesium and 34% for calcium. The plant achieved a reliable concentration of 1.7 mmol soluble phosphate despite very variable inflow concentrations (average 4.8 mmol P-PO₄ inflow wastewater).

Around ³/₄ of the precipitate was calculated to be struvite, and 1/3 calcium phosphate. The authors considered that the settled sludge, containing a mixture of small suspended solids from the screened wastewater and the precipitated phosphates, could be dehydrated to provide a soil conditioner or used in compost, because of the fertiliser value of the struvite.

The authors suggest that the process provides a simple and reliable method of consistently reducing phosphate and magnesium levels in piggery wastewaters, both reducing risks of struvite scaling and deposit problems and allowing phosphate recovery for recycling to agriculture.

"Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration". Water Research 36, pages 2991-2998, 2002.

K. Suzuki, Y. Tanaka, T. Osada, M. Waki, Waste Recycling Laboratory, National Institute of Livestock and Grassland Science (NILGS), 2 Ikenodai, Kukizaki-cho, Inashiki-gun, Ibarakai, 305-0901 Japan. szkazu@affrc.go.jp

Tennessee Optimising struvite recovery from swine wastes

Waste waters from two different piggeries were used for laboratory struvite precipitation experiments, to better define optimal conditions for struvite precipitation, as a means of reducing waste water phosphate content and to recover phosphates in a recyclable form.

High concentration supernatant was collected from a pull-plug pit under a pig farrowing unit (average around 1,000 mg/l phosphate, 51,000 mg/l COD). Low concentration supernatant was taken from a holding pond at a feeder pig unit operating a recycle flush system (average 230 mg/l phosphate, 410 mg/l COD).

Previous work by the authors had shown that a 90% reduction in soluble phosphate content could be achieved by adding magnesium to a 140,000 litre pig slurry holding pond, resulting in struvite precipitation. This work aimed to better define cost-effective conditions for struvite precipitation, and to try to achieve precipitation in a recoverable form, allowing separation from the slurry and recycling. (In "Environmental Technology" 22, pages 1273-1278, 2001 available at

http://www.nhm.ac.uk/mineralogy/phos/Nordwijkerhout/Environ mental Technology/Burns.doc

Experiments used 200 or 400 ml of waste water in a laboratory beaker, with addition of 60% magnesium chloride as a magnesium source, and in some cases sodium hydroxide to raise the pH. Magnesium chloride has the advantage of high solubility (ease of handling, effective reaction) but is slightly acidic, tending to reduce the pH of the wastewater when added, which is contradictory with the fact that struvite precipitation is facilitated by a pH increase.

Different reaction times of 10, 20, 30 and 40 minutes were tested, both at the wastewater's initial pH 7.4 and 7.5) and with pH adjustment to pH 8.5. A

reaction time of 10 minutes proved to be adequate, with an improvement in phosphate precipitation of only 1-4% when after 40 minutes. The pH increase, on the other hand, significantly decreased the residual phosphate concentration by a factor of 2-3. However, the authors note that the use of sodium hydroxide to adjust pH is unlikely to be economically viable.

Molar ratio

The effects of increasing the molar ratio of added magnesium were also tested. The authors' previous work cited above had suggested that the molar ratio of magnesium addition should be based on soluble phosphate and soluble magnesium (not total) with ratios significantly higher than 1:1 being appropriate. In this work, ratios varying from 1.6:1 to 3.5:1 were tested.

The results showed that the ratios higher than 1.6:1 soluble magnesium:soluble phosphate did not significantly improve phosphate precipitation. Further experiments would be needed to evaluate whether adequate precipitation efficiency could be achieved with ratios lower than 1.6:1 (the theoretical molar ratio of magnesium:phosphate in struvite is 1:1).

Seeding

Experiments were also made with the addition of struvite or of sand particles to attempt to "seed" the precipitation reaction and generate larger struvite particles, easier to separate from the waste water, recover and recycle.

The addition of struvite seed did not appear to usefully increase the size of precipitated struvite particles, nor to improve the phosphate precipitation. **The sand seed, however did result in an increase in precipitated struvite size**, after 1-2 hours, though the larger particles appeared by observation to be independent of the sand particles. Also the phosphorus removal was improved when the sand seed was added. However, the improvements gained were not significant enough to justify additional costs or manipulations. The authors suggest that more work is needed in this area.

The precipitated phosphate was analysed and showed the presence of both struvite (magnesium ammonium phosphate) and brushite (a calcium phosphate). The molar ratio of magnesium: ammonium: phosphate in the precipitate was 1:0.74:3.2, showing that it is not pure struvite, but has a **higher phosphate content** **than struvite** which would be positive for recycling. This also suggests that the molar ratio of magnesium addition could probably be reduced, thus reducing costs.

The authors concluded that further experimental work is needed on a number of parameters, and also the development of on-farm processes producing precipitated struvite in a form which can readily be recovered and recycled.

"Optimization of phosphorus precipitation from swine manure slurries to enhance recovery", paper presented at the IWA/NVA International Conference "From nutrient removal to nutrient recovery", Amsterdam, 2-4 October 2002, publication expected in Water Science and Technology http://www.iwaponline.com/wst/toc.htm

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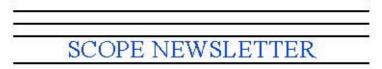
Struvite

Parameters for struvite deposits and recovery

The two papers on struvite precipitation chemistry and behaviour published by Doyle, Parsons *et al.* in "Water Research" provide a thorough summary of current knowledge and references in this area, and further new experimental evidence of the differences in struvite precipitation rates on different materials at different roughnesses.

The overview paper "*Struvite formation, control* and recovery" provides information on the impacts of struvite deposit formation in sewage works, struvite chemistry, precipitation and scale formation factors, struvite deposit prevention techniques, and struvite recovery for phosphate recycling.

Struvite deposits are an increasing problem in sewage works worldwide, in particular as a consequence of nutrient removal installation and of efforts to reduce sludge production, which both concentrate nutrients in sludge streams (and thus ammonia, phosphate and magnesium, which can react to form struvite – magnesium ammonium phosphate). Struvite deposits can reduce pipe diameters, increasing pumping costs or even



necessitating acid soaking to dissolve the deposits or pipe replacement, and can also affect filters, pumps and other equipment. Resulting costs for a medium size sewage works have been reported to easily reach US\$100,000/year.

Phosphorus recycling

Different work on the chemistry of struvite precipitation is reported, including a table of the **solubility constants** K_{sp} calculated by different authors. These vary significantly, probably as a result of pH and wastewater chemistry. Struvite is generally found to be least soluble (and so most likely to precipitate) at around pH9. Struvite solubility is particularly affected by the presence of calcium ions. The different models of struvite solubility ("Struvite", "Minteq+", and Mustovo *et al.* kinetic model) are discussed.

Struvite recovery from waste waters as a route for phosphorus recycling is presented. Struvite recovery is achieved by adding magnesium and/or increasing pH, the latter either by chemical addition or by aeration. Key experimental and pilot reactor experiences are referenced and tables show examples of waste streams with their struvite recovery potential and recovery costs as calculated by different authors.

Materials surfaces

The second paper "Struvite formation and the fouling propensity of different materials", presents experimental results concerning struvite precipitation rates on different materials' surfaces: stainless steel, acrylic (polymethyl methacrylate) and Teflon (polytetrafluoroethylene), smooth or roughened. The materials were attached to the stirrer in 1 litre beakers of anaerobically digested sludge centrate liquor from a sewage sludge treatment plant. The material surface was around 50 cm2.

Stirring at 150 rpm proved sufficient to increase the pH of the liquors from pH 7 to pH 8.2. The rate of deposit of struvite on the stirrer material samples was measured over 8 hour runs, with samples being used for three consecutive experiments to assess how the deposit rate changed with the progressive formation of a layer of struvite. The acrylic and Teflon materials were tested both smooth as new, and roughened homogenously with fine and with rough silicon carbide papers.

Struvite deposition was shown to be considerably lower on Teflon than on stainless steel, and considerably lower again on acrylic (less than one tenth of the rate on steel). However, for all materials, deposition increased with reuse, showing that once initial struvite deposits have started to form this can accelerate the process. Roughening of the acrylic and Teflon materials considerably increased struvite deposition rates (bringing acrylic up to nearly half the rate for steel).

This confirms previous work showing lower struvite deposit rates on smoother materials in a study comparing iron, glass fibre reinforced plastic, techite and PVC.

The authors note that these results mean that although smooth materials may initially result in lower struvite deposit rates in sewage works this effect may well not be durable, as the material is roughened by sand and grit in sewage.

"Struvite formation, control and recovery", Water Research 36, pages 3925-3940, 2002. J. Doyle¹, S. Parsons¹

"Struvite formation and the fouling propensity of different materials", Water Research 36, pages 3971-3978, 2002. J. Doyle¹, K. Oldring², J. Chruchley², S. Parsons¹.

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Water Research: http://www.elsevier.com/locate/issn/00431354

Water quality

Slovenia Phosphorus load estimates

The authors used material flow analysis to develop a phosphorus balance for the lower Krka River basin in Slovenia. This basin has an area of 650 km^2 (3.2% of the land area of Slovenia) with a population of 52,000 inhabitants, including the strongly urbanised and industrialised Novo Mesto town area upstream. 46% of the land surface area is forest, and around one third cultivated agricultural land, the remainder being pastures and wetland.

During 1996-1997, 17 sampling surveys of water quality from 5 different main river locations were carried out. In parallel, material flow analysis was carried out to estimate the total phosphorus loads from wastewater treatment plants septic tanks and direct discharges of sewage into the river, agricultural and land run-off and atmospheric deposition.

Around one third of the catchment's domestic sewage was collected (17,000 households) and treated in an activated sludge sewage works (nutrient removal not installed).

For households with septic tanks, 95% of phosphates are commonly removed after passing through a few metres of soil (Gilliom and Clayton 1983).

A hypothesis of improved sewage treatment was developed, based on Slovenian law (1996) which requires collection of sewage and nutrient removal in sewage works (80% P-removal expected).

Agricultural phosphorus losses were estimated on the basis of 1.5 kg/hectare/year, based on typical figures given by the US EPA (1984). Livestock discharges were estimated at 1% of total annual manure phosphorus production. An improved land management scenario estimated that agricultural loadings could be reduced by 10% by Best Management Practices including soil conservation, nutrient management, feedlot management, removing most polluting fields from production, etc.

Half of P-loads from sewage

Total phosphorus loads to the Krka river were estimated to be 81.8 tonnesP/year, and this estimate was confirmed by the rivers sampling and flow data (see Drolc 1998). Wastewater discharges were estimated to make up just over half of phosphorus loadings (52.2%), mostly via sewage works discharges (49.5% of total loads) with leaching via septic tanks making up only 2.3% of the total P load.

Agriculture was estimated to contribute 44.6% of total phosphorus loads, mainly through diffuse sources (only 3.9% of total from point sources – direct discharge of manures). Atmospheric deposition was also estimated to contribute 3.2%.

Wastewater treatment

The hypothesis of upgrading of sewage treatment according to current Slovenian law led to an estimated reduction in wastewater phosphorus loads from 42.7 to 16.1 tonnesP/year, that is a 62%

reduction. If at the same time, reductions in agricultural phosphorus loads were made by Best Management Practices and changes in land-use, this would reduce agricultural loads by around 10%.

In this case, wastewater would then provide only one third (33.1%) of total phosphorus loads to the river, with an overall reduction in all loadings of 18% being achieved.

"Estimation of sources of total phosphorus in a river basin and assessment of alternatives for river pollution reduction". Environment International 28 (2002) pages 393-400 www.elsevier.com/locate/envint

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Baltic Sea

Dissolved phosphorus linked to water movements

The Baltic Sea is semi-enclosed and brackish. Saltier, and so denser, water can flow into the Baltic from the North Atlantic, over the shallow sills of the Danish Straits, displacing the deep bottom water of the Baltic. 96 major inflows of this type have been recorded over the last century, but only a few since the mid-1970's and only two since 1980 (in 1983 and 1993).

The absence of such inflows is thought to have resulted in a "stagnation" of the bottom waters of the Baltic.

However, the widely used term "stagnation" appears to be inappropriate. The authors show that, contrary to expectations, the mixing of the Baltic was in fact greater during the long "stagnation" period 1983-1993. They suggest that the absence of major inflows reduces the salinity gradient in the Baltic, facilitating vertical mixing (the deep waters are not sufficiently more saline = heavier than upper waters to resist turbulent diffusion). Further, in between the major inflow events there have been many smaller inflows, which bring oxygenated water into the Baltic but may not enable the establishment of the salinity gradient which inhibits vertical mixing.

The authors show that during the prolonged "stagnation" 1983-1993, the area of hypoxic bottom waters (oxygen depleted) fell to only 5% of total



bottom water area (from a peak of 27% in the early 1970's). Also in this "stagnation" period, intermediate depth water (80-120m) had higher oxygen concentrations.

Implications for phosphorus

It is well documented that sediments can act as "sinks" for phosphorus from water when oxygen is available (in particular through P binding to iron) but that the phosphorus may be released back into the water in conditions of low or zero oxygen availability (hypoxic or anoxic conditions).

The authors show that, for the Baltic, changes in the pool of available phosphorus in the sea (water DIP = dissolved inorganic phosphorus pool) are effectively coherent with the changes in the area of hypoxic bottom water, and that oxygen concentrations were significantly negatively correlated to DIP concentrations in the hypoxic bottom waters. The DIP accumulation during expansion of the area of hypoxic bottom waters is about the same as the DIP losses during contraction.

Over the period of the study, total annual phosphorus loadings to the Baltic have varied within the range 23,000-37,000 tonnesP/year, without significant overall time trends. Although there have been reductions in fertiliser use and reductions in discharges through improved sewage treatment, these have not in fact substantially reduced total external phosphorus loadings (reductions of <1,000 tP/year).

Furthermore, the Baltic is estimated to export some 17,000 tP/year to adjacent sea basins, including 11,000 tP/year to the North Sea through the Danish Straits.

The variations in external P loads cannot thus explain the annual variations in the water phosphorus pool (DIP).

The authors conclude that large reversible variations in sediment phosphorus storage, related to climate events and water movements rather than to anthropogenic P loadings, will make it more difficult over the short term to manage phosphorus as the limiting nutrient in the Baltic.

"Hypoxia in the Baltic Sea and Basin-Scale Changes in Phosphorus Biochemistry", Environ. Sci. Technol. 2002, n°36, pages 5315-5320.

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Michigan, USA Nitrogen addition increases stream periphyton growth

Six different nutrient addition concentrations were tested for impact on periphyton response (algae growing on stream-bed surfaces) in continuously flowing natural streamwater: three N:P molar ratios (65:1, 17:1, 4:1) at high and low nutrient concentrations. Each combination was subject to 5 simultaneous replicates (total 30).

The experiments were run for 28 days using the University of Michigan Biological Station Stream Research Facility. This offers 30 parallel once-through "flumes" (2.8m long, 10cm wide, 7cm deep vinyl gutters) through which water from East Branch Maple River is continuously pumped.

Natural stream water

This stream flows through forests, draining Douglas Lake and receiving considerable groundwater inflows, thus offering stable concentrations of nutrients. The stream's nutrient concentrations, without N or P addition, corresponded to the high N:P ratio / low total nutrient concentration configuration (dissolved inorganic nitrogen DIN around 43 μ gDIN/l, soluble reactive phosphorus SRP around 1.4 μ gSRP/l). The low and medium N:P / low total nutrient concentrations were obtained by adding soluble phosphorus to the flume inflow (using peristaltic pumps), and the high TNC configurations by adding soluble N (up to around 140 μ gDIN/l) as well as soluble P.

Water velocity in the plumes was maintained at 35-40 cm/s, temperature was around 12-17°C and artificial shading was used to reduce light intensity to around 15% of incident light comparable to the natural forest shading of the stream itself.

Periphyton increase with nitrogen addition

Development of periphyton was examined on 70 previously sterilised clay tiles (49 x 35 x 10 mm) placed in each plume. Periphyton was collected from

randomly chosen tiles at days 9, 17 and 28 and chlorophyll-*a*, total periphyton biovolume and species composition were assessed. The 28 day period was long enough for the complete cycle of periphyton appearance, growth and sloughing off to have taken place.

Higher TNC resulted in significant increases in periphyton chlorophyll-*a* and biovolume at day 9, but with this effect being diminished by day 28, because of loss of biomass through sloughing by this time. The addition only of P (medium and low N:P ratios, low TNC) did not give any increase in periphyton biovolume or chlorophyll-*a* at day 9, and not clearly at day 17. Both biovolume and chlorophyll-*a* were, on the other hand, higher with high N additions. The authors indicate that this was "contrary to our prediction that P would limit periphyton growth based on the high N:P ratio in the source ratio and unamended periphyton mats".

The dominant algal group was diatoms (93% of periphyton biovolume). Of 11 common algal taxa counted, the relative abundance of 9 was affected by the changes in nutrient ratio or of total nutrient concentrations. Algal community structure was generally more sensitive to the changes than the overall algal volume.

The ratio N:P in the algal biomass mirrored closely changes in the water N:P ratio, driven mainly by changes in biomass %P. The %N in the algal biomass mirrored water N concentrations and was unaffected by the water N:P ratio.

The authors note that the stream N:P ratio (around 63:1) considerably exceeds the "Redfield Ratio" of 106C:16N:1P. The Redfield Ratio was empirically determined for oceanic seston, but is widely used for eutrophication modelling. Habitual eutrophication thinking would thus expect phosphorus to be the "limiting" nutrient in the stream. The authors conclude that, contrary to this expectation, algal growth was stimulated by N and not P concentrations: algal chlorophyll-a and biovolume were high in all high-N experiments and low in all experiments, whereas low-N increasing Ρ concentrations within a given level of N concentration did not result in increased algal biomass.

"Effects of N:P ratio and total nutrient concentration on stream periphyton community structure, biomass and elemental composition". Limnol. Oceanogr. 46(2) 2001 pages 356-367. R. Stelzer, G. Lamberti, Dept. Biological Sciences, University of Notre Dame, Notre Dame, Indiana 46556-0369, USA. Current postal address: R. Stelzer, Dept. of Biology and Microbiology, University of Wisconsin Oshkosh, Oshkosh, WI, 54901-8640, USA. stelzer@uwosh.edu

Lowland river Impact of sewage nutrient removal

A three-year study of the lowland river Wensum, Norfolk, England, published by the UK Environment Agency, examines dissolved and sediment phosphorus concentrations before and after sewage works P-removal implementation. Aquatic plant (macrophyte) populations were studied to assess the impact of this change in phosphorus loadings on populations.

The river Wensum is a prime example of a *Ranunculus* dominated calcareous lowland river specified in the EU Habitats Directive, one of England's 27 SSI (Site of Special Scientific Interest) designated rivers, and a proposed Special Conservation Area. The catchment studied (upper river) was 571 km2.

Around 50 point sources of phosphorus were identified in the catchment, with a total phosphorus load of 85 kgTP/day from sewage works and 43 kgTP/day from industrial point sources (mainly food processing industries). Of these, two municipal sewage works, Fakenham (19 kgTP/day) and East Dereham (32 kgTP/day), providing dominant contributions before implementation of Pimplementation, phosphorus removal. After discharges from these sewage works were respectively reduced to 6.95 kgTP/day (overall 77% P-removal) and 9.35 kgTP/day (88% P-removal).

Diffuse agricultural phosphorus loads to the Wensum river were estimated by using figures for per hectare releases from a dozen previous studies of similar catchments in Norfolk (figures quoted ranged from 0.075-0.101 to 0.231 kgTP/hectare/year). This corresponded to a predicted concentration of 53 μ gTP/l in the river, exceptionally low for this area of England at 12% of total phosphorus loadings to the river, increasing to **32% of total-P from agriculture** after P-removal implementation in the two sewage works.

The Wensum also has four tributaries unaffected by known point sources of nutrients, providing a valuable comparison for the study of plant communities, and of impacts of diffuse nutrient loadings. Mean concentrations of total phosphorus in these sub-catchments were 39-77µgTP/l, presumably corresponding to diffuse loadings.

Impacts of phosphorus removal

The point sources of phosphorus along the river were found to considerably influence the in-water phosphorus concentration, whereas the **levels of phosphorus in sediments were much more influenced by the presence of weirs** (phosphorus levels in sediments much higher immediately upstream of weirs, in the pool of impounded water, than immediately downstream).

The P-removal at these two principal sewage works proved not sufficient to bring dissolved phosphate concentration levels down to target levels for such a river (EPV0 10-60 μ g/l). However, **concentrations may be buffered by release of sediment phosphorus**, so that effects may become significant only after a few years. The levels of diffuse loads would also be an obstacle to achieving these objectives.

Macrophyte plant communities not correlated to nutrient concentrations

Plant communities were studied at 62 sites in the catchment, to compare populations in waters with different nutrient concentrations. Aquatic vascular plants populations characteristics, including density, species composition, species traits and community structure, were not found to be correlated significantly with nutrient concentrations over the range of soluble phosphorus 11-3600 µgSRP-P/l and ammonium 16-434 µgNH4-N/l. Sediment phosphorus availability was also not significantly correlated with plant characteristics.

"Assessment of the Impact of Nutrient Removal on Eutrophic Rivers" Environment Agency R&D Technical Report P2-127/TR,, November 2002. B. Demars, D. Harper, University of Lancaster.

http://www.eareports.com/ea/rdreport.nsf/e92ef76ffa1cc0b68025 6975002e8822/5cf5e368dce2e6a380256cda0043207d?OpenDoc ument

European Union Workshop Defining eutrophication criteria

The EU Commission's "Workshop on Eutrophication Criteria" (28-30 May 2002), chaired by the EU Directorate General for Environment, brought together scientific experts and representatives of the Member States. A clear and practical definition of "eutrophication", for different types of surface waters, is necessary for the implementation of key EU water legislation, in particular the Urban Waste Water Treatment Directive (91/271), the Nitrates Directive (1991/676) and the new Water Directive (2000/60).Framework The Workshop's objective was to start the process of establishing such an operational definition of "eutrophication", in order to enable Member States to decide and to engage appropriate actions to protect and restore surface waters as required by these Directives.

The Urban Waste Water Treatment Directive (91/271) requires Member States to identify "*eutrophication sensitive areas*" and to implement nutrient removal from sewage for all conurbations of >10,000 person equivalents in these areas (and also in smaller conurbations where appropriate). This Directive includes a definition of eutrophication:

"The enrichment of waters by nutrients ... causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the water balance of organisms ... and to the quality of the water concerned".

This definition thus clearly indicates that "eutrophication" must be assessed from the endpoints of ecological and water quality changes, and not simply on the basis of nutrient chemistry or even just of increased algal development (if this does not have detrimental impacts).

Definition and implementation

The Workshop agreed that this definition provided a good starting point. However, the EU Commission considers that "*Member States so far show some reluctance in designating sensitive areas*" and has recently drawn attention to the inadequacy of sensitive area designation in several states, including by taking certain states to the European Court (see

SCOPE Newsletters $n^{\circ}s$ 46, 47 – 2002 at *www.ceep-phosphates.org*).

This is indicative of the need to develop, starting from this outline definition of "eutrophication", operational criteria applicable to different types of water body.

The **Nitrates Directive** (1991/676) further requires Member States to monitor the eutrophication status and eutrophication symptoms, effects and trends of "vulnerable areas". This again requires an operational definition of "eutrophication" and of criteria and monitoring parameters for these criteria.

Eutrophication and "good ecological status"

The Water Framework Directive (2000/60) brings EU water legislation into a coherent integrated system, based on concerted catchment management and on the legal obligation to define and achieve "good ecological status" in all surface waters by 2015 (with the exception of heavily degraded/ modified water bodies), whilst maintaining the obligations of the Urban Waste Water and the Nitrates Directives. This therefore necessitates defining what "good ecological status" means in terms of eutrophication.

The challenge, as for the other aspects of water and biological quality, is to establish European guidelines for defining eutrophication which both allow harmonised European implementation of the Directive, monitoring and reporting, but also allow catchment managers to be responsive to local ecological specificities.

The Water Framework Directive's definitions relevant to eutrophication are coherent with that of the Urban Waste Water Directive. "Good ecological quality" is defined for phytoplankton (example of "lakes") as changes not "resulting in undesirable disturbance to the balance of organisms ... or to the physico-chemical quality of the water or sediment", and for nutrients "concentrations do not exceed the levels established so as to ensure the functioning of the ecosystem and ... the biological quality elements".

Taking these endpoint-based definitions as starting points, the Workshop concluded "It is important to use an operational approach when defining 'eutrophication', rather than a strict etymological approach. This means that **the attribute 'eutrophicated' should be given to ecosystems that exhibit deleterious effects of excessive primary** **production** (intense phytoplankton and/or macrophyte proliferation, increased toxic phytoplankton events, hypoxia in the bottom waters), but **not to ecosystems where there is only nutrient enrichment**, but no present or potential noxious effects on the ecosystems and/or on water use."

The Workshop thus agreed <u>an "operational</u> <u>definition" of eutrophication</u> could be: "A new state of enrichment of the ecosystem, compared with pristine conditions, creating clear degradation or nuisances both for human uses of water and for general water quality (shift of species with loss of biodiversity, flora and fauna morbidity)."

The Chairman therefore concluded: "The remaining task would be to move from definitions to a common understanding of the acceptable level of shift of structure and function of the ecosystem, compared with reference conditions and the degree of acceptable adverse indirect effects on the water quality and water use."

Eutrophication criteria for different types of surface water

Participants at the workshop emphasised that: "It is not only the specific nutrient concentrations as such that are important, but also the balance or ratio between Si:N:P and the deviation from the natural ratio. Natural eutrophication occurs (nonanthropogenic) all over the world; the difference between this and the man-made eutrophication is the speed at which they develop and, in many cases, the differences in magnitude of variation (amplitude)."

The reactions to nutrient enrichment and the significance of related changes in phytoplankton and other ecosystem dynamics vary considerably between different types of surface waters. This is also true of many other water quality factors, and the EU is therefore currently developing a classification of surface water types with as an objective Water Framework Directive implementation guidelines for each type. For example, some 100 different types have been identified just for coastal waters, with the objective being to rationalise this down to 30-50 types. An European Commission Joint Research Centre project currently underway aims to map a "<u>eutrophication risk index</u>" for all of Europe's coastal waters.

In some cases the **costs of achieving the "good ecological status"** required by the Water Framework

Directive may be unreasonably high, and it may thus be appropriate to try to assess what status of ecological quality can be economically achieved. This corresponds to the concept of "**Thresholds**". See article in SCOPE Newsletter n° 48 at *www.ceep-phosphates.org*

Case studies

A number of case studies of eutrophication problems in European waters and attempts to address these were presented. These showed the **difficulty of defining nutrient levels for ecosystem restoration or management**, and the complexity of ecosystem reaction to nutrients and to other man-made changes.

In several cases of inland lakes (Lade Constance, Lake Geneva, Lac du Bourget France, Neusiedlersee Austria, Lakes Mjosa and Gjersjoen Norway ...) considerable reductions of phosphate inputs have been achieved over the last 15-20 years, essentially through sewage treatment (nutrient removal), but phosphate inputs are still higher than "natural" loadings. **Nitrogen inputs have not been so successfully reduced, because of loadings from agriculture**. Recovery in these lakes has been variable, showing the differences between different water bodies, and in many cases has been slower than hoped because of internal loadings and because of the practical difficulty in achieving nutrient loadings as low as or near natural, pristine conditions.

H. Fleckseder (Austrian Environment Ministry) presented the successful restoration of Lake Neusiedlersee, emphasising the importance of sewage nutrient removal: "the total cost increment for that part of wastewater treatment that refers to the removal of nitrogen and phosphorus is relatively small compared with the cost of sewerage and wastewater treatment". The Lake's restoration also included re-establishing balanced natural fish populations, buffer vegetation strips on agricultural land, and harvesting of reeds to remove organic production.

Speakers emphasised the variations of ecosystem response to changes in nutrient loadings, with other **factors such as climate and transparency having considerable effects on algal development, and zooplankton populations playing an important role (grazing of algal biomass)**. The Workshop indicated that zooplankton should be monitored in lakes (species composition and abundance) and questioned why zooplankton were not included in the biological quality parameters for lakes listed in the Water Framework Directive.

For coastal/marine waters, OSPAR's current approach of moving beyond the existing 50% targets nutrient reduction towards targeted eutrophication management of coastal ecoregions, operational definition of also requires an eutrophication (OSPAR Common Procedure for the Identification of the Eutrophication Status of coastal and marine waters).

Case studies of coastal/ marine waters included the North Sea, the Baltic and the Mediterranean. Again, the considerable complexity of reaction to nutrient enrichment was apparent, with in coastal waters nitrogen often being the key limiting nutrient, but both nitrogen and phosphate levels and ratios having implications for development of toxic algal blooms.

<u>The Workshop concluded that:</u> "It would be advisable not to propose absolute threshold values for nutrient concentrations, as they cannot be considered alone as reliable risk evaluators because the hydrodynamics and physical characteristics (depth, turbidity) modulate strongly the nutrient role."

Eutrophication monitoring parameters

The Workshop considered that eutrophication monitoring should aim to assess whether the ecosystem is undergoing an "acceptable deviation" from reference ecosystem parameter levels. Eutrophication monitoring should therefore include:

a) causal and basic response parameters:

* total nitrogen

- * total phosphorus
- * chlorophyll_{-a}
- * water transparency (Secchi disk depths)
- b) ecosystem response parameters:
- * dissolved oxygen
- * macrophytes
- * phytoplankton index

(% blue greens, bloom frequency)

- * fish index
- * pH
- * benthic community index
- * autotroph index
- * algal growth potential (bioassays)

"Workshop on Eutrophication Criteria", Brussels 28-30 May, 2002. European Commission, Directorate General Environment (ENV.B1 – Water, Marine and Soil Environment)

Conference announcement Eutrophication of waters from diffuse sources.

The 7th International Conference on Diffuse Pollution and Basin Management (*DiPCon*) 17-22nd August 2003, Dublin

There is increasing awareness that diffuse sources of nutrients are a major component of the eutrophication of surface waters, and that build up of both phosphorus and nitrogen in ground waters originate from activities throughout a catchment.

In recent years, widespread improvement in phosphorus removal facilities at waste water treatment plants and reduction in supply of phosphorus from detergents has necessitated **a reassessment of source of nutrients to freshwaters**. There is an increasing focus on the relationship between land management and nutrient supply from a variety of diffuse sources. These are both difficult to quantify and control.

Since the first conference in Chicago in 1993, the International Water Association has organised a serious of conferences on diffuse pollution in Prague (1995), Edinburgh (1998), Bangkok (2000), Milwaukee (2001) and Amsterdam (2002). Parallel initiatives have occurred at national and international level. For example since July 1997 an EU COST (Co-operation in Science and Technology) Action has been operative to (i) develop a common technical understanding of the processes, forms and pathways of P loss in land run-off, and (ii) develop a methodological framework for identifying the relative contribution of different diffuse P sources at catchment level the farm and (see http://www.cost832.alterra.nl). Recently 3rd the International Workshop on Phosphorus Transport took place in Plymouth, England (reported in SCOPE *Newsletter* n° 46).

This attention to diffuse sources of nutrient enrichment has begun to unravel some of the mysteries of phosphorus and nitrogen movement from catchment to water. We now know, for example, that the majority of phosphorus can come off the land in only a few storm events in the year; that the mechanism of nutrient movements can be quite different between arable and grassland systems; and that inherent properties of the soil, past-history of fertilisation and antecedent moisture conditions can all be important controls on phosphorus transport. An equally complex, but different, set of factors controls net movement of nitrogen from land to water.

The new **Water Framework Directive** (2000/60/EC) requires that of activities within catchments that pose a risk to the maintenance of good water status are verified by monitoring, a programme of measures needs to be initiated that reduces impact on surface, ground and coastal waters. The implication for current agriculture and other activities, such as forestry, that provide the pressures to aquatic systems could be enormous.

Recent actions taken or initiated by the EU against member states for failure to comply with the Directives on Nitrates (*91/676/EEC*) and Dangerous Substances (*76/464/EEC*) suggest that compliance with the Water Framework Directive will also be carefully monitored.

The need, therefore, to understand the mechanisms that drive diffuse nutrient enrichment appears self-evident.

The 7th International Conference on Diffuse Pollution and Basin Management (*DiPCon*) 17-**22nd August 2003, Dublin, will bring together** researchers, practitioners and regulators from many countries, to share experience in understanding issues of diffuse pollution as it affects aquatic systems.

The conference in Dublin in 2003 will be the first time the regulatory aspects of pollution control will be given prominence. It will also be the first international diffuse pollution conference to have a major theme focusing on marine and transitional waters, in parallel with the traditional themes concerning urban and rural land-uses. 2003 also sees the start of the next major cycle of EU Common Agricultural Policy (CAP) review. The Dublin 2003 conference will provide an international forum to consider practical experience of agricultural support schemes with contrasting examples from North America, EU countries and elsewhere. The conference aims to play a role in developing best practice for World Trade Organisation compliant agricultural support mechanisms, consistent with state of the art understanding and management of environmental consequences.

The implications of the Water Framework Directive, which reflects international moves towards integrated environmental management, will provide a current



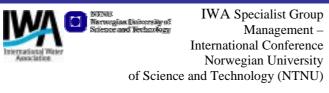
management context to the conference and one which is of relevance to all parts of the world.

The *Dublin 2003 Conference* will focus on opportunities and solutions relating to the diffuse pollution control aspects of water management.

Conference themes include:

- Integrated Water Resource Management (including impact of EU Water Framework Directive)
- Policy and Socio-Economic Considerations
- Agricultural Pollution Abatement Strategies (e.g. Cross Compliance)
- Sustainable Urban Drainage Systems (SUDS)
- Forestry and Mining Issues
- Maritime and Coastal Area Issues
- Groundwater and Baseflow Protection
- Aquatic Ecology and Dangerous Substances
- Organisation for Basin Management (including Transboundary Pollution Management)
- GIS Modelling and Remote Sensing
- Public Consultation and Awareness/Education
- Regulatory Framework

The 7th International DiPCon Conference on http://www.ucd.ie/~dipcon/dipcon.htm



BIOSOLIDS 2003 Wastewater Sludge as a Resource

Trondheim, Norway 23-25 June, 2003

Programme includes: sludge minimisation, sludge characteristics, sludge dewatering, pre-treatment and aerobic digestion, treatment technologies for land use –hygiene, case studies, **phosphate recovery (Wed. 25th June, 8h30-10h25)**, energy recovery, recovery of specific products, final handling of biosolids and future perspectives.

Phosphate recovery session includes: Recovery of phosphate from sludge – a Dutch analysis,
Phosphorous and coagulant recovery by alkaline sludge treatment, Phosphorus recovery by one- or two-step technology with use of acids and bases,
Recycling of sludge with the Aqua Reci – process

http://www.ivt.ntnu.no/ivm/Biosolids2003/

The SCOPE Newsletter

The SCOPE Newsletter is produced by the Centre Européen d'Etudes des Polyphosphates, the phosphate industry's research association and a sector group of CEFIC (the European Chemical Industry Council).

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.

The SCOPE NEWSLETTER is produced by CEEP - a sector group of CEFIC,

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SCOPE NEWSLE

Italy

NUMBER 49

Detergent phosphates

STPP

page 2 Rapid hydrolysis of detergent phosphates in sewage

rapidly polyphosphates (STPP) Detergent are hydrolysed in sewage. They are still detectable in the inflow to a sewage works with a very short sewer system, but not in sewerage networks with longer hydraulic residence times.

Phosphorus recycling

Low temperature heat page 3 **Recovering phosphate from bio-P sludges**

Low temperature heating (around $70^{\circ}C$) suffices to release nearly all the accumulated phosphorus from biological P-removal sewage sludge (EBPR), and the released phosphate readily precipitates under calcium addition without pH adjustment, giving a product offering interesting potential for recycling.

Japan

page 4

The Ebara struvite recovery process has been considerably improved, achieving 92% recovery rates, by adding a secondary process tank to keep seed particle size in the main reactor constant.

Twin tank struvite precipitator

Kinetics of struvite reactors

Japan

page 5

An experimental stirred reactor was used to study the kinetic conditions of struvite recovery, including stirring energy.

Turkey

page 6

Struvite from sewage and landfill leachate

Summarv text front page for Beaker tests show that 70-85% of ammonia can be removed as struvite (MAP) from municipal waste water and/or landfill leachates, enabling recovery for recycling.

Turkey Struvite from industrial wastewaters

page 7

Beaker tests show that struvite precipitation can achieve up to 83% ammonia recovery from wastewaters from tannery, opium and bakers yeast industries.

February 2003 page 7

Modelling P-recovery process

Following previous papers presenting successful Precovery experiments at the lab. scale, and the commissioning in 2001 of a full-scale pilot plant at Treviso sewage works, this paper a reactor operating model for P-precipitation.

Phosphate recovery page 9 Calcite and silicate seeding improves calcium phosphate precipitation

Experiments show that calcium carbonate (calcite) and Tobermorite (calcium silicate hydrate) seeds enable effective phosphate elimination from chemical solutions and from real wastewaters at pH 8. The effect seems to improve with re-use of the seed, possibly because of coating with calcium phosphate.

Phosphate precipitation chemistry page 11 Carbonate inhibition of calcium phosphate precipitation

A series of experiments show the interactions between calcium carbonate (calcite) and calcium phosphate precipitation. Calcite seed addition is shown not to facilitate calcium phosphate precipitation.

Aquatic ecology

page 11 **Brazil** Biomass as a key factor in tropical lakes *eutrophication management*

Studies in Brazilian lakes and reservoirs show that nutrient mass is not directly related to algal growth, and that biomass is the key management factor.

Tropical reservoir page 12 Factors controlling algal community structure

Blue green algal dominance is related to nitrate concentration, N/P ratio, temperature and light conditions.

Water treatment page 13 Sewage sludge management in Europe

A report for the EU Commission assesses options for sewage sludge disposal, implications of proposed tighter land spreading regulations, and costs of biosolids management options





STPP

Rapid hydrolysis of detergent phosphates in sewage

This paper provides the only recent data on the fate of detergent phosphates (sodium tri polyphosphate STPP) and other polyphosphates in domestic waste waters, and for the first time gives some indications as to the factors affecting the rate of their hydrolysis. Results are also given showing the degree of hydrolysis in laundry and dishwashing machines, the experimental rate of hydrolysis in raw sewage, and indications of the mechanisms involved.

The authors cite previous work by Jolley et al (1998, n°27 see SCOPE Newsletter at www.ceep*phosphates.org*) indicating that **polyphosphates were** not detectable in domestic sewage reaching the Lower Molongolo Sewage Treatment Works, Canberra. Australia. They indicated: "No pyrophosphate or triphosphate was detected: however, this was to be expected given that the sample was taken as the waste water entered the treatment plant, at which stage it might be expected that any condensed phosphorus species would have undergone hydrolysis ... This observation was not an artefact of the analytical technique used, which had been thoroughly validated ..." [with reference to: Jolley, D. Honours Thesis, University of Canberra, 1993.]

This new 2001 paper analysed polyphosphates (triphosphate and diphosphate) in sewage reaching the Whittlesea Local Treatment Plant (LTP domestic sewage treatment plant), Melbourne, Australia. The works served 425 homes and receives sewage that is almost entirely of domestic origin. The estimated average residence time of the sewage in the pipes before reaching the sewage works is 2.6 hours (from Cullen *et al.*, 1995).

The amount of detergent phosphate reaching the sewage works (as polyphosphate, not on a "high-washing" day) was 202-339gP/day. This is estimated to be **just over half (55%) the original amount of detergent phosphate entering the sewage** (370-621gP/day). Approximately 30% more detergent phosphates are thought to be used on a "high-washing" day.

Total phosphorus in the sewage works inflow was 4.6 - 21 mgP/l, so that the detergent polyphosphates (not

high washing day) made up 11-30% of total sewage works phosphorus inflow.

The authors compare this result with Jolley's 1993 data for sewage from the Lower Molongolo sewage works. "This is in contrast to the behaviour of triphosphate in larger municipal waste water systems ... where hydrolysis is complete or nearly so by the time the effluent reaches the sewage treatment plant"

Breakdown in sewage

The authors carried out experiments to assess the rate of hydrolysis of detergent polyphosphates in raw sewage at 15°C or 20°C, and also in autoclaved sewage (elimination of bacterial action) and with addition of solid particles or cations (calcium, magnesium). The sewage samples were spiked with triphosphate to an initial concentration of 2 mgP/l.

Detergent phosphates "were found to rapidly degrade in raw sewage. Unfiltered sewage samples ... contained no detectable levels of diphosphate or triphosphate 24h later". The half-life of detergent phosphates (triphosphate) in waste waters was measured to be 7.3 hours at 15°C and 3.0 hours at 20°C."

However, if the sewage sample was filtered to $<0.2\mu$ m, then no detectable hydrolysis occurred in the first 96 hours, presumably because of the removal of both bacteria and of particulate reaction substrates. Magnesium or calcium addition (100 mg/l) did not make a significant difference to the rate of polyphosphate hydrolysis, and nor did the addition of suspended solids (kaolin). Autoclaving the sewage, on the other hand, had a considerable effect, with in this case little hydrolysis over 10 hours compared to rapid degradation of polyphosphates over this time period with sewage which was still biologically active. This confirms the major role of bacterial action in detergent polyphosphate hydrolysis in sewage and in sewerage networks.

The authors also estimate that 20% of STPP will be adsorbed to particles in $>0.2\mu$ m in sewage.

Breakdown in washing machines

Several experiments using washing machines and dishwashers showed that **most of the detergent polyphosphates "survived" the wash cycles**, even at relatively high temperatures (55-65°C). The authors suggest that the relatively high pH in the wash cycle, and the short heating period, do not favour polyphosphate hydrolysis. Between 0% and 43% only

of the initial detergent phosphates were hydrolysed in the machine cycles, and the authors indicate "The stability of triphosphate during the washing process should be reassuring to detergent manufacturers in that it ensures the builder component of detergents functions effectively for the duration of the washing cycle".

thus The paper concludes that detergent polyphosphates (STPP) is not considerably broken down during washing machine or dishwasher but hydrolysed to operation, is soluble orthophosphate quite rapidly (half life of a few hours at 15-20°C) in sewage. This degradation is dependent on the micro-organism activity in the sewage (strongly reduced by sterilising or filtering the sewage). Thus only trace amounts of detergent phosphates will be found in the inflows to sewage works situated on sewerage networks with transport times of 12 hours or more, but detectable concentrations will enter sewage treatment plants with short sewerage networks (residence time of a few hours only).

"Hydrolysis of triphosphate from detergents in a rural waste water system" D. Halliwell^{1,2}, I. McKelvie¹, B. Hart², R. Dunhill³.

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Water Research vol. 35, n° 2, pages 448-454. 2001. http://www.elsevier.nl/gejng/10/42/34/34/27/37/abstract.html

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SCOPE Newsletter editor's note:

It can be expected that the hydrolysis of detergent polyphosphates will continue within the sewage works. For example, Finstein and Hunter 1967 showed that around 50% of detergent polyphosphates were hydrolysed in the aerobic compartments of sewage works, and a similar proportion in a trickling filter. Once finally degraded, the detergent polyphosphates give orthophosphates (PO_4^-), indistinguishable to the majority of phosphates in sewage coming from human and food wastes.

Low temperature heat Recovering phosphate from bio-P sludges

Bio-P sludge was produced simulating EBPR (Enhanced Biological Phosphorus Removal) sewage treatment cycles in a 500ml bench reactor, initially fed with fresh activated sludge from a municipal sewage works and then with synthetic waste water. The reactor used an 8 hour cycle (addition of synthetic waste water, 2 hour anaerobic phase, 5 hours aeration, 1 hour settling and removal of supernatant). This process enabled the sludge to accumulate 3.5 - 5 % polyphosphates, 4.3 - 6% total phosphorus (dry weight).

Release of the accumulated phosphates was then analysed under either anaerobic conditions or lowtemperature heat treatment. After 4 hours under anaerobic conditions (bubbling of nitrogen gas), polyphosphate release from the sludge was negligible without chemical addition (<5 mg/l P total P-compounds released after 6 hours). When the sludge was maintained in anaerobic conditions and 4g/l acetic acid added, around 20 mg/l of P compounds were released after an hour, rising progressively to nearly 80 mg/l after 6 hours.

However, when the sludge was subjected to lowtemperature heat, without any chemical addition, rapid release of polyphosphates was observed. At just 50°C, P-release was similar after one or two hours to release under anaerobic conditions plus acetic acid (as above). At 60°C, 60 mg/l total P release after two hours reached nearly 100 mg/l with around 2/3 as polyphosphates. At 70°C, nearly 120 mg/l P were reached after only one hour, with release even faster at 80°C or 90°C (but with not more P being released).

Staining of the sludge (DAPI) and use of a fluorescence microscope confirmed that at 70°C polyphosphates were indeed moving out of the sludge flocs into solution, but showed that DNA was staying in the flocs, showing that the **sludge micro-organismes were not undergoing disintegration**. The authors hypothesise that the heating is disrupting the cell membrane function, allowing polyphosphates to escape.

70°C optimal temperature

Treatment at 70°C was sufficient to release 90% of the sludge polyphosphates into solution. Apparently, almost all the phosphate released from initially the sludge was released as polyphosphates, progressively hydrolysing to other soluble forms of phosphate after release and with time. This was demonstrated by the decrease in polyphosphate levels occurring after release had stopped, paralleled by an increase in other phosphorus compounds in solution.

The initially-released polyphosphates at 70° C were shown (by PAGE analysis) to have a chain length of 100-200 phosphates. After 4 hours heat treatment, all polyphosphates of chain length > 100 P had disappeared. A part of the polyphosphates was shown (by HPLC analysis) to be hydrolysing to trimetaphosphate.

Calcium phosphate precipitation

The polyphosphates released from the sludge could be readily precipitated as calcium phosphates by adding calcium, without pH adjustment at room temperature (addition of 50 molar final concentration calcium chloride). 65% of total phosphorus present was precipitated after 30 minutes, rising to 75% after two hours. However, once the polyphosphates were hydrolysed, calcium phosphate precipitation was more difficult to achieve: only 20% total phosphorus was precipitated by calcium chloride addition without pH adjustment (but up to 90% at pH 10).

Elemental analyses showed that the product precipitated from the 70°C heat-released polyphosphates contained 16%P and 18% calcium dry weight, that is a phosphorus content comparable to mined phosphate rock. The authors examined the feasibility of this technique for recovering phosphorus from municipal wastewaters at pilot plant scale (submitted to Journal of Chemical Engineering of Japan, available on request). The wet pellets contained low levels of most metallic impurities and would be readily usable in the manufacture of agricultural fertilisers, for example.

The authors conclude that low-temperature (70°C) heat treatment of biological P-removal sewage

sludges, followed by calcium phosphate precipitation, offers a very promising – and to date unexplored – avenue for recovering phosphates for recycling from sewage.

"A simple method to release polyphosphate from activated sludge for phosphorus reuse and recyling", Biotechnology and Bioengineering, vol. 78, n°3, May 2002, pages 333 -338. Online at: www.interscience.wiley.com

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Japan Twin tank struvite precipitator

A laboratory scale 1.1-6.7 m³/day experimental struvite precipitation reactor was tested using anaerobic treatment liquors with total phosphate concentrations of 111-507 mgP/l and 177-862 mgNH₄-N/l. Struvite precipitation was achieved by adding magnesium and increasing pH by alkali addition.

A combination of aeration and recirculation enabled fluidisation of the bed of struvite seeds (0.5-1.5 mm). Raw water flow rate was $1.1-6.7 \text{ m}^3/\text{day}$ and circulation flow rate was 1-10x times higher (6.7-11.7) m³/day because of recirculation. Operating pH was around 8.3-8.4 and soluble magnesium was added to around 1:1 stoichiometry for total phosphate.

Previous work (including pilot and full scale test reactors, see references in SCOPE Newsletter n°44, **page 6**, at *www.ceep-phosphates.org*) has used a single reactor tank. However, the growth of the struvite seed particles then resulted in a decrease in the effective reaction surface area for struvite precipitation, and thus a loss of phosphorus-recovery efficiency. The seed particle growth also resulted in difficulties in maintaining the bed of particles in suspension (fluidised bed).

The authors therefore devised a process (see diagram) with a main reactor vessel with relatively large struvite seed particles (0.5-1.5 mm) maintained in suspension by liquor upflow achieved by recirculation. A smaller secondary reactor vessel contained fine struvite particles.

Particles >0.3 mm approx. sank in the secondary reactor and were manually taken out the bottom and

fed to the main reactor. Fine struvite particles forming in the main reactor, conversely, were transferred by air lift pump to the secondary reactor. Total upflow rate in the secondary reactor was 1 m³/day (0.13 m³/day raw effluent inflow rate, plus 0.87 m³/day recirculation).

This system proved successful in maintaining stable seed particle size in the main reactor vessel.

Stable phosphorus removal rates

The new two-tank process design proved efficient at phosphorus removal and recovery, achieving fairly stable soluble phosphorus concentrations in the process outflow (14.0-79.5 mgP-total/l). This corresponds to a **phosphorus recovery rate of 84-92%**.

The authors conclude that the two-tank system can provide an efficient and stable phosphorus recovery process applicable to domestic waste water liquors. They suggest that the system could also be adapted for calcium phosphate recovery, water softening processes by calcium carbonate precipitation, calcium fluoride recovery, etc.

"Development of a high-efficiency phosphorus recovery method using a fluidized-bed crystallized phosphorus removal system", International Conference "From nutrient removal to recovery" (International Water Association), Amsterdam, 2-4 October 2002 and published in Water Science and technology vol. 48 n°1, pages 163-170, 2003 http://www.iwaponline.com/wst/04801/wst048010163.htm

Also the Ebara Product Review n°196 (July 2002) http://www.ebara.co.jp/en/product/tech/abstract/196 en.ht ml#thing2

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Japan Kinetics of struvite reactors

A 2.5 litre laboratory reactor was tested for continuous struvite precipitation experiments, following beaker batch experiments.

The batch experiments used pure solutions (with dissolved phosphate, ammonium and magnesium) and the continuous experiments used anaerobic sewage sludge digestion liquors (after settling for 60 minutes: $198-290 \text{ mgP-PO}_4/l$, $441-591 \text{ mgN-NH}_4/l$).

The batch (beaker) experiments suggested that agitation, pH and quantities of struvite seed present were key parameters for reactor kinetics. Stirring and aeration were both tested as means of agitation, suggesting that **precipitation was significantly reduced at lower agitation**, with an upper limit for paddle speed of 200 rpm (G value of 40 1/s). Struvite seed volumes in the reactor were in the range 55-3,200 mg/l of mixed liquor.

Struvite particle growth

Two continuous runs were carried out using the laboratory reactor and real waste water digester liquor, for durations of up to 2 days.

The first run showed that precipitation was faster when the volume of struvite seed present in the reactor was higher (volumes tested were 37,000-140,000 mg/l mixed liquor, corresponding to 5-25% seeds by volume after settling). Using a magnesium / phosphate molar ratio of 1.1:1 and at a pH of 8.5, phosphate removal of 92% was achieved (soluble phosphorus concentration in reactor effluent of 17 mg P-PO₄/l) in **under 4 minutes residence time**.

In a second, longer run, struvite crystals were allowed to grow in the reactor, from an initial size distribution mainly <0.15mm reaching mainly 0.25-0.6mm after 43 hours. The seeds of >0.6mm were sinking to the bottom of the reactor, out of the mixing zone.

The precipitated product was analysed using Electron Spectroscopy Chemical Analysis (ESCA) and showed to be struvite. The product of solubility values K was calculated to be 7.8x10⁻¹⁵(mol/l).

"Removal and recovery of phosphate and ammonium as struvite from supernatant in anaerobic digestion", International Conference "From nutrient removal to recovery" (International Water Association), Amsterdam, 2-4 October 2002 – publication expected in Water Science and Technology http://www.iwaponline.com/wst/toc.htm.

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Turkey Struvite from sewage and landfill leachate

Domestic wastewater samples from the Yenikapi sewage works, Istanbul, and landfill leachates from two different sites near Istanbul (Kemerburgaz, Komurcuoda) were used, both separately and in different mixes, to assess the feasibility of struvite precipitation as a process for ammonia removal. For some samples, Fenton's oxidation was applied before struvite precipitation.

This follows a previous paper (see refs. below) presenting the co-treatment of landfill leachates and domestic waste waters, as a solution for both treating the landfill leachate and providing a sufficiently concentrated liquor with domestic wastewaters for effective anaerobic treatment

The struvite precipitation experiments used 500 ml closed flasks with magnesium (as magnesium chloride) and phosphate (as sodium hydrogen phosphate) added, both in either 1.1 to 1 or 1 to 1 molar ratios compared to the sample's ammonium concentration. The pH was adjusted using sodium hydroxide to pH 8.2 - 9.6 and the flasks were stirred rapidly for 5 minutes then slowly for 30 minutes, before being allowed to settle for 30 minutes.

Fenton's oxidation was carried out in stirred flasks with addition of ferrous sulphate and hydrogen peroxide at pH4 (adjusted using sulphuric acid). The sewage liquor had an ammonium concentration of 28-42 mgN-NH₄/l, a soluble phosphate concentration of 4-8 mgP-PO₄/l and total COD of 80-150 mg/l. Corresponding concentrations for the leachates were 610-2,740 mg/l for ammonia-N, near zero phosphate and 1,270-12,450 mg/l COD.

The samples studied used domestic wastewater sewage works inflow (after screening and de-gritting), untreated leachate from the Kemerburgaz landfill site, and anaerobically pre-treated leachate from the Komurcuoda landfill site in the following combinations:

- domestic wastewater
- domestic wastewater plus 2% pre-treated leachate
- domestic wastewater plus 2% non treated leachate
- domestic wastewater plus 3% pre-treated leachate

- domestic wastewater plus 3% pre-treated leachate, subjected to Fenton's oxidation
- pure pre-treated leachate

The Fenton's oxidation step did not improve the rate of ammonia recovery in struvite, but did significantly improve COD removal (up to 82%).

Ammonia recovery as MAP was improved by using the 1.1 to 1 molar ratio of phosphate and magnesium addition, and slightly by raising pH to around 9. At pH 9.2, ammonia removal rates of around 70% were achieved for most of the sample combinations indicated above, rising to 85% for the pure leachate (using 1:1 molar phosphate and magnesium addition).

The characteristics of the settled struvite were examined, showing a dry solids content of 20-25% and a capillary suction time (CST) of 50-70 seconds, indicative of easy dewaterability. Mass balances showed that the precipitated solids were indeed 85-90% struvite.

The authors conclude that struvite MAP precipitation can be a very effective process for removing ammonia from landfill leachates or mixtures of such leachates and of domestic wastewaters. The struvite can be used as a fertiliser, enabling effective recovery both of the ammonia removed and of the phosphates and magnesium used as chemical reagents in the process.

"Struvite precipitation from anaerobically treated municipal and landfill wastewaters" Wat. Sci. Tech. vol. 46 n°9 pages 271-278, 2002. Purchase article online at: http://www.iwaponline.com/wst/04609/wst046090271.htm

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and "A new process for the combined treatment of municipal wastewaters and landfill leachates in coastal areas", Water Science and Technology, vol. 46, n°8, pages 111-118, 2002. http://www.iwaponline.com/wst/toc.htm

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Turkey Struvite from industrial wastewaters

Two papers present experiments carried out to assess the potential of struvite precipitation as an ammonia removal and recovery process for industrial wastewaters. In one paper: application is assesses in tannery wastewaters (raw and after different stages of treatment); in the other: application to opium/morphine and bakers yeast product industries.

For tannery industry wastewaters, experiments used raw wastewaters (ammonium concentration approximately 120-140 mgNH₃-N/l) showed that struvite precipitation was efficient for ammonium removal from pH 8 upwards, being optimal from pH.

Ammonia removal of 75% was achieved at pH9, reducing ammonia concentration to 35 mgN/l. COD removal was also achieved (compared to 30% only by settling). Similarly satisfactory ammonia removal levels were achieved by struvite precipitation from settled and polyelectrolyte settled, chemically precipitated liquors. Application to biologically treated effluent however was not as successful, with significantly higher (60 mgN/l) residual ammonia.

The authors conclude that the complex nature of tannery effluent can reduce the efficiency of struvite precipitation as an ammonia removal process (as compared to results published by other authors using other types of wastewater). In particular calcium can interfere by producing calcium phosphate instead of struvite.

Opium and yeast industries

Beaker tests using effluents from an opium alkaloid processing plant and a bakers yeast plant (using molasses) used similar methods to the work by Altinbas et al. summarised elsewhere in this Newsletter.

For the opium wastewaters, ammonia recovery rates of 61-65% were achieved for effluents from different stages of a bench biological treatment plant, and 84% from effluent after Fenton's oxidation (for stoichiometric magnesium and phosphorus addition). Struvite precipitation is very effective for pH>8.5 and optimal at pH9.2. For the yeast industry effluent, taken from the existing on-site anaerobic and/or aerobic treatment plants, ammonia recovery of around 80% was achieved. After Fenton's oxidation, this rose to 89% (stoichiometric precipitation was effective for pH>9.5 and optimal at pH9.2.

For both industry effluents, the recovered struvite dewatered easily (20-25% dry solid content) and were shown to be around 90% pure struvite.

The authors conclude that struvite precipitation is an appropriate treatment for anaerobically treated industrial effluents with high ammonia content. Fenton's oxidation can improve removal of residual COD and colour. Struvite precipitation is also an effective treatment for high-ammonia industrial effluents prior to biological treatment systems.

"Assessment of magnesium ammonium phosphate precipitation for the treatment of leather tanning industry wastewaters", Water Science and Technology, vol. 46 n°4-5, pages 231-239; 2002. Purchase article online at: http://www.iwaponline.com/wst/04604/04/default.htm

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"Ammonia recovery from high strength agro industry effluents", Water Science and Technology, vol. 45 n°12 pages 189-196; 2002. Purchase article online at: http://www.iwaponline.com/wst/04512/12/default.htm

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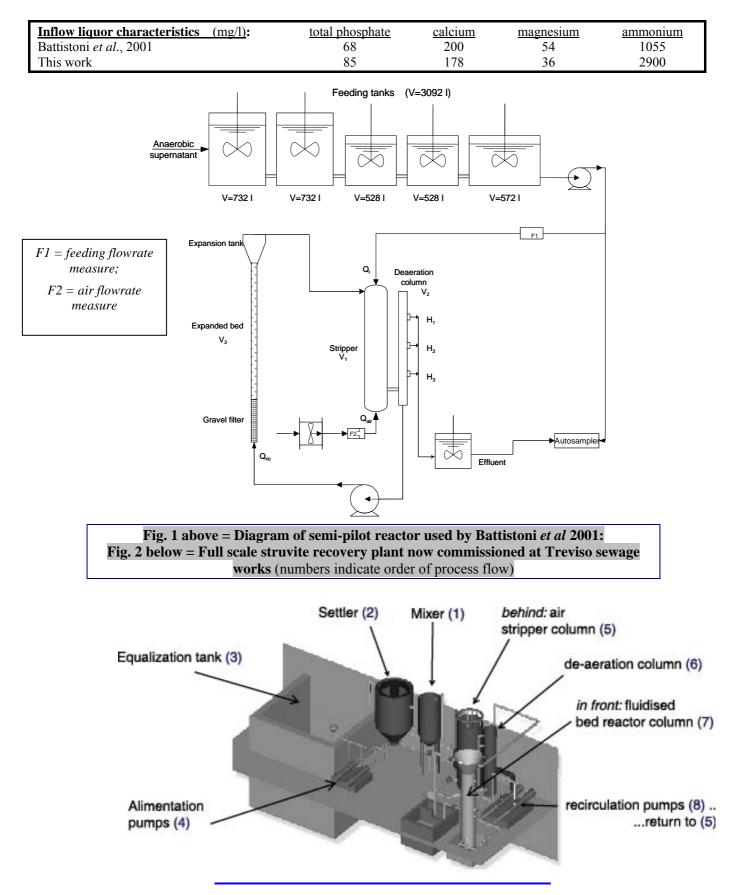
Italy

Modelling P-recovery process

In SCOPE Newsletter n°44 (www.ceep-phosphates.org), a semi-pilot P-recovery installation was presented (Battistoni *et al.*, 2001) and the commissioning of a full-scale pilot plant at Treviso municipal wastewater plant was announced. This paper uses the results from this semi-pilot plant to develop a detailed model for the operating parameters of the P-recovery reactor.

The semi-pilot plant used a robust fluidised bed reactor column (2m high, 13 litre capacity), using aeration to achieve a pH increase, and operating on anaerobic supernatants from the centrifugation section of a 100,000pe biological nutrient removal plant (A₂O configuration), Ancona, Italy. The layout (Fig. 1) was comparable to that of the fullscale plant now commissioned at Treviso (Fig 2).

SCOPE Newsletter – nº 49 - Page 7 - www.ceep-phosphates.org



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Results from 12 reactor runs (lasting up to one week) are presented. A pH of around 8.44 was achieved by aeration only (driving off CO_2), raised from the inflow pH of around 7.5.

The inflow liquor was similar to that used in Battistoni *et al.*, 2001, but with somewhat higher phosphate concentrations and lower calcium and magnesium levels.

Operating model

The paper develops a detailed model for the reactor operation, based on the following parameters:

- total phosphate inflow, total and soluble phosphate outflow
- magnesium inflow and outflow
- hydraulic residence times in: fluidised bed column, settling column, stripper (de-aeration column)
- fluidised bed porosity (function of expanded and settled bed volumes and mass of bed sand)

Precipitation efficiencies of 12 - 25% were achieved, principally as calcium phosphate, with total phosphate concentrations in the liquor outflow of around 20-30 mg/l.

The authors conclude that to achieve good reactor performance for P-recovery it is necessary to optimise both nucleation and precipitation. This requires optimisation of "contact time" in the reactor, which can most readily be achieved by re-circulating the liquor through the reactor: otherwise there is a risk of generating "fines" (small nucleated phosphate particles) which will be carried out of the reactor in the outflow, whereas the objective is to achieve precipitation onto the "seed" material in the reactor (bed sand).

"P removal from anaerobic supernatents by sruvite crystallisation: long term validation and process modelling".

P. Battistoni¹, *A. de Angelis¹*, *M. Prisciandaro²*, *R. Boccadorao¹*, *D. Bolzonella³*. *Water Research 36* (2002) pages 1927-1938. Elsevier Science http://www.elsevier.com/locate/watres

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Phosphate recovery Calcite and silicate seeding improves calcium phosphate precipitation

Previous work by the authors (see First International Conference on Phosphorus Recovery for Recycling http://www.nhm.ac.uk/mineralogy/phos/donner/donner.htm) suggested that the presence of calcium carbonate (calcite) particles as a seed improved the precipitation of calcium phosphates.

The further work presented suggests that this effect is real, depends on the characteristics of the calcite used (probably the surface structure), occurs also with Tobermorite (a calcium silicate hydrate). Significantly, the effect appears to increase with ongoing use (or re-use) of the seed material, suggesting that the formation of a layer of precipitated calcium phosphates on the particle facilitates further calcium phosphate surfaces precipitation. The experiments show that with such seeding, calcium phosphates can be precipitated from chemical solutions containing significant levels of soluble carbonates (known to be an obstacle to calcium phosphate precipitation) and also in the case of Tobermorite soluble organics (which also appear to inhibit calcium phosphate precipitation).

The **presence of soluble carbonate in waste waters** is known to be major obstacle to phosphate recovery for recycling as calcium phosphates. At the Geestmerambacht sewage works, The Netherlands, where calcium phosphates are recovered from sewage (by precipitation in a Crystallactor \mathbb{O} from a biological nutrient removal sidestream), it is found necessary to remove soluble carbonates by adding acid prior to the calcium phosphate precipitation at pH >8, which poses obvious problems of reagent consumption, increase in water salinity and cost.

The experiments used lake waters with calcium carbonate SI (Saturation Index) of -1.9 to +0.42, and local tap water, SI = +0.05. Phosphate concentrations used were 10 mgP/l, comparable to concentrations in raw sewage. Liquors from an industrial waste water treatment plant (secondary effluent, SI = -0.35, phosphate added up to 10 mgP/l), from a sewage works biological nutrient removal side stream (Phostrip©, with SI carbonate -0.18, approx 50 mgP/l) and from a laundry factory (liquor relatively high in organic carbon at around 150 mg/l) were also

tested. All experiments were carried out at the respective liquors' original pH's, which were around 8.0

Five different calcites (with Specific Surface Areas (SSA) from 0.3 - 70 m²/g), quartz sand (SSA 0.1 m²/g) and Tobermorite (a calcium silicate hydrate with SSA 30 m²/g, similar to the Tobermorite used by Moriyama, see SCOPE Newsletter n°36 and Second International Conference on Phosphorus Recovery for Recycling *http://www.nhm.ac.uk/mineralogy/phos/Nordwijkerhout/Moriyama.pdf*) were tested as seed crystals.

Simple beaker (up to 24 hour) precipitation experiments were first carried out, often with the seed materials being used several times (0.5 - 2 g of seed material for 200 - 500 ml of solution), followed by runs using a simple fluidised bed (column) reactor of 1 litre volume (residence time 1-8 hours).

Adsorption and surface area

24-hour beaker experiments near the saturation level (0.5g calcite/l = SI of +0.05, 10 mg P/l) showed the considerably better phosphate removal performance of calcite seeds with higher surface area (first use of virgin seeds): Socal-U3 calcite (grain size 0.015-0.025 μ m and SSA 70 m²/g) removed some 170 times more phosphate from solution per unit mass of seed crystal than Calcite Merck 2066 (grain size 2 μ m, SSA 1.1 m²/g), but this is approximately the same removal rate per unit seed surface area. The authors suggest that this is because this phosphorus removal from solution is essentially through adsorption onto the calcite surface in the calcite equilibrium state.

Comparison of waters with different saturation indices outside the equilibrium state (SI from -1.90 to +0.42), revealed that P removal was 70 times higher per unit surface area for Merck 2066 than for Socal-U3, despite the higher specific surface area (SSA) of the latter. This indicates that **surface morphology is important** and may influence calcium release into waters with low SI values.

When calcite seeds were re-used in several consecutive beaker experiments, it was found that the rapidity of phosphorus removal from solution was increased, so that P-removal in the initial 24 hours was considerably improved, and performance of different calcite seeds became more similar. FTIR-ATR and ESEM investigations suggested that after

reuse the seeds were coated with a layer of calcium phosphate.

Experiments also showed that the **effectiveness of quartz sand** (grain size 600-1,000 μ m, SSA 0.1 m²/g) as a seed was considerably increased by the addition of just 2% Socal-U calcite seed (using 10 mgP/l phosphate solution, carbonate SI=+0.2).

Problems with dissolved organics

Several beaker experiments with the real wastewaters showed considerable retardation of the phosphorus removal, and it is suggested by the authors that this is due to dissolved organic carbon (DOC) present in these liquors.

Tobermorite (details above) was also tested as a seed material. Good phosphorus removal from solution was obtained: 95% in artificial solutions, 83% in the secondary effluent and 67% in the laundry factory effluent in just ten minutes; rising to over 97% removal in all three cases after 24 hours. Interestingly, the Tobermorite was also removing 40% (ten minutes) and 67% (24 hours) of the 150 mg/l initial concentration of total organic carbon present in the laundry effluent. There was no significant change in effectiveness after several FITR-ATR again showed that reuses. the Tobermorite was being coated with calcium phosphate.

Long reactor runs

The column reactor was operated using a Tobermorite seed bed for a duration of over 3000 hours (residence time 1 hour). The initial phosphorus concentration of 10 mgP/l was consistently reduced to below 4 mgP/l, and to below 2 mgP/l for most of the time (at pH 8.3).

The authors suggest that Tobermorite seeding merits further investigation as a route for calcium phosphate recovery for recycling, as it appears to be fairly stable over significant time periods and only partly inhibited by the presence of dissolved organic carbon compounds found in wastewaters.

"Use of crystallisation for the P-recovery from waste water streams", poster presented at the IWA Aquatec Conference "From nutrient removal to nutrient recovery" 2-4 October 2002, Amsterdam, The Netherlands, plus background paper.

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Phosphate precipitation chemistry Carbonate inhibition of calcium phosphate precipitation

Both seeded and unseeded crystal growth experiments were used to assess the interactions between calcium carbonate (calcite) and calcium phosphate precipitation and results were compared with chemical kinetic modelling predictions, in particular to analyse the different forms of calcium phosphate that may be formed (tricalcium phosphate TCP, octacalcium phosphate OCP, hydroxyapatite HAP) in hard waters.

Calcite precipitation was studied for concentrations of 2.5 mmol/l calcium and phosphate concentrations of $0 - 500 \ \mu mol/l$ (as potassium phosphate KH₂PO₄), with calcite precipitation being initiated by the addition of calcite seed at pH around 8.5.

At relatively low phosphate concentrations (<20µmol/l), phosphate retarded calcite growth and phosphate was co-precipitated with the calcite, with the most rapid calcite precipitation kinetics occurring in the case of zero phosphate The precipitation rate of calcite decreased with increasing phosphate concentration.

With higher phosphate concentrations (50 - 500)were umol/l the solutions considerably supersaturated with regard to calcium phosphate compounds. In these experiments, calcite was not precipitated and calcium phosphate was instead formed as indicated by the much smaller ratios of Ca:P in the precipitate. The calcium phosphate precipitation appeared to be starting before the addition of the (calcite) seed material, and this was confirmed with experiments showing that the calcium phosphate growth rate was independent of the calcite seeding.

Theoretical calculations indicate that the solutions were supersaturated with respect to both HAP and TCP and it was possible, based on the results of other studies, that the calcium phosphate compound being initially precipitated was amorphous TCP, which was then

transforming (possibly via other phases) to the more stable hydroxyapatite (HAP).

Calcium phosphate precipitation was achieved at pH 7.3 to 9.0 for a calcium concentration of 2.5 mmol/l and phosphate concentrations of 50 to 500µmol/l (at 10°C).

The demonstration that calcite seeding did not facilitate calcium phosphate precipitation contradicts previously published work by other authors and suggests that calcite seeding is *not* a useful route to improve performance of calcium phosphate precipitation reactors in phosphate recovery for recycling processes.

The authors conclude that **unseeded calcium phosphate precipitation occurs in the presence of carbonate ions only if the Saturation Index (SI) for hydroxyapatite exceeds 9.4**. Further work is needed to better understand the role of the different interacting ions in this process.

"Precipitation of calcite in the presence of inorganic phosphate". Colloids and Surfaces -A - 203 (2002) pages 143-153.

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Brazil

Biomass as a key factor in tropical lakes eutrophication management

The author summarises key features of eutrophication in tropical lakes and reservoirs, emphasising that *"eutrophication problems actually originate from the formation of biomass and not from the mere presence of nutrients"*. The paper then presents a case study of lake Pampulha reservoir, Bello Horizonte, Brazil.

Tropical lakes differ from temperate water bodies in their response to nutrients and algal development in a number of ways. The interactions between nutrients and biomass formation in tropical lakes are particularly complex and only limited relevant information is available because they have been much less widely studied.

The relation between biomass production and nutrients depends on algal growth rates and on algal

losses through sedimentation and grazing, and these are both very important in tropical systems. This often leads to low measured nutrient concentrations in water (rapid nutrient uptake) but and low algal biomass. However, shallow tropical lakes can show very considerable variations over 24 hours, with alternations between stratification and mixing. Classifying such lakes as eutrophic or oligotrophic is thus difficult or misleading.

Tropical lakes and reservoirs:

difference when compared to temperate systems

- higher nutrient uptake by algae
 (higher light energy and temperature)
- * higher nutrient recycling rates
- rarer occurrence of "algal blooms", frequent occurrence of low algal densities but with high growth rates
- * higher mineralisation rates leading to sediments poor in organic matter
- higher settling velocities of organisms and nutrients

Lake Pampulha

Lake Pampulha, in the Bello Horizonte urban area, is a 2.6 km² artificial lake with a mean depth of 5m (max. 16m) and a catchment area of 97 km^2 . The lake is heavily impacted by untreated sewage and by sediments (soil erosion of many areas of the catchment). The deterioration of the lake's water quality prevents its use for either drinking water (its original purpose) or recreation.

Macrophyte blooms

Floating blooms of the macrophyte plant water hyacinth (*Eichhornia crassipes*) are frequent, often covering up to one third of the lake's surface. Biomass management, consisting of removal of these plant blooms over the 6-month growth season is regarded as the key tool for lake restoration, along with diversion of sewage.

Machinery has been developed capable of effectively harvesting the water hyacinths faster than they can grow. Some 10% of their biomass is left in place, in order to prevent algal development (competition, shading), because total removal has in the past led to blue-green algal growths. "The process of biomass formation as the key point in the restoration of tropical eutrophic lakes", Hydrobiologia, 342/343, pages 351-354, 1997.

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Abstract (free) and full text (subscriber access) at http://www.kluweronline.com/issn/0018-8158/current

Tropical reservoir Factors controlling algal community structure

Nutrient concentrations and physical conditions in the shallow tropical Juturnaiba reservoir (Rio de Janeiro State, Brazil, $22^{\circ} 33'$ S, $42^{\circ} 18'W$) were assessed over a one year period and compared with algal biomass and community composition. The reservoir has a maximum depth of 8m and an area of 43 km², in a hot, humid climate with a summer rainy season, >18°C in the coldest months.

Algal biomass and species composition showed two distinct periods: June 1996-November 1996; December 1996 – May 1997. Soluble reactive phosphorus (SRP) varied from around 0.3μ M to nearly 2μ M, with (not statistically significantly) higher levels in the first period (Winter-Spring). Dissolved nitrogen was also lower in the second period, with NH₄ below 2 μ M from October-March and particularly with NO₃⁻ low from October onwards (statistically significant) and non detectable in April-May.

131 algal species were recorded during the study. Diatoms and crytomonads dominated in the first period and cyanobacteria (blue-greens) in the second. Total algal biomass was lower in the first period with a peak in February (at 4.5x the annual average). This corresponded to a prolonged (5 month) blue-green bloom in period 2; dominated first by *Microcystis aeruginosa* then by *Anabaena spiroides* and *Cylindrospermopsis raciborskii*.

The dominant non blue-green species from the first period showed significant positive correlation with NO_3^- and with N/P ratio, and negative correlation with temperature and Secchi depth (water transparency). The dominant blue-green species from

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period 2 showed the inverse significant correlations, that is: low NO_3^- and N/P ratios were significantly correlated with dominance of blue-green algae.

The authors conclude that the phytoplankton assemblages proposed by Reynolds for temperate lakes apply quite well to this tropical reservoir. The first period is characterised by **D** and **Y** type species assemblages (**C** strategists = small, fast growing). The second period is characterised by **M** and then **H**, **H-Sn** assemblages (**S-R** and **R** strategists, adapted to first low light and then nitrogen deficiency conditions).

"Nutrient availability and physical conditions as controlling factors of phytoplankton composition and biomass in a tropical reservoir (Southeastern Brazil)" Arch. Hydrobiol. 153-3 pages 443-468, Feb. 2002. http://www.schweizerbart.de/j/archiv-hydrobiologie/

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Water treatment Sewage sludge management in Europe

Large quantities of Europe's sewage sludge production are currently recycled by agricultural spreading, effectively allowing both economic disposal and recycling of the nutrients (phosphate and nitrogen) and organic contents¹. However, this route is under significant pressure because of public concerns - objectively justified or otherwise - concerning risks of heavy metal, pharmaceutical pathogen or chemicals contamination of soils and/or of agricultural products (food). There is also concern about risks of run-off of such contaminants to ground and surface waters (drinking water supplies).

1: approximately 36.4% of European sewage sludge is spread on land, according to Rebecca Renner in "Sewage Sludge, Pros and Cons", Environmental Science & Technology vol. 34 - I.19 1, October 2000, text at: www.mindfully.org/Pesticide/Sewage-Sludge-Pros-Cons.htm

These concerns have led in some countries (eg. UK) to agreements between farmers organisations, water companies and supermarkets to limit levels of contaminants and to ensure pre-treatment of sewage

sludges before spreading, or in other countries (eg. Sweden, Switzerland) to farmers organisations recommending or legal implementation of bans on agricultural sludge use.

This EU report analyses the different options for sewage sludge disposal and concludes that agricultural use is the best environmental and economic solution. The development of the agricultural spreading route requires the improvement of both sludge qualities and of public confidence. Sludge quality guarantee and labelling systems will be a key tool to improve this, but with a significant cost to water companies. Research into sludge quality. pollutants and their fate in the environment and in food, and the publication of this research will be important in facilitating public acceptance.

Proposed tighter regulations

In order to develop public confidence, the EU is proposing a significant tightening of regulations concerning biosolids spreading (currently covered by *EU Directive 86/278*), to require fuller sludge pre-treatment before spreading, to lower soil and sludge limits for heavy metals, and to introduce limits for certain organic contaminants.

The report estimates that this will have little impact in countries where national sludge spreading regulations are already much more stringent than the existing EU Directive requirements (Denmark, Finland, Sweden. Netherlands. Implementation costs will however be significant in countries where existing national regulations are only somewhat more stringent (Austria, Belgium, France, Germany, Poland) or are similar (Greece, Ireland, Italy, Luxembourg, Portugal, Spain, UK, Estonia, Latvia) to the current EU Directive.

Who will bear the costs ?

The total cost implied by the proposed Directive tightening for the 15 EU Member States is estimated at almost **1 billion Euros/year**, with a large proportion of this cost being born by four EU states who currently recycle to agriculture large volumes of sludge (Germany 29% of total cost, UK 26%, France 16%, Spain 11%).

As a European average, sewage sludge disposal costs are estimated at 318 €tonne dry matter

(DM), that is at $0.12 \text{ } \text{€/m}^3$ of drinking water supplied, compared to total sewage costs of 0.87 €/m^3 , that is 14%. Total drinking water service costs (production and treatment) are estimated at 2.2 €/m^3 . Average sludge disposal costs are estimated to vary from 263 – 344 €/tonne DM. Landspreading of solid/semi-solid sludge is estimated to cost 110-160 €/tonne DM, of which 10-30% of the cost is covered by the fertiliser value of the sludge.

The report estimates that implementation of the proposed sludge spreading Directive tightening would result in 67% (short term) rising to 83% (long term) of sewage sludge failing limit values for heavy metals or organic pollutants in the absence of an effective "pollution prevention" policy to reduce the input of such contaminants to raw sewage. Such a policy could reduce the proportion of sludge failing limit values to around 25%. Despite this, the total cost to all stakeholders (water companies, farmers, industry, public / consumers, local authorities) of the new Directive *with* the pollution prevention policy could be around 15% higher than *without* such a policy.

A key difference is that *without* the pollution prevention policy, 60% of the costs are born by local authorities (ending up on the public's water bill), 20% by farmers and 16% by the general public (environmental and health impacts), whereas *with* the policy 60% of the costs are born by the pollution producing industries (discharge pollution prevention costs).

"Disposal and recycling routes for sewage sludge", report for the EU Commission – DG Environment – B/2, SEDE/ Arthur Andersen, January 2002. Available at: http://europa.eu.int/comm/environment/sludge/sludge_disp osal.htm



NTNU Norwegian University of Science and Technology

IWA Specialist Group on Sludge Management – International Conference Norwegian University of Science and Technology (NTNU)

BIOSOLIDS 2003 Wastewater Sludge as a Resource Trondheim, Norway 23-25 June, 2003

Programme includes:

sludge minimisation, sludge characteristics, sludge dewatering, pre-treatment and aerobic digestion, treatment technologies for land use –hygiene, case studies, phosphate recovery (Wed. 25th June, 8h30-10h25), energy recovery, recovery of specific products, final handling of biosolids and future perspectives.

Phosphate recovery session includes: Recovery of phosphate from sludge – a Dutch analysis, Phosphorous and coagulant recovery by alkaline sludge treatment, Phosphorus recovery by one- or two-step technology with use of acids and bases, Recycling of sludge with the Aqua Reci – process

http://www.ivt.ntnu.no/ivm/Biosolids2003/

1st IWA Conference on

Scaling and Corrosion in Water and Wastewater Systems 25th – 27th March 2003 Cranfield University, UK

Scaling and corrosion; Biofouling and biocorrosion Membrane fouling; Mitigation methods and processes Prediction and modelling; Test methodologies

Programme at: http://www.cranfield.ac.uk/sims/water/iwa/

In particular, **Thursday 27th March 11:30 Session on Struvite :** Struvite scale formation and control ; Potential for scale formation and control at wastewater treatment works ; Struvite Scale potential determination using a computer Model ; Struvite control through process and facility design as well as operation strategy



Cranfield The School of Water Sciences







The SCOPE Newsletter

The SCOPE Newsletter is produced by the Centre Européen d'Etudes des Polyphosphates, the phosphate industry's research association and a sector group of CEFIC (the European Chemical Industry Council).

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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CEEP Centre Européen d'Etude des Polyphosphates



Mexico

NUMBER 48

Nutrient management

Questioning nutrient "thresholds"

EU	Research
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page 2

The EU Commission's Research Directorate has launched a series of international workshops to try to define what is meant by a "threshold of environmental sustainability", taking the case of nutrients as an example. Report on the first workshop.

Netherlands

page 3 **Regional nutrient and ecological targets**

A research report for the Netherlands Environment Ministry suggests nutrient targets for different surface water types, concluding "very to extremely low" values. These are likely to be inaccessible in practice so that other approaches to addressing surface water quality will be necessary.

Nutrient sources

Danube basin More work needed on nutrient fluxes

page 4

A review of studies of nutrient fluxes to the Danube basin shows the considerable level of uncertainties concerning discharges and retention mechanisms. Households (with more than two thirds via sewage works) are considered to make up <30% of phosphorus discharges to the Danube. Diffuse particulate phosphate discharges and subsurface flows are systematically underestimated – the authors suggest a correction factor of x2.

Hungary page 5 Underestimates of diffuse lake phosphorus inputs

Diffuse sources are the major phosphorus (P) load to Lake Balaton, Hungary, and are probably considerably underestimated by standards monitoring methods.

Czech Republic page 6 **Challenges of agricultural nutrient run-off**

Nutrient run-off from intensive agriculture to the Zelivka reservoir is approaching the limits for drinking water, necessitating a concerted catchment action plan including soil conservation and management contracts with farmers.



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Ecosystems

Tropical lake nutrient resilience

Bioassays show that chemical factors do not prevent algal development in Lake Zirahuen's water. The lake's clear-water quality, despite high nutrient loadings, must therefore be the consequence of specific local tropical ecosystem mechanisms, preventing food-web nutrient mobilisation.

Winsconsin page 8 Daphnia and water clarity in eutrophic lakes

Observation of 13 eutrophic South Winsconsin Lakes showed that large-sized Daphnia could achieve grazing rates high enough to increase summer water clarity and delay blue-green algal blooms.

Ohio. USA page 8 **Importance of Daphnia in controlling algae**

In-lake column experiments show that Daphnia act on both total algal growth and blue-greens, whilst smaller zooplankton are less effective.

Norfolk Broads, England page 9 Fish, plants, zooplankton and control of algae

Studies of several shallow lakes in the Norfolk Broads show that the ability of zooplankton grazers to control algal development can be affected by fish predation or by the loss of plant (macrophyte) refuges.

Canadian lakes page 11 Daphnia control of filamentous algae

Enclosure experiments in an artificially nutrient enriched lake showed that Daphnia were able to strongly reduce densities of filamentous blue-green algae. Ammonia addition showed that this was not because Daphnia modified the N:P availability ratio and that other mechanisms are more important.

Denmark page 12 Varying lake reactions to reduced phosphorus

An 11 year study of 23 Danish lakes show clear biological community response to reductions in lake phosphorus levels, but not necessarily to external P loadings because of internal cycling. Eutrophic lakes showed less response. Biomanipulation of fish populations significantly increased response.





EU Research Questioning nutrient "thresholds"

The first of a series of workshops, organised by the European Commission Research Directorate General to address the question of "thresholds of environmental sustainability" (what is meant, how can they be defined, and as importantly used) taking as a starting point the case of nutrients, took place on November 6^{th} 2001. The workshop brought together scientific experts on nutrients from across Europe. The report from this workshop is summarised here. The second workshop took place on 18^{th} -19th June 2002.

The series of workshops aims to provide a definition of such "thresholds" as associated with ecological carrying capacities, and tools for translating these into environmental monitoring indicators and for coupling them with policy decisions reflecting costs and shortand long-term ecological impacts.

Public acceptability

The workshop accepted the "general public" definition of a threshold as a *'level beyond which undesirable effects tend to occur*". This means that a threshold is necessarily dependent on both specific characteristics of a given site or ecosystem and of a given time, but also on what are considered as "undesirable effects", which is a socio-economic consideration.

The workshop concentrated on nutrient enrichment of the marine environment as a case study, looking for operational definitions of the short- and long-term effects of marine nutrient enrichment, whether "thresholds" could be defined in this respect and how they could be used to support public policy making.

For the case of nutrients, the "threshold" was considered to be defined by six factors:

- the level (flux or loading) of nutrients considered to be compatible with acceptable ecosystem functioning

- the carrying capacity of the ecosystem: resilience, tolerance of nutrient inputs
- potential negative effects on the ecosystem
 dependence on the specific context: place (local ecosystem) and time

- concept of "critical" when applied to thresholds, leading to the need to fix "ecological quality objectives"

- the possibility of recovery of the ecosystem and/or the **costs of restoration**

The "threshold" can thus be defined variously as "a level causing unwanted negative impacts", a level "exceeding carrying capacity or system tolerance", a level leading to "restoration efforts which are difficult or prohibitively costly", a level giving "a high probability of unwanted impacts".

In particular, given nutrient loadings may or may not give undesirable impacts as a function of the **other factors and usages** impacting a water body.

Which nutrients to consider ?

The workshop decided to address the case of marine nutrient enrichment. Nitrogen is generally the key nutrient linked to negative effects in marine environments (for example, related to *Phyaeocystis* algal development in the Southern Blight of the North Sea – Christiane Lancelot) but the workshop decided that "nutrient thresholds" should consider **the sum of organic and inorganic nitrogen, phosphorus, carbon and silicon**.

Several case studies showed the deterioration of coastal ecosystems, in particular with algal blooms, related to increased nutrient loadings, including the Adriatic, the Baltic, the North Sea, Mediterranean, and the coast of Norway. Sources of nutrients cited include: agricultural run-off, atmospheric deposition and inadequately treated human sewage. However, all the speakers emphasised the difficulties in defining "nutrient thresholds" given both the lack of longterm data to support recommendations, and the need to define specific thresholds for different local circumstances. Even within given marine water bodies, reaction to nutrients varies considerably between local areas (eg. "It seems impossible to define one unique nutrient threshold in the Mediterranean according to the different effects of human nutrient inputs and to the non-steady state of these inputs" - J. Béthoux and D. Ruiz-Pino). N. Navarro and C. Duarte provided evidence of the major differences between different marine waters in Europe, contending that 'the unit of analysis should be the European Coastal Biogeochemical Provinces which are still to be defined".

The speakers emphasised that 'it is very difficult to predict the occurrence of harmful algal blooms from

resource supply" (Helmut Hillebrand). This is partly because of the influence of many other factors, for example residence time: "the fate of nutrients can be quite different depending on their residence time in a different environment" (Serrena Fonda Umani comparing the North Adriatic and the Gulf of Trieste). For the Mediterranean, Marta Estrada and Jordi Camp also emphasised that nitrogen/phosphorus ratios vary widely and "consideration of anthropogenic effects on physical properties in the environment must be integrated with that of chemical and biological factors".

Complexity

Christian Béchemin summarised these difficulties by underlining that "the definition of threshold (concentration, ratio, balance) is also connected to the biodiversity, to the special adaptation capacity of species ... requires to take into account the diversity, multiplicity of nutrients and their balance, as well as the diversity and multiplicity of organisms ... and finally the diversity of end-users".

The debate is rendered even more complex because in some cases **the unwanted effects of nutrient enrichment may exist irrespectively of and prior to human inputs**. J. Béthoux and D. Ruiz-Pino indicated that anoxia (oxygen deprivation) existed in the Black Sea was present before the increase of human activities, because of natural land weathering in the watershed, and that periodic anoxia in the Mediterranean also occurs naturally because of water circulation mechanisms.

The workshop concluded that nutrient thresholds are needed as a tool for communications between scientists, decision makers and the public, but that flexibility is necessary in their use because ecological processes are not reflected by the allocation of "pass/fail" status in response to numerical threshold values. Further **the definition of thresholds depends directly on the definition of ecological quality objectives** (or what is an "unwanted" effect) and this will vary between different stakeholders. Finally, thresholds must **take into account socio-economic factors** and a cost-benefit analysis.

"Thresholds of environmental sustainability – the case of nutrients" First Workshop Report. EU Commission, DG Research – Environment and Sustainable Development Programme, Policy Aspects, Unit I.1 – Research in Enclosed Seas series 11 – EUR 20170 – 2002.

Netherlands

Regional nutrient and ecological targets

The authors attempt to define nutrient standard values for different types of surface water occurring in the Netherlands, by assessing the nutrient level which would be necessary in order to achieve – by nutrient reduction alone – a switch in water quality conditions considered as appropriate ecological objectives for each water type.

This approach is comparable to that of the **EU Water Framework Directive 60/2000**, which requires surface waters to all be restored to "good quality status" by 2015 (save certain exceptions), this being defined for nutrients as enabling near-natural plant and animal communities to develop. The approach is also comparable to the US Environmental Protection Agency (EPA) currently ongoing definition of "ecoregional nutrient criteria" (see SCOPE Newsletter n° 44).

The authors consider 9 **different water types**: small streams, artificial ditches/drainage dykes, lakes, heathland lakes, moorland lakes, IJsselmeer, Vokerak, North Sea coastal waters and the Rhine (as it flows into the Netherlands).

Nutrient standards are suggested for some or all of: P (total phosphorus) and N (total nitrogen, nitrate nitrogen and/or ammonia nitrogen) concentrations in water (summer average) or loadings (inputs/hectare/year).

Nitrogen limitation in coastal waters

In the North Sea coastal waters, there are no clear indications that phosphorus limitation has ever occurred (that is, phosphorus levels do not appear to be the factor influencing algal growth), and **summer algal blooms appear to be nitrogen driven**. Considerable reductions of phosphorus loadings have already been achieved (through sewage treatment), but not significant reductions of nitrogen loads, yet a *further* 60-70% reduction of phosphorus loads would be necessary to achieve phosphorus Imitation of the spring algal bloom, according to the authors' estimates. It is difficult to see how this could be practically achieved. Nitrogen reduction thus appears to be the solution to reduce summer algal blooms and avoid toxic algae development.

For lakes, the Netherlands currently has "Maximum Tolerable Concentration" standards of 0.15 mgP/l and 2.2 mgN/l (summer averages, total P and N), corresponding to a "desired ecological quality" criterion of limited algal development (chlorophyll concentrations < 100 mg/l).

Other factors

The authors note that in some lakes this desired chlorophyll concentration target is achieved at total phosphorus levels higher than 0.15 mgP/l. In these lakes, algal growth is not limited by phosphorus, but by another factor, such as nitrogen concentrations or light.

The authors attempt to assess nutrient (N and P) concentrations which would be low enough to ensure switching of the relevant ecosystem types from a eutrophied to a near-natural conditions. These critical values "were found to be very low to sometimes extremely low" so that "nutrient reduction must be extreme" to enable ecosystem recovery. This suggests that in many cases such extreme nutrient reductions will be very difficult to achieve in practice and it may be appropriate to instead try to achieve ecosystem restoration by other actions.

These target concentrations are **up to ten times lower** than those derived from an analysis of the biological communities present in different types of surface waters in the Netherlands (data from several waterboards) – see SCOPE Newsletter n° 30. This previous study suggested quality levels for "specific environmental quality" (50% of sites achieving highest or nearly highest water quality) of for example 0.24 mgP/l (upper reaches) to 1 mgP:l (lower reaches) for hill streams, 0.15 – 0.36 mgP/l for lowland streams.

"Nutrient standards for nutrients in surface water types" (Watertypegerichte normstelling voor nutrienten in oppervlaktewater). In Dutch with summary in English. RIVM report 703715005/2002 for the Netherlands Environment Ministry. Z. van Liere, D. Jonkers.

Phosphorus and nitrogen targets suggested by the authors are as follows:

(summer average water concentrations)

*	small streams	0.02 mgP/l 0.28 mgNO3-N/l 0.02 mgNH4-N/l
*	ditches	0.23 - 2.3 mgP/l 1.3 – 3.3 mgN/l (plus loading limits)
*	lakes	0.05 mgP/l 1 mgN/l
*	IJsselmeer, Volkerak heathland, moorland lakes	0.05 – 0.06 mgP/l 5 – 10 kgN/ha/year (atmospheric)
*	coastal waters	0.6 mgDIN-N/l
	Rhine mit set to protect IJsselmeer mit set to protect coastal wa	1.8 mgN/l

Danube basin More work needed on nutrient fluxes

This paper presents the current state of the art as regards nutrient sources to the Danube basin, pathways and sinks, and transport to the Black Sea, including results of emissions estimates and the Danube Water Quality Model approach and comparisons with measured water monitoring data. Considerable knowledge gaps and margins of error are identified, and the paper concludes that considerable further work is required to achieve reliable estimates of nutrient sources and pathways.

The paper reports results from the EU study "Nutrient Balances for Danube Countries" (EU/AR102A/91, 1997) and the GEF/UNDP River Danube Pollution Reduction Programme. The Danube is nearly 2,900 km long with a catchment of 817,000 km2, including areas of 13 countries.

Total nutrient emissions to the catchment were estimated at 750 – 1,050 ktN/year and 90-130 ktP/year for 1996/1997. Of these totals, 21% of nitrogen inputs were estimated to come from households, of which just under 2/3 via sewage works. For phosphorus inputs, 29% were estimated to come from households, of which just over 2/3 via sewage works. Small amounts of phosphorus from agriculture and industry also go into sewage works, so that sewage works input in total is 33% of total estimated phosphorus inputs.

Underestimation of diffuse sources

If detergent phosphates make up around 30% of sewage phosphate levels, these figures mean that at present they would 30%x29% = 8,7% of catchment phosphorus – assuming no retention in sewage works. After implementation of EU legislation (P-removal in sewage works), they would contribute at most 30%x9% (part not going through sewage works) <3%. Both these figures are likely to be significantly lower because of the indicated underestimation of diffuse phosphorus inputs (up to 50%).

As well as inaccuracies and incoherence between different countries' data and estimates of diffuse inputs, the authors emphasise that total nitrogen inputs are inaccurate because of a lack of data on organic nitrogen. For total phosphorus, two systematic errors were identified: an underestimation because of low sampling frequency (so that large flows during high rainfall events, due to erosion, are not taken into account), and an underestimation because of the use of surface samples only. Total phosphorus concentrations measured in the river were found to be not representative of input estimates. The authors used a combined correction factor of 2 to adjust for these underestimations. They estimate that the use of surface samples only, for example, will inevitably cause an uncertainty in total phosphorus concentrations of up to 50%.

Furthermore, instream phosphorus concentrations are significantly affected by retention mechanisms, with a drop of around 25% occurring with sedimentation of phosphorus in the Iron Gates dam backwaters, for example.

The paper concludes with the **need for considerable further work to better understand nutrient inputs and pathways in the Danube**, in particular regarding agriculture, catchment retention, estimation of real river loads and impacts on the Black Sea. These issues are being addressed by the EU "daNUbs" project launched in February 2001.

"Nutrient fluxes from the Danube Basin to the Black Sea" Wat. Sci. Tech. vol. 46, n°8, pages 9-17. Article can be purchased at: http://www.iwaponline.com/ wst/04608/wst046080009.htm

M. Zessner, Institute for Water Quality, Vienna Technical University, Karlsplatz 13, A1040 Wien, Austria; and J. van Gills, Inland Water Systems, WL Delft Hydraulics, PO Box 177, 2600 MH Delft, The Netherlands.

Hungary Underestimates of diffuse lake phosphorus inputs

Diffuse sources (land and agricultural run-off ...) made up 60-70% of phosphorus loadings to Lake Balaton, Hungary, by the mid-1990's (Jolankai, 1997), mainly carried to the lake by tributary rivers and streams (see "Response of Lake Balaton to sewage nutrient removal" in this Newsletter). Of these, the largest tributary, the Zala river, drains nearly half of the Lake's watershed area (total 5776 km²) and has a mean flow of 7 m³/second.

Phosphorus loads have been monitored in the Zala river and in smaller tributaries 2-4 times/month since 1975, at the point of entry into the lake, and diffuse lake P inputs derived from them. This article assesses the inaccuracy in such load estimates, by using different statistical re-analysis of the available water quality and daily flow data for 5 lake tributaries:

- **unbiased ratio estimate**, where flow weighted mean concentrations based on discrete observations are multiplied by mean flows

- **cluster method**, where observed ranges of flows are grouped into clusters for which average loads are calculated

- **load-flow relationship**, where loads estimated using attentive seasonal regression analysis, differentiating between different seasons' typical loading patterns using 8-15 years' data.

The results of these different load prediction methods were then compared with loads estimated by the routinely used calculation method, where measured P

concentration for each sample is multiplied by sample flow (biased routine method).

Importance of flood flows and load underestimates

This analysis suggested that **nearly 25% of runoff** flow and 30-50% of phosphorus loads were associated with extreme flood flow events. This confirmed previous work by for example Bodo and Unny. This explains why the routine calculation methods tend to provide inaccurate river P load estimates. The error, for twice-monthly monitored small inflows lies in the range 15-80%, and varies according to the specific features of the river's watershed.

The biased routine method is assessed as giving a 5-20% underestimation of total phosphorus loads to Lake Balaton, and a 50-150% underestimate of loads to the Lake's Eastern bay areas.

In some cases, the loads recalculated using the historic seasonal regression analysis exceeded those given by the routine calculation method by factors of 2 or 3.

"Improving uncertain nutrient load estimates for Lake Balaton". Water Science and Technology, vol. 43, n°7, pages 279-286, 2001. http://www.iwaponline.com/ wst/04307/wst043070279.htm

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Czech Republic Challenges of agricultural nutrient run-off

The Zelivka reservoir provides the largest drinking water supply for Prague, as well as supplying the Central Bohemia and Jihlava regions. The reservoir contains up to nearly 257 million m^3 with a retention time of 1-2 years. This study looked at an 85 km² subcatchment of the Zelkiva watershed, the Sedlicky Brook catchment, which drains into the reservoir near the reservoir dam. The area comprises mixed arable and temporary grass fields, and is a high

risk area for soil erosion. Around one quarter of the area is covered by forest.

The water quality of the Sedlicky brook is mainly affected by **diffuse nutrient pollution resulting from intensive agriculture and soil erosion**. By 2000, diffuse nutrients were reaching the limits for drinking water quality.

The **annual average soil loss** was estimated as 1.8 - 4.1 tonnes/hectare and the annual average export of nitrogen from arable land as 2.5 gN/m^2 and phosphorus as 0.01 gP/m^2 .

Agricultural nutrient export

Long term trends for nitrogen (nitrate) and phosphorus loads being carried by the Sedlicky Brook into the reservoir were available from 1976 through to 2000. These indicated, considerable annual variations, but a trend of increases of both nitrate concentration (reaching 50 mgN-NO₃/l by 2000) and phosphorus (reaching 0.15 mgP-Total/l).

In response to this situation, a **catchment Clean Water Programme** was defined, involving local municipalities, the private water company operating the drinking water supply using the reservoir, and farmers. Prevention principles and best management practices were funded by the water company. Long term nutrient monitoring enabled maps defining particularly vulnerable zones to be established. Action can thus include targeted farmers to payments to appropriately manage specified areas to reduce nutrient export and soil erosion, in particular changes of land use and creation of "buffer zones" of permanent vegetation.

The total cost of the Clean Water Programme in the Zelivka reservoir catchment is estimated at 24-31 million €Euros/year.

"Integrated watershed approach in controlling point and non-point source pollution within Zelivka drinking water reservoir". Wat. Sci. Tech. Vol. 45 n°9, pages 293-300. Summary at: http://www.iwaponline.com/ wst/04509/wst045090293.htm

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SCOPE Newsletter – n° 48 - Page 6 - www.ceep-phosphates.org

Mexico Tropical lake nutrient resilience

Lake Zirahuen has a surface area of nearly 10 km² and lies in a catchment of 260 km² in the Central Mexico highlands around 19'N, 101'W, at an altitude of just over 2000m. The mean lake depth is 22M and the water residence time is long.

The lake faces considerable anthropogenic nutrient inputs, both from agriculture (60% of the catchment area) and from direct sewage input from around 24,000 inhabitants.

The lake's water temperature varied from $19 - 22.5^{\circ}$ C in the summer near the surface (stratification), falling to 16-17°C in winter (lake mixing) and was constant at 16.5°C near the bottom (1998). For the last 10 years, approximately, the bottom waters have regularly become anoxic at the beginning of the summer stratification period.

The significant external nutrient loadings to the lake and the potential for internal nutrient loadings due to sediment anoxia, contrast with the excellent condition of the lake, which shows highly transparent waters (whose blue makes the lake an important tourist attraction) and low algal biomass. Phosphorus loadings to the lake have been calculated at 0.25 gP/m² in 1987 rising to 0.34 gP/m² in 1996, but chlorophyll levels (highest surface concentrations 4 μ g/l chl_a) confirm the lack of response to nutrient loadings.

This paper presents algal growth experiments in lake water samples (bioassays) to which nutrients were added, carried out to test whether the low algal response in the lake was due to toxic inhibition of algal growth (one hypothesis suggested that copper pollution could be responsible for this). Bioassays were carried out using water from 5 sampling sites (4 in the lake, one in the La Palma stream, the lake's only inflow), each at four different dates (July, September, December, February). For each sample, four replicates were carried out for each of four treatments: control (no nutrient addition), addition of nitrogen (1000 µgN/l), addition of phosphorus (50 µgP/l), both nitrogen and phosphorus. The samples were filtered (0.45µm membrane) then placed in illuminated, test tubes, with a 40:60 proportion of air, at around 24°C, and shaken every 24 hours.

No response to nutrient loadings from La Palma waters.

In the lake water samples, the controls (no nutrient addition) consistently showed no algal growth potential (AGP), whereas in some seasons (particularly summer) the samples from the inflowing streams showed significant potential. In all tests with lake water, neither the addition of only phosphorus nor the addition of nitrogen only stimulated algal growth (compared to the control test), and stimulation resulted only from the combined addition of phosphorus and nitrogen.

The authors note that the absence of algal growth in the lake water (without nutrient additions) is **consistent with the observed absence of eutrophication symptoms in the lake**, whereas the algal growth potential in the inflowing stream water is consistent with the incoming nutrient loadings – and thus "*the Lake Zirahuen enigma continues*".

The good algal growth found for nutrient addition in the stream waters eliminates the hypothesis of copper inhibition from upstream industrial spills as the explanation of the low in-lake algal growth. The **authors conclude that the lake is co-limited for phosphorus and nitrogen**, and that algal response to nutrient inputs may be prevented by: (a) significant **subsurface flushing of the inflowing nutrients** (stream inflow waters were warmer, so lighter, than the lake bottom water in winter, but colder so denser in summer); and (b) internal control mechanisms preventing the mobilisation of nutrients into the food chain.

"Assessing trophic state of an endorheic tropical lake: the algal growth potential and limiting nutrients", Arch. Hydrobiol. 153 – 2, pages 323-338, Jan. 2002

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Winsconsin Lakes Large daphnia and water clarity in eutrophic lakes

13 eutrophic, summer-stratified lakes in South Winsconsin (USA) were selected for study on the basis of recorded occurrence of summer algal blooms, *Daphnia* grazing, and dominance by either *Daphnia galaeta mendotae* or *D. pulicaria*.

The lakes' areas varied from 78 - 3,985 hectares and their maximum depth from 8.5 - 25.3 m. In 6 of the lakes, *Daphnia* populations were dominated by *D. galaeta mendotae* (average size 1.0 mm, 5.9 µg dry weight), and in 6 by *D. pulicaria* (average 1.3 mm, 17.6 µg). In one lake, the dominant population of *Daphnia* changed from spring to autumn.

The population densities of *Daphnia* in the *D.* galaeta mendotae and *D. pulicaria* dominated lakes were similar (16 and 15 individuals/litre average respectively). However, the **larger** average size of *D. pulicaria* resulted in a higher *Daphnia* biomass/litre in the lakes dominated by this species (192 compared to 104 μ g dry weight/litre) and a significantly higher "mean filtration potential" – a measure of the capacity to graze algae (411 vs. 99 ml/l/day in May, 225 vs. 85 ml/l/day in June).

Clear water despite high nutrient levels

Total phosphorus concentrations were higher in the *D. pulicaria* dominated lakes (66 vs. 25 μ gP/l average May-July). Chlorophyll levels in both classes of lakes were similar in early spring and were found to then be related essentially to the *Daphnia* filtration rate. As a consequence, **the clear water phase in** *D. pulicaria* **lakes tended to start earlier, last longer and achieve better levels of water transparency** (greater Secchi disk depth) in May and June.

This study concords with the authors' previous work (Kasprzak & Lathrop, 1997), which used a series of bag experiments and indicated that *D. pulicaria* was a more effective grazer of algae than *D. galaeta mendotae* and that the difference is because of the greater body size and so filtration potential.

The authors also assessed the risks of blue-green algal blooms related to *Daphnia* grazing, because these algae can be inedible to Daphnia. Blooms of Aphanizomenon, a local problem blue-green, were related to interactions between nutrients, growth of other edible and inedible algae, and grazing. The study results suggest that sufficient abundance of large Daphnia may delay blue-green Aphanizomenon blooms: in the studied lakes Aphanizomenon did not develop in the D. pulicaria lakes where grazing potential was higher than 250 ml/l, with the opposite occurring in than D. galaeta mendotae lakes.

The authors conclude that high densities of large-sized *Daphnia* are a desirable goal in eutrophication management as natural lake populations can attain grazing levels high enough to increase summer water clarity. This confirms similar conclusions reached for lakes in Hungary (Grigorsky *et al.*, Hungary, 1998, reported in SCOPE Newsletter n° 39).

"Influence of different sized Daphnia species on chlorophyll concentration and summer phytoplankton community structure in eutrophic Winsconsin lakes", Journal of Plankton Research, vol. 21, n°11, pages 2161-2174 (1999).

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Ohio, USA

Importance of Daphnia in controlling algae

Six water column enclosures (1.4m diameter, 2.5m depth, from the lake surface to the sediments) were installed in spring (early June – end of August) in Crystal Lake, a small hypereutrophic man-made lake 5km west of Akron, Ohio, USA.

After an initial treatment to eliminate zooplankton and fish (CO_2 as dry ice), except in the "control" column, **two different types of native zooplankton population dominated in the columns** :

- the small cladoceran *Bosmina longisrostris* in three columns (including the control)

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- *Daphnia galeata mendotae* in the other three columns

The development of these two types of zooplankton population was fortuitous: other larger *Daphnia* species were in fact artificially introduced into certain columns but did not survive, and populations of these two native species instead appeared. A few fish (bullheads *Ictaluras melas*) were present in the control column (which had not been CO₂ cleared at the start) but none in the other five columns.

The *Daphnia* dominated columns showed average densities of nearly 100 *D*. individuals per litre, compared to near zero in the lake and the *Bosmina* dominated columns. The *B*. densities were on average 450 ind./l in the *Daphnia* dominated columns, around 2,000 in the *B*. columns (2.460 in the control) and around 1.000 in the lake.

Daphnia grazing effectiveness in controlling blue-greens

The Daphnia dominated columns showed algal counts five times lower than the B. columns, and three times lower chlorophyll levels. The main difference in algal biomass is due to a decrease in the relative abundance of the large, extensively sheathed, blue-green alga Edible Microcystis. primarily green algae, Scendedesmus (the most abundant green algae family in the lake) made up a relatively higher proportion of algal biomass in the Daphnia columns. The green colony alga Coelastrum developed only in the D. columns, to around 12% of algal biomass (this alga is probably inedible for Daphnia).

As a consequence water transparency was better in the *Daphnia* columns, whereas anoxic conditions appeared on occasions in the *B*. columns.

Are blue-greens edible for Daphnia ?

The authors note that other publications suggest that *Daphnia* cannot digest blue-green algae, although they may be grazed and pass through the *Daphnia* and no longer be viable after this passage. The apparent *Daphnia* control of blue-greens in this experiment may be related to differing levels of toxicity of for different strains of these algae, or for algae of different ages.

It may also be indirect results of *Daphnia* grazing which is in fact controlling blue-greens. Mechanisms for this could include the reduction of nutrient levels resulting from sedimentation of *Daphnia* facees (accelerated in this case as the *Daphnia* tended to congregate at the column base just above the lake floor sediments during the day), increased water transparency (green algae are more efficient than blue-greens in good light conditions) or lower pH (*Daphnia* grazing lowers total algal biomass, and thus primary production, and so pH).

"Direct and indirect effects of zooplankton grazing on phytoplankton in a hypereutrophic lake". Oikos 42, pages 291-302, Copenhagen, 1984. http://www.blackwellmunksgaard.dk/tidsskrifter.nsf/ti dsskrifter/Oikos/aimandscope?OpenDocument

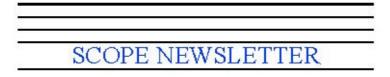
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Norfolk Broads, England Fish, plants, zooplankton and control of algal growth

Five lakes of the shallow Norfolk Broads lake system in Eastern England were studied for three years, from 1993-1995, over the growing season from April to September. Monitoring included sampling of zooplankton across the range of different macrophyte cover densities present in the lakes (from plant covered areas to open water), composition of lakeside vegetation, pointabundance sampling (by electrofishing) of small fish populations, and radio-tracking of piscivorous fish.

The surface area of the five lakes varied from 1.9 to 14.3 hectares and the mean depth from 0.9 - 1.7m. The average proportion of water covered by macrophytes varied from 0 - 91%.

In most of the Broads studied, the key zooplankton grazers *Daphnia sp.* Showed an early summer peak of abundance, followed by a rapid decline. Various pieces of evidence suggests that this population reduction is the result of predation by (small) planktivorous fish, and not simply a response to food limitation: previous studies showing correspondence to timing of development of populations of small fish, ability of even small populations of small fish to cause zooplankton population collapse and failure of *Daphnia* populations to develop in the Spring where significant populations of small fish over-winter.



Further, the relatively high concentrations of nutrients and of algae (chlorophyll) in the Broads suggest that food levels are rarely, if ever, limiting for zooplankton.

Role of macrophytes

Previous work (Stansfield et al., 1997) showed that the decline in Daphnia populations, even in the presence of dense small fish populations, tended to be delayed in the presence of macrophytes. This is thought to be because the macrophytes (plant vegetation) provides zones in which the zooplankton can shelter from fish predation (refuges), as is confirmed by observations of Daphnia behaviour, including grouping near the edges of macrophyte cover. Small fish tend not to enter macrophyte zones because of the high risk of attack by piscivorous fish (such as Northern pike Esox lucius) which can hide in such zones, and even when small fish, particularly roach (Rutilus rutilus) do enter macrophyte cover zones they may not feed on Daphnia because of the difficulty of capturing prey in structured environments.

Several studies have shown **diel horizontal migration of** *Daphnia*, that is moving out from macrohyte cover to open water at night (to graze algae) and returning to cover during the day. However, planktivorous fish are apparently capable of feeding in darkness (Townsend and Risebrow, 1982) so that a reduced predation pressure would still exist.

The presence of macrophytes tends to result in a zooplankton community shift from *Daphnia* dominance to smaller species such as *Simocephalus, Ceriodaphnia* and *Sida* species. Crucially, the latter three species appear to take over the principal grazing role from *Daphnia*.

The beneficial effect of refuges may also be enhanced by the presence of non-grazing copepods or macro-invertebrates in the vegetation, which provide an alternative food source for small fish, reducing predation on grazing zooplankton.

Conditions for zooplankton populations

Experimental work by Shriver *et al.*, 1995, in shallow lakes in Denmark, suggested that **macrophyte coverage of at least 20% of lake surface area and small fish density <2 fish/m² were necessary for zooplankton grazer population stability**. The figures suggested by this Norfolk Broads study suggest that the zooplankton community was here more fragile, requiring a minimum 40% macrophyte cover and small fish density $< 1 / m^2$. The type of fish predator appears to be a key factor.

Control of algal development

Stansfield *et al.*, 1997, illustrated that broads with cladoceran (grazing zooplankton) population densities > 30 individuals/litre achieved low algal development (chlorophyll_a concentrations < 25 μ g/l). Previous studies have suggested that a filtration rate (zooplankton grazing) of 300-400 ml/l/day would be adequate to prevent algal blooms and ensure clear water. This rate was effectively ensured by *Daphnia* in the early spring and then later by *Simocephalus* and *Ceriodaphnia* in this case.

Other studies have also shown that natural zooplankton grazer population densities can prevent algal development, for example Grigorsky *et al.*, Hungary, 1998, reported in SCOPE Newsletter n° 39.

Jepesen *et al.*, 1998, showed that it was **plausible that refuge-using zooplankton could effectively control algal growth at least until mid-summer**. However, an increase in fish densities (> 1 ind./m²) will not necessarily lead to algal blooms, which may be limited by other factors such as nutrient competition with macrophytes.

The authors conclude that zooplankton grazing is susceptible to control algal development in these eutrophic shallow lakes. However, even a low fish density (0.2 fish/m²) can eliminate all grazing zooplankton by mid-summer unless macrophytes are present. A cover of at least 30-40% may provide an effective refuge against fish for a range of grazing zooplankton, until a critical fish density is exceeded.

"The practical importance of the interactions between fish, zooplankton and macrophytes in shallow lake restoration" Hydrobiologia 395/396 (1999) pages 199-210.

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Canadian lakes Daphnia control of filamentous algae

Stoichiometric theory suggests that when significant populations of "phosphorus rich" zooplankton such as *Daphnia* develop (*Daphnia* biomass N:P ratio is lower than that of phytoplankton), then this should increase the ratio of available N:P in water and decrease the abundance of nitrogen-fixing blue green algae.

This paper reports on experiments carried out in the artificially nutrient enriched Lake L227 (North-West Ontario, Canada), where **development of filamentous blue-green algal populations (cyanobacteria) was examined in enclosures with/without** *Daphnia* populations, and with high/low soluble nitrogen:phosphorus ratios. The authors argued that, if *Daphnia* can affect blue-green algae by changes in N:P availability, then the effects of *Daphnia* on blue green algae would be expected to be greater in enclosures receiving low N:P loading.

The initial phytoplankton communities in the enclosures were dominated by the filamentous bluegreen *Aphanizomenon sp.*, with *D. pulicaria* being the main *Daphnia* species. Twelve 1m x 1.1m x 1.9m depth polythene enclosures were suspended in the lake on floating frames, including sediment in the bottom of each enclosure. The 1.9m depth was slightly greater than the mixing depth of the lake at the time of the experiment (June-July, duration 6 weeks).

D. pulicaria were collected from a nearby lake (L110) and added at an average density of 480µg/l in the with-Daphnia enclosures. Soluble phosphorus was added to all the enclosures at 23 mgP/m²/week, equivalent to the lake's phosphorus loading regime. For the high N:P ratio enclosures only, soluble nitrogen was added (as ammonia) to generate an N:P loading ratio of 33:1.

Daphnia survived well in all the enclosures to which they were added, dominating the zooplankton populations (>85% of biomass) and maintaining **densities comparable to those found in the lake surface waters** (average 300 μ g/l). *Daphnia* were nearly never found in the enclosures to which they had not been added.

Impact of Daphnia on algae

Daphnia presence had a strong negative influence on algal biomass, with mean phytoplankton biomass an order of magnitude lower in with-Daphnia than without-Daphnia enclosures. Furthermore, filamentous cyanobacteria made up 75% of algal biomass in without-Daphnia enclosures by the end of the experiment, compared to just 20% in with-Daphnia enclosures. Daphnia had a much stronger influence on algal biomass and community structure than did nitrogen addition.

In the with-Daphnia enclosures, total phosphorus decreased considerably because of greater sedimentation of particulate phosphorus. In contrast, total nitrogen did not change relative to without-Daphnia enclosures because losses of suspended particulate N were balanced by increasing dissolved nitrogen. This resulted in higher dissolved N:P ratios in with-Daphnia enclosures than in without-Daphnia enclosures (both for the with and without added nitrogen cases).

Because of the near-absence of a cyanobacterial response to ammonium addition, the authors conclude that **Daphnia** did not control filamentous cyanobacteria through changes in N:P ratios. They suggest that Daphnia control of cyanobacteria may have been achieved by grazing, or by damage to the algae in attempted grazing even if they were in fact inedible (average filament length $> 300 \mu m$). Alternatively, other nutrient changes related to the presence of Daphnia such as decreased Dissolved Inorganic Carbon (DIC) concentrations may have affected cyanobacteria and prevented their response to the changes in N:P ratios. DIC limitation may have occurred artificially in the enclosures as a result of reduced wind speeds at the enclosure surfaces (reduced aeration), due to the sheltering effect of the enclosure support structures above the water level.

The authors indicate that **the role of DIC in affecting cyanobacterial dominance remains poorly understood** and merits further study.

"The effects of Daphnia on nutrient stoichiometry and filamentous cyanobacteria: a mesocom experiment in a eutrophic lake", Freshwater Biology n°47, pages 1217-1233, 2002.

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Denmark Varying lake reactions to reduced phosphorus

Over 11 years (1989-1999), regular sampling of water total phosphorus concentrations, algal density (chlorophyll_{-a}), algal (phytoplankton), zooplankton and fish communities were analysed throughout the spring-summer period (May-September) in 18 Danish lakes showing significant in-lake phosphorus reductions, plus 5 reference lakes where in-lake phosphorus was fairly stable.

In four of the 18 P-reduction lakes, biomanipulation measures were taken, reducing cyprinid fish populations considerably (70% reduction in fish biomass in 1992-1994), thus limiting predation on zooplankton.

The P-reduced lakes had mean depths of 1 - 3.5m and areas of 0.9 - 4.9 km², with in-lake total phosphorus concentrations of $26 - 885 \mu gP/l$ (average 206 $\mu gP/l$ for the 14 non bio-manipulated lakes, 132 $\mu gP/l$ for the four biomanipulated lakes). The five reference lakes were considerably smaller (0.4 - 1.0 km² with low in-lake total phosphorus concentrations (20 - 59 $\mu gP/l$, average 31 $\mu gP/l$.

The summer chlorophyll levels in the 18 Preduction lakes declined significantly over the 11 year period, whereas no ch anges were recorded in the 5 reference lakes. In the P-reduction lakes, the proportion of non-heterocystous cyanobacteria (bluegreens) declined considerable, with heterocystous cyanobacteria and in some cases dinophytes and cryptophytes increasing. The effects were stronger in the biomanipulated lakes. No significant changes were noted for chrysophytes and diatoms.

In the P-reduced lakes, despite no significant changes in total zooplankton biomass, there were significant increases in the contribution of *Daphnia* to cladoceran communities, and an increase in the mean body mass of *Daphnia*. Because of the decrease in phytoplankton biomass, the zooplankton/phytoplankton biomass ratio increased and so the grazing pressure on phytoplankton increased. Again, these different effects were more marked in the biomanipulated lakes.

In the P-reduced lakes, the biomass of zooplanktivorous fish declined, while the

percentage of piscivorous fish increased markedly. The improvements in the lake water quality is therefore both an effect of enhanced "top-down control" (piscivorous fish eating zooplanktivorous fish and thereby releasing the predation pressure on zooplankton, which may then exert a high grazing pressure on the phytoplankton) and "bottom-up" control (less nutrients means less phytoplankton). In biomanipulated lakes, the role of top-down control was larger.

Internal phosphorus cycling

These different biological responses to reduced inlake phosphorus concentrations were particularly noticeable in the lakes with P concentrations of 1.2 mgP/l or lower, with only minor changes occurring at concentrations in the 1.2 - 4.0 mgP/l range.

The authors also note that the **biological changes are** recorded in response to in-lake phosphorus concentrations, but not necessarily to external phosphorus loading reductions, because of internal loadings.

"Response of phytoplankton, zooplankton, and fish to re-oligotrophication: an 11 year study of 23 Danish lakes", Aquatic Ecosystem Health and Management 5(1), pages 31-43, 2002.

http://www.aehms.org/5_1_jeppesen.html

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The SCOPE Newsletter

The SCOPE Newsletter is produced by the Centre Européen d'Etudes des Polyphosphates, the phosphate industry's research association and a sector group of CEFIC (the European Chemical Industry Council).

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SCIENTIFIC COMMITTEE

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SCOPE NEWSLETTER

NUMBER 47 Special edition

Fifty years of the Rhine commission : A success story in nutrient reduction

Photo : Laura Zito fotoforem@angelfire.com

This edition of the SCOPE Newsletter presents fifty years' action of the Rhine Commission, 1950-2000. We tell the story of how international co-operation through the Commission has restored the Rhine, from the point where most life had disappeared, to a state where salmon have returned to breed, migrating some 700 km up the river. 90% reductions have been achieved for many priority pollutants. We concentrate on one specific aspect of the Rhine's water quality: nutrient discharges and concentrations, and find that the successful reduction in phosphorus concentrations has not been matched for nitrogen. We conclude by looking to the future and to areas where further action is needed and to the Rhine Sustainable Development 2020 programme.

This Newsletter has been jointly written by Andrew Farmer, IEEP (Institute for European Environment Policy, London) and Marc Braun (International Commission for the Protection of the Rhine, Koblenz).









CEEP, SCOPE Newsletter : http://www.ceep-phosphates.org Rhine Commission : http://www.iksr.org



Map of the Rhine Catchment (approx 200,000 km²) showing the^{*} main water quality monitoring points referred to in this Newsletter.

INTRODUCTION



The River Rhine is one of Europe's most important and famous rivers. Originating in Switzerland it is 1,320 km long and flows via France, Germany and the Netherlands to the North Sea. With its tributary rivers it has a catchment of around 200,000 km². The river has been central to western European culture – from its time as a major corridor for the movement of prehistoric peoples and the effective boundary of the Roman Empire to is later role as a major shipping route and artery of commerce. It has been the source of inspiration for poets and writers and formed the centre for the early industrialisation of this region of Europe. While twelve other rivers in Europe have larger catchments than the Rhine, the river is probably only rivalled by the Danube in the underlying consciousness of European culture.

The Rhine catchment has acted as a significant source of settlement for many centuries. The Romans built the first important towns and cities in the region and later settlements thrived as the area acted as a major commercial, cultural and political cross-roads. Today the Rhine catchment holds a population of around 50 million people. Many benefit from the river itself, not least from commercial shipping – the Rhine being the most dense shipping route in Europe. At the mouth of the river lies the largest sea port in the world – Rotterdam – and this connects to the world's largest inland port at Duisburg. Industrialisation has grown considerably resulting in huge industrial complexes, such as those found in the Ruhr, Main and Rijnmond areas. A wide range of industrial activity is undertaken. For example, Europe's most important chemical plants are found along the river.

The transport opportunities are only part of the use to which the Rhine is put. For many years it has acted as a source of drinking water (today supplying over 20 million people), waste water disposal, energy generation and recreation. thoto : "Karl Auer kauer@bipine.com.au

This has created enormous pressures on the environment of the Rhine. However, it still remains an important location for many wildlife habitats as well as a corridor for species migration.

This edition of the SCOPE Newsletter is produced to mark fifty years of the Rhine Commission. It tells the story of the degradation of the Rhine to the point where most life disappeared and how international co-operation through the Commission developed ways to reduce pressures and restore the river. After providing a general overview of these issues, we concentrate on one specific aspect of the Rhine's water quality: nutrient discharges and concentrations. Finally, even though much has been achieved, such tasks are never finished. This Newsletter, therefore, concludes with a view to the future and what action remains to be undertaken.

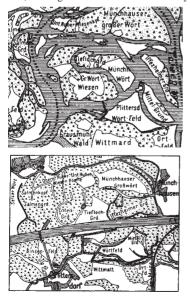


The deterioration of the Rhine

Centuries of human settlement and manipulation of the river have, not surprisingly, resulted in the degradation of the environment. It is also clear that conflicts can arise in the role of the Rhine for human purposes, eg between its role as a drinking water source and its use for waste water disposal.

Degradation started early. One of the earliest records of problems in the environment was noted in 1449. The effects of overfishing and of pollution had led to significant declines in the fish population. As a result the so called 'Strasbourg Regulations' were adopted. These formed the first international agreement to protect the Rhine. However, many more changes to the environment were to take place, before improvements would be seen.

One of the most dramatic changes to the river occurred between 1817 and 1874. During this period the German engineer Tulla undertook a major series of engineering works to alter the structure of the river channel. This included straightening of the river course, as well as numerous other riparian measures. The action was undertaken to improve navigation, reduce flooding, recover alluvial areas for farming and reduce incidents of disease. These changes (so called 'corrections') have continued since, well into the 20th century. The result of these changes was that the length of the river was dramatically shortened. Between Basel and the border of Hessen alone, the length of the river was reduced by 80 km.



Disappearance of tressing of the Rhine river near Pittersdorf, Upper Rhine, from 1817 to 1874, leading to loss of habitat diversity, fish spawning grounds, water purification capacity and other natural functions

Engineering works did not only focus on the river channel. The large volumes of water flowing down the river has proved attractive as an energy source. Along much of the Rhine many dams and weirs were constructed to hold water for power generation.

Overall the physical character of the river changed significantly. Meanders were cut off, flood plains reduced or lost and flow velocity generally increased. These effects also resulted in increased erosion in surrounding areas and a lowering of groundwater levels. Numerous important habitats were lost and the physical barriers erected across the river prevented the movement of migratory fish such as the Salmon. In 1870 the total catch of Atlantic Salmon on the river was 280,000. By 1950 this was reduced to zero.



Not all losses were the result of physical changes – pollution also had a large role. Amazingly, even though pollution problems had been highlighted in 1449, it was not until the 1960s that the issue became of high enough profile for action to be considered. However, by this stage water quality had deteriorated to the point that little aquatic life remained along much of the river. Discharges of organic wastes (eg from sewage) had reduced oxygen levels to below 2 mg/l, industrial discharges included large quantities of heavy metals, hydrocarbons, organochlorine compounds, pesticides, etc. Sediments became highly contaminated. Those providing drinking water had to employ increasingly more complex and expensive treatment methods. The river had become the sewer of Europe, as was noted by the poet Allen Ginsberg who, in 1979, published:

> 'Too much industry No fish in the Rhine Lorelei poisoned Too much embarrassment.'

International co-operation: the creation of the Rhine Commission

Solving the problems of the Rhine was only possible through international co-operation. The Rhine catchment states (Switzerland, France, Germany, Luxembourg and the Netherlands), therefore, established the International Commission for the Protection of the Rhine (ICPR) in Basel on 11 July 1950. Co-operation was strengthened particularly in 1963 with the signing of the Berne Convention on the Protection of the Rhine. The European Community formally signed this Convention also, in 1976. This SCOPE Newsletter, therefore, examines the achievements of the Rhine Commission to its fiftieth anniversary in 2000.

The first internationally agreed measures to tackle pollution in the Rhine were taken around 1970. This was twenty years after the creation of the Commission and, as we have seen, there was already significant evidence for environmental problems. It is not, therefore, unreasonable to ask – why the delay? The two main reasons usually given are that it took some time for mutual confidence building and co-operative mechanisms to be developed between the states and, more importantly, political commitment to tackling environmental issues was very weak until the late 1960s. It is often stated that the Torrey Cannyon oil tanker disaster in the English Channel highlighted environmental concerns and certainly, by 1974 a range of international conventions had been signed, such as the Marpol, Oslo and Paris Conventions. National governments were, therefore, willing to take necessary action.

Thus the 1970s and early 1980s saw a spate of activity in the Rhine catchment to reduce pollution. For example, between 1970 and 1985 more than Eur. 40,000 million were invested on industrial and municipal waste water treatment. The focus was on end-of-pipe techniques, rather than on preventive measures. The reduction in organic inputs led to a steady improvement in dissolved oxygen levels.

In 1976 the Rhine Commission adopted an International Convention on the Prevention of Chemical Pollution of the Rhine. This focused on a list of dangerous substances, in part taking forward the European Economic Community's 1976 dangerous substances Directive. Limit values for specific substances were agreed between the Rhine bordering states, but, due to potential consequences for the internal market, it was considered necessary for these to be developed by the EEC. Unfortunately, after some initial activity, progress became painfully slow and eventually ground to a halt at the Community level. The problem has been the very slow conversion of the ICPR-Recommendations for the reduction of single substances, in national law and the long list of substances (single substance approach in contrast to the BAT approach for industrial sectors).

Thus the 1970s and early 1980s saw some important initial action to reduce pollution to the Rhine. However, the initial impetus had become stuck in a mire of political disagreements which was leaving some issues unresolved and others making only slow progress. It took a major disaster to shock the national governments back into action.

The 1986 Sandoz accident: the creation of the Rhine Action Programme

The accident at the Sandoz plant near Basel resulted in the release of large quantities of toxic substances into the Rhine. These caused the death of almost all aquatic life for many kilometres downstream as far as the Lorelei, just upstream of Koblenz. The effect was equally dramatic politically, with popular concern heightened in all the Rhine states. In a short time three ministerial conferences had taken place addressing pollution to the river. These culminated in the 1987 Rhine Action Programme. The development of the Rhine Action Programme in so short a space of time contrasts markedly with the slow progress of previous years. Apart from the urgency felt from the Sandoz accident, it was also facilitated by environmental issues rising generally on the political agenda and, not least, by the preparatory work that the Rhine Commission had been able to undertake. The Rhine Action Programme marks an important step in international water management. It was by far the most detailed river basin programme agreed between sovereign states anywhere in the world.



The Rhine Action Programme set out a series of broad and challenging goals for the period up to the year 2000. These supported an integrated approach to river management, not merely tackling specific pollutants, but aiming to improve the entire ecosystem. The specific goals were:

- the ecosystem of the Rhine should be improved sufficiently for species such as salmon and sea trout to re-establish breeding populations;
- the production of drinking water from the Rhine should be guaranteed for the future;
- the pollution of river sediments should be reduced to levels compatible with the use of sludge for landfill or sea dumping.

The Rhine Action Programme also established more specific objectives to underpin these broad goals, such as that of reducing the input of dangerous substances to the river by 50% between 1985 and 1995. Concerns were again hightened in 1988 when enormous algal blooms occurred in the North Sea related to nutrient discharges from the mouth of the Rhine. As a result the Rhine Action Programme added a further broad objective for 2000:

• The improvement of the ecological state of the North Sea.

The Rhine Action Programme was divided into three phases:

- The Rhine Commission established a list of priority substances, including nutrients, analysing sources and discharges. It also developed a best available technology (BAT) approach to preventive measures for industrial and municipal discharges. Measures were also adopted to reduce the risk of pollution from accidents.
- 2. The second phase (to 1995) focused on the implementation of measures developed in the first phase;
- 3. The third phase (to 2000) focused on 'fine-tuning' identifying any additional measures necessary to tackle problems that may have remained.

Box 1: Key dates in the history of the Rhine Commission

- 1950: Following a Dutch initiative the Rhine bordering states created a common forum to discuss issues relating to pollution of the river.
- 1963: Signature of the Convention on the International Commission for the Protection of the Rhine against Pollution (Bern Convention) by the Rhine bordering states.
- 1976: European Community joins as contracting party to the Bern Convention.
- 1976: Signature of the Convention on the Protection of the Rhine against Chemical Pollution and signature of the Convention on the Protection of the Rhine against Chloride Pollution.
- 1987: Ministers approve implementation of the Rhine Action Programme.
- 1995: Ministerial decision to draft an Action Plan on flood control measures.
- 1998: 12th Conference of Rhine Ministers agrees Action Plan on Flood Defence and New Convention on the Rhine.
- 2001: 13th Conference of Rhine Ministers : adoption of the Rhine Sustainable Development Programme "Rhine 2020"

The organisation of the Rhine Commission

The organisational structure of the Rhine Commission has changed and evolved over the many years of its existence. The last major change occurred in 1995, with the introduction of action in relation to flood management. The political goals of the Rhine Commission are set through Ministerial conferences, which are held every two to three years. These also assess and evaluate the activities which the Rhine Commission was charged with undertaking. The Commission itself consists of senior officials from the member states. It meets annually and decides on work programmes, finances and formal procedures. A co-ordination group, meeting four times per year, is responsible for the actual planning and coordination of the work of the Rhine Commission.

The Commission has three permanent working groups which address the issues of water quality, ecology and emissions. The work of these groups is described in box 2. There is also one non-permanent project group which has a time-limited mandate and supervises the implementation of the Action Programme on Protection against flooding. The work of these groups is also supported by expert groups of national officials which address specific issues. The work of the Commission is supported by a small international secretariat based in Koblenz, Germany.

Box 2: The tasks of the three Working Groups of the Rhine Commission

Working Group A: Water Quality

- Supervises the development of the quality objectives for water, suspended matter, sediments and of residues in organisms.
- · Develops research programmes and evaluates the results.
- Assesses unusual concentrations of noxious substances through a variety of monitoring systems and tests.
- · Evaluates and reports on monitoring results.
- Periodically compares the state of the Rhine with target values.

Working Group B: Ecology

- Elaboration of the Ecological Master Plan for the Rhine in the context of integrated ecological protection.
- Drafting guidelines for a network of biotopes in the Rhine corridor and of proposals for necessary measures.
- Support and completion of the Salmon 2000 programme.
- Support and evaluation of ecological success.

Working Group C: Emissions

- Registration of sources of pollution and proposal of appropriate reduction measures, including, if necessary, economic incentives for point and non-point sources;
- Harmonisation of the Best Available Technology for significant industrial sectors along the Rhine and monitoring its application;
- Prevention of accidents and improvement of safety of industrial plants.

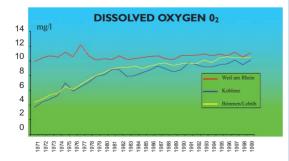
Management issues and achievements

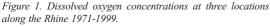
The nature of the problems relating to nutrient discharges and actions to tackle these will be discussed in detail in a later section. However, it is important to highlight action on the range of issues that the Rhine Action Programme addressed and were managed by the Rhine Commission. This illustrates the integrated river basin management approach.

Accident management and industrial pollution reduction

The management of accident prevention and containment is highly site specific. However, it is also important for management at the river basin level. In 1987 Ministers asked the Rhine Commission to develop a model to allow rapid and reliable prediction of how pollutants would travel along the river in the event of another accident. The Rhine Commission worked with the International Commission for the Hydrology of the Rhine and the Universities of Delft, Freiburg and Bern, As a result a model is available that can predict the timing of maximum pollutant concentrations following an accident, allowing for measures to be taken to reduce or avoid its effects. The model includes the Rhine from its outflow at Lake Constance to the Netherlands, including the estuarine rivers Ijssel, Nederrijn and Waal (although not tidal reaches), the tributaries of the Aare, Neckar, Main and Moselle, and the influence of standing waters.

The Rhine Commission also undertook a comprehensive inventory of all of the industrial plants along the Rhine which, in the event of an accident, could release significant pollution into the river. National authorities remained responsible for safety inspection. This work resulted in the Rhine Commission report 'Prevention of Accidental Pollution and Safety of Industrial Plants'. Since its publication the Rhine Commission has made a variety of recommendations concerning safety and the prevention of accidental pollution. Such recommendations included a focus on day to day pollution minimisation as well as prevention of major accidents.





See map page 2 for location of these sampling points.

To tackle industrial discharges, especially of toxic substances, the promotion of Best Available Technology (BAT) in pollution prevention has been important. BAT concerns improvements to industrial processes themselves (to reduce the likelihood of pollution production) as well as effective 'end-of-pipe' technologies to treat waste water prior to discharge. The Rhine Commission has assisted in the exchange of information on BAT between the Rhine bordering states and monitors its application.

These aspects of the Rhine Action Programme have been very successful. By 1994 the Rhine Commission reported that the 50% target for 1995 for the reduction in discharge of dangerous substances had been met in most cases and 90% reduction had been achieved for many. However, some problems remained, particularly for diffuse sources such as pesticides and nutrients from agriculture. However, the improvement has been dramatic in a short time.

Developing quality objectives

Effective management requires objectives. The Rhine Commission has, therefore, developed a system of quality objectives for the Rhine. These so called 'Zielvorgaben quality targets' are not absolute emission limits or ambient quality values. Their aim is to provide an easy quantitative assessment of the river quality and to act as a tool for priority setting when specific measures are developed for individual substances. These 'quality targets' include the most stringent values, such as no effect concentrations (NOEC) for aquatic life and drinking water abstraction requirements derived from EC legislation. They include standards for fisheries, suspended solids and also for sediments. The 'quality targets' is set at the strictest level for the most sensitive objective. For example, the drinking water standard for chloroform is 1.0 mg/l. However, toxicity tests on aquatic organisms showed that effects were possible above 0.6 mg/l. As a result the 'quality targets' for chloroform has been set at 0.6 mg/l. Currently 80 (since the Year 2000) substances or groups of substances are included. The list includes a quality objective for phosphorus (0.15 mg/l), but not for nitrogen.

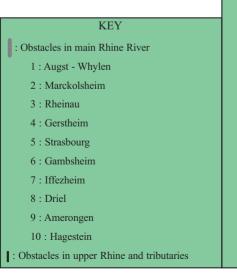
By the end of 1994 the implementation of the Rhine Action Programme meant that the objective concentrations for most substances (of the old list) were met. However, targets were not met for several metals (lead, mercury, cadmium, copper and zinc), for lindane, HCB and several PCBs and for ammonium. Many of these have significant diffuse sources or represent resuspension of contaminated sediments.

Reviving salmon populations

The Rhine Action Programme contained the objective of reviving sustainable salmon populations in the river by 2000. Salmon are an important indicator species for the general health of the river (requiring good quality water, spawning grounds and unhindered migratory access). They are also of importance to the public, which view the species as a symbol of the state of the river. The Rhine Commission considered that different measures would need to be undertaken in a short time frame. The reduction in discharges of dangerous substances was a necessary prerequisite, ensuring water quality was adequate for fish survival. A particularly important objective in this regard has been that to increase dissolved oxygen levels. Measures to control organic discharges (especially from waste water treatment works) were introduced and dissolved oxygen levels have increased significantly (see Figure 1 - for details of the monitoring stations see below).

Additionally, the large number of engineering works undertaken since the early 19th century posed many barriers to fish migration. A programme introducing fish passages at the necessary barriers was begun. Habitat restoration work was also required at the spawning grounds to provide the necessary conditions for successful reproduction. The 'Salmon 2000' project of the Rhine Commission culminated in the introduction of thousands of alevins from Scottish and French stock.

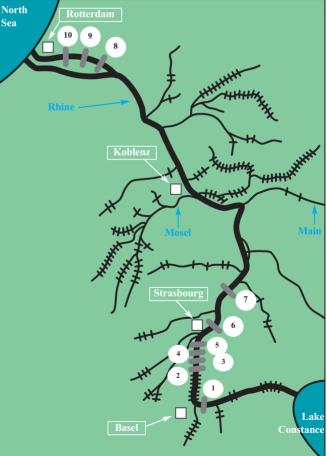
The results have been very encouraging. Since 1990 salmon and sea trout have returned to the Rhine and its tributaries from the sea and natural reproduction has been recorded since 1992. In 1995 nine salmon were caught at the Iffezheim barrier, just downstream of Strasbourg, proving migration had occurred more than 700 km upriver. However, significant barriers remain on the Franco-German border at locks such as *Iffezheim, Gambsheim, Gerstheim, Straßburg*, preventing further up-river migration at present.



The importance of the Salmon 2000 project is not just the species' symbolic function. It represents an integrated management approach. Measures had to be developed covering water quality, engineering, habitat creation, etc, each of which needed translating from the scale of the river basin to that of local action. The lessons learnt from this successful approach can also be utilised in other areas.

Flood management

River management concerns not only qualitative issues, but also quantitative ones. In 1994 the Rhine Ministers broadened the scope of co-operation to include quantitative aspects of the management of the Rhine. This decision was, in part, precipitated by disastrous floods in the middle and lower Rhine in 1993 and the need for action was confirmed by further extensive flooding in 1995. The Rhine Commission, therefore, took on the task of developing an international action programme for the management of flood problems.



Map showing barriers to fish migration in the Rhine and tributaries

By 1995 the Commission had developed the first international strategy for the management of flooding problems. The primary conclusion of the strategy was that flooding could not be prevented and, therefore, that action should be focused on floodplain management rather than flood management. Ten guiding principles were formulated as the basis for a multitrack management approach. The Rhine Commission undertook a complete inventory of all historically known and present day naturally flooding areas, as well as an inventory of current international alarm and warning systems along the Rhine, in combination with the international network of meteorological stations. The management of flooding on the Rhine focused attention on the need for international cooperation as decisions taken at the local, regional or national level were often insufficient (or even counter productive). For example flood defences or urbanisation may simply create an even worse problem further downstream. However, a major challenge remains, especially in integrating the sensitivities of all of the authorities and communities involved. The focus on floodplain management also allowed greater integration with the ecosystem restoration objectives from other areas of the Rhine Commission's work.

Nutrient discharges to the Rhine

The two nutrients of most interest are phosphorus and nitrogen. Plants (both phytoplankton – that is "algae" - and macrophytes – that is larger water plants) are limited in their growth by various factors. These include the availability of nutrients. In freshwaters phosphorus is often limiting, while nitrogen is more usually the limiting nutrient in marine waters. For the Rhine discharges of both are of concern, given the need to protect both the river ecosystem and that of the area of the North Sea to which to river discharges. Other factors are also important. One of these is light. In areas of high concentrations of suspended solids light penetration in the water column can be severely limited and, therefore, elevated nutrient concentrations would have less impact. This can also be an important issue along parts of the Rhine.

The Rhine Commission has undertaken two full surveys of phosphorus and nitrogen inputs in the Rhine catchment in 1985 and 1996. The sources are divided into two general source types – point sources (such as a waste water treatment and works, industrial discharges) and diffuse sources (such as agricultural and other land surface run off and drainage).

Phosphorus sources

The data show (Table 1) that, in 1985, point sources accounted for about 75% of the total phosphorus input to the Rhine, with urban (ie sewage) discharges being about twice that of industrial inputs. By 1996 the relative importance of urban and industrial sources to each other remained similar. However, by this time the relative contribution of point and diffuse sources was roughly equal.

Between 1985 and 1996 the total input of phosphorus from human activity reduced from 72,400 t P/a to about 25,400 t P/a. This is a reduction of about 65% and was well above the target in the Rhine Action Programme of a 50% reduction by 1995. The decline was driven overwhelmingly by a 77% reduction from urban point sources and a 76% reduction from industrial point sources. Diffuse source inputs were reduced by 59%. These changes are illustrated in Figures 2 and 3.



In 1985 more than a third of all phosphorus input to the Rhine arose from urban pollution from Germany. The 81% decline in this source by 1996 is highly important in driving improvement in the river. Early investment in phosphorus removal was driven by a domestic political agenda (both to improve conditions in the Rhine and also for other water bodies). In later years the requirements of the EC 1991 urban waste water treatment Directive (see below) were also important. The 1998 deadline in this Directive suggests that improvements in point sources have continued beyond 1996.

Nitrogen sources

In 1985 the contribution of point sources (284,000 t N/a) was slightly more than that from diffuse sources (249,000 t N/a) (see Table 2). By 1996 the diffuse source contribution had declined only slightly to 230,000 t N/a, while that from point sources was reduced to 162,000 t N/a. Overall this represents a reduction of 26%. This is only about half of the target of 50% for 1995 in the Rhine Action Programme. The largest decline derived from the industrial sector, which accounted for 15% of point source inputs in 1985, but only 5% in 1996 (or a 77% reduction in absolute emissions). This contrasts with a 27% reduction in discharges from sewage treatment works.



The largest single point source is, as with phosphorus, urban pollution from Germany. While some improvement has been made, this has not been so striking as for phosphorus. The large quantities of diffuse nitrogen pollution also remain of concern. However, the EC nitrates Directive had yet to be fully implemented by 1996 and it is expected that some further nitrogen reduction will have occurred as this Directive was implemented in subsequent years.

Figures 2 and 3: Percentage reduction in phosphorus and nitrogen discharges to the Rhine by source between 1985 and 1996 (note the percentage increase in P discharges from natural sources).

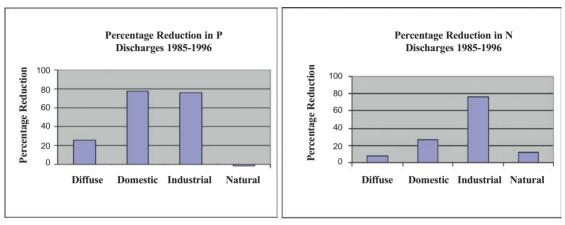


Table 1. Sources of total phosphorus in 1985 and 1996 to the Rhine. All values are in tonnes per year.

Country	Diffuse		Domestic point		Industrial point		Natural		Total	
	1985	1996	1985	1996	1985	1996	1985	1996	1985	1996
СН	448	449	2,300	900	150	35	98	138	2,996	1,522
D	8,987	6,452	25,970	4,925	3,370	590	625	605	38,952	12,572
F	2,190	1,527	3,520	830	1,280	410	108	108	7,098	2,875
NL	5,430	4,229	6,749	2,071	11,989	3,000	524	524	24,692	9,824
Total	17,055	12,657	38,539	8,726	16,789	4,035	1,355	1,375	73,738	26,793

Table 2. Sources of total nitrogen in 1985 and 1996 to the Rhine. All values are in tonnes per year.

Country	Diffuse		Domestic point		Industrial point		Natural		Total	
	1985	1996	1985	1996	1985	1996	1985	1996	1985	1996
СН	11,912	13,789	19,500	14,300	1,000	1,000	9,726	4,729	42,138	33,818
D	146,310	123,560	135,220	95,760	69,450	13,740	45,860	43,120	396,840	276,180
F	25,450	26,340	15,800	9,510	15,000	4,400	8,400	8,400	64,650	48,650
NL	64,847	66,149	22,780	21,377	5,221	2,160	3,794	3,794	96,642	93,480
Total	248,519	229,838	193,300	140,947	90,671	21,300	67,780	60,043	600,270	452,128

Waste water treatment in the Rhine states

Waste water treatment works have been important sources of both nitrogen and phosphorus to the Rhine. It is not possible in this space to detail the historical changes that have taken place in waste water treatment in each Rhine bordering state.

All states in the Rhine catchment area (except Switzerland and Lichtenstein) are required to implement the 1991 European Community Directive on urban waste water treatment (91/271/EEC). However, in Switzerland, in 1999, reports indicate that 73.8% of the total public waste water was treated to an advanced standard (usually nutrient removal).

The urban waste water treatment Directive, inter alia, established objectives for nutrient removal for discharges to waters that are eutrophic or that may become eutrophic. These objectives should have been met by the end of 1998. Member States had two options. They could either designate individual waters as sensitive, in which case waste water discharged from sewage treatment works serving a population equivalent of more than 10,000 would require either 80% phosphorus removal and/or 70% nitrogen removal (depending on the potential impact) or a combined phosphorus and nitrogen removal of 75%. Alternatively, Member States could designate their entire territories as sensitive and meet a 75% reduction for both parameters for all waste water treatment plants.



In November 2001 the European Commission published a short report detailing compliance with these requirements (COM(2001)685). For the relevant Rhine bordering states the main findings of the European Commission and other relevant sources were:

Belgium: a very small part with a low population density of the Wallonia region is in the Rhine catchment. The European Commission is critical of the Wallonia government for restricted designation of sensitive areas and only in 2000 did the Wallonia regional government state that it would consider the whole of its territory as sensitive. Thus, to date, many of the treatment plants in this region lack adequate nutrient removal. *France:* Although France is criticised by the European Commission for restricted designation of sensitive areas, the entire Rhine catchment in France is nonetheless designated. For the whole of France, at the end of 1998, 130 of 158 agglomerations in sensitive areas did not meet the requirements for nutrient removal. The most recent published material addressing France refers to 1996, when 58% of phosphorus was removed in the Rhin-Meuse catchment and only 30 of the 62 agglomerations above 10,000 population equivalent removed 70% or more of the nitrogen input.

Germany: the entire territory of the Rhine catchment part of Germany has been designated as sensitive. Much of this territory has extensive phosphorus removal, but additional treatment in many waste water treatment works is required to remove nitrogen.

Luxembourg: the entire territory has been designated as sensitive. While treatment removes more than 75% of phosphorus prior to discharge, additional investment will be required before the requirement for 75% removal of nitrogen has been met.

The Netherlands: the entire territory has been designated as sensitive. By the end of 1998 the Dutch reported that the requirement for 75% removal of phosphorus had been met, but that nitrogen removal at that date was only 60%. It is expected that full conformity with the Directive will be achieved by 2005.

The efforts made on phosphorus removal in Germany, Luxembourg and the Netherlands have been a major contributor to the significant improvements in water quality in the Rhine (see below). However, the focus of these countries has been on the potential eutrophicating effects of phosphorus in freshwaters, rather than the wider nutrient context. This is now changing. The European Commission is of the view that the North Sea (or at least parts of it) should be considered as sensitive. This means that significant controls on nitrogen discharges will be required for relevant waste water treatment works in the Rhine catchment. This will, therefore, require additional investment in some facilities in Germany, Luxembourg and the Netherlands.

The situation in Belgium and France has been less satisfactory. In Wallonia restricted designation has led to inadequate investment in waste water treatment. In France, despite designation of the territory of the Rhin-Meuse Water Agency the necessary treatment facilities have only been partially installed. In both cases further investment is promised and this, it is now clear, must include treatment to remove both nitrogen and phosphorus.

In conclusion, therefore, although there has been significant reduction in phosphorus discharges from waste water treatment works, reductions of nitrogen discharges have been limited. However, it is expected that some additional reduction in phosphorus discharges to the Rhine catchment from waste water treatment works will continue into the near future and that significant reductions in nitrogen discharges should be expected.

Nutrient concentrations in the Rhine

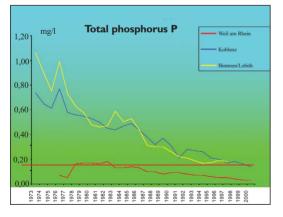
Water quality has been monitored for many years at different locations along the length of the Rhine. The accompanying figures present data from three locations (located progressively upstream):

- Bimmen/Lobith (1971-2000)
- Koblenz (1971-2000)
- Weil am Rhein (1977-2000)

Phosphorus

Phosphorus concentrations have shown a dramatic decline at all three monitoring locations (Figure 4), so that the target concentration has been met along much of the river. This trend has occurred since the mid-1970s in the mid/lower monitoring stations and since the early 1980s in the upper monitoring station (where phosphorus levels were already nearly at the target concentration). Phosphorus concentrations in the river have responded relatively well to changes in inputs and the significant decline in discharges (see above) is reflected in the improved river water quality.

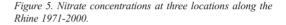
Figure 4. Phosphorus concentrations at three locations along the Rhine 1971-2000.

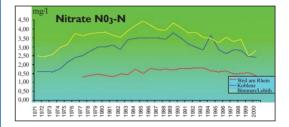


Nitrogen (nitrate)

The data at each location show similar trends but these are very different to the trends for phosphorus (Figure 5). Concentrations are higher at sampling points further downstearn, so that currently concentrations at Weil am Rhein are less than half those at Bimmen/Lobith. At all locations concentrations rose in the 1970s, reaching peaks in the mid to late 1980s or even early 1990s. At Koblenz concentrations of nitrate more than doubled, but smaller increases were found at the other two sites. In the late 1990s concentrations have begun to decline, but at no location have concentrations returned to those shown when monitoring started.

The decline in nitrate concentrations is certainly less marked than the relative decline in discharges (see above). Part of the reason for this may be the large contribution of diffuse sources, especially those entering via groundwater. There is a significant time lag (of many years) between nitrogen entering groundwater and its influence on the river. Thus it may be some time before improvements in river water quality fully reflect changes in pollution sources.





Rhine 2020 – The Rhine Sustainable Development Programme

Following the completion of the Rhine Action Programme in 2000, Ministers agreed in 2001 to a new programme to run to 2020. The programme builds on the successes of the earlier initiatives and takes forward action on ecosystem improvement, flood prevention and protection, water quality and groundwater protection. In each category a wide range of detailed targets has been established. These include a commitment to achieve compliance with target values of all substances in the Rhine, including phosphorus (for nitrogen there is no target value except the reduction required under the North Sea Conference) and to meet strict ecosystem objectives. This will require full implementation of measures on domestic and industrial pollution sources, and more environmentally sensitive farming practices.

The restoration of the ecosystem will be linked to flood prevention and will include restoring ecological continuity, restoration and reforestation of alluvial areas (1200km²) and reconnection of old branches and tresses of the river.

The Rhine Commission is also increasing its co-operation with non-governmental organisations (NGOs). This developed from a conference organised by the Commission called 'Living with the Rhine', which addressed all relevant issues and aimed to assist future policy development. National and international NGOs participated. In the framework of the new Rhine convention the NGOs have been integrated at the level of the plenary meetings and with the working groups.

Future management of the Rhine

1998 the 12th Conference of Rhine Ministers agreed the New Rhine Convention. The experience of the previous fifty years has underlined the importance of an integrated approach to the management of the river. The new convention has addressed and integrated all of the elements necessary for the future sustainable development of the Rhine. It has recognised the need for effective information exchange and co-operation with NGOs and for consensus on objectives and means. This principle not only means that there is inter-governmental agreement, but that citizens and communities are brought within the decision making process.

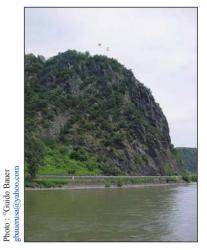
The history of the Rhine Commission's work also demonstrates the need for flexibility in implementation of programmes. Experience has shown that detailed prescriptive programmes take time to develop and tend to hinder implementation in some countries or regions. This flexible approach will also be taken in relation to polluters such as industry. Decisions of technical issues, investments, etc, can be better undertaken by these stakeholders rather than at the inter-governmental level.

The work of the Rhine Commission (and future developments) has become increasingly open and transparent. The reasons for objectives, actions, etc, must be clear and understood by the public. The Commission's information strategy will increasingly take advantage of the opportunities afforded by information technologies.



The EU water framework Directive

The water framework Directive (2000/60/EC) adopted by the European Union in 2000 requires Member States to take a river basin approach to qualitative and quantitative aspects of water management. Some aspects of the Directive owe much to the experience of international co-operation gained from the fifty years of the operation of the Rhine Commission. However, the Directive does impose additional obligations on the EU Member States that border the Rhine. In particular cooperation is being extended to the entire Rhine catchment, including eight states and the European Commission (six being EU Member States - Austria, Belgium, France, Germany, Luxembourg, the Netherlands - the other two being Lichtenstein and Switzerland) A steering group and preparation-group have been set up including both EU Member States and Switzerland and Lichtenstein. These groups will co-ordinate drafting of an international management plan for the Rhine river basin and are given practical support by the office of the International Rhine Commission within the available capacity. It will also need to address other implications of the Directive, such as setting ecological quality objectives and how its seven year plan review period links to action plans developed under the Rhine Commission. Ultimately, the framework Directive may lead to Member States taking further action to reduce nutrient inputs to water bodies, especially from those sources which have had less control until now, such as diffuse agricultural pollution.



Conclusions

The fifty year history of the Rhine Commission is a success story. While international agreement on environmental improvement was slow to be reached between the Rhine bordering states, increasing public concern and political reaction to the Sandoz accident did result in a wide ranging series of policy measures. Water quality has improved for many parameters, the physical structure of the river has been upgraded and salmon have returned.

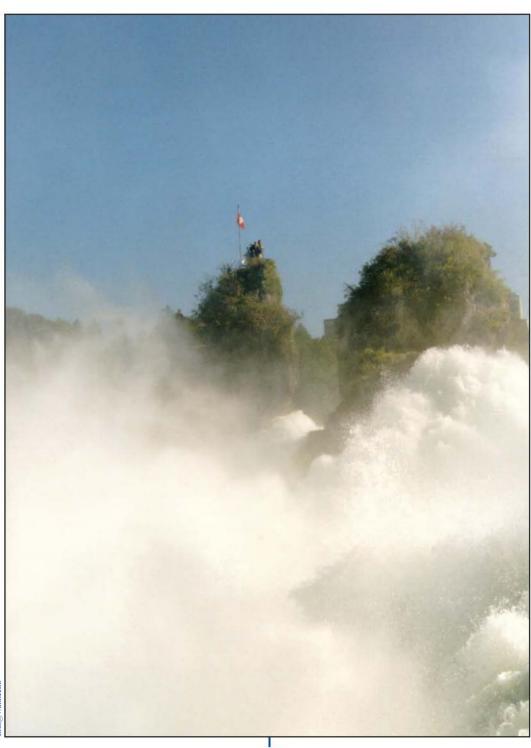
The general success story is repeated when one considers phosphorus discharges. Total discharges have fallen dramatically and water quality monitoring indicates that the target value for a sustainable ecosystem has been met along much of the river. This has largely been due to extensive investment in phosphorus removal in domestic and industrial waste water treatment works. Further investment has (or will) take place in selected locations due to pressure to implement EU legislation and, therefore, it is likely that further water quality improvements will be seen. Thus, when viewed as a whole, phosphorus is no longer a parameter of major concern in the Rhine.



Photo: [©]Karl Auer cauer@biplanr.com.au This success has not, however, been repeated for nitrogen. While there has been an important reduction in discharges since 1985, those that remain are highly significant, particularly given that they are carried by the Rhine into the North Sea coastal area where nitrogen loads are considered to be the key factor for eutrophication. The role of diffuse nitrogen pollution is of considerable concern. Minor improvement has been seen in nitrate levels in the Rhine water column, but concentrations are well in excess of the reduction targets. There is pressure at an EU level to invest in additional nitrogen removal on waste water treatment works and to reduce nitrogen applications in agriculture. It remains to be seen, however, what effect (and when) this will have on the water quality of the river and on nitrogen loads carried to the North Sea.

The future management of the Rhine will be more comprehensive in nature than anything previously. The new Rhine 2020 Program for sustainable development has detailed targets for many different management issues in the river and the implementation of the EU water framework Directive will result in a fully integrated management plan and a wider geographic consideration of the full catchment. It is not known what implications this might have for nutrient management. However, it is likely that attention will focus on any remaining significant point sources and on innovative measures to tackle diffuse sources.

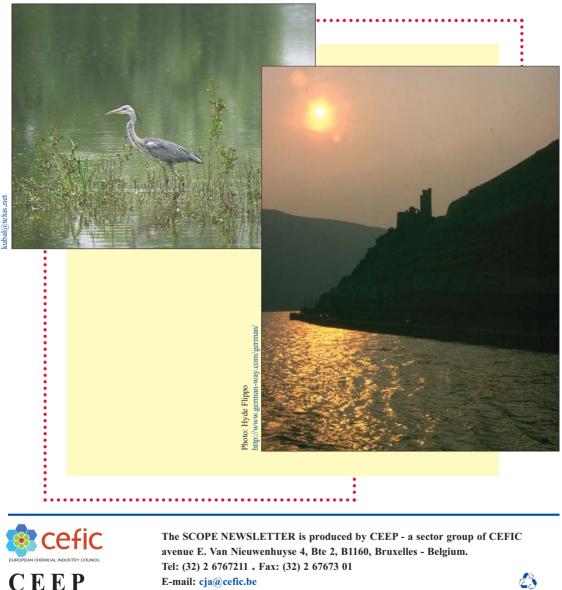




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Wastewater and Nitrates Directives implementation reports

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Reducing nutrient emissions to the Odra

Nutrient input modelling for the Odra river basin indicates that the 50% reduction targets set by HELCOM (Baltic Sea) are achievable by reducing point sources of phosphorus, but that nitrogen targets will only be met if an integrated set of measures is applied.

RHINE, ELBE, PO

Estimating agricultural nutrient loads

Contributions of agriculture to nutrient loads of the Rhine, Elbe and Po are quantified by modelling nutrient fluxes in these rivers for the period 1970-1995. It is concluded that the EU Nitrates Directive may not be stringent enough to substantially reduce nutrient loads in these rivers.

GERMANY

Complexities of lake restoration

Manipulation of fish populations, following diversion of wastewaters reducing nutrient inputs, has reduced eutrophication symptoms in the highly eutrophied Feldberger Haussee lake, but the stability of the improvements and the interactions between nutrients, fish dynamics and phosphate sedimentation are complex.

BRITISH COLUMBIA

Lake fertilisation and salmon populations

Nutrient addition to Chilko Lake, British Columbia, over five years, improved the size and survival rates of young Sockeye salmon, probably contributing to population recovery.

CONFERENCE

Restoring nutrients to ecosystems

400 scientists met to discuss nutrients and salmon ecosystems, concluding that nutrient addition to many ecosystems would improve the watershed productivity, and facilitate recovery of salmon populations.

PHOSPHORUS RECYCLING

SOUTH KOREA

Phosphate recovery using cow bone

Laboratory experiments suggest that sintered cow bone provides a good seed crystal for calcium phosphate precipitation.

INTERNATIONAL PHOSPHORUS TRANSFER WORKSHOP 2001 page 17

Soil Phosphorus inputs to aquatic ecosystems

Summary of the 3rd International Phosphorus Transfer Workshop, organised by the Institute of Grassland and Environmental Research, England) September 2001. This international workshop brought together relevant experts to forward understanding of the connections between agricultural soil Phosphorus and aquatic ecosystems and eutrophication.

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International Conference 'From Nutrient removal to recovery' Amsterdam, 2 - 4 October 2002

Organised by the <u>International Water Association</u> (IWA) in co-operation with the <u>Netherlands Association on Water Management</u> (NVA) and <u>Aquatech Amsterdam 2002</u>

- Societal and Economical Impacts of Wastewater Nutrient Removal and Recovery.
- Re-use of nutrients and wastewater in agriculture
- Nutrient recovery from concentrated liquid
- Nutrient recovery form diluted wastewater
- Improved/Advanced Biological Nutrient Removal
- Alternative Sanitation and Source Separation
- Nutrient (N,P,S) recovery and re-use technologies
- Centralised and decentralised techniques
- Hygienic aspects of re-use of nutrients
- Public perception of nutrient re-use
- Quantification and evaluation of sustainability aspects of nutrient recovery
- Modelling tools to implement nutrient recovery and re-use technologies
- Life cycle analysis of nutrient recovery technologies
- Novel biological, physical or chemical techniques for nutrient removal

http://www.iawq.org.uk/template.cfm?name=nutrient_removal

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WATER POLICY

European Court of Justice

European Court tells France to take account of nitrates in eutrophication

France has been condemned by the European Court for taking a too narrow definition of eutrophication. France had only being considering phosphate nutrient input in many areas and as a consequence was not applying the EU Nitrates Directive 1991/676.

On 27th June 2002, the European Court condemned France France for breaching the Nitrates Directive 1991/676 by taking a too narrow definition of eutrophication: effectively only considering phosphates for many types of water body (ignoring nitrates), thus excluding erroneously large areas of territory from application of the Nitrates Directive.

The French position, defined in the annexes to the national legislation currently transposing the Nitrates Directive, was that nitrate is "highly likely" to be the limiting nutrient in saline and shallow stagnant brackish waters (that is coastal waters and coastal lagoons), but not in flowing brackish waters (estuaries) and in hard freshwaters (stagnant or flowing). As a consequence, France has not designated estuaries and freshwaters as "vulnerable" for application of the Nitrates Directive.

The Commission argued that in all waters "nitrogen is a nutrient of prime importance in fostering eutrophication and must be controlled as preventive measure" and that nitrogen must be taken into account and managed, as well as phosphorus.

The Court accepted the main points of the Commission's position, noting that "understanding of the subject (causes of eutrophication) is still imprecise and incomplete", and stating that France's position on eutrophication is "too restrictive and consequently incompatible with the Directive". The Court noted that France's approach would result in large areas and many freshwater bodies never being classified as "vulnerable" even where eutrophication and nitrate pollution are a risk or even a fact

Further, in a second ruling at the same session, the Court ruled that France was wrong to not designate the Seine estuary and Normandy coast as a "vulnerable" area. Nitrate levels in these waters are high, mainly of agricultural origin, and nitrogen is recognised as being the most important limiting factor for algal development here. The Seine alone carries 100,000 tonnes of nitrogen per year into the Channel (2/3 of agricultural origin) out of a total nitrogen load from the Channel to the North Sea of 400,000 tonnes.

European Court Judgement reference: request Case C-258/00 at:

http://europa.eu.int/jurisp/cgi-bin/form.pl?lang=en

European Union

EU acts to get water Directives implemented in Member States

The EU Commission has taken further action to obtain correct implementation of EU water quality legislation by Austria, Belgium, France, Greece, Italy, Luxembourg, The Netherlands, Portugal, Spain and Sweden. The Commission has made public the audits of "sensitive area" designation in different countries, showing considerable inadequacies and the UK has already announced the designation of 33 further "sensitive areas"

The EU Commission is maintaining its very active and visible stance over implementation of EU water quality Directives, with actions being furthered against a number of Member States and publicised through press and web communications.

A number of Member States (Belgium, France, Greece, Spain and Sweden) have received "Reasoned Opinions" (the first step in the EU's legal implementation procedure) for failure to provide adequate information concerning the implementation

of the EU Urban Wastewater Treatment Directive 1991/271. This follows publication earlier this year of the Commission's "Implementation Report" concerning this Directive (see this Newsletter), a proactive communications campaign "Name and Shame" emphasising the failure of many states to implement adequate sewage treatment (see Scope Newsletter n°45) and legal actions already launched against Belgium, France and Greece for failure to designate "sensitive areas" and to treat adequately the sewage flowing into them.

The Commission has published the audit reports verifying the designation procedure for "sensitive areas" (Urban Waste Water Treatment Directive) and "vulnerable areas" (Nitrates Directive) for 10 Member States. These reports confirm that large areas of Europe have not been designated to date, but require designation because of their potential susceptibility to eutrophication – so that nutrient removal in domestic sewage works and reduction of agricultural nitrate inputs will then (after correct designation) become legally necessary in these areas. Major cities concerned by such areas include London, Paris, Athens and Dublin.

For the moment, certain of these reports identify in their summaries (eg France) only areas where there are significant cities or towns (so that designation would automatically imply the necessity for nutrient removal in the relevant sewage works). In France, the summary thus only includes areas with a town of >10,000 population. This however ignores the fact that the Directive criteria target "agglomeration" of "population equivalent > 10,000" (which could mean groups of several towns <10,000 – also a population equivalent of 10,000 generally corresponds to around 6,000 actual inhabitants). It also ignores the Directive's requirement for "appropriate treatment" of sewage in smaller agglomerations, and in eutrophication sensitive areas this can be taken to necessarily mean nutrient removal.

In 1994, the UK designated a first wave of 36 "sensitive areas" (considered potentially subject to eutrophication and in which nutrient removal is obligatory in sewage works), followed by a further wave of 41 areas in 1998. The EU "Implementation Report" (referred to above) considered that many estuaries, coastal waters and Loughs which are nutrient sensitive had still not been

designated. The UK responded in June 2002 by designating as "sensitive" a further 33 river and coastal areas. When added to 180 areas designated under the Bathing Waters Directive, and 7 under the Nitrates Directive, this makes a total of 297 designated areas in the UK to date.

Italy, Portugal and Sweden are facing action under the Nitrates Directive 1991/676, for failure to adequately designate "nitrate vulnerable" zones and to implement programmes to reduce pollution of these zones. Austria is also being targeted for failing to designate mountain areas as "vulnerable" and for inadequate manure storage capacities.

Belgium, Luxembourg, The Netherlands and Portugal are facing action for failure to implement the Dangerous Substances Directive 1976/769, for failure to adopt programmes to reduce emissions of listed dangerous substances. Portugal and Spain face action for breaches of the water quality objectives fixed by the Drinking Water Directive 1998/83 and Spain for contravening the Bathing Water Directive 1976/160 at several beaches in Galicia.

EU Commission press release: type reference IP/02/973 at http://europa.eu.int/rapid/start/cgi/guesten.ksh

EU Commission audit reports on "sensitive" and "vulnerable" areas designation: http://www.europa.eu.int/comm/environment/water/wa ter-urbanwaste/vunzones.html

European Union

Wastewater and Nitrates Directives implementation reports

The EU Commission has published Implementation Reports for the Urban Waste Water Treatment Directive 91/271 and the Nitrates Directive 91/676, both of which show that progress is being made but that a lot of work still needs to be done by Member States to implement EU water protection legislation.

The Commission's Implementation Reports for the Urban Wastewater Treatment Directive 1991/271and the Nitrates Directive 1991/676 show that the considerable "investments dedicated to urban wastewater treatment will be inefficient regarding nutrients if a parallel effort is not devoted to an effective reduction of agricultural nutrient losses" (Commission summary on web). According to the European Environment Agency EEA, application of the Waste Water Treatment Directive, however, for discharges other than nitrates (and in particular for phosphorus) "implementation of the Directive's requirements leads to most parameters being below levels that normally give rise to poor quality" (Presentation by the EEA's Executive Director, Brussels, 19.3.2001)

The Commission's summary of the implementation status of the Nitrates Directive 1991/676 shows that "20% of EU groundwaters are facing excessive nitrates concentrations, with a continuous increasing trend" whilst 30-40% of rivers and lakes either carry high nitrogen fluxes to coastal areas and seas or show eutrophication symptom. 50-80% of the nitrogen inputs to EU waters are of agricultural origin. EU farmers use some 9-10 million tonnes-N of inorganic fertiliser, and generate some 8 million tonnes-N of manures from cows, pigs, sheep and poultry. Problems are accelerated by the disappearance and draining of wetlands which play a natural role in removing nutrients and purifying water (in France, for example, 67% of wetlands have been destroyed over the last century).

Agricultural nitrogen surpluses

Nitrogen surpluses (difference between inputs and outputs in crops, meat and milk production) reach 300 KgN/ha/year in agricultural areas, related to intensive livestock production, or to intensive maze, cereal or other crops. Nitrate losses are worsened by practices such as bare agricultural soils over winter.

All Member States have begun implementation of the Nitrates Directive and have transposed the Directive, set up monitoring networks and codes of good practice, but significant nitrate affected areas have not yet been designated as "vulnerable zones" in Spain, France, Ireland, Portugal and Sweden. The Commission has opened 56 legal cases against Member States concerning the Nitrates Directive, resulting in 8 European Court condemnations with 6 cases still open.

The Commission concludes that significant progress has begun to be achieved over the last two years and success stories in nitrate pollution production are already visible in some areas (Denmark, some German Länder, East France, Algarve). However, the effects of action programmes will often only be visible after some years because of the time-scales of inflow to and movement of subsurface water bodies. In other countries, the proper application of the Nitrates Directive will only be possible through rectification of Common Agricultural Policy measures.

Inadequate implementation of Urban Waste Water Treatment (UWWT)

The Commission's Implementation Report for the UWWT Directive 1991/271 confirms the information already made public by the Commission's press conferences and press releases, that many countries are considerably behind deadline in implementation and/or have not designated adequately "sensitive areas" (resulting in nutrient removal not being planned in areas where it is in fact necessary). See details in Scope Newsletter n°45).

The Implementation Report underlines that whenever water bodies are "eutrophic or which may become eutrophic if protective action is not taken" then they must be designated as "sensitive areas", as well as those concerned by drinking water or other water Directive quality objectives, plus effectively the catchments of all such water bodies. The Commission underlines that all agglomerations of 10,000 pe. or more discharging into such water bodies or their upstream into their catchment must have nutrient removal installed and, on

the basis of a specific audit study by ERM, that "a large number of Member States had not taken sufficient account of the degree of eutrophication of their waters". In particular Belgium, France, Greece, Ireland, Italy, Finland, Portugal, Spain, Sweden and the UK have not yet installed adequate nutrient removal in sewage works discharging into interior or coastal waters.

In order to incite Member States to improve their designation of "sensitive areas" the Commission has had two reports drawn up: "Criteria used for the Definition of Eutrophication in coastal/marine waters" ERM April 2000 and "Criteria use for the identification of freshwaters subject to eutrophication" EC Joint Research Centre January 2001.

The Commission concludes by underlining that out of 527 EU agglomerations of more than 150,000 pe, at the end of 1998, 96 cities were still discharging all or much of their sewage untreated into the environment, including Brussels, Athens, Barcelona, Cork, Dublin, Florence, Milan, Marseilles and Porto.

Further information concerning the status of waste water treatment in Europe is provided by the Commission's statistical bulletin EUROSTAT (Theme8 – 14/2001). By the end of the 1990's, 77% of the EU's population was connected via sewerage to a waste water treatment plant, with corresponding figures of 96% and 78% for Switzerland and Norway. More than 80% of Sweden's population are connected to sewage works with nutrient removal, followed by 78% in The Netherlands, 72% in Germany and 64% in Austria.

IEEP (1999) previously estimated that 39-45% of all phosphorus in domestic sewage was removed in waste water treatment works by the end if 1994, but that this figure would increase to 56-62% once the EU Urban Waste Water Treatment Directive was implemented.

Effectiveness of wastewater treatment where implemented

The European Environmental Agency's assessment of impacts of wastewater on rivers, lakes and seas emphasises the effectiveness of the investments required by the Urban Wastewater Treatment Directive 1991/271: "Member States that are ... still facing major investments can rest assured that investments in urban

waste water treatment in accordance with the Directive will result in measurable and significant improvements in water quality". Concerning eutrophication the EEA concludes that despite improvements, "it may be necessary to reduce the diffuse load of phosphorus from agriculture. In many places this contribution is substantial and at the same level as the input from waste water treatment plants. Nitrate from agriculture ... also plays a major role in eutrophication".

The EEA cite Finland as a "best-practice" example of waste water treatment. Sewage treatment has reduced phosphorus emissions by 88% (total P load) since the 1970's as a consequence of waste water treatment implementation.

Over most of Europe, phosphorus concentrations have fallen steadily in all sizes of river (from small to very large) over the last decade as a consequence of waste water treatment, and a similar success story is presented for lakes and in coastal waters influenced by river inflow. Nitrogen concentrations however have tended to be stable or even increase.

European Environmental Agency "The effects of urban waste water treatment on the quality of rivers, lakes and seas" 19.6.2001 :

http://org.eea.eu.int/pressroom/documents/speeches/br ussels.pdf

EU Commission Implementation Report on the Urban Waste Water Treatment Directive 91/271:

http://europa.eu.int/comm/environment/water/waterurbanwaste/report2/2001_1669_en.pdf

EU Commission Implementation Report on the Nitrates Directive 9119/676:

http://europa.eu.int/comm/environment/water/waternitrates/report.html

EUROSTAT "Waste water in European Countries" 2001:

http://europa.eu.int/comm/eurostat/

Choose English then enter "waste water in european countries" (in inverted commas) in the search form.

IEEP (Institute for European Environmental Protection) 1991 "Implementation of the 1991 Urban Waste Water Treatment Directive and its role in reducing phosphate discharges": http://www.ceepphosphates.org/publications.htm

NUTRIENTS AND AQUATIC ECOSYSTEMS

River basin management

Nutrient loadings to the Danube

The main source of nutrients to the Danube river basin is agriculture and land run-off. Improving sewage treatment to EU Directive standards will nonetheless reduce N and P by 16 and 20%.

Several papers published in Water Science and Technology (special edition devoted to "Management of large river basins") show the difficulties of reducing nutrient loadings to the Danube, and consequently to the Black Sea.

The papers published cover the methodology for assessing nutrient loads and sources to the Danube, difficulties and the degree of accuracy of such assessments⁽²⁾, and possible strategies for reducing these nutrient loadings. An overview⁽¹⁾ is also presented of the political process of river management in the Danube catchment, the environmental programme, and implementation of the 1994 Strategic Action Plan.

A clear breakdown of sources and pathways for phosphorus (P) loadings to the Danube is provided by Lampert and Brunner⁽³⁾. This shows that a total of 22% of a total P loading of 105,000 tonnesP/year (1992) came from households, of which two thirds (14%) passed through sewage treatment plants and one third (8%) did not (direct discharge plus contribution to base flow). Industrial loadings are estimated as 7% of the total via sewage plants, plus 6% as direct discharges.

This is coherent with the figures suggested by Somlyody et al.⁽⁴⁾ indicating that "around 20% of total P load comes from households, and 33% from "municipal and industrial point sources".

It is also coherent with Iijas et al.⁽⁵⁾ who calculate a total phosphorus loading from domestic sources of 22,410 tonnesP/year (1995).

The corresponding figures for total nitrogen (N) loadings are comparable. Lampert and Brunner estimate that N from households contributes 19% of the

total basin loading of 825,000 tonnesN/year (1992) and 10% of industrial loadings, whereas Somlyody et al. indicate that 25% of N loadings come from municipal and industrial point sources.

Agricultural nutrient loadings

The majority of nutrient loadings are of agricultural origin (57% for P, 51% for nitrogen). However, the economic transition caused a decrease in both the use of mineral fertilisers (-55% and -65% for N and P) and a 30% decrease in manure application. Much of this decrease had occurred at the time of the loading data used here (1992). It is expected that in the future agriculture will recover in the transition countries which cover much of the Danube basin, bringing a corresponding considerable increase in nutrient loads.

Implementation of EU sewage treatment Directives

Somlyody et al. estimate that implementation of the EU Waste Water Treatment Directive 91/271 (which requires nutrient removal in all sewage works in villages or groups of villages of total population equivalent >10,000, corresponding to a population of around 6,000 persons) would result in a reduction of total nutrient loads by 16% for nitrogen and 20% for phosphorus. This Directive requirement is applicable to all sewage works serving such populations and discharging into "sensitive areas", that is water bodies which are potentially susceptible to eutrophication, which is clearly the case for the whole Danube basin given that it flows into the Black Sea.

This is coherent with Lampert and Brunner's figures of 14% of total P from households plus 7% industry passing through sewage works, in that P-removal in sewage works is required by EU legislation to achieve 75-80% P-removal, but in fact can readily and reliably achieve >95% P-removal.

It is suggested that a move to phosphate-free detergents could provide a further 10% P reduction, but this does not seem to be supported by the figures. The introduction of P-free detergents will not significantly reduce the P-load being discharged from sewage works, in that where P-removal is installed the discharge P-

concentration is a consequence of operating choices (dictated by discharge consents) and not of inflow concentrations. In any case, the 20% P-reduction estimated for implementation of the EU Directive 91/271 apparently effectively reduces sewage works P discharge to near zero.

Modern phosphate-based detergents contribute around a quarter of total household sewage phosphates (the majority comes from natural human bodily functions and food wastes). This is confirmed for the Danube basin by Iijas et al. who calculate that in 1995 detergents contributed 5,154 tonnesP/year to surface water out of a total contribution of 22,410 tonnesP/year from domestic sources (that is 23%).

A maximum estimate for a further reduction to be expected from introducing P-free detergents once EU wastewater treatment legislation is implemented can thus be established as follows. The reduction in P from domestic sources would be 23% x 1/3 (proportion of domestic P discharges not passing through sewage works, see above), plus 23% x 2/3 (discharges to sewage works) x 20% (80% P-removal at least in sewage works), plus at most 1% for sewage passing through the remaining small sewage works not operating in which P-removal may not be required, that is a total of <11% of P from domestic sources. Households make up 22% of total P loadings (see above), so the overall additional reduction resulting from introducing P-free detergents would be <22% x12%, that is less than 2.4%. The real figure will be lower as detergent formulations have evolved since 1995 resulting in lower phosphate dosages, whilst at the same time it is likely that agricultural phosphate loadings to the Danube have increased, as indicated above.

(1) "Danube river basin: progress with the environmental programme", T. Botterweg, D. Rodda, pages 1-8

(2) "Use of ambient water quality data to refine emissions estimates in the Danube basin", A. Clement, K. Busas, pages 35-42 and "Nutrient balances of the Danube basin: the role of uncertainties", K. Buzas, pages 51-58

(3) "Materials accounting as a policy tool for nutrient management in the Danube basin", C. Lampert, P. Brunner, pages 43-49 (4) "Nutrient balances for Danube countries: a strategic analysis", L. Somlyody, P. Brunner, H. Kroiss, pages 9-16.

All the above in Water Science Technology, vol.40 n°10 special edition "Management of large river basins", 1999

http://www.iwaponline.com/wst/04010/10/default.htm

(5) "Removal of phosphate from detergents in the Danube basin", I. Iijas/Senator Consult, PHARE project EU/AR/205/91

Baltic sea

Reducing nutrient emissions to the Odra

Nutrient input modelling for the Odra river basin indicates that the 50% reduction targets set by HELCOM (Baltic Sea) are achievable by reducing point sources of phosphorus, but that nitrogen targets will only be met if an integrated set of measures is applied.

The Odra river basin covers over 110 000 km² in Poland, the Czech Rpublic and Germany, with a population of around 15.5 million. Different models (MONERIS, MODEST and NIIRS) were used to estimate nutrient inputs (P,N) from point sources and various diffuse pathways. These were based on data for river flow and GIS (Geographical Information System) digital mapping statistics. See SCOPE Newsletter n°37 for further information about these models, and their application to the Rhine and Elbe rivers.



Total phosphorus emissions into the Odra river basin were estimated at around 12 840 tP/year (for 1993-1997), similar to the total emissions to the Elbe river basin. These represent around 60% of total emissions to the Rhine river basins (see SCOPE 37). Total nitrogen emissions to the Odra (same period) were estimated at around 124 260 tN/year.

The comparison of emissions modelling with real river nutrient loads showed a mean deviation (between estimated and real loads) of around 21% for nitrogen and around 32% for phosphorus. An underestimate of real river phosphorus levels was caused by the release (desorption) of phosphorus from high eutrophic and polymictic lakes in parts of the catchment.

The balance between different sources/pathways for P and N is however very different. Whilst over 62% of total P emissions to the Odra are estimated to come from point sources (mainly sewage works) and a further nearly 12% from urban area runoff, only 36% of nitrogen emissions come from point sources.

Total and diffuse nutrient emissions into the river systems of the Odra by country in the period 1993-1997 (the percentages in bold and italic are related to the total emissions of the Odra; the other percentages are related to the total emissions of each country).

		Czech Republic		Poland		Gern	nany	Sum	
		total	diffuse	total	diffuse	total	diffuse	Total	diffuse
Phosphorus	tP/a	1,030	500	11,480	4,220	330	150	12,840	4,870
	%	8.0	48.5	89.4	36.8	2.6	45.5	100	37.9
Nitrogen	tN/a	14,020	10,900	105,690	65,170	4,540	2,900	124,260	78,980
	%	11.3	77.7	85.0	61.7	3.7	63.9	100	63.6

As a consequence, it was estimated that a realistically achievable reduction in emissions of phosphorus from point sources (mainly municipal sewage works) of 70% would suffice, for the Odra basin, to achieve the HELCOM target of a 50% reduction in phosphorus loadings to the Baltic Sea. Levels of 90% P-removal or higher are usual for modern sewage works equipped with P-removal, and indeed a level of 80% P-removal is required for "sensitive areas" by EU legislation (Urban Waste Water Treatment Directive 91/271). Because it flows into the Baltic, the Odra basin is a "sensitive area" within the terms of this Directive. The "transition arrangements" for negotiated with the EU in the Accession process accord until 2010 for the Czech Republic and until 2015 for Poland for the implementation of this Directive.

The HELCOM objective of a 50% Baltic Sea loading reduction is however more difficult to achieve for the Odra for nitrogen. 27% of N emissions to the Odra basin were estimated to come from ground water and tile 26% agricultural drainage. from Full implementation of the EU Urban Waste Water Treatment Directive is expected to eventually lead to a 65% reduction in point N sources and a possible reduction of the N surplus on agricultural areas could bring a 17% reduction of diffuse inputs. However, these two mechanisms combined would only achieve approx. 44% reduction of total N emissions from late 1980's levels

Additional measures will thus be necessary to achieve a 50% reduction in N emissions, for example restoration of drained wetlands, buffer vegetation strips between agricultural land and rivers and streams, creation of small retention reservoirs ...

Summary at:

http://www.igb-

berlin.de/institut/deutsch/2001/Research/nutrient_heav ymetal_emissions.pdf

"Nutrient Emissions into river basins of Germany." UBA-Texte 23/00, 266 pages (2000).

Poster: "Nutrient emissions of point and diffuse sources, transport and retention within the Odra Basin and its main tributaries", International Odra Conference, 16-19 June 1998, Krakow, Poland http://odra.ing.uni.wroc.pl/iorc/

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Rhine, Elbe, Po

Estimating agricultural nutrient loads

Contributions of agriculture to nutrient loads of the Rhine, Elbe and Po are quantified by modelling nutrient fluxes in these rivers for the period 1970-1995. It is concluded that the EU Nitrates Directive may not be stringent enough to substantially reduce nutrient loads in these rivers.

The authors report estimations of nitrogen and phosphorus loads to the Rhine (upstream of The Netherlands), Elbe and Po river basins for the period 1970-1995. These basins cover around 400,000 km², of which some 45% is used for agriculture. They include areas in 11 countries and cover a population of around 85 million people.

Previous estimations of the agricultural contribution to surface water nutrient loads are reported, ranging from 42-81% for nitrogen and 21-50% for phosphorus :

Region	Year	N (%)	P (%)	Reference
North Sea basin	1987	60	25	Lidgate (1987) in Isermann (1990)
West Germany	1989	50	40	Isermann (1990)
West Germany	1987/1989	46	30-40	Werner et al. (1991)
East Germany	1988/1989	42	25	Werner & Wodsak (1994)
Italy	1986	62	33	Gaggino et al. (1986) in Isermann (1990)
Po river	1990	56	32	Italian Ministry of Environment (1992) in Stanners & Bourdeau (1995)
The Netherlands	1989	68	21	RIVM (1992) in Stanners & Bourdeau (1995)
The Netherlands	1990	60	40-50	Boers (1996)
Denmark	1981	81	22	Christensen et al. (1993) in Stanners & Bourdeau (1995)
Poland	1990	62	34	MEPNRF (1991) in Stanners & Bourdeau (1995)

The estimates of agricultural nutrient loads in this study were established using two different models, as reported previously in De Wit, M.J.M. (1999). Modelling nutrient fluxes from source to river load: a macroscopic analysis applied to the Rhine and Elbe

basins. Hydrobiologia 410: 123-130 ; and De Wit, M.J.M. (2001). Nutrient fluxes at the river basin scale. I: The PolFlow model. Hydrological Processes 15, pp. 743-759. The models differ in the way the way the transport, retention, and loss of nutrients in the soil/groundwater system and river network is described. In Model 1, the proportion of the surplus nutrients reaching the river outlet is estimated on the basis of the area specific runoff in the upstream basin (see article "Nutrient Retention" in SCOPE Newsletter n°37) and of the nature of the groundwater system (rock type). Model 2 (PolFlow) is GIS-based, and takes into account soil, lithology and runoff characteristics, as well as general river characteristics.

Both models are run with estimated data for direct inputs to the river (from households and industry) and indirect inputs from (agricultural) land, based initially on the calculated nutrient "surplus at the soil surface". This surplus is taken to be the agricultural nutrient surplus, that is manure production plus fertiliser consumption, minus nutrients in crop yield (calculated for five-year periods). These agricultural data were based on coefficients (for example: manure nutrient production for different livestock, nutrient uptake coefficients for different crops) and administrative agricultural data for areas of average size 1.000 km². The models have been validated with river loads derived from discharge, and N and P measurements from sixty monitoring stations all over the Rhine, Elbe, and Po basins. Although Model 2 is more complex and more closely related to local physical characteristics influencing nutrient transport, its predictions of river nutrient loads were no better than those of Model 1. Differences in results between the two models are therefore indicative of the degree of accuracy of the results.

Direct and indirect nutrient sources

Fertiliser consumption fell (particularly for phosphorus) while crop yield increased in both the Rhine and Po basins over the period 1985-1995, leading to a decrease in the agricultural surplus of N and (particularly) P. In the Elbe basin, a more drastic decrease in both fertiliser consumption and livestock numbers (and so manure) followed the political and

economic changes of 1989-1990. Nonetheless, most of the variation in river N and P load between 1970 and 1995 can be explained, in all three rivers, by differences in the direct nutrient inputs (household and industry). Average river loads of phosphorus from households and industry (direct inputs) fell from 66 to 18 million kg/year in the Rhine and from 31 to 13 million kg/y in the Elbe (figures pre-1990 not given for the Po). Agricultural loads show no clear trend (differences in estimated loads over the period are smaller than differences between results from the two models).

The authors estimate from the model results that agriculture, in the early 1990's, was contributing :

* for N: 43-49% of total N loads in the Rhine, 28-58% in the Elbe and 47-57% in the Po

* for P: 13-21% of total P loads in the Rhine, 11-16% in the Elbe and 22-25% in the Po.

Overall, they estimate that agriculture was contributing around 45% of total nitrogen loads to these rivers, and 20% for phosphorus. However, this only includes loads related to fertiliser use and manure in agriculture, not those relating to soil erosion, which can be significant in some cases, which may explain why these figures are lower than those given previously by other authors.

A model simulation of the implementation of the EU Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources shows that the average livestock manure application rates in the three basins only exceeds the given Directive threshold (170 kg N ha-1 yr-1) in relatively few regions. Implementation of this Directive requirement is not susceptible to thus significantly reduce river nutrient loads. The Directive also requires (in general terms) that the land application of fertilisers should be based on a balance between the requirements of the crops and the supply to the crops from the soil and from fertilisation. The modelling exercise shows that only a move to such "balanced farming" could substantially reduce river nutrient loads.

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http://www.ewaonline.de/journal/2002_03.pdf

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Germany

Complexities of lake restoration

Manipulation of fish populations, following diversion of wastewaters reducing nutrient inputs, has reduced eutrophication symptoms in the highly eutrophied Feldberger Haussee lake, but the stability of the improvements and the interactions between nutrients, fish dynamics and phosphate sedimentation are complex.

Feldberger Haussee Lake is situated 150km north of Berlin, in the Baltic Lake region. The lake was slightly eutrophic in the early twentieth century, but the installation of sewage collection and a sewage works discharging into the lake from the nearby town of Feldberg in the 1960's led to the lake becoming highly eutrophied. Municipal waste water made up 90% of the lake's nutrient inputs.

The lake has an area of 135 hectares, a maximum depth of 12m and a mean depth of 6.3m, and a hydraulic retention time of around 5 years. It is typically stratified from May to September (very little mixing between deep water and surface water).

In 1980, the sewage works discharge was diverted away

from the lake, but the accumulated nutrients in the lake meant that it was still highly eutrophic, and no improvement in the water quality was observed. The annual mean concentration of phytoplankton (algae) in the water did not show a detectable decrease, and worse, a general dominance by green phytoplankton before 1980 changed increasingly to dominance by blue-greens. (Kasprzak et al.).

Manipulation of fish populations

Long term biomanipulation consisting of removal of planktivorous fish and enhancement of piscivorous fish was therefore carried out from 1986-1998 to try to restore the lake's water quality, and in particular transparency.

The objective has been to reduce the populations of fish which consume Daphnia and other species of zooplankton, which naturally consume and so control algal populations. These planktivorous fish species in the lake are mainly roach (Rutilus rutilus) and bream (Abramis brama). This has been achieved both be removing these fish manually using a net (a 800m long 16-20 mm mesh beach seine) and also by enhancing the population of piscivorous fish which predate these zooplankton-consuming fish. Piscivorous fish populations were enhanced both by stocking (addition of young pike-perch (Stizostedion lucioperca), pike (Esox lucius) and perch (Perca fluviatilis)) and by protection of these species (forbidding their removal by fishermen and anglers).

The fish manipulation actions can be divided into three periods:

- 1986-1989: removal of planktivorous fish only
- 1990-1995: removal of planktivorous fish and stocking of piscivorous fish
- 1996-1998: above plus protection of piscivorous fish

Varying responses to biomanipulation

Water transparency improved somewhat at the start of the fish manipulation, but then deteriorated again during 1990-1995, before again improving since 1996. Overall, water transparency had increased from 1.66m to 2.55m (+54%) over the biomanipulation period. Algal concentration (measured as chlorophyll-*a*) and

primary production on the other hand fluctuated until 1989, and peaked in 1991, 1993 and 1995.

Water transparency was predictably inversely correlated with algal concentration and primary production (these by definition reduce transparency), but also with piscivorous fish population and weakly with Daphnia biomass.

Algal concentration and primary production were correlated with nitrate concentration (N-NO₃) and with the N:P ratio, which is coherent with Kasprzak et al.'s conclusions that the lake is nitrogen and not phosphorus limited.

The authors suggest, from their assessment of the changes in the different variables and indicators of the lake's state over this period, that the improvement in the lake's water quality was due to both the delayed effects of the diversion of municipal sewage away from the lake and to the fish biomanipulation.

The understanding of the effects of the nutrient loading reduction is made more complex by the variations in nutrient patterns. Lake total phosphorus concentrations stabilised only in the last few years of the biomanipulation period (at around 100 μ gP/l) despite external loadings having been reduced to 0.2 – 0.3 gTP/m²/year from 1980. Increased calcite precipitation during the biomanipulation period, binding phosphorus into the sediment, had an important influence of the phosphorus decline. Nitrogen levels fluctuated during much of the biomanipulation period, only falling during the last few years.

They suggest that the rate of removal of planktivorous fish was probably too low to enable biomanipulation to be very effective (the yield of fish in the seining net remained constant over the period 1990-1998 so that the population had apparently not been significantly affected overall, probably by less than 50%). Other examples of lake fish biomanipulation which have been more successful in improving water quality after 1-3 years involved removal of 75% or more of the planktivorous fish population.

The stocking of piscivorous fish alone was not effective in increasing the proportion of such fish in the seine net catches. This only increased once the piscivorous species had also been protected by stopping commercial fishermen and anglers from taking these species.

The authors conclude that the Feldberger Haussee Lake experience shows that biomanipulation can contribute to restoration of stratified lakes, when combined with reductions in nutrient loads, providing effective measures to reduce planktivorous fish are adequately chosen and are implemented over the long term.

"Restoration of a stratified lake (Feldberger Haussee, Germany) by a combination of nutrient load reduction and long-term biomanipulation". Internal. Rev. Hydrobiol. 86, 2001 – 2 pages 253-256.

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"Applicablility of the food-web manipulation in the restoration program of a hypertrophic stratified lake: model studies for Lake Haussee (Feldberg, GDR)". Limnologica (Berlin) 19(1), July 1988, pages 87-95.

P. Kasprzak, J. Benndorf, R. Koschel, F. Recknagel.

British Columbia

Lake fertilisation and salmon populations

Nutrient addition to Chilko Lake, British Columbia, over five years, improved the size and survival rates of young Sockeye salmon, probably contributing to population recovery

A number of papers have been published concerning nutrient addition to lakes as a tool to facilitate salmon population recovery, either to improve salmon fisheries or to restore threatened salmon species (see for example SCOPE Newsletter n°27). The work presented in this paper, on Lake Chilko, on the Fraser River, British Columbia, is unique in the existence of a 44year record of salmon spawner, smolt and adult abundance in the Lake and in the possibility to compare population changes in this Lake during the five-year fertiliser addition period with changes in population in 7 other similar lakes in the Fraser watershed.

Chilko Lake is on the eastern side of the British Columbia Coast Mountain range, at an altitude of 1,172m. It is 70 km long and 3-5 km wide with a total area of 185 km². The Chilko River, which flows out of the Lake, travels some 180 km before meeting the Fraser River, which then travels some 350km to the Pacific Ocean. The lake has a mean depth of 123m and a maximum depth of 330m, with a residence time of 17-25 years.

Chilko Lake is oligotrophic (nutrient poor) with natural total phosphorus and nitrogen concentrations of 3 and $7 \mu g/l$.

Effects of nutrient addition

The Lake was fertilised for five years (1988 and 1990-1993) by nitrogen and phosphorus addition during the summer, at a rate of 100 mgN and 4 mgP per m² of total lake area weekly (for 6 weeks in 1988 and for 14 weeks in 1990-1993).

In the years in which nutrients were added, primary production effectively increased in the lake, as did algal abundance (measured by chlorophyll concentration) and macrozooplankton biomass.

Young salmon (smolts) were significantly larger during the nutrient addition years, with estimated average increases in weight of +34% and +54% for one and two

year old smolts respectively. Also, the survival of the young salmon (rate of return to the Lake as adults after the migration to the sea) was above average for the nutrient addition years.

By using the other lake populations to control for variations in survival outside Lake Chilko, the mean productivity (returning adults per spawning female in the lake) was estimated to be increased by +73% during the nutrient addition years, although the uncertainty of this estimate was considerable.

The authors conclude that this paper provides additional evidence to the existing belief, from previously published work, that nutrient addition to lakes increases the size of juvenile salmon leaving the lake, and thus the rate of survival in the sea and of return to the lake to breed, thus overall increasing the salmon population. They suggest that the fertilisation programme in Lake Chilko may have prevented its salmon suffering the decline undergone by Sockeye salmon populations elsewhere in the Fraser River basin over recent years.

"Biological responses of Sockeye salmon to the fetilization of Chilko lake, a large lake in the interior of British Columbia". North American Journal of Fisheries Management, 2, 2000, pages 661-671.

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Conference

Restoring nutrients to ecosystems

400 scientists met to discuss nutrients and salmon ecosystems, concluding that nutrient addition to many ecosystems would improve the watershed productivity, and facilitate recovery of salmon populations.

A joint conference of the American Fisheries Association http://www.fisheries.org and the Canadian Aquatic Resources Section (Eugene, Oregon http://www.fisheries.org/cars/en/index.htm), April 2001, looked at latest developments in the science and management of marine-derived nutrients around the North Pacific Rim and the Scandinavian countries. The conference, entitled "Restoring Nutrients to Salmonid Ecosystems" particularly addressed the question of how to put back into these ecosystems the nutrients necessary to improve salmon populations.

A number of papers have previously been published showing **the positive effects on salmon reproduction and survival of artificial nutrient addition to ecosystems** (see SCOPE Newsletter n° 27 and in this issue). John Stockner or Ecologic Ltd, West Vancouver, summarised modern understanding by stating that we need to "change our perception of nutrient enrichment from one of pollution to one of restoration".

Natural nutrient cycles have been broken by man's intervention. Logging, for example, exports nutrients out of watersheds (each log truck carries away 200 kg of phosphorus). Because salmon die in rivers and lakes after spawning, their carcasses return significant levels of nutrients to these aquatic ecosystems. The decline in salmon populations accentuates nutrient impoverishment, further reducing productivity, and thus putting further pressure on salmon reproduction Consultant Jim Lichatowich estimated that historic, natural salmon runs in Oregan, Washington and California represented 150-250 million kgs of salmon flesh deposited in rivers, releasing considerable quantities of nutrients, compared to only 11-13 million kg today, as a result of salmon population decline.

Washingto State DBR biologist Jeff Cederholm concluded that, to allow salmon populations to recover, "we should not be fishing salmon at all".

Stream nutrient enrichment

Bob Bilby, Weyerhaeuser Company, presented studies of **stream nutrient enrichment using salmon carcasses**, carried out since the 1980's. These show a dramatic increase of survival of young salmon (50 - 80x) as a result of the carcass enrichment. The young salmon ate the carcasses directly, and also benefited from an increase in the number of aquatic insects which they consumed as prey. This work suggested that some 200 carcasses per mile of stream was adequate to improve salmon populations, but this would correspond to an abundance of spawning salmon no longer found in most Northwest streams.

Other work showed that adding logs to streams also improved salmon reproduction, presumably by **retaining nutrients**.

The importance of salmon in nutrient cycling was illustrated by T. Reimchen, Dept. of Biology, University of Victoria, British Columbia, who showed that 75% of nitrogen in old Sitka spruce wood was originally derived from salmon. The nutrients are transferred out of the water to the terrestrial ecosystem when salmon are caught as food by predators such as eagles, bears and otters. Younger Sitka spruce trees show a much lower proportion of nutrients coming from salmon, reflecting recent salmon population declines.

Conference workshops addressed: historic and future salmon population levels, linkages and nutrient cycling between terrestrial and aquatic ecosystems, the contribution of salmon carcasses to aquatic ecosystems, the effects of salmon carcasses on waterside vegetation, protocols for artificial nutrient addition (fertilisation) of salmon ecosystems, methods for increasing salmon carcasses, water quality and productivity effects of carcass decomposition.

"Restoring Nutrients to Salmonid Ecosystems" conference web site: http://www.gpafs.org/confnutr

Conference proceedings are expected to be available via this web site during 2002.

PHOSPHORUS RECYCLING

South Korea

Phosphate recovery using cow bone

Laboratory experiments suggest that sintered cow bone provides a good seed crystal for calcium phosphate precipitation.

Lab-scale batch calcium phosphate precipitation experiments, with residence times up to 6 hours, were used to assess the influence of different conditions of calcium concentration, carbonate concentration, pH, and temperature, using different seed crystals. Residual soluble phosphate concentration was measured as an indicator of the effectiveness of phosphate precipitation.

The two see crystals tested were cow bone sintered for 3 hours at respectively 600°C and 400°C, then ground to pass through a 0.5mm sieve. The cow bone before sintering consisted of 57% hydroxyapatite = HAP (calcium phosphate) and 33% gelatinous material. Lee et al. had previously shown that HAP content and the ability to increase pH of cow bone are improved by sintering at higher temperatures. The seed was added to the batch experiments at 0.1% (by weight of solution volume in ml). Experiments were stirred at 150 rpm.

Optimal conditions

All experiments used initial soluble phosphate concentrations of 3.5 mgP-PO₄/l, comparable to those found in municipal waste water treatment plants.

Three first sets of experiments tested varying calcium concentrations (0-120 mgCa/l), pH (8–9.5), seed dosage (0 or 0.1% of 600°C sintered bone), carbonate concentration (0 – 300 mgCO₃/l) and reaction temperature (10 – 35°C). These showed that phosphate precipitation effectiveness increased significantly with higher calcium concentrations up to around 50 mgCa/l (at which concentration >70% phosphate precipitation was achieved for all pH's 8–9.5). Phosphate precipitation also increased with higher pH, but residual soluble phosphorus concentrations of below 1 mgP/l could be achieved

with 50 mgCa/l, pH8 and 0.1% 600°C seed.

As reported previously by other authors, **bicarbonate concentrations appeared to inhibit calcium phosphate precipitation.** At the above conditions, 95% phosphate precipitation was achieved in half an hour with no added bicarbonate, whereas only 90% was achieved after 2 hours under addition of 100 mgCO₃/l. These results enabled reaction rate model constants to be evaluated.

Higher temperatures, as could be expected, accelerated phosphate precipitation, enabling kinetic model constants to be evaluated.

Cow bone calcination

A fourth set of experiments compared the effectiveness of the two sintered cow bone powders (400°C and 600°C) at the following conditions, considered as optimal and realistic on the basis of the first three sets of experimental results:

3.5 mgP-PO₄/l 50 mgCa/l pH 8 100 mgCO₃/l 0.1% seed dosage temperature 25°C 0 - 6 hours residence time

The 600°C calcinated cow bone performed significantly better than the 400°C product, probably because of lower organic content and improved pH adjustment characteristics.

Under the above conditions and using 600°C sintered cow bone seed, **residual soluble phosphate** concentration was reduced to around 0.5mgP-PO₄/l (85% P-removal) in one hour. The authors conclude that cow bone to be used as a seed material should be sintered at 600°C.

"Phosphorus removal using cow bone in hydroxyapatite crytsallization" Water Research 36 (2002), pages 1324-1330.

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INTERNATIONAL PHOSPHORUS TRANSFER WORKSHOP 2001

Soil Phosphorus inputs to aquatic ecosystems

The 3rd International Phosphorus Transfer Workshop took place in Plymouth, England, in September 2001, following on from previous such workshops in 1995 and 1998. The objective of the meeting was to bring together relevant experts to forward understanding of the connections between agricultural soil Phosphorus and aquatic ecosystems and eutrophication.

Phil Haygarth (Institute of Grassland and Environmental Research, England) wrote in the workshop introduction that "Point sources of P entering surface freshwaters are now relatively easily isolated and abated, but agriculture persists as the major diffuse source. Farms often import excess P via animal feeds and fertilisers and discharges in waters from plot studies have shown that total P loads often exceed 3 kg/ha/year, with concentrations of >100 µg/l."The workshop addressed four themes :

- sources of P on the farm and the initiation of P transfer
- hydrochemical connectivity
- impacts of agriculture-derived P on water quality
- integrated catchment management and mitigation of P transfer

Further conference information is available at: http://www.iger.bbsrc.ac.uk/igerweb/NWNew/IPT W/iptw2001.htm

Sources of P on the farm and the initiation of P transfer

As indicated by **D. Nash** et al. (Agriculture Victoria Ellinbank, Australia), phosphorus (P) exports from agricultural land are a worldwide problem, with soil P losses resulting both from dissolution and from physical processes (erosion of soil particles, carrying particulate P). It is necessary to try to assess both systematic P export (base losses into run-off

and drainage water) and incidental P-loss (related to farm management, such as grazing, manure or fertiliser applications).

Phosphorus dissolution results from both chemical and biological soil processes. As **B. Turner** et al. (Northwest Irrigation and Soils Research Lab., Idaho, USA) explained, these biological mechanisms in soils are not well understood, and there is a need to relate a developed understanding of the molecular-level mechanisms of P-release processes and patterns of P movement occurring at larger scales.

J. Quinton (Cranfield University, England) indicated that overland flow is an important source of P reaching surface waters, contributing both dissolved and particulate P. He described three mechanisms for the detachment of particulate P from soils and its release into overland flows: the physical impact of raindrops, the physical erosion effects of water flow over the soil surface, and physico-chemical dispersion. The interaction between overland water flow and soil detachment processes is difficult to predict. Frequent, small erosion events have been shown to account for more P transfer than infrequent heavy rain events, so that P transport associated with sediment run-off may be even more widespread than previously thought.

M. Bechmann et al. (Jordforsk Centre for Soil and Environmental Research, Norway) presented results from four catchment scale (65-680 ha) and two field scale (4-6 ha) studies for the Autumn 2000 in South-East Norway. High precipitation levels (2 -14xcompared to previous studies) resulted in much higher P losses (4-20x), particularly through an increase in sub-surface losses of suspended solids and P. The increase in P losses was much greater at the catchment than at the field scale, possibly because of erosion processes occurring in the streams. Concentrations of P in the run-off water stabilised during this prolonged period of high precipitation, at higher levels for the field with the highest soil P content.

R. Hodgkinson et al. (ADAS, England) also showed the importance of sub-surface P losses. Results from four experimental catchments showed that P loss in subsurface flow in tile drainage accounted for 55% of P losses in the Rosemaund catchment, Herefordshire (where arable fields were the most important sediment source and 30% in Trent catchment (pasture fields most important source).

R. Maguire et al. (University of Delaware, USA) presented leaching results from soil columns from fields in the Delmarva Peninsula. Leachate P concentrations were frequently greater than those reported to cause eutrophication. Mehlrich-3 P [Al+Fe] appeared as a good indicated of risks of P loss to subsurface waters, and suggested that it may be possible to achieve a soil P status sufficient for agricultural production whilst reducing soil P losses.

G. Toor et al. (Lincoln University, Canterbury, New Zealand) presented P leaching results from lysimeter experiments on stony grassland soils following application of dairy shed manures. Total P levels in leachates were up to over 1,000 μ gTP/l, with 70-80% of P losses occurring as particulate P. The manure contained equal proportions of soluble and particulate P, suggesting the importance of adsorption in soils, converting soluble to particulate forms.

R. Simard et al. (Agriculture & Agri-Food Canada) also presented P loss results from fields, in this case maze crop fields near Lennoxville, Quebec, treated with either liquid pig manures or inorganic fertilisers. Most of the P loss was in surface run-off was as particulates (90%), but 30-44% of losses in drainage waters were as dissolved reactive P (higher for inorganic fertilisers). Average P transfer was 2.6 - 10 kg/ha/year.

Posters presented also showed that soil Olsen-P or soil total-P do not necessarily provide good indicators of the risks of P leaching after manure application (R. Anderson, Queen's University Belfast, Northern Ireland) and gave further figures for P losses from agricultural land, eg. 0.12-0.16 mg P/l in run-off (E. Azazoglu et al., Vienna University of Agriculture, Austria); 0.15-3 mg P/l (P. Brookes et al., Rothamsed Experimental Station, England); 0.08 –2.3 kg/ha/year mainly as particulate P in

surface run-off and strongly related to annual rainfall (N. Fleming et al., South Australian R&D Institute); 115-307 µg P/l in leachate (G. Toor et al., Lincoln University, Canterbury, New Zealand; annual P-losses of 0.4 kg P/ha/year on a clay soil, 2.1 and 2.6 on peat soils, and up to 3.7 kg P/ha/year on a sandy soil (C. van der Salm et al., Alterra Green World Research, Wageningen, Holland); 8 mg P/l (Morgan-STP) in drainage water from heavily manured fields in Northern Ireland (H. Tunney et al., Johnston Castle research Centre, Ireland): average total P 0.6 – 1 mg P/l in run-off from sloping grassland (T. Vollmer et al., ETH Zurich, Switzerland); 0.19 - 0.83 mgTP/l in run-off from dry grass-clover grazing land (A. Melland et al., University of Melbourne, Australia); total P concentrations in surface run-off from sheep pastures in Victoria, Australia 0.19-1.28 mg P/l (A. Melland et al., University of Melbourne, Australia); mean total-P concentrations of .02 mg P/l in a slow draining catchment compared to 0.055 mg P/l in a freely draining catchment of agricultural livestock areas in Devon, England (A. Joynes et al., IGER, Devon, England).

Several posters showed the variation in P transfer for different land/management situations. In Florida, P run-off was 0.75 kg/ha for summer pastures (planted with bahiagrass (Paspalum notatum) but only 0.15 kg/ha for winter pastures on natural wet prairie land with somewhat lower stocking densities (D. Graetz et al., University of Florida). In the UK, re-seeding of pasture land resulted in a loss of 7.5 tonnes/ha of soil and 3.75 kg P/ha over just 16 days, compared to normal annual losses of 0.8 kg P/ha on undisturbed grass (P. Butler et al., Institute of Grassland and Environmental Research, England). W. Jokela, D. Meals et al. (University of Vermont; New England Interstate Water Poll. Cont. Commission) see article in SCOPE n°45, showed that the use of vegetation buffer strips along watercourses reduced P and suspended solids run-off, with 15 m buffers being more effective than 7.5 m buffers.

Hydrochemical connectivity

The different papers presented on this theme showed the wide variability in space and time of P losses from agricultural soils, resulting particularly from complex interactions between soil structure (and preferred water flow pathways such as cracks and macropores), climate, and the P-status of the soil.

C. Stamm et al. (Swiss Federal Institute of Technology, Zurich) emphasised the differences between results from the Lake Sempach region of Switzerland, where a few high water flow events dominated annual P losses, and from Devon, England, where smaller rain events were more important.

W. Gburek et al. (USDA-ARS Pennsylvania, USA) emphasised the importance, but also variability, of how water transfers from a catchment to the draining stream. The area of soil actually contributing run-off and infiltration water to the stream outflow will vary seasonally, and with the intensity of rainfall events.

J. Cox et al. (CSIRO, Adelaide, Australia) showed that generally-used soil characteristics could only explain a limited proportion of variability in P mobility in soils: 24% for all soil chemical parameters, and 21% for all soil physical parameters. Lower residence time of P in the soil increased P loss, because P was unable to contact soil adsorption sites. Macropores allow rapid movement of water through soil (preferred pathways) thus reducing residence time and allowing P movement even in clay soils or other soils with high P adsorption capacity. Combining the soil physical and chemical parameters with saturated hydraulic conductivity, total exchangeable cations and microporosity enabled around 90% of variation in P mobility to be explained.

D. Ryan et al. (Oak park Research Centre, Carlow, Ireland) also showed that a simple parameter based on the volume of air-filled pore space in soil was a good indicator of water flow behaviour for fields at three Irish sites with drainage problems.

I. Foster et al. (Coventry University, England) suggested, from work on two UK Midland field sites, that soil cracks, wormholes and gaps left by plant roots can provide a network of macropore

channels accelerating water movement through the soil, and resulting in rapid delivery of eroded soil sediment to drainage water. At one site at Rosemaund, Herefordshire, sediment transported in field drains reached nearly 100 tonnes/km²/year, of which 75-85% was from the topsoil.

Other papers on this theme looked at the fate of different forms of P reaching the aquatic environment from agricultural soils, and their potential to contribute to eutrophication. The importance of dissolved inorganic phosphates has long been recognised, but significant proportions of P transferred from agricultural soils are in organic or particulate form. It is now becoming apparent that these forms can also contribute significantly to eutrophication as a function of local conditions.

I. McKelvie et al. (Monash University, Victoria, Australia) presented results showing that organic phosphates, which have generally not been measured or been ignored, can be substantially released to inorganic (biologically immediately available forms) under estuarine mixing conditions.

D. Baldwin at al. (Muray-Darling Freshwater Research Centre, Albury, Australia) argued that agriculture-derived P often moves with sediment P, and can be progressively released by abiotic and biotic processes.

M. McGechan (Scottish Agricultural College, Edinburgh) showed that macropore flows through the soil to field drains, carrying colloidal P, are a significant component of input to surface waters. Phosphorus transfer was high when liquid manure (livestock slurry) was spread on wet soil (with waterfilled macropores), but negligible when slurry was spread on dry soils (macropores not containing water).

These themes were also largely explored in poster papers. In South-West Finland, annual field P-loss was calculated to be 0.92 kg P/ha/year, of which 87% was in particulate form. Although <7% of this was desorbable in an aerobic environment, 10-80% (average >30%) was released in low redox conditions.

Phosphorus levels in drain (ditch) water were shown to evolve differently, increasing as water moved down an grassed ditch (P release from organics) but decreasing along an earth drain (K. Barlow et al., Agriculture Victoria. Australia). Work in Herefordshire UK on the River Arrow showed that of a total P flux from fields of nearly 3 kg P/ha/year, only 1.41 kg P/ha/year actually reached the river, with the difference being considered to be retained in field vegetation and local re-infiltration. (M. Silgrum et al., ADAS Wolverhampton, England). Channel erosion in rivers and streams was estimated to contribute only 12% of suspended sediment, whereas agricultural transfers are likely to be a significant source of river P (F. Wood et al., IGER, Devon, England).

Phosphorus being carried in storm run-off in different streams in the Belgium-Luxembourg Ardennes showed a strong correlation between suspended solids and total P, but levels are higher at the start of storm events than during their continuation, so that P transfer cannot be adequately calculated using a simple concentration x discharge equation (M. Salvia-Castellvi et al., Fondation Universitaire Luxembourgeoise, Arlon, Belgium).

Impacts of agriculture-derived P on water quality

Several papers emphasised the importance of the EU Water Framework Directive (2000/60) in the evolution of agricultural nutrient transfer management, and in particular the need to assess the biological impact of nutrient inputs and not simply the water nutrient concentrations. Historically, there has been little linkage between monitoring of nutrient levels and biological parameters. (R. Dils et al., UK Environment Agency, Wallingford).

Different work was presented concerning models to estimate the transport and fate of P in river systems and the impact on the ecosystem. Pers et al. (Swedish Met. & Hyrd. Institute SMHI) presented modelling of biota response to nutrient input changes and fish management in a eutrophic lake, showing that planktivorous fish would increase algae (by removing grazer zooplankton), that algal levels were not responsive to P inputs other than a move towards N-fixing algae, whereas increased N inflow increased plant development. Wade et al. (University of Reading, England) showed modelling work suggesting that flow rate was more important than in-stream P concentrations for controlling macrophyte development in River Kennet, England. **P. Ekholm** (Finnish Environment Institute) showed that suspended solid concentrations and the Pcontent of suspended solids explained 71% of the variation in dissolved reactive P in agricultural runoff in Southern Finland

P. Chambers et al. (Environment Canada) indicated that P losses from agricultural land in Canada have accelerated eutrophication of certain rivers, lakes and wetlands, leading to changes in habitat and loss of biodiversity. In Alberta, P concentrations exceeded the interim provincial guideline value of 0.05 mg-totalP/l in >85% of samples, particularly in areas of intensive farming, but also even in areas of low-intensity farming. M. Chandra Sekhar et al. (Regional Engineering College Warangal, India) also emphasised the need to control non-point nutrient sources for effective surface water quality management.

Integrated catchment management and mitigation of P transfer

"All fields are not created equal when it comes to P export", stated T. Burt (Durham University, England). It is thus necessary to develop spatially explicit models to indicate where in the landscape the risk of P-transfer is highest, in order to then target management practice improvements in the most sensitive locations. This was confirmed by E. Ampontuah et al. (Reading University, England): geographically low-resolution data inputs to models may not accurately reflect transport processes and are likely to underestimate P losses. D. Collentine et al. (Swedish University of Agricultural Sciences) also indicated that compounded problems at the field or small catchment scale are one of the key problems in trying to design integrated models taking into account hydrology, soil and economic aspects.

A number of speakers presented modelling work using Geographical Information System data inputs concerning factors such as soil type and land use, but according to J. Freer et al. (Lancaster University, England) these will need conditioning with local observations. Modelling at a larger scale can be effective for identifying surface waters which exceed water quality guidelines for nutrients, which should be targeted for remedial work (C. Jordan et al., Dept. Agriculture and Rural Development, Northern Ireland). In Denmark, estimated particulate P transfers from 15 catchments were lower than measured levels, with the difference possibly resulting from stream bank and soil erosion (B. Kronvang et al., National Environment Research Institute, Sikeborg, Denmark). L. Heathwaite et al. (University of Sheffield, England) suggested that modelling should be based on a three-tier approach: land cover and management, climate - soil topography, routing and connectivity to receiving waters.

As J. Weld et al. (Pennsylvania State University) concluded, management and financial impacts of P strategies depend on factors such as farm location and animal density, making implications farm specific. M. Hart et al. (Summit-Quinphos, New Zealand) also indicated the need to identify high risk of P-loss areas on each farm, and appropriate case-by-case management strategies. The three driving factors for P-loss (surface run-off, erosion and transport of particulate-P, release and transport of soluble P) are all effectively highly locally variable.

Conclusions

Overall, the Workshop emphasised that despite considerable scientific progress, the popular recognition that phosphorus (P) run-off occurs widely from soils is only recent, and there is a considerable need to make farm managers and decision makers aware of this issue and to present research results in a form accessible to them. Thus the next challenge is communication and extension of information to stakeholders.

Concerning the technical understanding of the causes and mechanisms of P transfer, the Workshop emphasised the importance of organic and particulate P forms, alongside the more established recognition of the importance of soluble inorganic P; and the importance of storm and heavy rain 'event related' 'incidental transfers', especially following fertiliser or manure additions to soil.

The Workshop papers showed that significant transfers of P can occur from soils at all levels of soil phosphorus.

Different forms of P vary in their perception with different scientific/professional background. In general, agronomists and agricultural technicians are particularly attentive to inorganic P forms, whereas eutrophication scientists and water managers are more attentive to organic and particulate forms.

Because it is such a complex, multi-scaled and multi-disciplined problem, it is difficult to unequivocally 'prove' the link between agriculturerelated P and eutrophication. In this context, the best available option for eutrophication management is a combination of the use of hydrochemical parameters (eg. surface water and run-off P limits) and biological parameters. Such a combination is the approach taken by the EU Water Framework Directive.

There is a particular need to better understand the effects of land-use choices in controlling P runoff levels and levels and patterns. There is also a need to improve the understanding of interactions between Fe, Ca and Al and P availability / run-off during transport

Although often referred to in conceptual terms, in practical terms it is difficult to distinguish between sub-surface and surface transport. There is a need for further work developing tracing sources of P run-off from agricultural land and different run-off pathways

The Workshop concluded that way forward lies with integrated catchment management, involving all stakeholders. This must develop strategies for P-transfer prevention, looking for long-term sustainable solution, and not only act in response to the appearance of eutrophication symptoms.

Further conference information is available at: http://www.iger.bbsrc.ac.uk/igerweb/NWNew/IPT W/iptw2001.htm

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WATER POLICY

EUROPEAN UNION

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Member States under attack for failure to implement EU water policy

The Commission has strongly criticised many Member States' failure to implement adequately the Urban Waste Water Treatment 91/271, initiating a number of actions in the European Court against many Member States for failure to implement both this Directive and other water quality Directives: Nitrates Directive, Bathing Water Directive, Shellfish Water Directive and Drinking Water Directive.

MARINE EUTROPHICATION

Nitrogen discharges remain problematic

Recent reports by the European Environmental Agency and the Baltic Commission HELCOM suggest that marine eutrophication is decreasing in Europe, but that progress is being limited by the failure to address diffuse nitrogen sources, in particular from agriculture. Improved sewage treatment has enabled phosphorus emission reduction targets to be largely met.

EUROPEAN UNION

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Developments in EU water policy and implementation

The EU Water Framework Directive 2000/60 is beginning a complex implementation process, whilst at the same time Europe has adopted an Integrated Coastal Zone Management (ICZM) policy and is starting work on a Soil Framework Directive.

UK

WWF calls for action to reverse coastal eutrophication

A WWF UK report states that eutrophication of the UK's estuaries is leading to massive losses of biodiversity and of important fish nursery grounds. Many estuaries need to be urgently designated "sensitive areas" and sewage-works nutrient removal plus agricultural run-off reductions must be enacted.

NUTRIENT MANAGEMENT

FRANCE, UK, GERMANY

Nitrate emissions too high and increasing

For nitrates, France is far from respecting the OSPAR commitment to halve nutrient emissions to the North Sea, whereas phosphorus emissions have been considerably reduced. Nitrates are also posing problems in the UK and Germany.

VERMONT USA

Effectiveness of river bank restoration and protection

A paired watershed study in an agricultural area of Vermont, USA, shows that restoring river banks and preventing livestock access to streams can significantly reduce river nutrient and bacteria levels.

SYSTEMS APPROACH

Imbalance of nitrogen cycle

Energy-intensive human nitrogen fertiliser production has now reached around 37% of total natural nitrogen fixation by terrestrial and aquatic biological systems, leading to widespread and rapidly increasing eutrophication. A new approach must be developed, to reduce accumulation and develop recycling.

AQUATIC ECOSYSTEMS

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Alternative states in a eutrophied lake

Addition of pike to an experimentally eutrophied lake led to massive increases in large zooplankton, resulting in intensive grazing and reduced algal biomass. This state was accompanied by changes in the C:N:P ratios in the water and in the water residence times of nutrients, contributing to the stability of the alternate food-web state.

USA FLORIDA LAKES

Algal polyphosphates provide P-sink to sediment

Polyphosphates synthesised and bio-accumulated by algae can be sedimented and remain geochemically stable for decades. This provides a significant "sink" mechanism in lakes with excessive enrichment and removes available P from the aquatic ecosystem.

NORTH CAROLINA

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Effects of nutrients on phytoplankton and bacteria in dark-watered rivers

Bioassay experiments in waters from two "blackwater" North Carolina rivers showed that phytoplankton (algae) development was limited by nitrogen, but not by phosphorus, but that both nutrients could stimulate the development of heterotrophic plankton (bacteria).

NORTH CAROLINA

Muted river response to nutrient input reductions

Analysis of nutrient inputs to the Neuse river, North Carolina, over the last 20 years shows that reduction of point sources has reduced river phosphorus levels, but that downstream river nitrogen levels show no consistent patterns in response to changing watershed nitrogen inputs.

LOWLAND ENGLAND

Seasonal phosphorus retention in a river system

Assessment of catchment inputs to a good-quality lowland river showed a reasonable correlation with loads carried in the river water, but significant retention of phosphorus in the river system in spring and summer followed by release in autumn-winter.

HUNGARY

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Response of Lake Balaton to sewage nutrient removal

Chlorophyll levels (algal development) in part of the large, shallow Lake Balaton in Hungary have responded rapidly to reductions in nutrient loadings obtained by sewage treatment and river management, but in other parts of the lake algal blooms have instead increased.

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CANADA

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International Conference **'From Nutrient removal to recovery'** Amsterdam, 2 - 4 October 2002

Organised by the <u>International Water Association</u> (IWA) in co-operation with the <u>Netherlands Association on Water Management</u> (NVA) and <u>Aquatech Amsterdam 2002</u>

- Societal and Economical Impacts of Wastewater Nutrient Removal and Recovery.
- Re-use of nutrients and wastewater in agriculture
- Nutrient recovery from concentrated liquid
- Nutrient recovery form diluted wastewater
- Improved/Advanced Biological Nutrient Removal
- Alternative Sanitation and Source Separation
- Nutrient (N,P,S) recovery and re-use technologies
- Centralised and decentralised techniques
- Hygienic aspects of re-use of nutrients
- Public perception of nutrient re-use
- Quantification and evaluation of sustainability aspects of nutrient recovery
- Modelling tools to implement nutrient recovery and re-use technologies
- Life cycle analysis of nutrient recovery technologies
- Novel biological, physical or chemical techniques for nutrient removal

http://www.nva.net/agenda/conference200210_2-4.htm and http://www.iawq.org.uk/template.cfm?name=nutrient_removal

The SCOPE Newsletter is produced by the CENTRE EUROPEEN D'ETUDES DES POLYPHOSPHATES, the phosphate industry's reserach association and a sector group of CEFIC (the European Chemical Industry Council).

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 reader are invited on all subjects concerning phosphates, detergents, sewage treatment and the environment. You are invited to submit scientific papers for review.





PREVIOUS NEXT

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WATER POLICY

EUROPEAN UNION

Member States under attack for failure to implement EU water policy

Both the Commission and the EU Parliament seem determined to accelerate effective implementation of existing water quality directives. The Commission has published an assessment of implementation of the Urban Waste Water Treatment Directive 91/271, criticising many Member States for failure to adequately designate "sensitive areas" and for failure to implement adequate sewage treatment. The Commission has also initiated European Court procedures against a number of Member States for failure to implement adequately this Directive and/or the Nitrates Directive 91/676, the Bathing Water Directive 1976/160, the Shellfish Water Directive 1979/923/68 and the Drinking Water Directive 1998/83, the relevant obligations of all of which are implicitly maintained in the Water Framework Directive. Meanwhile. the EU Parliament has reacted by announcing a draft resolution criticising delays in implementation of the EU Waste Water Treatment Directive.

The Commission launched an active communications campaign addressing implementation of the Urban Waste Water Treatment Directive 91/271 with a press seminar presented as "Name and Shame" in March 2001. The accompanying press release stated that "the vast majority of Member States show major delays and shortcomings in implementation. 37 large cities are still discharging untreated waste water into the environment, and many others are discharging large quantities of effluent after inadequate treatment".

Sewage "name and shame"

In a reply to a European Parliamentary question concerning non-compliance with the Urban Waste Water Treatment Directive, in July 2001, Environment Commissioner Mrs Wallström confirmed that *"the* *Commission will not hesitate to take all the necessary steps ... to ensure full compliance*", and by the end of 2001 the Commission had sent "Reasoned Opinions" to seven Member States concerning failure to implement this Directive. This is the Commission's last formal step before a European Court of Justice procedure.

Concerning the Directive's requirements for nutrient removal from sewage, the Commission states that **Member States have designated Sensitive Areas in a** *"restrictive fashion"*, not taking account of the sensitivity of waters downstream from the immediate discharge point. **London, Paris, Athens and Dublin** are cited as amongst major cities where incomplete designation of Sensitive Areas has resulted in nutrient removal not being planned where it is in fact required. This is coherent with the European Environment Agency report on marine eutrophication (see Scope Newsletter n°44) which identifies the **Seine** as a major contributor of phosphorus and nitrogen to the Channel sea area.

Nutrient removal

The Commission's documents show that 67% of the 1017 agglomerations of more than 10,000 inhabitants discharging into Sensitive Areas in the 11 Member States which provided data were not providing adequate nutrient removal. Only Austria and Denmark were close to compliance with the December 1998 deadline for implementing nutrient removal. France and Germany had not provided any information whatsoever with regard to the treatment of their urban waste water at 31 December 1998, a situation described by environment Commissioner Margot Wallström as "unconstructive ... a barrier to transparency and proper information to the public".

The EU Parliament has also reacted to the delays in implementation of the EU Waste Water Treatment Directive, with a resolution voted on 13th March 2002 to underline the legally binding nature of the timetable of implementation deadlines in the Directive and the responsibility of Member States to



enact these.

The motion voted emphasises that "are major shortcomings in the implementation of the urban waste water Directive due to the failure of Member States to enforce the more than ten year-old Directive, whereas the urban waste water Directive is a cornerstone of European water legislation. ... underlines the importance of the legally binding timetable of the urban waste water Directive and stresses the importance of ensuring that the, in some cases, already considerable delay of the Member States in implementing the Directive is not further added to"

Inadequate definition of "sensitive areas"

Commission criticism covers nearly all Member States. Germany has not classified most of its **Danube basin** area as sensitive, which is inconsistent with reducing nutrient loads to this river and to the Black Sea, as agreed by the Danube Commission. In **Spain**, the Commission estimates that there are 44 areas which have not at present been designated as Sensitive, but which should be so.

For **France**, also, the Commission identifies a number of areas which have not been designated as sensitive but should be so, in particular the Seine river basin in which Paris and other large cities are situated, rivers and coastal waters in Brittany, areas of the Vendée, the Mediterranean coastal lagoon of Thau ... France has also failed to provide information concerning conformity of its sewage works.

The **Wallonia region of Belgium** is criticised for not only failing to have installed adequate, or in some cases any, sewage treatment (since late 2000, one third of Brussel's sewage receives secondary treatment, but the sewage works to treat the remainder is still only at the planning stage!), but also for failing to identify as Sensitive Areas rivers which flow into the Flanders area (which is designated as Sensitive).

Italy has failed to designate as Sensitive the **Po river tributaries** (despite the Po being historically concerned by problematic eutrophication, in particular as a result of agricultural loadings), meaning that the cities of Milan and Turin should be equipped with nutrient removal. Indeed, in December 2001, the Commission initiated a European Court action against Italy for inadequate treatment of Milan's sewage, because discharge is into the Po river which flows, 300 km downstream, into the (designated) nutrient Sensitive Area of the Po Estuary.

The **UK** designated 36 sensitive areas in 1994 and a further 40 in 1998. However, even after this second "wave" of designations, many estuaries and coastal waters which the Commission considers as Sensitive are not designated, including major estuaries such as the **Thames** and Humber, as well as certain loughs and estuaries in Northern Ireland including Lough Foyle, Carlingford and Belfast Loughs and the Bann Estuary.

This is consistent with the report published by WWF concerning eutrophication of UK estuaries, see this Newsletter. Of the 207 conurbations in already designated sensitive areas in the UK, only 19 were had nutrient removal installed in their sewage works in compliance with the Urban Waste Water Treatment Directive by 1998. On top of this backlog will be agglomerations in the areas which the Commission considers should be designated sensitive but have not been to date, which includes cities such as London, Leeds, Hull and Southampton.

In Austria, which considered that none of its territory was Sensitive, the Commission identifies 3 rivers as requiring designation, as well as several areas which are in the Rhine, Elbe or German lake catchment areas – but in this case nearly all the agglomerations concerned already have nutrient removal installed.

This criticism for inadequate designation of Sensitive Areas is reiterated by the EU Parliament motion (see above) which "Underlines that several Member States have been restrictive and unhurried in their designation of sensitive areas" and "Urges the Commission to initiate infringement procedures in cases where criteria for designating sensitive areas have not been respected or ignored"



European Court condemns Member States

The Commission is also acting to enforce implementation of the Urban Waste Water Treatment Directive and other water protection Directives (Nitrates Directive, Bathing Water Directive, Shellfish Water Directive, Drinking Water Directive ...) through European Court actions against Member States.

On 7 December 2000 the European Court of Justice (case C 1999/069) judged that the UK had not adequately implemented the EU Nitrates Directive 91/676, by failing to identify adequately nitrate polluted waters and to designate nitrate "Vulnerable Zones".

The UK had in fact omitted from consideration all surface and ground waters not being used for the extraction of drinking water, thus inappropriately limiting the areas. Since the decision, designation processes have been re-launched in England, Scotland and Wales. This could lead to around 80% of England being designated.

In October 2001, the Commission followed up the Court decision by a "Letter of Formal Notice" reminding the UK of its obligation to complete the identification of all nitrate polluted waters. The Commission's press release recalls that the Commission has power to act against a Member State which does not comply with a European Court judgement, including the possibility to impose financial penalties.

On 8 November 2001, the European Court of Justice again condemned a Member State for failure to implement the Nitrates Directive 91/676 – this time Italy (case C-127/1999). This follows a 1999 judgement that Italy had failed to designate nitrate Vulnerable Zones. The 2001 judgement states that Italy has failed to establish the action programmes for the protection of waters against agricultural nitrate pollution required by the Directive, failed to carry out fully the required monitoring, and failed to provide adequate reporting to the Commission. The judgement however also criticised the lack of case-specific evidence and information supplied by the Commission.

Actions have also been launched against Finland,

Portugal and Luxembourg for non-respect of the Nitrates Directive.

On 8th March 2001, the European Court ruled against France for failure to comply with the 50 mg/l nitrates limit in drinking water in Brittany. Early 2002, the Commission followed this up with a Letter for Forma Notice (a first written warning) for not complying with this judgement, considering that no effective measures have been taken to reduce this nitrate pollution problem.

On 13 November 2001, the European Court also condemned the UK for failing to meet minimum water quality standards at over 10% of designated bathing beaches in 1996 and 1997 (Quality of Bathing Water Directive 76/160). The UK acknowledged the breach, and indicated that compliance has been better since 1998.

On 24th July, the Commission also began actions, by sending formal warning letters (Reasoned Opinion) against **France** and **Spain** for **breaches of standards set by the Drinking Water Directive (1980/778)** and against a number of countries for failing to transpose into national legislation by the 25/12/2000 deadline the updating of this Directive (1998/83)

The same day, the Commission announced action against **France**, **Belgium and Greece for non-respect of the Urban Waste Water Treatment Directive**. France is targeted for having failed to designate as "Sensitive Areas" various nutrient effected bodies of water, and for failing to adequately treat sewage discharging into them. Belgium is late in designating "Sensitive Areas" and in installing sewage treatment, including for Brussels. Greece is faced by three actions, for failure to equip Athens' new sewage treatment plant with nutrient removal despite the nutrient affected state of the Gulf of Sarinokos, for failure to install nutrient removal in the Elefsina area, and for failure to designate the Thermaikos Gulf as a sensitive area.

On 22nd February 2002, the Commission issued a press release emphasising the various procedures launched against Member States for failure to comply with the Urban Waste Water Treatment Directive and other



water quality Directives. As well as the actions indicated above, this announced referral to the European Court of Belgium, France, Germany, Ireland, Luxembourg, Spain and the UK. Belgium is stated to have not finalised transposition into legislation in Flanders or Wallonia of the updated 1998 Drinking Water Directive; France is pinpointed for not providing bathing water monitoring results for 1999, for polluting freshwater hydroelectric plant discharges into the Etang de Berre in contradiction to the Mediterranean Sea protection protocol and for failure to transpose the Drinking Water Directive; Germany's federal legislation, according to the Commission, fails to provide adequately for wastewater treatment monitoring; Ireland has failed to implement a pollution reduction programme to respect the Shellfish Water Directive; Luxembourg has failed to transpose Drinking Water Directive; Spain and the UK have also not finalised transposition of the Drinking Water Directive.

Portugal, on the other hand, has obtained the first ever sewage treatment derogation to be accorded under the Urban Waste Water Treatment Directive 91/271. This Directive states that the water treatment standards defined may be "relaxed" in specific cases where Member States designate waters as "less sensitive" to eutrophication and microbiological pollution. Portugal applied for a derogation from the Commission for the Estoril conurbation (720,000 population equivalent) on the Atlantic coast. The Commission's decision (2001/720/EC) allows discharge to be subject to primary treatment only, plus disinfection during the bathing season. The Commission decision indicates that the emission point is situated a long way from the bathing waters, and that this coastal zone offers "exceptional" marine conditions "some of the most favourable of European coastal waters for the dilution and dispersion of pollutants". ENDS Daily (12/10/01) indicates that two other requests for derogations re currently being examined by the Commission, both concerning small conurbations.

Accession States

Concerning Accession Countries, the Commission estimates that implementation of the Waste Water Treatment Directive will cost in total around €30 bil-

lion but that good progress has been made in preparing the financial strategies to achieve this. As regards nutrient emissions, implementation in the Accession countries is expected to reduce these by 40-50% overall from current levels.

To date, transitional arrangements regarding implementation of this Directive have been negotiated and agreed with the following countries (in brackets, the deadline accorded for Directive implementation): Cyprus (2012), Czech Republic (2010), Estonia (2010), Hungary (2015), Latvia (2015), Lithuania (2009), Poland (2015), Slovenia (2015).

EU sewage treatment "name and shame" press release http://europa.eu.int/comm/environment/nsf/index.htm

EU water pollution fact sheets page http://europa.eu.int/scadplus/leg/en/s15005.htm

EU DG Environment press releases http://europa.eu.int/comm/environment/press/index.htm

Information about implementation of EU environmental Directives in Accession States http://europa.eu.int/comm/environment/enlarg/home.htm

EU Parliament Resolution: http://www.europarl.eu.int/plenary/default_en.htm then go to "Texts adopted by Parliament" -> "By date" -> March 13th 2002

MARINE EUTROPHICATION

Nitrogen discharges remain problematic

Both the EEA (European Environment Agency) and HELCOM (the Baltic Marine Environment Protection Commission) have published recently overview reports assessing progress on addressing marine eutrophication. These reports indicate that objectives for phosphorus emission reductions have been widely achieved (up to 50% reductions) through improved sewage treatment (installation of P-removal). Diffuse nitrogen emissions, on the other hand, have not been successfully reduced or have



even increased. Diffuse agricultural phosphorus releases from agriculture in West European Baltic countries have also increased, despite reductions in phosphate fertiliser applications.

The EEA report emphasises that inadequate data was available for the Mediterranean, the Bay of Biscay and the Iberian Atlantic Coast. In fact, effective monitoring data is indicated as available for the North Sea, Skagerrak, Kattegat, Belt Sea, Baltic open sea, Gulf of Riga, Gulf of Finland and Gulf of Bothnia areas ; partial data are available for the Channel, North Atlantic, Iceland coast, Celtic Sea and Baltic coastal areas ; but " almost no measurements on eutrophication variables " are available for the Bay of Biscay, Iberian coast and Mediterranean Sea. This confirms previous reports that marine eutrophication science and policy in Europe is centred on the North Sea areas and is not necessarily relevant to other marine ecosystems (see eg. Vidal, Duarte and Sanchez "Coastal eutrophication research in Europe: progress and inbalances", Marine Pollution Bulletin 1999).

The report indicates that eutrophication in the Mediterranean is limited to certain specific coastal areas, and discharge of untreated sewage, in addition to agricultural run-off and fish farming are the main nutrient sources. Only 72% of the 290 major towns on the Mediterranean coast have secondary sewage treatment to date, and even fewer operate nutrient removal.

In the North Sea, there has been a significant reduction in phosphorus loadings since the 1980's, but **no reduction in nitrogen loadings, primarily because of agricultural releases**. The drop in phosphorus loadings has continued with a 20% fall over the 1990-1996 period, resulting from improved sewage treatment.

Ecosystem effects

The report indicates that there are **no symptoms of eutrophication for the marine areas of the Irish coast, the North Atlantic coasts of the Shetland Isles and Norway**. In the remaining areas of the Channel, North Sea and Skagerrak, nutrient levels are closely related to the localisation of river inflows, and nutrient enrichment appears mainly in coastal areas near river outlets and in estuaries. Nitrogen and phosphate levels in the Baltic appear to vary considerably with aquatic biological denitrification processes and with phosphorus adsorbtion into/release from sediments (depending on the oxygenation or not of the sea bottom).

Chlorophyll-*a* concentrations, an indicator of algal development, showed a slight correlation with winter concentrations in the marine waters, even in the low range of $0-50 \mu$ MN. Chlorophyll levels were not correlated with phosphorus concentrations or with any other variable. Sea bottom oxygen concentrations were not correlated to nutrient or chlorophyll levels, but only to the vertical stratification of the water column (degree of mixing), and possibly to the related sedimentation rates.

The report concludes that *"The main source of nitrogen is run-off from agricultural land brought to the sea via rivers"* and emphasises the need for more thorough data collection.

Nitrogen challenge in Baltic

In the Baltic Sea, nitrogen loads have dropped very slightly, as a result of reductions of agricultural intensity in Eastern European countries. Phosphorus loads have been very significantly reduced, on the other hand. The HELCOM target objective of a 50% reduction has been achieved for phosphorus from point sources, in particular through installation of sewage treatment with P-removal, so that diffuse sources and in particular agriculture are now the main cause of concern. According to HELCOM's 2001 report " Most of the nitrogen discharges are coming from agriculture. The challenge is to gain control over diffuse sources within the agricultural sector ".

HELCOM indicate that the 50% reduction for phosphorus from all sources has been achieved by almost all Baltic Sea countries, but that most did not achieve this for nitrogen. Reductions in the 1990's were lower for Finland, Western Germany, Sweden and Denmark, because they had already achieved point source reductions through nutrient-removal in sewage works in the 70's and 80's.



Sweden and Finland are estimated to be now achieving an overall 90% removal of phosphates from municipal wastewater, and had by 1995 the lowest per inhabitant load of phosphorus from municipal sources at <0.2 kgP/inhabitant/year after sewage treatment.

Agricultural phosphorus losses did not fall in Sweden, Germany and Finland, despite lower fertiliser application rates, probably because of high soil P levels. Agricultural nitrogen losses have been reduced in all of the Transition Countries except Poland, but this is linked to 30-40% drop in agricultural production.

A HELCOM press release in March 2002 confirmed that pollution from the agricultural sector is *"conside-red to be the main reason for eutrophication"*.

"Eutrophication in Europe's coastal waters" European Environment Agency Topic Report 7/2001, Copenhagen, 2001. European Environment Agency http://www.eea.eu.int eea@eea.eu.int

" Working Document on Evaluation of the Implementation of the 1988 Ministerial Declaration regarding Nutrient Load Reductions ", Helsinki Commission, Katajanokanlaituri 6 B, FIN-00160 Helsinki, Finland, August 2001 <u>helcom@helcom.fi</u>

HELCOM press release, 7th March 2002 " The 2002 Helsinki Commission Meeting " <u>http://www.helcom.fi/helcom/pressroom/pressre-</u> leases/07032002.html

EUROPEAN UNION

Developments in EU water policy and implementation

EU water policy is currently in a phase of rapid development, with the definition of a Recommendation concerning coastal zone management and the start of the implementation process of the Water Framework Directive 2000/60. The latter involves a considerable body of consultative and scientific work to define the practical meaning and application of the Directive's obligation for Member States to achieve "good ecological quality" in all surface waters (except for specific exceptions) by 2015: how should this ecological status be defined and measured in the field ?

The Water Framework Directive provides extensive annexes outlining the criteria for assessing whether water bodies have achieved the required "good ecological quality". The Directive requires that objectives and action plans for achieving this quality status should be defined in the field on a catchment basin basis. However, these annexes specify the different criteria to be assessed, but do not generally give limit values or numerical objectives to be achieved. Good ecological quality is defined as water quality such that the ecosystem functioning (eg. species variety and balance, compatibility with water usages ...) do not differ significantly from the natural state.

The Commission published in May 2001 a strategic guidance document "Common Strategy on the Implementation of the Water Framework Directive", with the aim of achieving a coherent and harmonious implementation across Europe, in particular where river basins cross national boundaries. This is the first time that an EU Directive has been accompanied by such an implementation guide. The Common Strategy establishes a series of expert and working groups to take forward various aspects of the Directive. The expert groups assist the European Commission in developing policies in areas that are not yet (or are inadequately) addressed in the text of the Directive, such as priority substances, groundwaters and reporting. The ten working groups each address specific technical issues, ranging from the typology of waters and defining 'heavily modified waters', to monitoring and the use of GIS. The working groups each have two lead institutions, at least one of which is a Member State, to take forward the initiative. The Common Strategy recognises that while there is significant expertise and experience of 'best practice' in the Member States, the Water Framework Directive requires extensive innovation in many areas (eg in defining "ecological status"). The objective is, therefore, to



draw on experience to assist in this innovation, not necessarily to achieve standardisation across the EU, but to avoid duplication and promote integration.

Other important components of the Common Strategy include an **emphasis on capacity building, involvement of stakeholders and public awareness and the need to integrate implementation of the Directive with other legislation and policy areas.** The latter issue includes transitional arrangements (eg on reporting) for those Directives that are repealed by the framework Directive and integration with the remaining EU water Directives and policies - such as integrated product policy.

Coastal management and soil directive

In October 2001, the European Council adopted a Recommendation concerning **Integrated Coastal Zone Management (ICZM)**. At the time of going to print, this was pending final (2^{nd} reading) approval by the European Parliament. This gives Member States five years to develop national strategies for coastal management, integrating land use and marine water protection, including international cooperation for regional waters, and information systems for monitoring and dissemination.

Also in October, the EU Commission (DG Environment) issued a **"Soil Protection Communication"**, intended as a consultation document to lay the foundations for a future "soil framework directive".

EU document "Common strategy on the implementation of the Water Framework Directive" download (WWF site)

http://www.panda.org/europe/freshwater/pdf/WFD-CSImpl.pdf

EU Commission's "Soil Protection Communication" http://europa.eu.int/comm/environment/agriculture/pdf /soilpaper2.pdf

Common Position (Council-Commission, 13th December 2001) on Integrated Coastal Zone Management (ICZM), COM2000(547)final <u>http://europa.eu.int/eur-lex/en/com/cnc/2000/com2000</u> _0547en01.pdf

UK

WWF calls for action to reverse coastal eutrophication

"Current policy is threatening and reducing biological diversity" in the UK's estuaries according to WWF UK. Nutrient levels in some UK tidal rivers and estuaries are up to 100x higher than levels officially recognised as problematic, posing a threat to marine habitats and species, including eelgrass meadows, seahorses, and different commercial fish species. Of Britain's 155 estuaries, only 20 still possess eelgrass beds of one hectare or more (a decline in 85% of estuaries since the 1920's). Important international conservation areas are threatened by loss of biodiversity. WWF suggests that the UK's eutrophication strategy has concentrated on fresh waters, ignoring estuaries and coastal waters, but that this is inconsistent with international commitments such as OSPAR. The particular threats of fish farming are also emphasised.

The WWF report indicates that phosphorus and nitrogen are the two key nutrients which can contribute to problems such as algal development, leading to turbidity and changes in biodiversity. Nitrogen is usually the critical "limiting" nutrient and there is some evidence that disproportionately reducing phosphorus inputs may increase the competitive advantage of some "undesirable" species. **Many estuary ecosystems may be sensitive to relatively small increases in nutrient levels.**

Symptoms of increased nutrient levels emphasised by WWF include growth of annual seaweeds, which can form thick mats of weed, and smother perennial plants such as kelp and eelgrasses. Floating algae (phytoplankton) and small surface algae (epiphytes on the surface of larger plants) can also develop, causing the water to become turbid, and preventing light from reaching depths where perennial plants grow. This rapid development of different plant forms can provide food, for example for sea snails which then are eaten by brent geese, but can also cause a change



towards smaller phytoplankton species, which provide lower food value for fish.

Submerged eelgrass meadows are a very important ecosystem, in particular the subtidal species Sostera marina, providing shelter for species such as seahorses, pipefish, cuttlefish, and fish nursery areas for commercially valuable species such as bass. Eelgrass has declined massively in UK estuaries, and there is significant evidence that this is related to increased nutrient levels.

Many UK estuaries, which are nature conservation areas of international status (SACs and SPAs), are currently being deteriorated by eutrophication.

OSPAR commitments

In 1987, under OSPAR, the North Sea countries committed themselves to reduce nitrogen and phosphorus inputs to the sea "by the order of 50%". The UK has not implemented this commitment. In 1998, the "OSPAR Strategy to Combat Eutrophication" committed all parties including the UK to not only meet this 50% reduction target, but also to take further measures to ensure that by 2010 a healthy marine environment is achieved "where eutrophication does not occur".

WWF recommends that the UK now urgently address these commitments, which will inevitably have to be met in time, since the EU is a signatory of OSPAR and will ensure enforcement. WWF also suggests that many estuaries should be designated as nutrient "sensitive areas" under the EU Urban Waste Water Treatment Directive 91/271 provisions, which would then require 75% nutrient removal in sewage works. Many should also be designated as "nitrate vulnerable zones" under the EU nitrates directive 91/676.

WWF identifies as the actions required nutrient removal in sewage works, addressing agricultural nutrient pollution (reducing nitrogen loads to fields, restoring vegetation buffer zones alongside rivers), and rewilding of the land around lower estuary areas.

Specific action is also called for to limit nutrient releases from fish farming. Fish farming on the West and North coasts of Scotland are estimated to release the same levels of phosphorus as raw sewage from 9.4 million people, in an area where the ecosystem is particularly diverse and sensitive to nutrients. The report emphasises that there are reasons for hope given the experience from Denmark which shows that when nutrient inputs to estuaries are reduced then important species, such as eelgrasses, and biodiversity in general slowly recover.

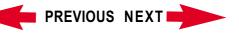
"Out of sight – out of mind – Marine eutrophication in the UK". Malcolm MacGarvin/ ModusVivendi for WWF UK, August 2001.

Report :

http://www.wwf-uk.org/filelibrary/pdf/nutrientoverview.pdf

List and map of affected estuaries : http://www.wwf-uk.org/filelibrary/pdf/nutrientmap.pdf





NUTRIENT MANAGEMENT

FRANCE, UK, GERMANY

Nitrate emissions too high and increasing

The French Environment Institute (IFEN) has published a summary of analysis of ten year's figures for nutrient loads carried by France's rivers (the full data will also be available shortly). This estimates that the country's rivers carry each year some 646,000 tonnes of nitrogen (N), mainly as nitrate, into surrounding seas, along with 43,800 tonnes of phosphorus (P) and nearly ten million tonnes of sediment (averages for the last ten years). Trends are compared to the commitment made by OSPAR states, which include France, to reduce nutrient inputs to the North Sea by 50% from 1985 – 1995.

Figures over the last 10 years were analysed from 90 French rivers discharging either into the sea or into the transboundary Rhine river. River nutrient loads were calculated by comparing monitored concentrations with data for river flows. The authors note that this may induce considerable inaccuracies for the Mediterranean rivers such as the Rhône, in particular, where large loads of nutrients are carried in sediments related to short flood/high flow events.

Even in the Seine, which carries 85% of France's phosphate emissions to the Channel sea area, only 44% of this is soluble, showing **the importance of sediment phosphorus fixing mechanisms.**

The Institute's study shows a complete difference between trends for nitrates, and those for phosphorus. **Phosphorus emissions have been significantly reduced, as have ammonium emissions (in both cases, probably as a result of improved waste water treatment installation), whereas nitrate emissions have note fallen.** Phosphorus emissions have fallen significantly, for example by around 50% 1990-2000 for the heavily populated Seine and Rhône rivers, although emissions have remained stable in the Loire (predominately agricultural). Total phosphorus emissions in 1999 at 375,000 tP/year were nonetheless considerably higher than the OSPAR target, of around 200,000 tP/y.

Nitrate emissions from the two main catchments flowing into the North Sea, the Seine and the Loire, are actually still increasing, leading the authors to state that "an imaginable deadline for achieving the OSPAR objective cannot be given".

The nutrient emissions from North Brittany and Normandy are relatively high, reaching 33 KgN-NO₃/hectare/year and 2.5gP/inhabitant/day for Brittany, indicating the contribution from agriculture. The study results also show that **smaller rivers make a contribution which is signific ant** overall, and can be locally determining, to coastal marine eutrophication.

Nitrates also the problem in UK rivers

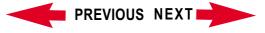
A similar situation to that in France is reported by the UK Environment Agency. **Rising nitrate concentra-tions** stand out as the black spot in the "best ever" results for river quality reported in the UK Agency's five yearly survey for the year 2000. 94% of rivers achieved "fair or good" chemical quality in 2000, leading the Agency to state that rivers are now "probably cleaner than they have ever been since the industrial revolution".

Nutrient data show an improvement in phosphate levels, with a halving of the percentage of rivers classed as having "excessively high" levels. On the other hand, nitrate levels have increased with 31.7% of river sections having "high" concentrations in 2000, whereas only 30.3% did so in 1995.

EU Court action on nitrates

Germany, meanwhile, has been condemned by the





European Court of Justice for allowing farmers to spread too much manure on land, in contradiction with the EU's 1991 Nitrates Directive 91/676. According to the judgement, member states must precisely apply EU limits defined for farms' nitrate application in "nitrate vulnerable zones", including where the nitrates are spread in manures. This will also affect The Netherlands and Italy, who face similar enforcement actions from the EU Commission.

France: "Les données de l'environnement – numéro 72". IFEN – Institut Français de l'Environnement, 61 bd. Alexandre Martin, 45058 Orléans Cédex 1, France. Available at: <u>http://www.ifen.fr</u> Available spring 2002: "10 ans de flux de nutriments des fleuves de la France" (text and CD)

UK: Environment Agency National maps and summary tables of river quality classification

http://www.environment-agency.gov.uk/ yourenv/eff/water/213902/river_qual/

Germany: se European Court by entering C-161/00 in "Case number" at

http://www.curia.eu.int/jurisp/cgi-bin/form.pl?lang=en

VERMONT USA

Effectiveness of river bank restoration and protection

Some 71% of the annual phosphorus loads to Lake Champlain, the US's sixth largest freshwater lake, come from non-point sources, and most of this is from agricultural land. The Lake is undergoing eutrophication, and the management strategy calls for reductions in the phosphorus loadings.

This study looks at rivers in the Missiquoi river drainage sub-catchment of Lake Champlain, in Vermont, in the North East of the USA. The area has annual temperature ranges from -34° C to 33.2° C (average max and min), annual precipitation of just over 1,000 mm and annual snowfall of around 290 cm. This is the most intensively agricultural region of the Lake's catchment, contributing the greatest non-point phosphorus load of any of the Lake's tributaries (around 82 tonnesP/year) for the second largest volume of water. The rivers in the area are typically deteriorated by nutrients, bacteria and organic matter originating from animal wastes from dairy farms, crop production and livestock activities near the rivers.

Mainly dairy grassland farming

The study compares two watersheds, the Godin Brook (1422 hectares), in which a river bank restoration programme was launched, and the Berry Brook (954 ha) control (no management actions). These catchments range from 150 – 400 m altitude, and are similar in terms of land use, with **around 60% coverage by mixed woodland, very little urbanisation, and around one third agricultural land. This agricultural land is primarily grass production for livestock, either grazing pasture or hay growing. The numbers of farm animals reported in the two catchments (larger farms only reported) were respectively 1,656 and 333 "animal units" (that is, equivalents to around 450 kg of animal), predominately dairy cattle.**

Restoration work

The river bank restoration work in the Godin Brook catchment involved 11 landowners. Action carried out included protecting both sides of 2300m of stream and wetland with fences to keep livestock out, bank stabilisation including planting willow trees, a 300m stabilised livestock track and bridge. The fenceprotected riverbank areas varied from 2 to 8m in width, and grass and shrubs were allowed to re-grow naturally on these areas.

The paired watershed method involves monitoring both watersheds before the management actions to allow comparative regression factors to be defined ("calibration"), then comparing differences in evolution of the monitored parameters following the implementation of management actions on one of the watersheds but not in the other. **The paired monitoring enables changes to be better attributed to the actions taken**, as effects of external factors (climate, precipitation, ...) should



affect both watersheds similarly. In this case, the two watersheds were "calibrated" by monitoring over 3 years (Spring 1994 – Spring 1997), then monitored in 1998 (following management work in the Godin Brook catchment in 1997). Post-treatment monitoring was expected to continue for an additional two years.

The first year of post-action monitoring showed significant decreases in river total phosphorus concentrations (-25%), river bacteria counts (-46% to -52%) and in total phosphorus export out of the watershed (-42%). All these figures are considerably higher than the margin of possible error indicated by the calibration period results (20%).

The author concludes that livestock exclusion and riparian restoration can be "an effective tool for reducing nonpoint source pollutant concentrations and loads from livestock grazing in agricultural watersheds".

"Water quality response to riparian restoration in an agricultural watershed in Vermont, USA". Water Science and Technology, vol. 43, n° 5, pages 175-182, 2001.

http://www.iwaponline.com/wst/04305/wst043050175.htm

D. Meals, New England Interstate Water Pollution Control Commission/ Vermont Dept. Environmental Conservation, 103 S. Main Street, Waterbury, Vermont 05671 USA. <u>dmeals@wcvt.com</u>

SYSTEMS APPROACH

Imbalance of nitrogen cycle

Although nitrogen is present in the air, rocks and sediments in huge amounts, these N-minerals are mostly too inert to be accessible to biological systems, so that organically available nitrogen has been and continues to be the main limiting factor for global biomass production. Natural biological nitrogen fixing and denitrification mechanisms are approximately balanced, but man has massively altered this situation with the development of mineral nitrogen fertiliser synthesis, in particular with a tenfold increase since the 1960's. Mineral fertiliser synthesis now fixes around 90 million tonnes of N per year, compared to biological nitrogen fixation estimated at 240 million tonnes N worldwide. There are few other elements for which human impact has been so dramatic.

The doubling of the world population between 1960 and 2000 would probably not have been possible without the increase in agricultural production enabled by nitrogen fertiliser use, but at the same time the industrial fixation of nitrogen in fertilisers increased by a factor of 10.

Global warming

The considerable increase in biologically available nitrogen in ecosystems has a number of negative impacts. The authors cite the development of bluegreen algae, which can be toxic and problematic for water supplies, the oxidation of ammonia in surface waters which can lead to low aquatic oxygen levels, overproduction of plant and algal biomass in surface waters, and the loss of biodiversity.

Lower water oxygen levels can lead to incomplete denitrification, resulting in the production of NO and the greenhouse gas N_2O , and the decomposition of overproduced biomass in aquatic sediments can generate another greenhouse gas methane. These contributions to global warming gas increases are little understood and have received little attention to date. They add to the impact of the energy consumption necessary for nitrogen fertiliser synthesis.

The average retention time of organic nitrogen in the biosphere is around 7000 years. Industrial fixation of nitrogen in fertilisers is making a considerable contribution to total nitrogen fixation and is not balanced by natural denitrification, thus leading to an ongoing accumulation of available nitrogen in the biosphere, the long-term effects of which are not known.

Systems approach

Only 10-15% of nitrogen fertiliser applied to land



actually ends up in food protein, the rest feeds into the environment. Further, only 1-2% of organic nitrogen in food is actually used by the human body, the rest going to sewage. The result of these inefficiencies is mirrored in the economic value of different products containing organic nitrogen (US\$/kgN) :

- * mineral fertiliser 0.5
- * wheat protein 9
- * pork protein 55
- * milk protein 90

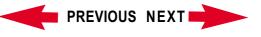
Less than 5% of the world's sewage receives tertiary treatment involving nitrogen removal, and even if this were massively increased, this is a very inefficient 'solution' as it involves investing in expensive capital equipment and running costs to break down organic nitrogen which has been synthesised using energy input. The authors estimate this "negative value" of sewage nitrogen at 3 US\$/kgN.

The authors suggest that it is therefore necessary to develop a systems approach to nitrogen fixation and reuse in agriculture and aquaculture. The aim should be to move away from the current inbalance and accumulation of organic nitrogen in the biosphere, towards nitrogen recycling and towards a much more efficient use of nitrogen in crop and food production.

"The nitrogen cycle out of balance", Water 21 (IWA – International Water Association), August 2001, pages 38-40.

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AQUATIC ECOSYSTEMS

CANADA

Alternative states in a eutrophied lake

L227 is a 5 hectare, 10m max. depth headwater lake situated at the Experimental Lakes Area of North-West Ontario, Canada. It is usually strongly thermally stratified. The lake had been experimentally eutrophied since the early 1970's in a classic study reported elsewhere. From 1990 onwards, nitrogen was no longer inlcuded in the lake fertilisation regime, so that it was receiving an input of 0.56 gP/m²/year and no other nutrient addition. Before 1993, the fish population was made up only of small fish (cyprinid minnows, dace ...) with no piscivorous fish. Densities of these small fish were thought to be comparable to that in other eutrophied lakes in the area, at around 100 kg/ha. In the springs of 1993 and 1994 a total of 160 piscivorous fish (pike, total weight 143 kg) taken from nearby lakes were added.

From 1992-1996 the lake was monitored every 7 or 10 days from May – September for algae, zooplankton, water nutrient chemistry and other parameters. Small fish abundance was assessed monthly using fish traps. The addition of the pike decimated the small fish population within 2 years and by 1996 had apparently been exterminated, so that by that year zooplankton effectively no longer had vertebrate predators in the lake.

Larger zooplankton

Summer average zooplankton size changed little through to 1995, but increased fourfold in 1996. This corresponded to a slight appearance of smaller *Daphnia* species in 1993-1995, and a dramatic increase in the larger *Daphnia pulicaria* in 1996 (98% of zooplankton biomass in July 1996). At the same time, the N:P ratio of zooplankton biomass declined, down to a lowest level of 17:1 in 1996.

In the summer of 1996, zooplankton biomass included more than 32% of epilimnetic phosphorus, compared to

less than 1% in previous years. The zooplankton thus effectively acted as a "sink" for available phosphorus, leaving less available to produce algal biomass. This was accompanied by a fall in the seston (mostly algae, some bacteria, but not including zooplankton) biomass C:P ratio.

Sedimentation rates of phosphorus were greatest in 1996, presumably because of the effect of the large zooplankton to "pack" phosphorus into relatively large, rapidly sinking particles (fecal pellets, zooplankton decay remnants ...). Also C:N and C:P ratios in sedimented material were significantly lower in 1995 and 1996 than in previous years.

However, the dense Daphnia population in 1996 did not last, and crashed from 375 μ g/l on 24 July to 2.1 μ g/l Daphnia biomass. This was associated with high densities of invertebrate predators such as diving beetles and notonectids. Total zooplankton biomass also declined with this Daphnia population crash, but nonetheless remained higher than in previous years, being dominated by the omnivorous calanoid copepod Epishura lacustris.

In 1996, during the large Daphnia population development, dissolved phosphorus (TDP) and nitrogen (TIN) concentrations in the lake water were both significantly higher they had been in the Springs of 1992-1995. However, the dissolved nitrogen increased over 4x whereas dissolved phosphorus only around twice, so that the TIN:TDP ratio also doubled in Spring 1996. After the Daphnia population crash in the Summer of 1996, TIN concentrations declined.

Blue-green algae

The proportion of nitrogen-fixing cyanobacteria ("blue-greens") in the lake algal population had begun to increase from 1990, when nitrogen had been removed from the normal experimental fertilization regime. This trend continued in 1992-1995.

However, in 1996, with the Daphnia population deve-



lopment, phytoplankton (algal) biomass plummeted, and cyanobacteria were almost absent. The result was a phytoplankton population assemblage (mix of different species) similar to that present in the lake 25 years earlier, before high external nitrogen and phosphorus inputs occurred.

Alternate states

In 1997 and 1998, despite continuing near absence of small fish, zooplankton remained low and the Daphnia population did not develop as it had in 1996. Dense cyanobacterial algal blooms thus returned.

This is consistent with stoichiometric models of grazer – algae interactions, which predict that highly eutrophied lakes can have two different stable states, one with high grazer populations and low algal development, the other with few grazers and algal blooms. The non-linear response of the zooplankton – phytoplankton system thus strongly limits the feasibility of predicting lake ecosystem reactions to nutrient inputs and food web alterations.

"Pelagic C:N:P stoichiometry in a eutrophied lake:responses to a whole-lake food-web manipulation". Ecosystems (2000)-3 pages 293-307.

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USA FLORIDA LAKES

Algal polyphosphates provide P-sink to sediment

The authors report studies of sediment cores from the widely-studied hypereutrophic Lake Apopka, near Orlando, Florida, USA. This is a shallow, subtropical lake, situated at 28°4' North and 81°4' West, with an average depth of 1.7 metres. The lake was macrophyte dominated with clear water before the 1920's, when eutrophication began with sewage and citrus-fruit processing discharges.

In the 1940's, the lake area was reduced from 210 to 125 km², as "muck farms" were created on drained lake and marsh land. The lake then became dominated by large growths of phytoplankton (algae) and turbid water. By the 1990's, pumping of nutrient-rich farm drainage water provided 85% of the phosphorus loading to the lake (0.42 gP/m²/year from this source). Because of the high P-loading, phytoplankton growth in the lake is nitrogen limited.

Organic sediment phosphorus

As is the case for other Florida lakes, the shallowness of the lake and frequent resuspension mean that the sediments are exposed to aerobic conditions before permanent deposition. Consequently, the sedimented organic material is mainly "refractory", that is not readily biodegradable. Primary production by phytoplankton is sufficient to account for sedimentation rates and TC:TN [total carbon : total nitrogen] ratios suggest that most of the sedimented material is indeed of phytoplankton origin. The sediment in Lake Apopka has a relatively high organic content (~65%), and the phosphorus present is not bound to cations (Fe, Al, Mn) so that P release is not redox potential dependent.

Six sediment cores were taken from the lake and the different forms of phosphorus present were analysed chemically (total P, water soluble P, 0.1M NaOH available P, 0.1M NTA pH7 available P, polyphosphates) and with bioassays (the latter using cultures





of Scenedesmus quadricauda). Polyphosphates were measured using heat extraction that has been shown to liberate cellular polyphosphates stored by algae (Fitzgerald and Nelson 1966 methodology). Core samples were aged using estimates based on temporal patterns of sedimentation rates and ²¹⁰Pb dating work carried out previously to develop core sediment chronologies in the lake (Schelske 1997).

Cellular polyphosphates

The bioassay available P surprisingly represented only a small proportion of the NaOH and total P. NTA-P and water available P were correlated with bioassay P; whereas NaOH-P and cellular polyphosphates were correlated with total P. Among the P fractions measured, **cellular polyphosphate levels in the sediments were the most sensitive indicator of the lake's phosphorus enrichment history.**

Whether samples were freeze-dried significantly affected the results of these analyses. For example, water soluble P was greater in freeze-dried samples from recent periods when sedimentation was dominated by phytoplankton, but not in older samples (macrophyte sedimentation). Cellular polyphosphates were not measurable chemically in the freezedried samples, and were higher in phytoplankton than in macrophyte sediments that were analysed wet. Similarly to polyphosphates, NaOH-P was higher in wet samples, and like water soluble P, bioassay-P was higher in freeze-dried samples.

The authors conclude that the freeze drying of samples causes cellular polyphosphates to be released, becoming available for uptake in bioassays. This corresponds to other work showing that phytoplankton cells can remain intact, and indeed viable, in sediments for decades, and that cellular polyphosphates were a significant fraction of phosphorus even in sediments over 100 years old (Newnans Lake, Florida).

Implications for understanding eutrophication

The comparisons of different sediment samples show that as phosphorus loading to the lake has increased in the past, so phosphorus has been accumulated by phytoplankton as internal polyphosphate "reserves", with this uptake probably becoming the dominant mechanism for removal of P from the water. Under experimental conditions, phytoplankton populations from Lake Apopka converted 83% of added soluble phosphate into cellular polyphosphates in less than 2 hours (Newman *et al.* 1994).

The authors conclude that the sinking and burial in sediment of intact phytoplankton cells is a significant factor of P sedimentation in Lake Apopka, thus storing phosphates in a non geochemically available form, and effectively removing P from the aquatic ecosystem. The mass of phosphorus sedimented annually in Lake Apopka equals the total phosphorus present in the water column and is at least 65% of the annual P loading to the Lake. This is probably a significant P-removal process in many eutrophic systems with excessive supplies of P for phytoplankton growth.

Conclusions

The authors draw three main conclusions from this work : 1) that cellular polyphosphate concentrations are the most sensitive indicator in sediments of historical P-enrichment of lake waters; 2) that the different forms of P present in sediments must be measured on fresh wet-kept samples as freeze-drying causes the disintegration of cell structures in the sediment and thus the release of non-geochemically available phosphorus (cellular polyphosphates); 3) that phytoplankton uptake of soluble phosphate from water (beyond cellular needs), storage as polyphosphates, and then sedimentation, can be an important process for the removal of P from eutrophic aquatic ecosystems towards a non-available sediment "sink".

"Changes in polyphosphate sedimentation: a response to excessive phosphorus enrichment in a hypereutrophic lake", Can. J. Fish Aquat Sci 58, pages 879-887, 2001. W. Kenney¹, C. Schelske², A. Chapman³.

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NORTH CAROLINA

Effects of nutrients on phytoplankton and bacteria in dark-watered rivers

Nutrients were added to water samples from two "blackwater" rivers, as different forms and combinations of nitrogen (N) and phosphorus (P), in order to asses the reaction of the ecological system to nutrient enrichment.

"Blackwater" river systems are typical of the coastal plains of the US Gulf Coast, from Virginia to Florida, and are characterised by **low topography, sand sediments, extensive flood plains and high concentrations of organic matter**. Phytoplankton is often low, as a result both of low nutrient levels (due to soil type and retention in flood plains) and light limitation (due to water coloration).

A major nutrient source to these coastal plain areas is industrial pig and poultry production, which is widespread from the Delaware Bay to North Carolina. Traditional agriculture, and industrial and municipal point sources also input nutrients to certain "blackwater" rivers.

The bioassay experiments used triplicated 3-litre samples of river water collected together from the Black River and from the Northeast Cape Fear River, both in south-eastern North Carolina. The rivers are respectively 40 and 50m wide and 4 and 9m deep at the sampling points.

Nutrient addition

The following **combinations of nutrients** were added to the samples in 1 mg/l concentrations:

- no added nutrients (control)
- inorganic phosphate only
- ammonium only
- inorganic phosphate and ammonium (both at 1 mg/l) urea only
- soluble organic phosphate (glycerophosphate) only

The experiments were run for 6 days in July, August, October and November 1996 and in January, March,

April, May and June 1997. Furthermore, in February and July 1997, experiments using higher nutrient additions (10 mg/l) were carried out. The samples were held in floating cubitainers at ambient river temperature, and subjected to light irradiation comparable to those at a depth of around 0.25m in the Northeast Cape Fear River (by appropriate screen shading).

Samples were analysed after 1, 3 and 6 days for chlorophyll-*a* and for ATP concentrations. **Chlorophyll-***a* **is considered to be a good indicator of phytoplankton (algal) development**, as it is the pigment present in all green algae and used for photosynthesis. ATP is a useful indicator of microbial biomass (development of all micro-organisms, including algae, zooplankton, and heterotrophic microbes), because it is present in all living matter and the ratio of ATP:organic carbon is relatively uniform across all such organisms. Where chlorophyll-*a* levels were high, samples of phytoplankton were also analysed for taxonomic data (identification of distribution between main species).

The river water samples showed **low turbidity** (low levels of light-inhibiting suspended matter), but light penetration was reduced by the water coloration. Dissolved oxygen levels were low in summer. Inorganic nutrient concentrations were also generally low, with total nitrogen around $1,000 - 1,200 \ \mu g/l$ (of which 76% organic in summer) and total phosphorus around $75 - 95 \ \mu g/l$ (of which 65% organic in summer).

Nitrogen inputs and algal blooms

The bioassay results showed that both inorganic or organic nitrogen inputs, alone, stimulated phytoplankton development in most cases, but phosphorus inputs alone generally did not. The authors conclude that both inorganic or organic nitrogen loadings to theses rivers could potentially generate algal blooms. The indications are that the phytoplankton physiologically had a higher requirement for N than for P.

The authors conclude that phytoplankton development in these rivers appears to be generally nitrogen, not phosphorus, limited.

Phosphate inputs alone, particularly organic phosphorus, did result in increased ATP concentrations in many



cases (especially in summer). In other cases, ATP concentrations increased in response to nitrogen addition only. The authors conclude that these ATP responses are probably the **result mainly of stimulated development of heterotrophic bacteria.** Such development could pose environmental problems by increasing oxygen demand, either by the activity of the bacteria, or by their decomposition on death, depending on water mixing and other factors.

"Effect of nitrogen and phosphorus loading on plankton in coastal plain blackwater rivers". Journal of Freshwater Ecology, vol. 6, n°3, September 2001.

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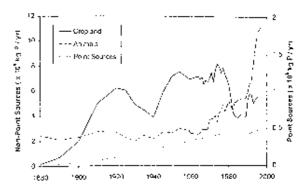
NORTH CAROLINA

Muted river response to nutrient input reductions

The Neuse River estuary in North Carolina, has shown significant and problematic symptoms of eutrophication over recent years (mid 1990's). This is despite significant reductions to river phosphorus inputs. The river and estuary P concentrations have fallen, in line with these reductions, but river and estuary nitrogen concentrations have not reflected changes in inputs – raising the question of what effect can be hoped for from planned reductions in nitrogen loads of 30%.

The Neuse river is 320km long with a $16,100 \text{ km}^2$ watershed, made up mainly of farmed land (35%) and forest (34%).

Cropland phosphorus application in fertilisers began to increase around 1900, and rose irregularly through to the 1970's (to over 8,000 tonnesP/year), when it fell significantly in the 1980's, before recovering slightly in the 1990's. Animal phosphorus sources were low steady until the 1970's, when they began to increase, tripling to 12,000 tonnesP/year by today. Point sources rose steadily from the late 19th century through to the late 1980's, when they fell by 20-25% as a consequence of a detergent phosphate ban and improvements to sewage P-removal.



Estimates of annual anthropogenic Phosphorus loadings within the watershed from cropland, animals and point sources. The vertical line corresponds to the first year for which loading estimates were calculated.

River phosphorus concentrations have responded to changes in inputs, both upstream and downstream. They dropped significantly following the construction of a 35 km² dam in 1983, then again following the detergent phosphate ban and improved sewage treatment in the late 1980's.

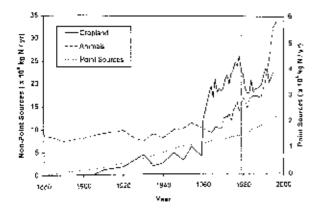
Nitrogen inputs

Cropland nitrate inputs increased rapidly and by a factor of around 4 in the 1960's, remaining high if irregular since then. Point source nitrogen inputs have increased steadily since around 1900 (with population increases). Animal nitrogen inputs, like animal phosphate inputs, have increased rapidly since 1960, and particularly since 1990, with an overall near quadrupling from 1960 to today.

Like phosphorus, river nitrogen concentrations fell upstream with the construction of the dam, but unlike phosphorus, **no consistent patterns in river nitrogen levels are visible further downstream**, although there does appear to have been an increase over the period



approximately 1985-1995, followed by a recent decrease at monitoring stations downstream from the major point sources.



Estimates of annual anthropogenic Nitrogen loadings within the watershed from cropland, animals and point sources. The vertical line corresponds to the first year for which loading estimates were calculated.

Muted response

The authors note that the absence of a clear increase in river nitrogen loads (amounts carried by the river water) is surprising, given the ongoing increases in watershed inputs, and in particular the recent large increase in animal manure inputs. For phosphorus also, loads carried by the river, do not appear to have responded to the recent increases in inputs within the watershed.

The authors estimate that in fact only around 10% of the inputs of nitrogen and phosphorus into the river in the watershed are in fact carried out by the river into the sea, probably because of storage in groundwater, riparian zones and losses during river and stream transport (denitrification, transfer to sediments).

They conclude that even if the proposed objective of a 30% nitrogen input reduction is achieved, several years may be necessary before any detectable change will result in river concentrations or in loads carried to the estuary (at least four years, even if the reduction were made as a single step). Also, it would appear that the watershed was already receiving excess nutrients in the

1970's and earlier, so that resolving the problem in a short time-scale may be difficult. Indeed, the release of sediment-stored nutrients could mean that **reductions in inputs may not lead to improvements in the river and estuary ecosystems, even after a "substantial" number of years.**

"Long-term changes in watershed nutrient inputs and riverine exports in the Neuse river, North Carolina". Wat. Res. vol. 35 n°6 pages1489-1499, 2001.

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LOWLAND ENGLAND

Seasonal phosphorus retention in a river system

Inputs of total phosphorus to the upper River Cherwell, Oxfordshire (in England's Midlands) were estimated from populations connected to sewage works and from export coefficients related to land-use coverages. These estimations were then compared with the loads of phosphorus being carried out of the catchment in the river water, according to monitoring data. The results suggested that the input estimates were reasonably accurate (within 15%) and that there was a significant seasonal retention phenomenon in the river, with phosphorus being stored in the system in spring and summer, then released downstream in autumn – winter.

The upper River Cherwell catchment studied covers just over 17,500 ha upstream of Banbury i Oxfordshire, GB, with mainly clay soils, so that the river is fed mainly by surface rather than underground water flows. **Water quality on this 34km section of river is classified as "good"** by the UK Environment





Agency, with a variety of fish present including roach, dace, chub, grayling and trout. The catchment includes a number of smaller tributaries, with five up to 17 km long but most less than 3 km long.

Much of the catchment is tilled (ploughed) farmland (48.9%), with a further 31% meadows and grassland. Only 1.6% is forested and 8.9% is urbanised. Annual total phosphorus losses for each land cover type were estimated using the export coefficient method (Johnes, 1996), in particular using values of 0.65 kgTP/ha/year for the tilled land and 0.3 kgTP/ha/y for the meados/grassland.

This method suggested a **total annual phosphorus run-off from land of 8,759 kgTP/y, of which 64% from tilled land**, 19% from meadows/grassland, and 15% from urbanised areas.

40% of river phosphorus from sewage

Annual total phosphorus discharges from the 12 significant sewage works discharging into the studied catchment (with population equivalents ranging from 150pe to 3,500pe) were estimated by calculating 0.73 kg/pe/year, in the absence of monitoring data. This gave a total estimated output of 6,900 kgTP/y from the sewage works, that is 40% of the total catchment phosphorus inputs to the river system.

The total load of phosphorus being carried downstream out of the catchment by the river was estimated from daily river flow data and total phosphorus concentrations measured every four days. This gave a total outflow load of 13,425 kgTP/y for the study year (March 1998 – February 1999), lower than but within 15% of the estimated total inputs to the river (15,700 kgTP/y).

However, the phosphorus load being carried downstream out of the catchment by the river showed strong seasonal variation. A number of authors have shown that high river flow events can carry significant proportions of catchment phosphorus outflow. However, in this case, despite spring storms in April and high monthly water flows at this period (55% of annual water flow in the Spring), the seasonal total phosphorus load carried by the river was much higher in winter (56% of TP load for only 37% of the year's water flow in winter, compared to 20% of TP load for spring). Autumn TP load was significant (19%) despite low water flows (6%), and in summer both the TP load (4%) and the water flow (3%) were very low.

The authors conclude by emphasising the significance of this seasonal variation in river phosphorus loads, resulting from an apparent retention in spring and summer. **Total phosphorus has little impact on river ecology during high flows (which occurred in autumn and winter), and during the period of the year when algae are not susceptible to develop (again, autumn and winter)**. On the other hand, in the spring and summer when phosphorus may contribute to algal development, it appears to be retained in the river system and be suppressed in the river load by seasonal variations.

"Seasonal export of phosphorus from a lowland catchment: upper River Cherwell in Oxfordshire, England". Science of the Total Environment 269, pages 117-130, 2001.

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Response of Lake Balaton to sewage nutrient removal

Lake Balaton is a 596 km² shallow (3.2 m deep), calcareous lake in Hungary, around 80 km long by 10-15 km wide, and separated into four basins by narrower stretches of water. Increases in nutrient loa-



ding in the 1970's led to eutrophic conditions in the upper basins of the lake. Outflow rates in the lake's exit canal from basin 4 can be up to 40 m3/s in late winter, but are generally zero from spring to autumn.

Significant actions were undertaken to reduce nutrient loading, targeting the Zala river which flows into the upper end of the lake (basin 1) and which carried over 90% of nutrient inputs, in particular **opening of two retention reservoirs on this river in 1985 and in 1993, and the introduction of phosphorus removal at the Zalaergerszeg municipal sewage works** (65,000 inhabitants) in 1991. Nutrient loads to the other lake basins were also considerably reduced in the 1980's, mainly by sewage diversion from the shoreline settlements of basins 3 and 4 and by installation of P-removal in sewage works in the catchment. Overall, these measures reduced the lake phosphorus load from 0.5 to 0.3 mg/m²/year.

The authors examine the changes in a number of monitored factors over this period, both in the lake and in this main tributary river, the Zala. These include total phosphorus, calcium, suspended solids, chlorophyll, algal blooms as well as loading ratios between particulate (organic) and dissolved phosphorus and lake phosphorus sedimentation rates.

Carbonate makes up some 50-60% of Lake Balaton's sediments (dry weight). Unlike in many calcareous lakes, the main process for phosphorus sedimentation in the lake, however, is not carbonate precipitation but sorption and mineralisation of detrital and organic phosphorus in the sediments. **The construction of the pre-reservoirs significantly changed the dissolved:particulate phosphorus ratios** in the inflowing river (from around 1.4 to 0.7 for the hypertrophic upper reservoir in 1985, then to around 2.5 with the opening of the reed-bed lower reservoir in 1993). This is thought to have considerably modified phosphorus sedimentation rates. The introduction of phosphorus removal in the sewage works, on the other hand, did not significantly change this ratio.

Rapid recovery of the upper lake basin

The upper lake (basins 1 and 2) responded rapidly and positively to the nutrient management actions undertaken, with both total aquatic algal biomass (measured by chlorophyll concentrations) coming down to pre-1970's levels by 1995-1997, and also nuisance algal blooms effectively being eliminated by this same date.

The authors note that the type of management measures taken probably had significant impacts on the rate of phosphorus sedimentation in the lake, because of induced changes in factors such as the dissolved:particulate phosphorus ratio, inflowing suspended solids and calcium. This seems to have resulted in rapid immobilisation of phosphorus in the sediments, leading to ecological recovery of the lake's upper basins, but is certainly "not a universal phenomenon" and would be hard to predict in other lake systems.

Furthermore, and surprisingly given the interconnectivity, at the same time as this described recovery of the two upper basins of the lake, the two lower basins (basins 3 and 4) actually showed definite eutrophication and an accentuation of blue-green algal blooms. A first analysis of monitoring data suggested that this might be the result of increased hydraulic residence times in the lower lake, resulting both from climatic factors (draught years with low precipitation) and from the cessation of pumping of karstic water into the lake (closure of a bauxite mining operation).

However, the hydraulic residence time of Lake Balaton is relatively long, so that the lake is not subject to flows high enough to "flush out" algal development. Although the increase in residence time was thus significant (from around 2 to 4-7 years), it was considered that this could not account for the increased algal development in the lower basins.

Blue-green algae

As phosphorus inputs were reduced, basins 3 and 4 of the lake showed increasing nuisance blooms of the blue-green cyanobacterium *Cyclindrospermopsis rasiborskii*. This is a subtropical species which appeared in the lake in the 1980's, and may have been able to develop because of the eutrophied state of the lake combined with unusually warm late summers.



The authors suggest that the blooms of this cyanobacterium, occurring despite falling external phosphorus loads, may result from its ability to mobilise internal (sediment) stored phosphorus sources. *C. rasiborskii* may be efficient in doing this because of its **high shade tolerance and high affinity for phosphorus and ammonium uptake**, allowing it to reach very high biomass concentrations, thus producing a powerful "drain" for mobile phosphorus from sediments. Calculations based on estimated phosphorus requirements of the observed algal biomass levels were coherent with this hypothesis.

The development of the blue-green algae can be considered surprising given the changes in P:N loading ratios resulting from the improvements in sewage treatment (ratio increased from 16 to 27 by weight). Indeed, field data suggest that during the algal blooms only around 10% of C. *rasiborskii's* nitrogen needs were being supplied by fixation of atmospheric nitrogen.

The authors conclude that specific morphological features of the lake, and not nutrient loadings, may

have led to the blue-green algal dominance. The completely different response of the lower and the upper basins of Lake Balaton to external nutrient loading reductions show the **difficulty in predicting lake recovery and lake response to eutrophication management policies.**

"Factors influencing lake recovery from eutrophication – the case of Basin 1 of Lake Balaton". Water Research vol.35 n°3 pages 729-735, 2001. See also:

http://phytoonline.ocean.org.il/Lakes/L_Balaton/ body_l_balaton.html

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"Cyanobacteria-mediated internal eutrophication after load reduction in shallow Lake Balaton". Water Research, in press. Above authors plus A. Clement.





NUMBER FORTY-FOUR

PHOSPHORUS RECYCLING

BIOSOLIDS MANAGEMENT

Phosphate recovery improves sludge management

Phosphate recovery for recycling from municipal wastewater treatment works can improve biosolids management by lowering P:N ratios (and thus facilitating agricultural reuse), reducing sludge quantities or incineration ash production, and enabling other disposal routes.

SWEDEN

PAGE 4

PAGE 2

Life cycle assessment of sludge disposal routes

Energy recovery appears as the most important environmental factor in choices between different sewage sludge processing routes.

JAPAN	PAGE 6

Phosphate recovery experience

Several pilot scale experiences of phosphate recovery from swage, by calcium phosphate or struvite crystallisation, produced reliable phosphate granules.

PIG MANURES

Struvite recovery for ammonia removal

Struvite precipitation was tested on effluent from an anaerobic digester treating pig manure and showed to be able to remove nearly 90% of ammonia, recovered as struvite.

ITALY

Successful on-site testing of sewage P-recovery pilot

Results from a 13 litre (approximately half full-scale) pilot phosphate precipitation reactor tested at Ancona sewage works, Italy, show that up to 80% P-recovery can be achieved using aeration only (no chemical addition).

NUTRIENTS AND ECOSYSTEMS

FRANCE

PAGE 12

P run-off from sewage sludge on fields

6m² plot simulation of rain events suggests that sewage sludge spread on fields reduced losses of total phosphorus but increased soluble phosphate.

USA

PAGE 13

PAGE 14

NOVEMBER 2001

National assessment of US estuary eutrophication

The US National Ocean Service has published the conclusions of a seven year study of 138 estuaries (90% of estuarine waters), showing that 65% of these waters are subject to high or moderate eutrophication, and that this situation is likely to become worse.

EUROPE

Assessment of nutrients in Europe's waters

Phosphorus emissions have been reduced in some parts of Europe, over the last 10-20 years. In contrast, the nitrate level in many European rivers has risen over the same period.

UK

Phosphorous solubilisation in soil following drying and rapid rewetting

The solubility of soil phosphorus, and thus the risk of runoff to surface waters, increases significantly as weathering dries and re-wets the soil.

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NUTRIENT MANAGEMENT

USA

PAGE 16

EPA publishes "ecoregional nutrient criteria"

The US "Clean Water Act" requires state and tribal areas to set water quality criteria. Recognising the regional variation in environmental effects of nutrient levels, the EPA has published 17 ecoregional nutrient criteria for guidance of local authorities.

THE NATURAL STEP

PAGE 17

A systems-orientated approach to the phosphorus cycle

A systems-oriented approach to managing phosphorus enrichment of surface waters concludes that phosphorus recycling, both in agricultural sewage sludge reuse and by P-recovery processes, must accompany improved phosphate use in fertiliser and other applications.

SEPTIC TANKS

PAGE 18

Natural soil iron can precipitate P from sewage

Available carbon compounds in sewage can cause iron compounds in soils to dissolve, by "Reductive Iron Dissolution", and these in turn can then precipitate phosphates.





PAGE 8

PAGE 10

PHOSPHORUS RECYLING

BIOSOLIDS MANAGEMENT

Phosphate recovery improves sludge management

The authors give an overview of the technico-economic feasibility of P-recovery from municipal wastewaters and of the impact an sewage sludge production and management. Conclusions are that P-recovery is feasible in biological nutrient removal plants but that the economics will vary considerably as a function of the local context and wastewater treatment plant operation. P-recovery will reduce sewage sludge production by a small amount, but may significantly facilitate agricultural spreading (by improving P:N ratios which can be a limiting factor), thus reducing transport distances to fields. Ash production will be considerably reduced where sludges are incinerated, and co-combustion in cement works facilitated (by lower sludge P levels).

This work is based on a literature survey to assess the feasibility of phosphorus recovery in European municipal wastewater treatment plants (WwTPs); interviews with 33 experts in the water industry, national water regulators, the phosphate industry, agricultural biosolids utilisation, fertiliser and other relevant sectors; and a water industry WwTP process model of WwTP biosolids production and management. It examines the hypothesis of phosphorus recovery as struvite (MgNH4PO4) or as calcium phosphates, via precipitation or crystallisation. The authors conclude that for P to be recovered by precipitation or crystallisation of calcium phosphates or struvite using technologies likely to be developed into economically reliable processes in the short-medium future, a liquor stream in the WwTP must exist or be generated by mixing or pre-treating (settling, anaerobic holding ...) of existing streams, which offers : relatively high soluble phosphate levels ([P soluble] $\geq 10 \text{ mg/l}$) and relatively low suspended solids (SS 150-200 mg/l).

This means that the WwTP must run with the activated sludge process, must be equipped with a biological phosphorus removal process, and must have an anaerobic zone in the sludge treatment line (sludge digestion, holding tank) where soluble P will be released. After this, the sludge must usually go through a separating unit (settling for instance) to lower suspended solids levels

Implications for WwTP operation and sludge diposal

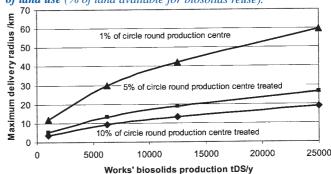
Possible positive impacts for WwTP operation include: limitation of P-rich flows returning to the head of the WwTP, thus facilitating effective biological P-removal; reduction of nuisance struvite deposits which can cause pipe blocking, clogging of belts in sludge presses.

The effect of P-recovery on sludge production was estimated using a water industry process model, published data on sludge compositions, and expert opinion concerning the interactions between organic matter removal and sludge phosphate metabolism. For Precovery in a biological P-removal WwTP, overall average reductions in biosolids production (dry solids) are estimated at 2 - 8%.

Biosolids use in agriculture

Nitrogen and phosphorus are often the limiting parameters for agricultural use of wastewater biosolids, and there are already areas in Europe where the soils have enough P for crop needs, so that P is a limiting factor. In this context, decreasing the P-concentration in biosolids could mean either improving agricultural spreading (reducing risk of P run-off to surface waters, better adapting application levels to crop needs), or reducing the area used for spreading and thus reducing the costs of transportation necessary to reach these application sites. This transport effect was modelled for the UK using soil P data, data on sewage sludge production and processing, estimates of P levels in sludge and their agricultural availability, and a model of average sludge transport distances to fields as a function of land use. The average availability of P in biosolids was taken to around 35% that of single superphosphate fertiliser (after Smith et al., 2000).

Model of haulage radius for sustainable use of biosolids phosphate for different sizes of works and different intensities of land use (% of land available for biosolids reuse).



Potential for P-recovery in WwTPs

ʒ/l ; % suspended vo	solids = 70% ;	F/M ratio = Food on
60 %	75%	90%
2,3%	3%	3,5%
3,4%	3,8%	5,2%
	60 % 2,3%	2,3% 3%

If 20% of all phosphates in municipal wastewater in England and Wales were recovered, the related transport cost saving for agricultural reuse is estimated to be in the range £217,000 to £1.4 million, that is £50 to £320 per tonne of P recovered. The most likely scenario in this range (200 facilities spreading on 5% of the total land within their distribution radii) would give an annual saving of £450,000. This is £101 per tonne P recovered, which is around half the market price of imported, mined phosphate rock (£207/tP), but the difference may be offset by the greater purity compared with phosphate rock and delivery from the recovery site to the point of use. The reductions in transport distances would also offer environmental advantages.

Implications for biosolids incineration and cocombustion in cement production

Sewage sludge incineration reduces dry solids by a factor 6. This means that the reductions in biosolids resulting from P-recovery (see above) will then lead to a **reduction** in incineration ash residues of between 12 and 48 %. If an approximate cost of landfill is 228 \notin /t ash (average year 2000 price in France) the saving could be about 70 \notin /t of initial ash production. Further work is necessary to confirm these results given by mass calculations.

Although not very widespread, co-combustion of sewage sludge in cement production is an interesting energy recovery route because it does not produce waste (the ashes are trapped and used in the making of cement). However, high levels of phosphorus in cement lowers the short-term resistance. An OFEFP technical document recommends a limit value of 0.5 % P2O5 in cement. Reducing the phosphorus content of biosolids by P-recovery can address this problem, which is also dependent on the proportion of biosolids in the charge to the cement kiln.

Other costs, savings, revenues and regulatory issues related to P-recovery

Other costs and revenues (operating savings, sale of recovered phosphates) are likely to be very dependent on the local context. The sale of the recovered phosphate product, by comparison with imported phosphate rock or wholesale fertiliser prices, is likely to cover only the chemical reagent costs of P-recovery but not operating and investment costs.

The authors conclude that driving forces for Precovery are thus very dependent on the particular national context. P-recovery is already registered as a national objective in Sweden, and this notion of recycling is expected to become a regulatory requirement. In other countries, P-recovery answers different needs:

- The quality of the recovered product is better than some imported mined phosphate rock, in particular as regards the heavy metal contents.
- Sustainable development in the phosphorus industry via the recycling of a recovered product this is

regarded as particularly attractive in the Dutch context.

- P-recovery can be a way to avoid internal problems at some wastewater treatment plants (where scaling is a problem) and to improve biological P-removal

Summary of costs and revenue/savings related to P-recovery operation.

Expenses	Financial benefits	
- Investment and depreciation costs	- Sale of the recovered phosphates	
- Consumption of reagents and of energy	- Savings due to the suppression of problems of struvite deposits	
- Additional labour costs / time	- Possible reduction of transportation distances for agricultural reuse.	
- Specific training of the operating staff	- Savings on the landfill of incineration ashes.	

There are two scenarios that are likely to lead to a significant development in P-recovery:

- **Local feasibility:** locally, P-recovery can be a significant solution to case-specific WwTP operation problems or to sustainable biosolids utilisation or disposal. In this case, the costs of P-recovery will be covered by the water company through resulting specific local WwTP operating savings.
- **National or European political decision:** the arguments of sustainable development (phosphorus recycling) or of better quality of the recovered product may lead to P-recovery being stipulated as a national or European political objective. In this case, the consumers and/or taxpayers will share any net costs.

In any case, the development of phosphorus recovery strongly depends on regulations not being an obstacle to recycling. The current classification of the recovered product as a "waste" is a major obstacle to the development of recovery and reuse in areas such as The Netherlands – Belgium – Northern Germany – South-East UK because it renders cross-boundary transport impractical.

"Technico-economic feasibility of P-recovery from municipal wastewaters", Environ. Technol., 22 (11) 2001 in press – this summary is reproduced with authorisation of "Environmental Technology" and is copyright of this Journal. No reproduction or use without prior authorisation from the Journal at www.Environ.Technol.co.uk.

Also, papers by the authors at the 2nd International Conference on Phosphate Recovery for Recycling, Noorwijkerhout, March 2001 - CD available on request from : cja@cefic.be

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SWEDEN

Life cycle assessment of sludge disposal routes

A Chalmers University of Technology (Gothenburg, Sweden) masters thesis compares the environmental life cycle assessment (LCA) for four different processing and disposal routes for municipal sewage sludge: spreading sludge on agricultural land; co-incineration of sludge and household waste; incineration of sludge combined with phosphorus recovery by the Bio-Con process; fractionating sludge with the Cambi-KREPRO-process.

Around one million tonnes of sewage sludge is generated annually in Sweden's sewage works. Until recently, most of the sludge was spread on agricultural land or deposited to landfill. Agricultural use of sludge means that the phosphorus, plant-available nitrogen, other nutrients and organic material contained in sludge are re-used as soil improvers and recycled to crop production. Nevertheless, agricultural spreading of sludge on land is increasingly regarded as an insecure handling route, because sludge also contains heavy metals, viruses, bacteria and persistent organic pollutants which can be transmitted to human beings and animals by the food. As a consequence of reports of sewage containing such undesirable substances, the Swedish farmers' organisations have recently recommended farmers to stop using sewage sludges for agricultural purposes.

Currently almost 50% of Swedish municipal sewage sludge is deposited to landfill. In 2000 a tax was introduced on depositing sewage sludge at landfills making this disposal route increasingly expensive. Furthermore, in accordance with EU Directive 99/31, from 2005 it will not be permitted to deposit organic waste to landfill.

The aim of this study was therefore to compare the environmental impacts (using LCA) of four different alternatives to landfilling of sludge. The handling of digested and de-watered sludge from the Rya municipal sewage treatment work in Gothenburg is considered.

Pilot processes

Apart from agricultural spreading, the other three process routes examined are currently at the pilot phase in Sweden. **Co-incineration of sludge and household waste** has only recently been tested in Sweden. The **Bio-Con** and **Cambi-KREPRO** sludge treatment processes, are still in the development phase. However, a full-scale Bio-Con plant is planned in the city of Falun and a Cambi-KREPRO in the city of Malmö.

For co-incineration of sludge and household waste, a ratio of 5-10% sludge/household waste is generally used. Recovery of elements such as phosphorus from the generated ash is theoretically possible, but unrealistic, given the dilution with household wastes, and the study assumes that the ash and slag will be landfilled.

The Bio-Con process (developed by Bio-Con A/S, Denmark), is a sludge incineration system which integrates recovery of phosphorus and other chemicals. The energy recovered can be used for district heating. The installation has three sections; drying, combustion and a 4section recovery process. In the drying process the dewatered sludge is dried to some 90% dry matter. Some of the energy generated in the combustion phase is used in the drying process. The ash and slag that remains after combustion is treated chemically by dissolving in sulphuric acid. In this process up to 90% of phosphorus and precipitation chemicals are recovered. The acid solution enters a set of ion exchangers. The first section is a cation exchanger where the iron ions are recovered (regeneration using sulphuric acid gives iron sulphate, a chemical used for sewage P-removal and water purification). The next section is an anion exchanger in which sulphate is recovered in the form of potassium sulphate. In the third section phosphate is recovered (in the form of phosphoric acid, after regeneration with hydrochloric acid, suitable for use in the phosphate or fertiliser industries). In the fourth section, which is a cation exchanger the heavy metals are recovered.

The Cambi-KREPRO sludge fractionation process is a modification of the KREPRO process, developed by Kemira Kemi Kemwater, in co-operation with the municipality of Helsingborg and Alfa Laval Separation. The technique is by high-temperature hydrolysis and precipitation, separating the sludge into four products: one stable organic fraction (used as a bio-fuel); one iron phosphate fraction, one heavy metal fraction and a carbon source that can be re-circulated to the waste water treatment plant where it can be utilised to "feed" biological nutrient removal processes (reducing the need for an external carbon source, usually ethanol). The iron phosphate fraction generally contains more than 75% of the phosphate contained in the sludge and can be spread on fields (work is underway to assess its value as a fertiliser). The heavy metal fraction is dealt with by a separate company for treatment, recovery, or landfill as appropriate.

Different environmental values

The treatment of the sludge on-site at the Rya sewage works is not included in the analysis, since it is assumed to be similar for the four alternatives. For the agricultural spreading route, however, hygienisation at the sewage works is included since this is expected to be required in a near future for all agricultural reuse. The environmental impact from producing electricity and fuels, which are used in the four alternatives, is included in the study.

Sludge has an energy value of 12-13 MJ/kg dry matter, but on the other hand has very high water content. In those alternatives where heat can be produced, it is assumed this energy will be used for district heating and will replace heat from other energy sources in Gothenburg. It is assumed that the sludge will be incinerated evenly during the year, irrespectively of the variations in need for district heating.

Four characterisation categories are used in the study's environmental impact assessment: acidification, eutrophication, global warming and resource depletion. The author concludes that LCA methodology is shown to be suitable for studying the environmental impacts of sewage handling and management. Energy consumption, transport, incineration and consumption of chemicals can all be adequately assessed. It is, however, complicated to compare spreading of sludge on agricultural land to the other alternatives as the "products" and the emissions from these are so dissimilar. For land spreading, the phosphorus, nitrogen and organic matter are recycled; the three other alternatives predominantly provide savings of fossil fuel, but the Bio-Con system also allows recovery of the phosphorus in a recyclable form.

P-recycling

Concerning phosphorus, it is open to question whether the priority should be energy recovery (reducing fossil fuel consumption) or phosphorus recycling (reducing consumption of phosphate rock reserves). On this question, the author points out that phosphorus is essential nutrient to living organisms and cannot be replaced by any other element.

Indeed, the Swedish government has mandated the Swedish Environmental Protection Agency (2001) to develop an action programme with the aim of achieving a practical and achievable scale of recycling/recovery of phosphorus contained in sewage sludge, whilst at the same time ensuring protection of health and environment. A recovery rate of 75% of phosphorus by 2010 has been discussed in Sweden but is not indicated in the Government's mandate.

The study's main conclusions are as follows :

- The energy that is recovered from the incineration is of great importance, which makes co-incineration with household waste to be the preferable alternative, followed by Bio-Con and Cambi-KREPRO.
- Spreading sludge on agricultural land is, in most aspects, the one of these four alternatives which is the least preferable from an environmental point of view.
- The issues of depletion of phosphorus resources and toxicity of metals are somewhat hidden in the characterisation- and weighting methods used in this study. A satisfactory way of including these matters in the assessment is missing.
- Normalising the results against the total environmental impact in Sweden gives the result that phosphorus and nitrogen recycling to agriculture and emissions of metals to land are important issues.
- The recycling of precipitation chemicals and carbon sources is of minor importance compared to the total environmental impact.
- The Bio-Con results would be improved if one

made the assumption that Bio-Con's flue gas cleaning system will be of the same high standard as those in household waste incineration plants.

"Life Cycle Assessment of four sludge disposal routes", Master Thesis at Chalmers University of Technology, Gothenburg, Sweden, 2001. Available at http://www.esa.chalmers.se/Publications/PDF-files/Thesis/ ESA2001_4.pdf (In Swedish with English summary).

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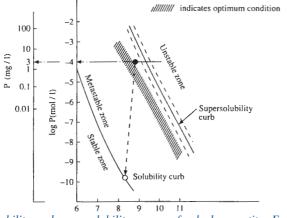
JAPAN

Phosphate recovery experience

A 1996 paper [1] summarises work into the chemistry of phosphate recovery from sewage, industrial waste streams and landfill leachate, and presents results from three pilot plant experiences in Japanese sewage works.

This paper starts by summarising beaker experiments using pure phosphate solutions, carried out to determine the saturation curves of calcium phosphates. Results are shown in figure 1 and the author suggests that in the unstable zone many fines of calcium phosphate will be produced by spontaneous crystallisation, making recovery difficult, whereas in the metastable zone crystallisation will only occur in the presence of seeds. Experiments comparing different seed materials were carried out and showed that phosphorus rock was a better seed material than bone char, activated carbon, marble or calcium carbonate.

Calcium phosphate precipitation



Solubility and supersolubility curvess for hydoxyapatite. From Hirasawa [1] with permission

An earlier paper ([2], 1981) presents a **100** m³/day pilot plant constructed and operated for 18 months in 1978-**1979** at Morigasaki sewage works (Tokyo Municipal Council). This pilot used a fluidised bed reactor to precipitate calcium phosphate onto calcium phosphate seeds. This work showed that the process was feasible and operated reliably after a stabilisation period of several months, but that decarbonation (CO₂ removal) of the influent stream (filtered sewage works effluent) was necessary for phosphate to precipitate effectively. With a filtration stage between the decarbonation and the fluidised bed reactor, the process reduced total phosphate concentrations from around 1.5 to around 0.3 mgP/l (around 0.5 mgP/l without this filtration step).

Another paper ([3], 1983) compares operation of a 100 m³/day pilot fixed bed calcium phosphate precipitation process in a sewage works with a pilot plant fed with biologically treated night soil liquor and consisting of a 10.8 m³/day fluidised bed reactor along with a 3.6 m³/day fixed bed reactor. These plants both included prior decarbonation by acid addition. The sewage plant fixed

bed reactor was able to recover 77% of influent phosphorus, taking total phosphorus concentrations down from 1.3-2 mgP/l to 0.2-0.37 mgP/l. This plant included, however, a sand filter between the decarbonation tank and the calcium hydroxide addition tank, upstream of the fixed bed reactor, and it seems probably that there would be a loss of phosphates by precipitation within this filter. The plant treating night soil liquor reduced total phosphorus concentrations from 8-19 mgP/l to 3-6 mgP/l after the fluidised bed reactor, and then to 0.2-0.5 mgP/l after then flowing through a sand filter and the fixed bed reactor.

A 12,000 m³/day experimental plant was then constructed at Morigasaki Sewage Works, in 1987. This used a continuous-flow precipitation reactor in which the seed material was fixed in the bed, with phosphate recovery being achieved by periodic backwashing to detatch the grown calcium phosphates. Ion sensitive electrodes allowed stable automatic control of calcium addition, decarbonation (by nitrification) and use of a sand filter.

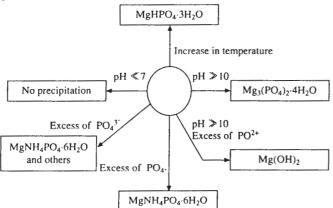
A plant was also constructed to recover phosphates from night soil secondary effluent (with phosphate concentrations of 10 - 30 mgP/l). This involved a 20 m³/day fluidised bed precipitation reactor with recirculation enabling fluid velocity to be adjusted. This plant demonstrated the need to inject the influent water and chemical reagents into the very bottom of the fluidised bed reactor, so that any "fines" precipitated should then agglomerate onto larger particles in the reactor.

A 2 m³/day reactor was also tested for 40 days with a 15 m³/day pilot biological P-removal plant at a sewage works, treating a sidestream from the anaerobic zone of the bio-P process. This used a 2.5m high fluidised bed reactor and phosphate rock seeds (size around 0.35mm). Calcium chloride and sodium hydroxide were dosed at the base of the reactor to maintain calcium levels around 80 mg/l and the pH at 9.5. The use of this phosphate recovery reactor proved to enable the biological phosphate removal plant to respect a 1 mgP/l effluent limit which was exceeded when the reactor was stopped. The reactor removed 40-70% of influent phosphate to be grown.

Struvite recovery

Following scaling problems in sludge digestion circuits in Tokyo, investigation was carried out into struvite (magnesium ammonium phosphate) crystallisation as a means of recovering phosphate in a form useable as a fertiliser. **Experiments using a stirred batch reactor with pH adjustment** suggested that an excess of ammonium ions, a pH in the range 9-10 and a magnesium-phosphate molar ratio >1 were optimal conditions for phosphate precipitation. The author presents a summary of how reactor conditions lead to the precipitation or not of different phosphate forms.





X-ray diffraction showed that a 1-1 magnesium-phosphate molar ratio produced typical struvite crystals, whereas with a molar ratio of 2 crystals tended to form agglomerates and at 4 they became needle like and fines appeared.

The author also presents similar work into the removal of iron and calcium carbonates from different industrial waste streams.

[1] : "Study on the recovery of ions in wastewater by crystallization". Memoirs of the School of Science and Engineering, Waseda University, n° 60, 1996 (in English)

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[2] : "Study on phosphorus removal from sewage by contact phosphorus removal process". Gesuido Kyokaishi, vol. 18, n° 203, 1981/4. In Japanese.

K. Okada, Y. Hoshino, Tokyo Municipal Government Sewage Bureau and K. Shimada, M. Osanai, I. Hirasawa, Ebara Infilco Company, Japan.

[3] : "Studies on phosphorus removal from sewage by contact phosphorus removal method". Suishitsu Odaku Kenkyu vol. 6, n° 4, 1983. In Japanese.

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PIG MANURES

Struvite recovery for ammonia removal

Struvite precipitation, achieved by the addition of magnesium and phosphate ions, was tested at the laboratory scale as a process for removing ammonia from effluent from an 84 litre anaerobic sequencing batch reactor (ASBR) treating pig slurry. Results were compared with precipitation predictions calculated using the US EPA's MINTEQA2 v3.11 geochemical equilibrium speciation model.

The authors explain that anaerobic reactors are often preferred for treating relatively concentrated waste streams, such as sewage sludges or animal manures, because they enable conversion of significant proportions of BOD and odorous organics into energy in the form of methane. Struvite precipitation is well documented problem in animal manure treatment installations, including pig and poultry wastes, as well as in various food industry waste streams (seafood canning, wine distillery effluents).

98% ammonia removal in beaker tests

Initial beaker studies were carried out using chemical solutions comparable to concentrations in the effluent from the ASBR reactor (ammonia > 3,000 mg/l). This enabled predictions from the MINTEQA2 model to be confirmed, and mixing time, flocculation and settling characteristics to be optimised.

250 ml beakers were used, with mixing at 150 rpm, followed by settling, and then a centrifuge at 5,000 rpm to separate precipitates. A mixing time of 5 minutes was found to be sufficient (no detectable improvement of ammonia removal with longer mixing times), whereas a small increase (approx. 6%) was observed when settling time was extended from 15 to 60 minutes. **Ammonia removal was consistently very high** (98%+) for pH's over the range 8 – 10, but pH's below around 9.5 should be maintained to limit losses of ammonia to air (and consequent odour problems).

Optimal ammonia removal efficiencies were obtained when both magnesium and phosphorus were at least 1.25x stoichiometric concentrations.

Struvite precipitation for phosphorus removal

In another series of beaker experiments waste sludge from the Ames Water Pollution Control Plant, a trickling filter/solids contact process, was used (initial ammonia mg/l and soluble phosphate concentrations 700 and 39 mg/l respectively), and no additional phosphate added (only magnesium, as MgO), in order to assess the feasibility of reducing soluble phosphorus concentration by struvite precipitation. In this case **ammonia removal varied from 50 – 59% and soluble phosphate removal from 9 – 39% for Mg:NH4 molar ratios (magnesium addition) of 1.08 - 3.4.**

pH9 optimal pH for struvite recovery

The lab-scale ammonia removal (by struvite precipitation) experiments used a 4 litre decanter, filled daily from the ASBR decant cycle. Phosphate and magnesium ions were added to this reactor in order to achieve stoichiometry with ammonia levels in the treated waste. Phosphate and magnesium concentrations in the wastewater itself were both insignificant compared to levels needing to be added to reach stoichiometry with ammonia.

At first, magnesium hydroxide and phosphate fertiliser were used, but these caused clogging of inlet pumps, so that they were then replaced by magnesium oxide and potassium phosphate, which were more expensive but fully soluble. The phosphate fertiliser was also causing the reactor pH to drop, and this problem was also avoided by the use of potassium phosphate.

After chemical addition, the reactor was mixed at 150 rpm for 5 minutes, then allowed to settle for 20 minutes. The precipitated solids were then pumped out of the bottom, and the supernatant tested for residual ammonia concentration and pH.

The MINTEQA2 model was used to calculate an optimal pH for struvite precipitation, giving approximately pH9 when phosphate and magnesium were in excess compared to ammonia. This model does not include struvite in its thermodynamic database, so that these calculations had to done manually.

At pH 9 – 9.5, the bench experiments showed that over 88% of ammonia could be removed from the wastewater.

The pilot reactor was operated for one month, with the operating problems (plugging of chemical inputs ...) being sorted out during the first couple of weeks. Inflow ammonia concentration was around 1700 mg/l and magnesium and phosphate were added respectively to around 1.2x and 1.5x molar ratios. By the end of this period, ammonia removal of over 99% was being achieved, taking ammonia concentrations down to below 10 mg/l.

Once the struvite precipitation reactor was achieving reliable operation, its supernatant was returned with the raw feed waste to the ASBR inflow (replacing dilution usually carried out using tap water) at approximately one part raw feed to one part supernatant. This showed to have **no negative influence on the ASBR operation or performance.**

The authors conclude that struvite precipitation could be a good way to recover nutrients from anaerobic treatment of animal manures, thus providing a source of revenue to offset treatment costs.

"Struvite precipitation potential for nutrient recovery from anaerobically treated wastes", Water Science and Technology

vol. 43 n°11 pages 259-266, 2001. Available at : http://www.iwaponline.com/wst/04311/wst043110259.htm and "Recovery of nitrogen and phosphorus from anaerobically treated wastes using struvite precipitation", Proceedings of the ASCE National Conference on Environmental Engineering, Chicago, 7-10 June 1998, pages 161-166.

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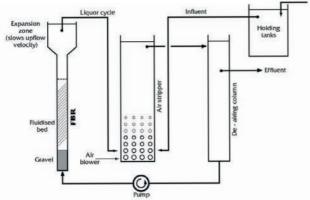
ITALY

Successful on-site testing of sewage P-recovery pilot

Previous lab-scale work, see SCOPE Newsletter n°s 35 and 33, were carried out using liquors from the dewatering of anaerobic digesters sludges at the Ancona sewage works, Italy (100,000 pe, A2O biological nutrient removal process). This work used aeration only (no chemical addition) to increase the pH of the treated liquors, followed by a simple fluidised bed reactor to precipitate the phosphates onto sand seed material.

The experimental work presented used an installation similar to that used in the previous lab work (NB. and indeed to the full-scale pilot now operational at Treviso sewage works, Italy), with a reactor consisting of three column tanks : an aeration "stripper" column (which causes pH to be increased by CO_2 stripping, a de-airing column (where excess air then comes out) and a simple "fluidised bed reactor" (FBR). In this case, the FBR was a 0.09m diameter and 2m high (13 litre capacity) Perspex column. NB. For information, the full-scale pilot at Treviso has a 0.6m diameter, 3m high (approx 1 m³) capacity FBR.





The FBR used water through-flow up the reactor to maintain sand particles in suspension, on which the phosphates precipitate. Partial recycling of the liquid back through the aeration and de-airing columns allows the up flow rate to be adjusted to ensure that the sand is maintained in suspension, but not carried out over the top of the FBR column (see diagram). The set-up of the pilot plant is characterised by four different hydraulic retention times. Among these, the authors distinguish the hydraulic retention time of the expanded FBR bed : this is a function of the liquor recycle ratio and of the contact time of the liquor with the seed material in the bed (which is mainly a function of bed porosity and of liquor flow rate). A layer of large gravel particles (approx 0.03m diameter) in the base of the FBR column ensure that the inflow is well mixed and prevent the sand particles falling back into the inflow pipe during pump stoppages. 9.5 kg of 0.21-0.35 mm diameter sand was initially loaded into the FBR reactor.

Digested sludge centrifugeate

The liquor treated by the pilot P-recovery reactor system was untreated centrifuge water from the dewatering of anaerobic digester sludge, stored in a holding tank. Soluble phosphate concentrations were 40 - 90 mgP/l, around half the concentrations which were in the same liquors during the earlier lab experiments a consequence of a modification having been made in the plant management in the intervening time. Significant changes in soluble phosphate concentrations were noted, depending on changes in the digested sludge characteristics and in the centrifuge operation, but also related to the time the liquor remained in the holding tank upstream of the reactor system (during holding, contact with air caused some of the soluble phosphate to change to insoluble forms, probably by spontaneous precipitation of calcium phosphates and struvite, as reported previously).

Calcium, magnesium and ammonium concentrations each exceeded the stoichiometric ratio necessary for precipitation of all the phosphate present as calcium phosphate or as struvite. **Fifteen experimental runs of 16-44 hours were carried out, enabling 16 reactor operating parameters to be tested.** The aeration column enabled the pH to be increased from around 7.6 in the influent liquor to up to 8.4 - 8.9.

pH and reaction efficiency

Reaction efficiency (% precipitation of soluble phosphates) was strongly related to operating pH, as had previously been noted in the laboratory experiments. A pH above 8.5 gave over 70% efficiency, and the highest pH achieved (pH 8.8) gave 80% efficiency.

pH variation explained 85% of variation in efficiency, which was also related to the "contact time" (see above). These two factors used together in a model formula gave an explanation of variations in phosphates precipitation efficiency, showing that 70% efficiency can be achieved at the readily attainable pH 8.5 with a contact time of half an hour.

Interference with calcite precipitation

Analysis of the sand from the FBR reactor at the end of the experimental work showed that grain size had increased significantly (near doubling of mass after a total of 400 hours operation), and that the phosphate precipitated on the grains effectively accounted for all the phosphate calculated as having been precipitated (difference between inflow and outflow).

However, the phosphorus content of the grains were disappointingly low in the deposited layer (EDX analysis results on grain surface, thus not taking into account initial sand), with on average 15% struvite, 2% calcium phosphate and 83% calcium carbonate (calcite) as molar distribution. This was confirmed by heating the grains, and showing the typical weight loss at 800°C associated with carbonates.

These significant levels of calcite precipitation, leading to

a recovered product with low phosphorus content, were not observed in the previous laboratory studies. The authors suggest that this is probably because of the higher soluble phosphate concentrations in the liquors used in this previous work.

The authors conclude that this work shows the accuracy of the mathematical model of phosphate precipitation conditions (in particular the relations with pH and contact time) and that the possibility of achieving high phosphate precipitation efficiencies is confirmed.

Further work is clearly necessary, however, to try to achieve higher P contents in the precipitated product by avoiding the precipitation of calcium carbonate. This is achieved by, for example, certain Japanese struvite precipitation plants by adding significant concentrations of magnesium, which lead phosphates to be precipitated as struvite (which does not seem to be inhibited by calcite formation, rather than calcium phosphates). The challenge lies in achieving phosphate precipitation without chemical addition (as in this paper), whilst still avoiding significant calcite precipitation (which reduces the P content of the recovered product).

"Phosphorus removal from a real anaerobic supernatant by struvite crystallization". Wat. Res. vol. 35 n°9 pages 2167-2178, 2001.

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NB. A full-scale pilot installation has since been commissioned at Treviso sewage works, Italy, and is currently operational, ensuring phosphate removal from sewage thickening liquors (thus facilitating biological P-removal operation and reducing sludge production), whilst at the same time permitting further testing of reactor operating parameters.

NUTRIENTS AND ECOSYSTEMS

FRANCE

P run-off from sewage sludge on fields

Three rain events were simulated on a 6m² plot of bare field in Brittany, France, one week after application of sewage sludge (from a works operating biological Premoval), in order to study effects on soil erosion, water and sediment run-off and phosphorus run-off. Liquid sludge (23 g dry solid/litre, 2.65% P/dry matter) was applied to half the plot, at 12 litres/m2 (giving 2.8 tonnes dry matter/ha and 73 kg P/ha), consistent with local agricultural practice and with plants needs for nitrogen. Run off was distinct and collected separately for the two (adjacent) half plots (each 4m long parallel to run off and 0.75 m wide).

The field had been sown with maze for silage in May, harvested in November. The experiments were carried out in March of the following year, when the soil was still bare, with remains of the maze stalks. The soil was loamy, on a 4.5% slope, with a total P content (before sludge application) of 0.91 g P/kg dry solid. The sludge application was followed by a 20cm manual tillage to restore soil surface roughness.

Simulated storm events

Three rain events were simulated over the 6m² plot, with 40 mm of water over 30 minutes each time. The first such event was one week after application of the sewage sludge to half the plot, with the second and third events following at 5h30 and 17h30 intervals.

The sludge spreading significantly reduced run off and erosion from the soil. The total amount of water collected as run off during the three events was 134 m³/ha for the treated plot, compared to 290 m³/ha for the untreated one. Similarly, the quantity of sediment (suspended particles) carried off in the run off was 500 kg/ha compared to 1200 kg/ha. The average sediment/litre of run off is similar, and the lower quantities of soil particles being carried off is clearly mainly a result of the lower water run off volumes.

The authors suggest that these differences in run-off are related to changes in splash erosion and physical run off patterns (puddle connection and rill = rivulet formation). They observed that the sludge tends to form a film on the soil surface, thus increasing resistance to splash erosion and so slowing the physical changes in the soil surface which allow run off rather than water retention and infiltration.

Total and soluble phosphorus run off

The sludge spreading resulted in a significant increase in the concentration of soluble phosphate in the run off water (from 0.15 to 0.57 mg P/l) but did not lead to a change in concentrations of particulate phosphate, or in the phosphate concentration in the sediments being carried off. Consequently:

(i) total phosphorus run-off decreased on the treated plot, roughly in proportion to the decrease in the volumes of water running off, from 2.7 to 1.2 kgP/ha;

(ii) on the other hand, the quantities of soluble phosphorus being lost were greater for the sludge treated plot, despite the much lower water run off volumes (see table).

Soluble P in run off (kg solubleP/ha)

Rain event	First	Second	Third	Total
Untreated plot	11.8	15.6	17.1	44.5
Sludge spread plot	13.5	34.9	29.6	75.4

Higher soluble-P/total-P ratios in samples analysed after transport to the laboratory than those analysed in the field showed that particulate matter was releasing soluble phosphorus, by a desorption or dissolution mechanism.

Soil phosphorus concentrations and organic matter levels showed significant variability aver the plot areas after the three rain events, probably as a result of erosion patterns and run off having moved the soil. This variability was greater in the sludge treated plot.

Implications for surface waters

The authors emphasise that it is soluble phosphorus which is bio-available, and thus susceptible to contribute to eutrophication if run off carries it to surface waters. These results indicate that the spreading of sewage sludge may increase this run off of bio-available phosphorus during storm events – and it is generally recognised that often 70-80% of soil phosphorus loss is related to storm events. Furthermore, the authors indicate that the particulate phosphorus carried off the sludge treated plot tended to be more labile (liable to become soluble) than that from the untreated plot.

"Phosphorus losses from sewage sludge disposed on a field: evident from storm event simulations". Water Science and Technology, vol. 42, n°9, pages 179-186, 2000.

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USA

National assessment of US estuary eutrophication

The US "National Estuarine Eutrophication Assessment", published in September 1999, draws on a national workshop held in 1998, on the results of a national estuary survey carried out from 1992-1997 and on other available data, input from 300 experts, and modelling. It covers 138 estuaries, representing over 90% of the USA's estuarine surface area, plus the Mississipi river plume.

The report concludes that "high" expressions of eutrophication are present in 44 estuaries (40% of total estuarine water area) and "moderate" expressions in an additional 40 estuaries, making **a total of 65% of total estuarine water area affected.** 67% of estuarine water area is affected by one or more of the following symptoms: depleted dissolved oxygen levels, loss of submerged vegetation, nuisance algal blooms. All coasts are affected, but particularly the Gulf of Mexico and the Middle Atlantic coasts.

This results in **impairment of human uses of 69 estuaries,** in particular loss of or deterioration of commercial and/or leisure fishing and of shellfish production.

Of the 44 highly eutrophication affected estuaries, most (36) were considered to be strongly influenced by human activities. All were considered by the experts to be naturally very or moderately susceptible to eutrophication (nutrient inputs likely to result in biological changes), whereas only 6 in fact had high levels of nutrient inputs. Conversely, most of the 38 non-eutrophication affected estuaries showed low susceptibility (28) but also had low nutrient inputs (31).

Consequently, management policies must vary considerably as a function of the different combinations of potential susceptibility to nutrient inputs and actual levels of these. Priority of management efforts should be given to the 10 estuaries (3% of water area) with high susceptibility but presently low nutrient inputs (in order to avoid potentially rapid deterioration), and to the 23 estuaries with high susceptibility and high nutrient inputs (10% of water area) where sustained and considerable nutrient reductions will be necessary to achieve water quality improvements.

The report concluded that eutrophication symptoms could be expected to worsen over the next two decades in 86 estuaries (including 43 which are currently unaffected), unless significant preventative nutrient management is undertaken. It also noted that data was considered inadequate (low confidence levels) for 48 estuaries, so that accentuated monitoring of both nutrient sources and eutrophication symptoms is necessary in many places, as well as further research into the relationships between nutrient input and effects such as algal development, and into the nutrient assimilation capacities of different estuary systems.

"National Estuarine Eutrophication Assessment – Effects of Nutrient Enrichment in the Nation's Estuaries". US Dept. of Commerce – National Oceanic and Atmospheric Administration – National Ocean Service, September 1999.

Copies available from : Pam Rubin, NOS Special Projects Office, National Ocean Service, 1305 East-West Highmay, Silver Spring, MD 20910-3281, USA pam.rubin@noaa.gov and http://spo.nos.noaa.gov

EUROPE

Assessment of nutrients in Europe's waters

The European Environment Agency has published, in its "Environmental Assessment Series", an overview of nutrient sources to European waters, environmental impacts and curative measures.

The European Environment Agency's report is based on data collected from national contact points in 30 European countries, as well as existing national and international reports and data bases. The report follows on from the first Dobris assessment report which identified anthropogenic nutrients in European ecosystems as a major environmental issue (1995).

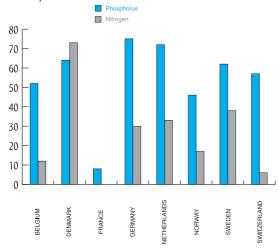
The report emphasises that nutrient loadings to surface water have increased considerably with man's activity, in particular from agricultural sources (fertilisers, manures), from domestic and industrial sources, and as a result in changes of land use and physical river conditions. In many areas of Europe, farming practices have significantly increased rates of soil erosion, thus causing nutrients to be carried into surface waters, while much of the agricultural land is drained and large areas of marshland, wetlands, ponds and lakes have disappeared, reducing the capacity of freshwater systems to retain nutrients.

Most of the phosphorus loading to inland surface waters comes from point discharges (sewage and industry), whereas most nitrogen loading comes from agricultural activities, in particular fertiliser and manure spreading. **Phosphorus emissions have been reduced in some parts of Europe, over the last 10-20 years. In contrast, the nitrate level in many European rivers has risen over the same period.**

Phosphorus sources

Fig. 1: Expected reduction of N and P emissions from municipal waste water treatment plants between 1985-1995.

From EAA publication indicated at end of article, page 123. Source of data : Table 8 OSPAR 1995 Nutrients in the Convention Area. With permission.

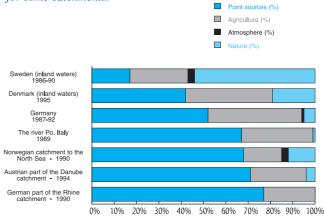


The report suggests that most of the phosphorus loading to surface waters in densely populated areas is from human excretion, with phosphorus production being 1 - 1.5 kg/person/year in industrialised countries. 50% (Southern Europe) – 80% (Northern Europe) of the population is connected to sewage works, with both the connection rate and the quality of treatment achieved in sewage works improving significantly over the last 10-15 years. By 1995, over 80% of sewage treated in Nordic countries, and over one third in Western Europe, received tertiary treatment (phosphorus/ nutrient removal).

Phosphorus fertiliser application rates are estimated at around 20-50 kgP/ha/year in Northern and Western Europe, and 10-30 kgP/ha/y in Southern Europe. A consequence is that around 20% of agricultural soil is saturated with phosphorus, leading to leaching. Levels of phosphorus in the aquifers below the Po river valley, for example have reached 1 mgP/l, probably due to fertiliser use on overlying rice fields.

Fig. 2: Source appointment of phosphorus loads.

From EAA publication indicated at end of article, page 32, with permission. Source of data : compiled by ETC/IW from state of the environment reports, Windolf 1996, Swedish EPA 1994, Umweltbundesamt 1994, BMLF 1996, Ibrekk et al 1991, Italian Min. Env. 1992. Note: atmospheric contribution considered only for some catchments.



(the bars at the bottom of the figure have the highest proportion of point source pollution)

Excess nutrients

Eutrophication, etymologically, means an elevated supply of nutrients. However, the term is generally currently taken to mean a situation where an increased supply of nutrients results in "an 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" (definition from the EU Urban Waste Water Treatment Directive 91/271).

The OECD has suggested indicative limit values for phosphorus defining different nutrient classes of water :

Total annual average P concentration µg/l

ultra oligotrophic	<4
oligotrophic	4-10

mesotrophic	10-35
eutrophic	35-100
hypereutrophic	>100

These are compared to the levels which one would expect to find in "natural" pristine lakes, unaffected by human activities, from $0.3 - 25.7 \mu gP/l$ in shallow lakes (average depth 10m) to $3.1-11.4 \mu gP/l$ in deep lakes (200m).

The report concludes by suggesting values above which phosphorus concentrations can be considered "excessive", but indicates that these are intended only for guidance :

rivers	100 µgP/l
lakes	25 µgP/l
marine waters	site specific

The nutrient levels in lakes across most of Europe (all except sparsely populated Northern areas) are significantly increased by man's activities, and although phosphorus levels have fallen somewhat (mainly as a result of improved municipal waste water treatment), nutrient levels continue to pose water quality problems in many lakes. In rivers, phosphorus is "present in excess" at almost all of the around 1,000 monitoring stations surveyed, but elevated chlorophyll levels are often not detected, probably because the rivers are not sensitive to eutrophication for reasons other than nutrient concentration (permanent turbidity, presence of toxic substances ...)

In large estuaries, the main events occurring with elevated nutrients levels are the flocculation of organic matter and clay, and the death of river phytoplankton. Algal development in estuaries is often not limited by nutrient concentrations, but rather by other factors such as water movements (flushing), light penetration (related to suspended solid levels), mixing depth, grazing, tidal effects ... Algal development in estuaries may however be limited by nitrogen or phosphorus, depending on the ratio between the available concentrations of these elements, but also on algal populations and other factors, and may in some cases also be limited by silicon or iron.

In coastal marine waters, nitrogen loadings may have a positive effect (improving productivity, and thus fish catches) but may also pose problems if algal blooms occur. Atmospheric nitrogen fixation seems to be less significant in marine waters than freshwaters, and the control of algal development cannot be achieved solely through phosphorus load reductions : nitrogen loadings, and pollutants which are involved in mobilising phosphorus from marine sediments must be addressed.

Water Framework Directive

The EU Water Framework Directive 2000/60 completes existing water protection regulations (in particular the Urban Waste Water Treatment Directive 91/271) with the general obligation for Member States to reach "good" ecological status for all surface waters within a given time-scale (generally by 2010) using appropriate local measures. Concerning nutrient levels, this Directive defines "good" ecological status as such that « Nutrient concentrations do not exceed the levels established so as to ensure the functioning of the ecosystem and the achievement of the ... biological quality elements ». The EAA concludes that implementation should result in significant reductions of excessive nutrient loadings, particularly from agriculture.

"Nutrients in European Ecosystems" (Environmental Assessment report n°4), 156 pages, 1999. Available from the Office for Official Publications of the European Communities http://europ.eu.int (or national sales outlets). European Environmental Agency : http://www.eea.eu.int Figures reproduced with kind permission from EAA, and for Fig. 2 from OSPAR (the data indicated are originally taken from table 8 of OSPAR 1995).

NUTRIENTS MANAGEMENT

USA

EPA publishes "ecoregional nutrient criteria"

The US "Clean Water Act" requires state and tribal authorities to achieve, wherever possible, water quality adequate for the healthy development of fish, shellfish and wildlife, and for recreational water uses. This approach is comparable to that taken by the new EU "Water Framework Directive" (60/2000 which requires local authorities to achieve "good water quality" in all surface waters (except justified exceptions) by 2015, where this "quality" is defined for nutrients as levels which are compatible with natural species and biodiversity.

The US EPA's new nutrient criteria are the result of a process started when a report to congress, stating that 40% of US waters did not meet the Clean Water Act's overall quality standards, led to the Clinton administration's March 1998 "Clean Water Action Plan". The 1996 National Water Quality Inventory indicated that 40% of US rivers, 51% of lakes and reservoirs, and 57% of estuaries were adversely affected by eutrophication. Despite a national move to Pfree laundry detergents and some investments in municipal waste water treatment, excess nutrients were reported to have degraded almost 3.5 million acres of lakes and reservoirs, and over 84,000 US miles of rivers and streams to a point where they no longer supported basic uses or aquatic life. At the time, the only national water quality criteria for nutrients in existence in the US were 10 µg nitrate-N/l for drinking water supplies and 10 µg total-P/l for marine and estuarine waters - but these were based on conservative toxicology and not on possible eutrophication effects.

The new nutrient criteria, published in December 2000, are intended as recommendations to states and tribes, are set for **17 different "ecoregions"** and are developed as Technical Guidance Documents for streams and rivers, lakes and reservoirs, estuaries and coastal waters, and for wetlands. The 17 "ecoregions" cover 8 climate areas/ecosystem types for lakes and reservoirs, 8 for rivers and streams, and 1 for wetlands. **They provide suggested baselines for numerical values for both nutrient concentrations (total phosphorus and nitrogen) and for symptom effects (chlorophyll-a concentrations, turbidity – or for wetlands, periphyton). These are intended to help states and tribes identify problem waters, provide a basis for establishing local quality criteria (on a catchment basis) and evalute success in reducing eutrophication.**

As a result of the regionalised approach, aggregate reference conditions vary widely, for example for "streams and rivers" : from 10 to 76 μ gTP/l; 0.12 to 2.18 mgN/l; 1.3 to 9.89 NTU turbidity between ecoregions II (Western Forested Mountains) and VI (Corn Belt and Northern Great Plains), and from 0.4 μ gChl-a/l in ecoregion

XII (Southern Coastal Plain) to 8.59 in ecoregion VI.

Similarly, ecoregion aggregate reference conditions range from 8 to $37.5 \ \mu gTP/l$ and from 0.1 to 1.68 mgN/l for lakes and reservoirs.

However, as well as these inter-ecoregion ranges for aggregate reference conditions, a range of reference conditions is also given within each ecoregion : for example, the aggregate references of $10 \ \mu gTP/l$ and $0.12 \ mgN/l$ for "rivers and streams" in ecoregion II in fact corresponds to ranges of reference conditions for subecoregions of 5.3-21.5 $\mu gTP/l$ and $0.1 - 0.8 \ mgN/l$.

These new ecoregional criteria are expected to be taken into account with the development of local water quality standards by 2004.

The Ecoregional Nutrient Criteria and the waterbody-specific Technical Guidance Manuals are available at the EPA's nutrient website : www.epa.gov/ost/standards/nutrient.html or from : US National Service Center for Environmental Publications (NSCEP), 11029 Kenwood Road, Cincinnati, OH 45242, USA.

THE NATURAL STEP

A systems-orientated approach to the phosphorus cycle

This article examines phosphorus enrichment of surface waters from a systems perspective, suggesting that past approaches have been mainly based on endof-pipe (P-removal from sewage) or end-of-field approaches (buffer vegetation zones). The author argues that decision makers need to look beyond current market contexts (for example, comparison of mined phosphate rock prices with costs of recovered P) to develop cyclic and sustainable solutions, including phosphorus recycling, and equally improved phosphate use in both fertiliser and detergent applications.

The author's starting point is the definition of sustainable development, as an objective of achieving end-of-state sustainability of the system as a whole, and not just incremental improvements in current non-sustainable business-as-usual scenarios. This is summarised the "The Natural Step" system conditions (adapted from Holmberg et al. 1996).

In the sustainable society, nature is not subject to systematically increasing...

- 1. ...concentrations of substances extracted from the Earth's crust
- 2. ...concentrations of substances produced by society
- 3. ...degradation by physical means and, in that
- society...
- 4. ...human needs are met worldwide.

Current use of phosphate minerals is clearly in contradiction with such a system, as resources of phosphate rock are being depleted, whilst at the same time phosphorus is accumulating in surface waters and their sediments. This results in water quality problems in surface water: in the UK for example, current phosphorus concentrations in surface fresh waters are estimated to be an order of magnitude higher than natural background levels. Phosphate mineral consumption also results in other collateral problems such as heavy metal release from the mined phosphate rock, environmental impacts of rock extraction and transport ...

Unsustainable P use in farming

Of phosphates extracted from mined phosphate rock and consumed in agricultural applications today, around 60% goes to developed countries, although these hold only 35% of the world's agricultural land and 24% of its population. Crop species and cultivars are no longer selected for their adaptation to local soil and climate, but for short term profitability, on the basis of large inputs of mineral fertilisers.

Fertilisers are not even used efficiently: in Sweden, for example, an average of three times more phosphorus is added to fields than leaves it in animal or vegetable products. Of the phosphorus contained in this produce, only around 20% is ploughed back into the land, with 80% ending up in sewage, and then on to sewage sludge and landfill.

The author identifies three main pathways for improving the sustainability of agricultural phosphate use: better phosphorus application, taking into account the phosphorus already present in soil and the crop's real needs; soil conservation (avoidance of soil erosion, as a large proportion of P loss from fields is carried with soil particles being lost); use of "end-of-field" retention zones such as buffer strips of vegetation or wetlands.

Phosphorus recycling cost-benefits revisited

Recovery of phosphorus from waste streams and its recycling is seen by the authors as a centre stone for a sustainable phosphorus cycle. One way to achieve this is by reuse of sewage sludges in agriculture, but the author recognises the current pressure against this from for example the retail sector.

P-recovery from sewage, animal wastes and other waste streams, to produce a product which can be recycled is presented as a key to sustainability, and to avoiding the accumulation of this element in natural systems.

The author suggests that it is "necessary to challenge predominant thinking about the costs and benefits associated with the delivery of more sustainable cyclic uses of phosphorus and other resources. Most analyses of the economics of recovery and reuse of phosphorus from effluent are based firmly on today's probable market prices. Yet most people would accept that we live in a fast-changing world in which sustainability pressures lead to increasing resource costs and scarcities, a declining capacity to dispose of waste, ever more stringent regulatory requirements, and greater public and customer pressure for more environmentally and socially responsible practice. The economic climate will therefore inevitably change considerably in coming years, favouring inherently more sustainable practice as the adverse effects of today's unsustainable norms become more evident. This changing economic climate, together with the economic multipliers of the coincidental closure of reuse cycles for other resources (some noted in this article), may more rapidly become favourable to phosphorus recovery for reuse."

"Taking a Systems-oriented View of Phosphorus Enrichment in Fresh Waters". Freshwater Forum 2001, 15, pp.35-54.

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SEPTIC TANKS

Natural soil iron can precipitate P from sewage

The organic matter in sewage (labile carbon) causes iron in soils to become soluble, and this soluble iron can precipitate the phosphorus out of sewage down to below 0.05 mgP/l, forming stable solid coatings on soil particles. This may explain why up to 85% of phosphorus from septic tanks is precipitated into soil within a few metres of infiltration pipes. The author proposes structured application of this "Reductive Iron Dissolution" (RID) mechanism as a P-removal process for smaller sewage works and septic tanks.

The author's first experiment was a 2-week lab test, in which natural soil sediment in a 25cm column was dosed with filtered sewage. This successfully showed that soluble iron increased from 0.05 to 0.3 mgFe/l as the sewage descended the column.

This was followed by a two year laboratory experiment where approx. 60 ml/day of filtered sewage first passed through 360g of RID medium (fine particles of B-horizon soil fine, collected in Ontario, Canada, with a total iron content of 67gFe/kg dry soil) and then through a 70 cm column of sand. The iron content increased from around 0.16 mgFe/l in the influent sewage to around 1 mgFe/l after a residence time in the RID medium of 1.4 days.

Redox potential

There was a significant variation in iron dissolution, and this was attributed to the storage time of the sewage samples used. These were collected monthly from the sewage works, and the redox potential increased in the stored sample (from around 100 mV when fresh, to nearly 390 mV after one month's storage). Lowest RID iron levels were consistently noted at the end of each month's "batch" of sewage, when redox potential was highest.

This problem was resolved in a pilot scale field trial conducted during the non-freezing periods from May 1997 to August 1999. This experiment used untreated, filtered sewage from a domestic septic tank. The sewage was pumped into an 1m high lysimeter with three compartments at approx 1.3 litres/day. The first compartment (8 l volume) was simply a holding tank, the second (again 8 l) contained the same RID medium (Ontario soil), and the third one medium-grain sand (19 l). Residence times were respectively around 7, 2.2 and 3.6 days.

In this field experiment, the fresh sewage was thus not stored for more than a few days (in the first holding compartment), and **this gave consistently low redox potentials (140-180 mV) and high soluble iron from the soil (2.5 - 9 mgFe/l).**

P-removal

In the field trial, inflow soluble phosphate levels were around 10 mgP/l, and the lysimeter system brought this

down to around 3 mgP/l after passage through the RID medium, and down to levels below the detection limit (0.05 mgP/l) after the sand column : a P-removal of over 99%.

SEM micrographs showed that the phosphates were being precipitated on the sand particles as thick (10-30 μ m) grain coatings, containing 6 – 12%P, with a fairly uniform molecular composition consistent with the mineral mitridatite [CaFe₂(PO₄)₂(OH)2.8H₂O]. This is consistent with work by Leckie and Stumm which suggests that Fe-III is very effective at precipitating phosphates.

The Fe:P ratio in the precipitated phosphates is around 1, suggesting that around 9 mg of Fe would consume 5 mgP. Analysis of the soil used as RID medium in the 2-year laboratory and experiment showed that only around 0.2% of the initial iron present had been leached, showing that the process system could remain effective for years or decades before renewal of the RID medium would be necessary.

Septic tanks

The author notes recent work by other authors looking at the solids near the outflows of septic tanks. Zanini et al. 1998 showed that **phosphates generally precipitated close to the septic tank outpipes (<1m)** and suggested that this occurred by Fe-II to Fe-III conversion at the redox oxidation front. Harman et al. (1996) showed that 85% of outflow phosphorus from a septic tank precipitated within 3m of the outflow pipes.

This could correspond to the RID mechanism functioning, with the natural soil in the infiltration area providing the required iron.

The author suggests that the mechanism can also be adapted to remove phosphorus from sewage, using only low-cost and readily available materials (soil, sand), in a passive flow system. This would be appropriate for application in small sewage works or septic tanks.

"Treatment of wastewater phosphate by Reductive Dissolution of Iron", J. Environ. Quality 29, 1678-1685 (2000).

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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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P-RECOVERY CONFERENCE

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Recycling phospates from detergents - a reality within a decade?

Over 260 representatives of the water treatment industry and of regulators met in March in The Netherlands to discuss the recovery of phosphates from sewage and animal wastes for recycling.

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Fertiliser value of struvite

A 1968 document for the International Chemical Fertiliser Centre summarises a number of pot and application trials of struvite and concludes that it is an effective, added-value fertiliser for a variety of applications, providing plant available nitrogen, phosphorus and magnesium.

AUSTRALIA

PAGE 5

Making a business from recovering struvite

Project to commercialise a P-recovery process (as struvite) in Australia, targeting piggery wastes and in sewage works

JAPAN

P-recovery from sewage sludge incineration ash

High temperature process for producing phospate fertiliser from sludge incineration ash.

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The EU Commission's presentation at a WWF conference underlines the essential role of wetlands in water basin environmental management.

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Costs of sewage treatment and nutrient removal

Operating costs for Austrian municipal waste water treatment plants are compared between 1989/90 and 1997 as well as with Germany and Sweden.

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Implementing the US Clean Water Act

The requirement to define TDML's (Total Maximum Daily Loads) for nutrients for listed waterbodies will put increasing pressure on agricultural practices and on land application of sewage biosolids. However, in some areas, the significant reduction in nutrient loading necessary to achieve significant impact on eutrophication problems may not be compatible with maintaining conventional agricultural activity.

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Nutrient loading increases bivalve productivity

Analysis of 14 shallow Danish estuaries suggests that higher nutrient loadings have a clear positive effect on shellfish biomass.

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Installing ponds as nutrient traps for drainage and runoff water (reducing nutrient load to downstream water bodies) as well as creating valuable wetlands.

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Respiration rates vary with zooplankton populations

Data from four lakes over 7 years allow a comparison of crustacean zooplankton populations (resulting from manipulation of fish stocks) and nutrient addition with respiration and other parameters. Nutrient loadings led to increased respiration, but at significantly different levels as a function of zooplankton grazing.





Phosphorus recyling

P-RECOVERY CONFERENCE

Recycling phosphates from detergents - a reality within a decade ?

Over 260 representatives of the water treatment industry and of regulators met in March in The Netherlands to discuss the recovery of phosphates from sewage and animal wastes for recycling. The Second International Conference on Phosphate Recycling, three years after the first ever meeting on this subject, brought together technical experts and policy planners from private and public water companies, scientists and consulting engineers and regulators (including four national Environmental Protection Agencies/Environment Ministries from across Europe).

Participants were present from Australia (where Brisbane Water is testing a pilot phosphate recovery installation, see SCOPE Newsletter n°41), the USA, Canada, Turkey, Malaysia, and from a dozen European countries.

The conference was jointly organised by CEEP - the West European phosphate industry's joint research association (a sector group of CEFIC), editor of the SCOPE Newsletter, STOWA (the Dutch water industry research organisation) and CIWEM (Chartered Institution of Water and Environmental Management).



Over 260 decision makers and engineers met in Holland this spring to discuss phosphorus recycling.

Phosphate recycling is already happening

The conference included presentations of several full-scale phosphate recovery installations which are already operational, in The Netherlands, Italy and Japan. Phosphates from the Geestmerambacht sewage works (230,000 pe), near Edam in The Netherlands, are already recovered as calcium phosphates, and are recycled in the phosphate factory of Thermphos BV at Vlissingen, where they are used in the manufacture of elemental phosphorus, used to produce sodium tripolyphosphate (for detergents) and other industrial phosphates. In Japan, several full scale phosphate recovery installations are already operational in sewage works (Unitika Ltd and Kurita Water Ltd processes) and the recovered phosphates are sold as a premium value fertiliser ("Green MAP") for use on rice and on vegetable cultivation. The product is a high quality product, marketed by two fertiliser companies, who emphasise in their advertising that it is an environmental recycled product. The delegates from Unitika explained that they sold the phosphates, recovered from sewage as struvite (magnesium ammonium phosphate) for around 27,000 yen/tonne (price at the sewage works, the transport costs being covered by the buyer). The fertiliser, after mixing with other products to provide a potassium content, is then sold to the public for 1 - 2,000 yen per 20kg bag.

The conference heard from several water companies that they were currently planning the construction of pilot plants. Several of them also agreed on the need to carry out simple fertiliser tests of struvite to update knowledge of the product's agronomic properties and fertiliser value, particularly in a European context. Representatives of the fertiliser industry also confirmed their interest, and the European Fertiliser Manufacturing Association, EFMA, has already decided to carry out pot trials of recovered struvite.

Several North American delegates underlined the considerable interest in recovering and recycling phosphates from Animal Wastes (eg. Tennessee, North Carolina). A full scale plant is already operational recovering potassium ammonium phosphate from 700,000 tonnes/year of veal calf manures at Putten in the Netherlands, and DEP Stichtung told the conference that the construction of a full-scale plant to recover phosphates from chicken manure from around 600 poultry farms is being built (ZLTO/Mestac project, treating around 300.000 tons of poultry litter per year).

Sustainable development policy

Bjorn Wallgren of the Swedish Environmental Protection Agency explained to the conference that the Swedish Committee on Environmental Objectives has proposed a regulatory objective of 75% recovery for recycling of phosphates from sewage and from other biological wastes. The Committee proposed that recovery and recycling should include the return of phosphates to soil for use by crops. Because sewage sludge spreading on agricultural land has nearly ceased in Sweden, through a combination of regulatory pressure on contaminants in sewage and rejection of the practice by farmers for foodimage reasons, this would mean that phosphates would have to be recovered from sewage and recycled as fertilisers or in the phosphate industry. This objective is currently under discussion, but the environmental courts in Sweden have already begun to condition operating authorisations for sewage sludge incineration on the

implementation of phosphate recovery. The cities of Ekilstuna, Falun, Halmstad, Malmö, Södertälje and Stockhom are already subject to such a requirement, or the issue is now being addressed.

In other areas, such as South-East England, most sewage phosphate is already recycled through the agricultural application of sludge as a fertiliser, so that the phosphates can contribute to fulfilling crop needs. Several papers looked at the fertiliser availability of phosphates in sewage sludge and many delegates underlined the need to maintain this ecological route of phosphates recycling (and of recycling of the other nutrients and organic materials in sewage), by ensuring safe and well managed sludge spreading in areas where adequate agricultural land is available.

Nina Sweet of the **UK Environment Agency** indicated that their strategy "includes a specific action to work with others to promote the development and uptake of P recovery and recycling technologies and practice within the UK".

The conference concluded that several factors are now pushing strongly towards the recovery and recycling of phosphates, as a function of local or national contexts. These can include optimising biological phosphate removal from sewage (in order to protect surface waters and reduce sewage treatment operating costs), pressure on sewage sludge spreading (phosphate recovery will reduce the quantities of sludge needing spreading or incineration), regulatory decisions and policy towards sustainable development.

The detergent phosphate industry reaffirmed its commitment to recycling phosphates and to thus changing the idea of phosphates, the only recyclable detergent ingredient, from an objective into an industrial reality.

The SCOPE Newsletter will publish a summary of the Conference discussions in the Autumn 2001, and selected papers presented at the conference will be published in "Environmental Technology" journal – available on request from CEEP, see rear cover.



Willem Schipper, Thermphos BV, The Netherlands. The company has fixed an objective of replacing 20% of its current phosphate rock consumption by phosphates recovered from recovered materials within 5 years

FERTILISER INDUSTRY MANUAL

Fertiliser value of struvite

A paper prepared by Dr. G. Bridger of the Georgia Institute of technology for the fertiliser industry manual "New Fertiliser Materials 1968" concludes that magnesium ammonium phosphate (struvite) "has been shown to be a highly efficient source of magnesium, nitrogen and phosphorus for plants. Furthermore, its rate of release to plants can be controlled by use of different granule sizes, and it can be applied in massive doses without burning". The paper indicates that struvite had been produced commercially in a number of countries, and was at the time in the USA for horticultural applications, but that it potentially has wider uses.

Magnesium ammonium phosphate (struvite) was first prepared by de Fourcroy in 1789 and its use as a fertiliser was first suggested in 1857 by Murray. Patents for its use as a fertiliser were granted to different persons from 1932 through to the date of writing (1967). it is to be noted that one of these patents was taken out by amongst others the author of this paper, so that he is thus an interested party.

According to the author, the release of nutrients from struvite in soil is determined by bacterial nitrification (rather than solubility) and the rate of release can be controlled by the granulation (particle size) of the material.

The paper presents routes for synthesising struvite and indicates that industrial production has been described in Germany in the 1920's - 1930's and at the time of writing in the United States.

Fertiliser value test results

Leiser, 1963, published results of a series of tests comparing struvite with other fertilisers.

Four-month growth chamber tests of the fertiliser effectiveness for ryegrass, compared struvite with ammonium nitrate and urea formaldehyde. Conditions were non-leaching, and nitrogen, phosphate, potassium and magnesium applied at the same rate to all plants. The cumulative growth achieved with struvite (average for the three particle sizes used) was marginally better than for ammonium nitrate, and significantly better than urea formaldehyde.

Tests using Merion blue-grass under leaching conditions (1-2 inches of water every two weeks to simulate heavy rainfall), compared struvite (-6+16 mesh granule size) with urea formaldehyde. In this case, nitrogen, potassium and magnesium were applied at the same rate to all containers, but phosphorus rates were higher for the struvite treated plants. Again, struvite gave significantly higher cumulative growth than urea formaldehyde (nearly 2x).

Greenhouse tests using buckwheat compared struvite with triple super phosphate fertiliser, using both at application rates of 40 - 640 pounds of phosphate acre. Potassium was

also dosed, and nitrogen was added as ammonium nitrate as required. Eight successive crops were grown and harvested. In almost every case, the yield was greater with struvite as a phosphorus source than with triple super phosphate fertiliser – in some cases being twice as high. **Phosphorus uptake was calculated from analyses of the first five crops and showed to be about 20% greater for struvite than for triple super phosphate at the higher application rates and marginally higher at the lower application rates.**

Leiser also gave results comparing planting of several woody species used for roadsides using cow manure in the planting hole, no fertiliser or 1 or 4 ounces of struvite. Struvite gave significantly better results as measured by plant development during the second growing season.

Bridger *et al*, 1962, published results of field trials of struvite on potatoes in a magnesium deficient soil. NPK fertilisers were amended with struvite, soluble magnesium and no magnesium. The soluble magnesium gave 20% more marketable potatoes than with no magnesium, and struvite 42% more (although some of this increase may have been due to increased nitrogen contained in the struvite).

Lunt et al, 1961, 1962, 1964, published results of trials of struvite with ornamental chrysanthemums. Plants grown with struvite incorporated into the potting medium (sand and moss) performed as well as those supplied daily with soluble nutrients in the irrigation water.

Lunt et al, 1964, also published trials with poinsettias, as did Tawagan & Bodley, 1963, showing excellent results with struvite and potassium nitrate incorporated into the potting medium. Other authors, 1962-1964, have published results using struvite with azaleas, cherry laurel, pyracantha, cornus racemosa, ligustrum ovalifolium, taxus cuspidata expansa, carnations and divers bedding plants.

Bridger et al, 1962, also included results of field tests for several species of ornamental plants, comparing 2 or 4 ounces the use of struvite in the planting hole with 1.6 ounces of conventional NPK fertiliser applied similarly. Struvite gave generally better growth in height and similar diameter, but with little plant mortality, whereas the conventional fertiliser led to substantial plant death.

Grambell et al., 1964, published results comparing surface application around the planting hole of struvite with similar application of conventional fertilisers for young peach trees. After one year, the struvite fertilised trees achieved greater volumes and trunk diameters.

Several authors have shown that struvite has proved a good fertiliser for planting forestry seedlings and transplants, and the author indicates that struvite was being used at the time of writing by the California Division of Forestry for a variety of trees (mixing with planting medium). Voth et al., 1963, published results of trials with winter planted strawberries in row-raised beds (soil pH 6.5). For equivalent nitrogen application levels, struvite (-6+16 mesh granule size) gave better yields than (in order of decreasing yield) resin coated, bloodmeal, ammonium sulphate, urea formaldehyde or no nitrogen fertiliser. Fruit size and appearance were also superior with struvite.

Koritskaya and Remen, 1962, published results from several experimental field stations in Russia comparing fertilisation of several field crops including mangel beets (4 year test), winter wheat (6 years), potatoes (3 years) and tobacco. Struvite proved better or equivalent to superphosphate and to fused magnesium phosphate.

Bridger, 1962, also gives results of field tests for tomatoes in Maryland and Florida. Yields with struvite were respectively 71% and 37% higher than with conventional NPK fertilisers.

Magnesium potassium phosphate

The paper also quotes unpublished test results (Leiser *et al.* of the Grace Fertiliser Company) of the fertiliser value of magnesium potassium phosphate (sometimes referred to as K-struvite). These suggest that this compound can be as effective a fertiliser for ryegrass, bushbean and tomatoes as are triple super phosphate plus potassium sulphate.

SCOPE editor's conclusions : This paper contains a remarkable number of interesting references concerning the fertiliser value of struvite. Unfortunately, key data such as soil pH (which is an essential factor influencing fertiliser solubility) are scarcely ever given. Also, it must be born in mind that as a holder of a permit concerning the fertiliser application of struvite, the author can possibly not be regarding as completely neutral. SCOPE is currently trying to obtain the various original publications quoted by the author of this paper, in order to see to what extent these contain more complete information concerning the tests in question, but many of these are not only relatively old documents, but also from journals which are not easily available.

"New Fertiliser Materials 1968" – Centre International des Engrais Chimiques – Noyes Development Corporation – pages 236-284 "Magnesium Fertilisers - Section 3 – Magnesium ammonium phosphate and related compounds". G. Bridger, Georgia Institute of Technology, Atlanta, Georgia, USA.

NB. Pot tests of struvite as a fertiliser were reported in Scope 42 (page 13) using the Japanese vegetable Komatsuna. The Latin name of this plant was however omitted : it is a kind of cabbage, *Brassica campestris* L.

AUSTRALIA

Making a business from recovering struvite

The struvite crystallisation process can contribute to the sustainability of pig-rearing, municipal water treatment and other industries by removing and recycling nutrients (phosphorus and nitrogen) from waste waters.

A paper presented at the Second International Conference on P-Recovery (Holland, March 2001), summarised here, describes the market research and a business plan for selling such a process in Australia. The by-product of the struvite crystallisation process, MAP (magnesium ammonium phosphate), is a valuable slow-release fertiliser that allows recovery of the limited resource phosphorus.

Current trends suggest that the Environmental Protection Agency (EPA) in Australia is to issue environmental licences that specify lower nitrogen and phosphorus discharge concentration limits. This requires that farmers, industry and government invest in technology to remove the nitrogen and phosphorus from wastewater.

The Struvite Crystallisation Process (SC Process)

The struvite crystallisation process can cost-effectively remove the pollutants nitrogen and phosphorus from wastewater. The Japanese company Unitika Ltd. has been marketing a technical implementation of the struvite crystallisation process (SC Process) under the name of Phosnix since the early 1990s (Katsuura, 1998). This paper examines the possible market for the struvite crystallisation process in Australia.

The SC Process would principally target :

- Animal production plants (piggeries, abattoirs, feedlots, poultry, aquaculture such as prawn farming, dairy, rendering plants, etc.)
- **Domestic wastewater treatment plants** with anaerobic digesters (where anaerobic digesters are used for sludge treatment, they produce waste sidestreams that are high in nitrogen and phosphorus).
- Fertiliser production plants.

Table 1. Concentrations of nitrogen and phosphorus for nutrient-rich wastewaters.

Type of wastewater	Total N (mg/L)	Total P (mg/L)	Reference
Sidestream from domestic wastewater treatment plant with anaerobic sludge digestion	800 to 1000	60 to 150	v. Münch and Barr (2001)
Piggery effluent prior to screen	2175	850	Kruger et al. (1995)
Piggery effluent after pond treatment	384	44	Kruger et al. (1995)
Piggery sludge after pond treatment	2617	1696	Kruger et al. (1995)

Application to piggery effluents

Piggery effluent is very amenable to be treated with the SC Process for the following reasons:

- Piggery effluent and sludge are very high in nitrogen and phosphorus (Table 1).
- Unintentional struvite crystallisation occurs in a majority of effluent treatment facilities of piggeries, showing that it is very easy to produce struvite from this wastewater.
- Many piggeries recycle their effluent for cleaning and flushing, and this increases the nitrogen and phosphorus concentration of the effluent even further.
- **Piggery owners could use the MAP** by-product as fertiliser on their farms.

Application to municipal wastewaters

Research has been performed into the SC Process applied to municipal waste waters at the pilot scale in Australia (143 L pilot reactor) by v. Münch and Barr at the Oxley Creek wastewater treatment plant in Brisbane (see Scope Newsletter n° 41, page 23).

The SC Process is not intended to treat raw sewage but rather nutrient-rich sidestreams in a domestic wastewater treatment plant. It is often due to these sidestreams (also referred to as sludge dewatering liquors) that it is impossible to achieve extremely low levels of nitrogen and phosphorus in the effluent. This is particularly the case for plants with enhanced biological phosphorus removal, because phosphorus is released in anaerobic digesters and then not removed in the sludge. With the SC Process, a biological nutrient removal (BNR) wastewater treatment plant can be upgraded to significantly improve its nitrogen and phosphorus removal performance.

Where the SC Process is intended to be used for a domestic wastewater treatment plant, it is ideally required that:

- the plant is a **BNR plant** with enhanced **biological phosphorus removal**
- the plant has **anaerobic digesters** for sludge digestion (because of their potential to produce biogas/energy from wastewater, anaerobic digesters will play an increasingly important role in wastewater treatment in the future).



Figure 1. Photograph of MAP produced from the pilot-scale SC Process at the Oxley Creek wastewater treatment plant.

The recovered struvite

Unlike many other wastewater treatment processes, the SC Process produces no harmful by-products. The by-product that is produced, MAP (that is : struvite = magnesium ammonium phosphate), is commercially valuable (note: this MAP is not to be confused with mono-ammonium-phosphate, which is also often referred to as "MAP"). MAP is produced as a powder (Figure 1) or a granule of various granule sizes. MAP can be used as an ingredient in mineral fertilisers.

The theoretical composition of MAP on a weight basis is 9.9% magnesium, 5.7% nitrogen, 12.6% phosphorus with the remainder being crystalline water. MAP satisfies a need for mineral slow-release fertilisers and has many potential uses in horticulture, for nurseries, golf courses, etc. MAP is likely to be of most benefit to customers as a "boutique" fertiliser. An alternative to supplying the product directly to end-users is to sell it in bulk to a fertiliser manufacturer for use as a raw ingredient in their products.

Market survey results

85% of the respondents were convinced that the EPA limits would become stricter in the future with respect to nutrient discharge limits.

All but one respondent thought that animal production industries had effluent problems with respect to nitrogen and phosphorus.

Piggeries were quoted by 70% of the respondents as having the most effluent problems compared to other animal production industries, followed by poultry and abattoirs (multiple answers were possible).

45% of the respondents thought that piggery operators would pay a separate company for effluent treatment if such a service was offered (45% were undecided).

60% of the respondents knew of unintentional struvite crystallisation, and piggeries and anaerobic digesters were cited as examples.

A market survey was carried out by contacting agricultural waste and water treatment professionals, giving the main conclusions shown in the table.

Pig industry analysis

Fresh manure production and characteristics depend on the type of production. For example, for a 100 sow "farrow to bacon" unit, about 21.7 kg nitrogen and 7.3 kg phosphorus is produced as manure per day (Kruger et al., 1995). From the phosphorus that is contained in the manure, about 21 t/yr. of MAP could be produced for a 100 sow unit.

The Australian pig industry is experiencing significant waste management problems which threaten the future viability of the industry. Meo and Cleary (2000) show that the number of pig producers has reduced from approximately 40,000 in 1969 to approximately 3000 in 1999, however the pig population has remained fairly stable over this period (Figure 2). The average herd size has increased from 8 to over 100 pigs. This trend towards fewer piggeries, but larger concentrations of pigs has resulted in a greater concentration of pig waste. This trend favours the development of the SC Process, which may be prohibitive to small producers.

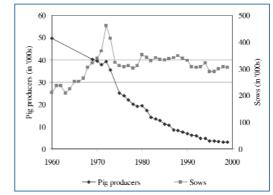


Figure 2. Structure of the Australian pig industry: Number of pig producers and breeding sows from 1960 to 1999.



Figure 3. Australian piglets at a piggery; for every sow on a piggery there are approximately 9 other pigs.

Local government wastewater treatment analysis

Because of the "economy of scale" for wastewater treatment operating costs, there is a general trend for large centralised wastewater treatment facilities, at least in the major cities of Australia. Such large facilities are more

likely to invest in sidestream treatment than smaller wastewater treatment plants.

There are only about 750 domestic wastewater treatment plants installed around Australia (which is a small number per capita compared to the fragmented water industry in some European countries). The top ten wastewater treatment plants treat around 50% of the total wastewater generated in Australia (AWA, 2000). Twenty WWTPs were identified that have anaerobic digesters, and hence sidestreams that would be amenable to the SC Process.

Sales forecast and operating costs

(Prices are quoted in Australian dollars which equalled $0.59 \in at$ the time this paper was written).

The market research undertaken indicates that the **potential market** sizes are:

- About 105 units in the pig industry (based on about 52.5 ML/d of effluent produced by the 300,000 sows in Australia)
- About 20 units for local government wastewater treatment plants (this is a conservative estimate).

The sales price for the MAP has a significant impact on the economics of operating the SC Process. Until a separate business plan for the MAP has been completed, a sales price has to be estimated. **Based on the nitrogen and phosphorus content alone, a sales price of \$234/t is possible.** This would be the price if the MAP was to be used in broad-scale agriculture. However, the intention is to use MAP as a "boutique" fertiliser for specialised applications. For those applications, a much higher sales prices can be achieved. **In Japan, a sales price of \$3800/t has been reported (Taruya et al., 2000).** For our business plan we have used a conservative estimate of \$500/t.

The construction and installation cost of one standard SC Process is estimated to be \$400,000. Unitika Ltd provided this cost for manufacture in Japan, but further work will be undertaken to obtain a more precise cost estimate under Australian conditions.

The cost for the magnesium solution that has to be added is estimated to be around \$450/t if magnesium hydroxide solution, MHS-60, manufactured by Orica is used. This is a very conservative estimate. To reduce this cost, waste streams from other industries containing magnesium will be sourced

The standard SC Process unit requires about 50 t/yr. of magnesium hydroxide solution and produces about 80 t/yr. of MAP. This calculation is based on a wastewater containing 63 mg/L phosphorus and 92 % phosphorus removal by the SC Process, leading to an effluent ortho-P concentration of 5 mg/L (without supplemental phosphorus addition to removal all nitrogen from the wastewater).

Other **operating costs** (labour and electricity) are negligible compared to the costs for magnesium, but are estimated to be:

- Labour: One person for one hour per day at a rate of \$100 per hour
- Electricity: \$10 per day (the electricity costs will be negligible in the overall scheme)

The operating costs detailed above have been used to determine the fixed and variable costs to charge the customer to operate at a profit :

- a fixed component of \$12,000 per month covers the transfer of process knowledge and provision of the plant.
- a variable component of \$540 per ML is charged for effluent treated.

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JAPAN:

P-recovery from sewage sludge incineration ash

Introduction

Japan Sewage Works Agency and Sanki Engineering Co., Ltd. have developed the technology of producing the phosphate fertilizer from sewage sludge incineration ash.

The source for phosphate fertilizers is normally produced from the phosphate rock. Japan imports one million tones of phosphate rock every year (three hundred fifty thousand tones if converted to P_2O_5), but nowadays the good quality phosphate rock has been dried up worldwide. In the meantime, it is expected that 40 to 120 thousand tones of phosphate is contained in sewage sludge in Japan if converted to P_2O_5 (it is figured out based on the assumption that sewage sludge of 1.86 million dry solid tones per year is produced at 1997. Ash is assumed 21% of the sewage sludge. P_2O_5 is assumed 10-30% of the ash). In addition to phosphate, the materials useful for vegetable such as silica, magnesium, etc. are included in the sewage sludge incineration ash. We have developed the recycled method to efficiently utilize those materials as fertilizer.

The phosphate fertilizer that we have developed for the purpose of producing recycled product is the "fused phosphate fertilizer" (which is widely recognized as fused calcium magnesium phosphate fertilizer in Japan), the phosphate of which shows solubility to the citric acid. The phosphate fertilizer is conventionally produced under the process where serpentine is added to the main material of phosphoric rock, and then is melted and cooled down immediately. The composition of this phosphate fertilizer is very similar to that of sewage sludge incineration ash (see table-1) and the production process is also very similar to the melting process of sewage sludge incineration ash.

We have so far confirmed the feasibility of fertilizer at laboratory level, and now continue to confirm this technology at the pilot plant level. We apply this technology for patent jointly with Japan Sewage Works Agency.

Market for Fused Phosphate Fertilizer

Annual production volume of fused phosphate fertilizers is 133 thousand tones, which is equivalent to 27 thousand tones if converted to P_2O_5 (production from July 1997 to June 1998). It is expected on the other hand that total

Table-1	Example - Composition	of Sewage Sludge	Incineration Ash and Fused

Phosphate Fertilizer						
Sample	P_2O_5	MgO	CaO	SiO ₂	Al_2O_3	Fe ₂ O ₃
			%			
Incineration Ash - A	22.7	2.30	13.5	25.4	21.2	9.52
Incineration Ash - B	27.9	2.92	11.0	13.7	9.93	1.30
Fused Phosphate Fertilizer	22.2	14.3	32.5	24.8	0.60	1.67

volume of phosphorus contained in the sewage sludge in Japan is 40 to 120 thousand tones per year if converted to P_2O_5 and thus sewage sludge incineration ash is considered as the substituted resource for fused phosphate fertilizers.

In producing the fused phosphate fertilizer, the raw material of phosphate rock is procured at 12 yen per kilogram while the finished product of fused phosphate fertilizer is sold at 40 - 50 yen per kilogram. On the other hand, the disposal for the incineration ash costs 5 - 10 yen per kilogram (which does not include transportation cost). Therefore, the effect of the cost-benefit is significant if the phosphate fertilizer is produced from the incineration ash.

Production Method of Phosphate Fertilizer

This fertilizer is produced under the process that the calcium and magnesium (which are necessary composition for fused phosphate fertilizer) are first added to the sewage sludge incineration ash. Then, those are melted by heat at the furnace $(1,350~1,500^{\circ}C)$, and finally crushed by immediate water cooling for production of phosphate fertilizer.

At the basic experiment at laboratory test level, we have find out the best composition rate for sewage sludge incineration ash and its additives to produce the fertilizer.

Trial Product

We have produced the trial product with use of main material source of sewage sludge incineration ash, at the experimental room level where electric furnace and black led melting pot are used. We have produced Product A (with use of incineration ash A) and Product B (with use of incineration ash B), both of which fully satisfy, as shown below, the Requirements of Phosphate Fertilizer described in Japanese Fertilizer Regulations.

At the result of this test, we have confirmed the possibility that we can produce the phosphate fertilizer from the sewage sludge incineration ash. We consider by this finding that the possibility to recycle the sewage sludge incineration ash as the substituted new source of phosphate increases.

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Product Name	Usage Rate of Ash	Solubility (P ₂ O ₅)	Solubility (MgO)	Alkali	Cd
	%	%	%	%	% (note 1)
Regulation		17 or above	12 or above	40 or above	0.00015 or less
Product A	53	19.8	18.0	53.8	0.000005
Product B	65	18.6	15.4	49.4	0.000005

Note: Value per 1% content rate of solubility (P₂O₅) to the citric acid

SEWAGE TREATMENT

WETLANDS

Delivering the objectives of the Water Framework Directive

A presentation by the EU Commission at the second World Wide Fund for Nature (WWF) conference on the implementation of the EU Water Framework Directive "The role of wetlands in river basin management" emphasises that wetland conservation will be essential in delivering the objectives fixed by this important new Directive.

The requirements of the Water Framework Directive with regard to wetlands

The purpose of the new Water Framework Directive is to protect and enhance inland surface waters, transitional waters, coastal waters and groundwater. For the first time in European legislation for all these water categories a good status is defined which Member States have to achieve within 15 years. With regard to wetlands the Directive aims at the prevention of their further deterioration and the protection and enhancement of those wetlands directly depending on aquatic ecosystems.

Wetlands are not directly included in the definition of good surface water status, but through the hydromorphological elements, which need to be addressed when the good water status is determined, a link to the water needs of wetlands is established. The definition of good groundwater quantitative status goes further and incorporates the water needs of wetlands into the objectives of the Directive. It is required that the level of groundwater is not subject to anthropogenic alterations such as would result in any significant damage to terrestrial ecosystems which depend directly on the groundwater body.

River basin management plans with programmes of measures are required by the Directive as the main instrument to reach the objectives. The entire river basin management process is subject to public participation. Within the river basin management plans all protected areas in a river basins have to be identified and a map with all protected areas have to be produced. The areas identified under the Birds Directive (79/409/EEC) and under the Habitats Directive (92/43/EEC) need to be included. Moreover, the impacts and pressures on these areas have to be analysed and specific monitoring requirements for the status of the protected areas are defined. In the programme of measures the re-creation and restoration of wetlands have to be included, whenever these measures are necessary to reach good water status.

With these requirements for River Basin Management the Water Framework Directive establishes a new spatial planing instrument to manage the water needs of wetlands. Furthermore a new co-ordination mechanism between existing legal instruments like the Birds Directive and the Habitats Directive is introduced.

One further requirement within the River Basin Management Plan is to produce an economic analysis that allows to make judgements about the most effective combination of measures in respect of water uses based on the potential costs of such measures. As wetlands doubtless have positive effects on the purification of waters, all measures aiming at the re-creation and restoration of wetlands shall be included in the economic analysis.

Wetland functions and threats

Wetlands are extreme complex and dynamic systems. They serve very important ecological and cultural functions. The Ramsar Convention of 1971 already addressed their importance and their multifunctionality. The Ramsar Convention distinguished between 35 different categories of wetlands which indicates the wide range of different functions wetland ecosystems may serve. But wetlands may only serve their functions when the related ecological processes are largely undisturbed and in particular their water needs are satisfied.

However the understanding of the functions and the related ecological processes is a key factor for successful management of wetlands. All management strategies should take into account the following functions:

- wetlands belong to the most productive ecosystems with an extreme rich biodiversity
- wetlands can serve very important purification purposes for surface and groundwater
- wetlands are important for the ecological processes of all aquatic ecosystems
- wetlands are very effective natural retention areas for floods
- wetlands are important for recreation.

The first three functions are of high importance for the status of surface waters and groundwater and should get very special attention in the River Basin Management Plans. One hectare of wetland, for example, may under specific conditions have the same purification capacity as an urban waste water treatment plant for 500 people. But wetlands can only serve these functions, as long as pollution does not jeopardise the natural ecological processes and as long as they are part of a hydrological regime that serves their water needs.

Although the Birds Directive and the Habitats Directive are effective instruments for the protection of wetlands, the European wetlands are still under high pressure by human activities. The Communication on wetlands (1995) estimated that 2/3 of the wetlands were destroyed since the beginning of the century.

The major threats for wetlands were and still are:

- regulations of rivers and lakes for flood protection, hydropower and shipping

- land drainage for agriculture
- over exploitation of ground and surface waters
- pollution.

Moreover, the sector oriented policies and the fragmented water management approaches in the past have added to these threats. The outdated engineering approaches to flood protection - more and higher levees - are one of the most outstanding examples .

River Basin Management - a chance to improve wetland management

The effective implementation of the Birds Directive and the Habitats Directive will play a key role in improving the status of wetlands in Europe. The implementation of the Nitrates Directive and the Urban Waste Water Directive will continuously improve the quality of the water status and thereby contribute to the protection and enhancement of wetlands. Although all these legal instruments are of great importance for a wetland policy they do not sufficiently address one of the key factors for successful wetland management: the water needs of wetlands.

The wise use guidelines of the Ramsar Convention and the Communication on wetlands already stressed the importance to include wetlands into a River Basin Management approach. The conservation strategies for the protection of biological singularities do address the negative effects on wetlands. But the great importance of water for all ecological processes and functions of wetlands need to be better addressed by modern management strategies for wetlands. The approach of the Water Framework Directive provides the instruments to include the water needs of wetlands in a river basin oriented water management with an appropriate spatial scale.

The reporting and monitoring requirements of the Directive will contribute to the assessment of the status of wetlands and will increase the knowledge of the role of wetlands for the status of the surface waters and the groundwater in a river basin. In many cases the analysis will show the great importance of wetlands for the water status. Moreover, the co-ordination requirements of the Directive are forcing the different administrations and stakeholders to work together in setting up the programme of measures and are therefore a chance to overcome the old sectoral management approaches with their negative effects on wetlands.

The economic analysis which is required as a basis for the design of the programme of measures and in particular to optimise its efficiency can help to **assign an economic value to wetlands and thereby demonstrate their economic relevance** within the programme of measures to improve the water status.

All these specific monitoring, co-ordination and management tools of the Directive will increase the transparency and are thereby a great chance to improve the awareness for wetland protection and management. One of the objectives of the river basin management process should be the creation of wetland networks within the river basins. This will create a win-win situation for the water status and the wetlands. The Water Framework Directive provides an efficient spatial planing instrument to reach this objective.

Presentation by the EU Commission at World Wide Fund for Nature (WWF) conference on the implementation of the EU Water Framework Directive n°2 "The role of wetlands in river basin management", 9-10 November 2000, Brussels.

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The EU Water Framework Directive is now valid legislation (under the title Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy) having been published in the EU Official Journal L 327, vol. 43, 22nd December 2000. It can be downloaded at : http://europa.eu.int/eurlex/en/oj/2000/l_32720001222en.html

AUSTRIA

Costs of sewage treatment and nutrient removal

This paper is based on a comparative study of 13 Austrian municipal waste water treatment plants (wwtps) in 1989/90 and again in 1997, and on comparisons with published studies of wwtps in Sweden (Balmer and Mattsson, 1994) and Germany (Bohn, 1998). The author concludes that expenses directly related to the wastewater load (energy, chemicals) make up only around 20% of total costs, with labour costs being the highest operating cost item. In Germany, however, sludge management/disposal costs were already reported as 6 Euros/p.e./year (P.e. = person-equivalent) and reached around 25% of total operating costs. The additional costs for nutrient removal in wwtps have only a small influence on total operating costs.

On the basis of a range of reported figures, the author estimates that average loads to European municipal wwtps range, per capita p.e., from around 110 to 120 g/day for COD; from 9 to 12 g/d nitrogen; and around 1.7 g/d phosphorus (with lower loads of 1.3 - 1.5 g/d phosphorus for wwtps receiving a high proportion of industrial waste waters in their inflow).

In 1990, only five of the 13 Austrian wwtps studies were operating phosphorus removal (although all were operating biological nitrification and partial nitrogen removal). In 1997, all 13 of the plants were operating phosphorus removal, as nutrient removal had become compulsory in Austria : nitrogen removal for all wwtps > 5,000 p.e. and phosphorus removal for all wwtps > 1,000 p.e. The 13 Austrian wwtps had a mean load of 42,300 p.e. in 1989/90,

rising to 45,700 in 1997. Operating data from the plants were checked against calculated mass balances, and this led in one case to additional measurements being taken and the operating data being corrected.

Energy cost and balance

The energy cost at the Austrian wwtps was the same in 1997 as in 1989/90 at 2.1 Euros/p.e./year. The average energy consumption was 35kWh/p.e./y, of which 11 kWh was produced on site by methane production from sludge digesters.

The average cost at the Austrian plants for chemicals for phosphorus stripping was 1.3 Euros/p.e./year in 1997, not significantly different to the cost for the plants already equipped with chemical phosphorus removal in 1989/90.

Sludge disposal costs were relatively low for the Austrian plants studied in both 1989/90 and 1997 (below 2 Euros/p.e./year), and the author notes that most of the plants were using either local landfill or agricultural spreading as disposal routes. Sludge disposal costs reported in the German study (1997) were however 3-4 times higher.

By far the highest operating cost for the Austrian wwtps studied was that of "repair and maintenance, personnel and administration", reaching 8 Euros/p.e./y in 1989/90, increasing to 12 Euros by 1997. The author explains that these different types of cost are grouped together, because of the difficulty of separating them in many wwtps where repair and maintenance are carried out partly or to a large extent by wwtp staff.

Thus these **repair**, **maintenance and personnel costs make up around 75% of the total wwtp operating costs in Austria** in 1997. The proportion is very similar in the 1992 Sweden study, but somewhat lower at around 55% in Germany 1997 (because of higher energy and sludge disposal costs reported for Germany).

Overall, the total operating costs for the wwtps studied in Austria rose from 12 Euros/p.e./year in 1989/90 to just over 16 Euros in 1997. The author suggests however that a well designed and operated wwtp (design capacity 100,000 p.e. operated at a load of 60,000 p.e.) should be able to achieve a total operating cost under current economic conditions of 12.5 Euros/p.e./year.

This paper confirms the author's previously published work demonstrating that the additional costs for nutrient removal (nitrification, nitrogen and phosphorus removal) make only a small difference to municipal waste water treatment plant operating costs (Nowak 1991, "Auswirkungen auf die Betriebskosten" in German).

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NUTRIENT MANAGEMENT

Implementing the US Clean Water Act

This paper (which can be consulted on the web at www.gfreedlee.com) offers a review of current knowledge of the relationship between nutrient loadings to surface water and eutrophication symptoms, and discusses how this can be applied in the definition of Total Maximum Daily Loads for nutrients, as required by the US Environmental Protection Agency in implementation of the Clean Water Act. Amongst other issues, the authors emphasize the need to base nutrient management strategies on nutrient loadings to waterbodies, rather than aquatic nutrient concentrations. They also suggest that in some circumstances eutrophication symptoms can best be managed by changing the physical conditions and/or hydrology of the waterbody

Many waterbodies in the USA are listed as "303(d) impaired" because of excessive algal and/or plant growth related to eutrophication and the number of waterbodies listed is expected to increase considerably as the US EPA and states develop chemically based nutrient (N and P) water quality criteria. A further concern, as regards nitrogen loadings, is the nitrate pollution of groundwaters. This paper provides guidance on the application of existing scientific knowledge concerning the relationships between nutrients and water quality, and on how to define nutrient load limits for waterbodies.

Limiting nutrients and critical concentrations

In many cases, water managers identify phosphorus as the "limiting nutrient" in fresh waters simply because the N:P ratio is higher than the "Redfield ratio" of 7.5:1 (mass) and conclude that reducing phosphate loadings will reduce algal development. The authors indicate, however, that in many cases both available phosphate and nitrogen (soluble inorganic forms which algae can take up) may be in excess of algal growth needs (surplus) where further algal growth is limited by other factors, in many cases light.

In order to establish whether a nutrient is indeed a limiting factor, the authors suggest that the actual dissolved concentration at peak biomass must be measured. Concentrations of around 5 μ g P/L as soluble orthophosphosphate and 20 μ g N/L as nitrate+ammonium are generally growth rate limiting. If concentrations are higher than this, then algal growth is being limited by other factors, often light.

Light limitation of the ultimate total biomass development by inorganic turbidity and water colour will generally only occur for Secchi depths of less than around 0.2 m. However, in more transparent conditions light limitation can slow algal growth rates and self-shading can limit algal development.

The authors question the US Environmental Protection Agency (EPA)'s attempt to develop "critical nutrient

[&]quot;Expenditure on the operation of municipal wastewater treatment plants for nutrient removal", Water Science and Technology, vol. 41, n°9, pages 281-289, 2000.

concentrations" (concentration limit values) for ecoregions for different waterbody types. They suggest that this is likely to lead to inappropriate regulation and management. Critical loads of nutrients should instead be defined on a site by site basis, taking into account the physical characteristics of each waterbody, but also management objectives as a function of differing social expectations of the waterbody. The water quality objectives in waterbodies will depend on the leisure (recreational) purposes, ecological context, type of fish population targeted, use of the waterbody as a domestic water supply, etc.

The US EPA's National Water Quality Inventory 2000 concludes that some 45% of US waterbodies have "impaired" water quality due to nutrients. 30% are "impaired" by agricultural pollution and 12% by wastewater discharges. The US EPA's proposed nutrient criteria/standards concentrations will result in the designation of many more waterbodies as "impaired", and therefore lead to the definition of TDML (Total Maximum Daily Loads) for nutrients and management programmes to control nutrient loads.

Managing eutrophication

The authors present a summary of the results of the Vollenweider OECD international eutrophication study which relate normalised phosphorus load to lakes (nutrient load / hydraulic residence time) to expected average chlorophyll levels and to expected fish production yields.

Using these models, algal development levels can be predicted from nutrient loadings, and discrepancies between predicted and observed conditions can be used to identify possible ecosystem malfunctioning (such as toxic effects which might reduce grazing of algae by zooplankton).

The models however are only applicable to planktonic algae, and to not reliably predict how nutrient concentrations may be related to attached algae or floating water weeds and macrophytes.

These OECD study results give some indication as to how changes in nutrient loadings may modify water quality. However, the authors also emphasize that it cannot be considered in eutrophication management that "every little bit" of nutrient load reduction helps. They state that in fact at least a 20 to 25 % reduction in a nutrient load to a waterbody is necessary to produce a discernible improvement in the eutrophication-related water quality (see Jones and Lee, 1986). In certain cases, such a significant reduction of nutrient loading can be achieved by treating one large point source (eg. a municipal wastewater discharge). In most cases, however, eutrophication management programmes will only be effective by addressing all sources of available nutrients to the watershed.

The authors believe that the US EPA's approach, focusing on nutrient concentrations rather than nutrient impacts, can provide unreliable indications as to the appropriate nutrient control. Instead, eutrophication management should focus on specific local water quality problems of concern in a given waterbody, evaluate the factors which influence how each nutrient impacts this water quality problem and assess how changes in the loading of each nutrient will effect water quality.

Agricultural nutrient loads

Also, the US EPA approach is based on total nutrient concentrations, whereas **the OECD Vollenweider models referred to above are based on the statistical analysis of waterbodies where most of the phosphorus input was in an algae-available form.** In many cases, however, a large proportion of the phosphorus load to waterbodies is from soil erosion and agricultural and urban runoff, only around 20% of particulate phosphorus may be readily converted to an algal available form.

In many cases, it may prove difficult to reduce agricultural nutrient loads to the extent necessary to improve eutrophication-related water quality (that is, to bring nutrients down to levels where they become limiting for algal development). Agriculture in the Chesapeake Bay watershed is finding a 40% nutrient reduction objective difficult to meet, and similar problems are reported in the Lake Erie watershed. It may indeed, in many cases, be impossible to achieve the nutrient reductions necessary for water quality objectives whilst maintaining conventional agricultural methods and an economically viable agricultural system.

Physical characteristics

The response of a waterbody to changes in nutrient loadings will depend on its physical characteristics. The OECD Vollenweider models are not applicable without appropriate modification, for example, to waterbodies with relatively short hydraulic residence times (less than one year).

A **phosphorus residence time,** calculated as the total mass of phosphorus in the water column divided by the annual phosphorus load, analogous to the hydraulic residence time, can be used to evaluate the rate of recovery of a waterbody upon altering the phosphorus loads to a waterbody. For example, Lake Michigan's hydraulic residence time is around 100 years, but its phosphorus residence time is only around 6 years. The recovery time for a lake following changes to phosphorus loads can be estimated as approximately three times its phosphorus residence time.

In some cases, responsibility for eutrophication-related water quality problems can be considered to not only lie not with nutrient sources but with other human activities. The authors present the case of the San Joaquin River where algal development regularly leads to oxygen depletion problems. These problems are considered to be caused by the **excavation of a deep ship canal in the river, which considerably increases hydraulic residence time, and by the upstream diversion of water to Central**

and Southern California, which reduces flow to the channel. The authors argue that in this case the financial costs of management should therefore be born by the port authorities and water users responsible for these changes and that one of the best solutions may be aeration of the channel waters to eliminate the low dissolved oxygen that occurs in the ship channel due to the death and decay of algae.

The authors also emphasize the **importance of sewage biosolid spreading as a source of agricultural nutrient loads**, suggesting that this is often inadequately accounted for in nutrient source assessments, but that – with mineral fertiliser and manure spreading – it can represent a significant nutrient load with real opportunities for improved management.

"Evaluation of inorganic and organic nutrient source impacts in nutrient TMDLS". Paper accepted for presentation at the AWWA – WEF – CWEA Joint Residuals and Biosolids Management Conference San Diego, February 2001. A Jones-Lee, G. Lee, 27798 E. El Macero Drive, El Macero, California 95618, USA. Email : gfredlee@aol.com Paper downloadable from www.gfreedlee.com

SEWAGE TREATMENT

DANISH ESTUARIES

Nutrient loading increases bivalve productivity

The abundance and biomass of macrobenthos (seabed fauna, in fact mainly bivalve molluscs) was compared with nutrient loadings (nitrogen and phosphorus), spring algal bloom nitrogen stocks, and with estuary flushing rates. Of the two nutrients, the highest correlation was found with nitrogen loadings, and so only nitrogen was used in the data analysis. The loadings of nitrogen and phosphorus were closely correlated, and were both correlated to the freshwater inflows to the estuaries.

Correlation coefficients	N-load	P-load
Total macrobenthos biomass	0.64	0.47
Macrobenthos production (g/m²/year)	0.77	0.66

The data used to compare the 14 estuaries studied was local authorities' monitoring data for physico-chemical and biological variables, mainly from the period 1989-1995, with a total of 474 samples, each with 5-10 replicates.

The nutrient loadings to the estuaries varied widely, from 2 -200 gN/m^2 /year for nitrogen and $0.1 - 12 \text{ gP/m}^2$ /year for phosphorus (taken over the total estuary surface areas which varied from $2 - 315 \text{ km}^2$). Residence times were not significantly correlated to freshwater inflows, reflecting the fact that exchange with the adjacent sea area played the major role in flushing.

The seabed biomass in the estuaries studied was dominated by molluses, often >80% of total bottom biomass. Dominating bivalves were Mytilus edulis, Cardium edule and Mya arenaria, all filter feeders. Such suspension feeding bivalves can be very efficient consumers of primary production (algae): Gerritsen et al., 1994, showed that more than 50% of annual algal production can be consumed by such populations. In the shallow Danish estuaries, frequent wind mixing of the water is also likely to make algal production rapidly available to the seabed filter consumers.

The benthic biomass of these estuaries was thus considered to be a good indicator of secondary production. This biomass was compared to the nutrient supply as indicated by the total calendar year nitrogen load (Ntot), to this total corrected for export out of the estuary during the four non-productive winter months (NA) and to the nutrient pool available for the spring bloom at the beginning of March (N_{SBNP}).

Response to nitrogen loadings

Benthic biomass clearly increased with the total nitrogen loading up to around 35 gN/m²/year, but above that level showed some tendency to decrease. Secondary production showed a similar pattern, whereas the density of individuals did not show a clear trend.

Clearance times (based grazer biomass and literature feeding rates) were significantly higher than the water residence times for most of the estuaries and total benthic biomass was shown to be quantitatively coherent with the total nitrogen load, assuming a 20% efficiency of transfer. Comparisons suggested that the biomass yield (secondary production : nutrient loading ratio) was higher in estuaries with a lower nutrient load and higher water residence time, and lower in estuaries with higher nutrient loads and shorter residence times.

When corrected for residence time, the benthic biomass was proportional to the estimated nitrogen pool available for the spring bloom (N_{SBNP}).

The authors conclude that the studied data's most clear signal is the positive effect on benthic grazer biomass of increasing nitrogen loadings to the estuaries, over a wide range of loadings $(2 - 200 \text{ gN/m}^2/\text{year})$. They suggest that this is probably the result of increased phytoplankton production resulting from the increased nitrogen loading, although the data do not provide evidence for this, and note that the relationship between grazer biomass and N-loadings found in this study have nearly the same slope as literature values for the relation between N-loadings and primary production (Nixon et al., 1996).

The study suggests that increased nutrient loadings will often not result in adverse effects of eutrophication or ecosystem disfunctioning in relatively well-flushed estuaries. The authors indicate that similar results were obtained by Balls et al., 1995, who showed that a Scottish estuary with a residence time similar to the Danish estuaries studies here (around 5 days) showed no increases in chlorophyll levels despite a 5-fold increase in nutrient loadings over 30 years.

The study does not, however, provide information as to which of nitrogen or phosphorus is the limiting nutrient, because of the strong intercorrelation between their respective loadings.

"Nutrient retention by benthic macrofaunal biomass of Danish estuaries: importance of nutrient load ans residence time". Estuarine, Coastal and Shelf Science 50, pages 205-216, 2000. A. B. Josefson, B. Rasmussen, National Environment Research Institute, PO Box 358, DK-4000 Roskilde, Denmark. <u>Email : aj@dmu.dk</u>

SWITZERLAND

Using ponds as nutrient traps

The Swiss lake of Sempachersee near Lucerne lies in an intensively farmed countryside. The nutrient load to the lake has led in the 1970's and 1980's to an increase in lake phosphorus concentration, reaching 165 mgP/m³ in 1985. Concerted actions to reduce the load (including tertiary sewage treatment and advice to farmers) and actions in the lake itself (forced water circulation and oxygenation of deep waters) succeeded in reducing lake phosphorus concentrations to below 50 mgP/m³ today, but this concentration still needs to be reduced by a further approx. 50% to restore the lake to a mesotrophic status.

The installation of retention ponds in the catchment area of the lake is one measurement to achieve this objective through the nutrient retention function of these artificial wetlands. With the sewage treatment and land management measures already in place, the phosphorus load to the Sempachersee has been brought down to an estimated 15 tonnes/year, but the objective of reducing it further to 11 tonnes/year has been defined. **To achieve this goal, it will be necessary to prevent the phosphorus loading from the farmland around the lake from reaching the lake water.**

In an initial study in 1998, 24 potential sites for the installation of retention ponds in the "Kleine Aa" river basin were identified. In 1999, work started on the pond at Sonnhof. A second pond was installed at Hungerbühl near Neuenkirche in 2000 and a third is currently in the planning stage. The Sonnhof pond is situated at the point where drainage and surface water of 20 ha of farmland flows into the river. Two cascading ponds result in two artificial pools of around 2,400 m² total area and a maximum depth of 100cm. The water flows from the upper pool over a sand dam into the lower pool. The construction of the two ponds using a sand dam enables them to function as filter, with the water moving through them during low flow periods.

The pond system is designed to ensure a retention time of 10 days, which is sufficient for the natural processes (plant, phytoplankton and microbial growth) to absorb both phosphorus and nitrogen from the inflowing surface and drainage water. Microbial activity makes the largest contribution to absorbing phosphorus, which is then transferred to sediments by settling and stabilised by natural chemical reactions.



Sohnhof nutrient retention pond

Natural habitats

As well as acting as a nutrient retention system, the ponds create wetland areas which are of significant local interest as natural habitats. This is particularly true in this area of Switzerland where intensive agriculture and the drainage of natural wetlands has severely affected many amphibians and other wetland species. The ponds also add diversity to the agricultural countryside. The artificial wetland also plays an useful role in local water management, both contributing to the replenishment of underground water supplies (by providing a surface of water for all year round downward infiltration) and by reducing peak spate flows (at their usual water level, the ponds offer an available retention volume of around 550 m³).

"Ponds for nutrient retention" (Nährstoffrückhalt mittels Retentionsweihern), UFA Revue 10/00. Rolf Heinrich, Schattweid Ecology Centre, 6114 Steinhuserberg, Switzerland and Josef Blum, Office of Ecology 6210 Sursee, Switzerland. Email : josef.blum@lu.ch

WHOLE-LAKE EXPERIMENTS

Respiration rates vary with zooplankton populations

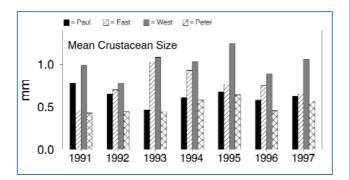
Four small lakes situated near Land O'Lakes, Wisconsin (46°N, 89°W), each with an area of <4 ha and an average depth of 4-6m, were studied over 7 years (1991 to 1997). Different parameters were measured weekly over the summer season and the annual average taken for each lake, giving 4 lakes x 7 years = 28 data points for analysis.

Paul: One lake (Paul Lake) served as a "control" (unmanipulated) ecosystem. This lake has a single fish species, largemouth bass (Micropterus salmoides).

Peter: At the start of the seven year period, and subsequently as necessary to maintain populations, Peter Lake was stocked with a high density of several species of planktivorous fish (predators of the crustacean zooplankton which graze algae), and piscivorous fish were removed from this lake.

East and West: The other two lakes were created by dividing Long Lake (using a rubber curtain) into two independent ecosystems, see description published by Carpenter and Pace, 1997, reviewed in SCOPE n°36 pages 3-4. In West Long Lake, existing populations of piscivorous fish were reinforced by stocking (thus suppressing planktivorous fish), whilst in East Long Lake DOC (dissolved organic carbon) concentrations increased and the water became darkly stained, leading to very low fish populations.

As a consequence of these manipulations of fish populations, the mean size of crustacean zooplankton (which graze algae) was greatest in West Long Lake, generally somewhat higher in East Long Lake than in the "control" Paul Lake, and lowest in Peter Lake.



From 1993 onwards, in Peter, East and West Long lakes, nutrients were added (soluble phosphorus and nitrogen), with nitrogen in excess (N:P ratio > 30). Phosphorus loadings in the three fertilised lakes, after 1993, were thus increased to $50 - 200 \ \mu molP/m^2/day$ (comparable to eutrophic lakes), compared to around 10 $\mu molP/m^2d$ in the unfertilised Lake Paul.

Respiration measurement

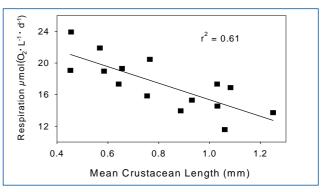
Respiration was measured by the "dark bottle method". This consisted of filling (four duplicate) 300 ml opaque bottles in the surface layer of lake water (depth approx. 1m) at around 13h00-15h00 and then leaving them immersed near the lake surface for 24 hours. Dissolved oxygen concentration was measured initially (at the time of collection/immersion) and after the 24 hours, and the difference used to calculate the amount of oxygen being taken up (per litre per day).

Mean oxygen consumption for the different lakes varied from 7 to 25 μ molO₂/l/day, so that the changes of concentration in the bottle were always well above the analytical detection limit.

Other parameters monitored included chlorophyll-a concentration at various depths, primary productivity (measured by 14C uptake), bacterial abundance (acridine orange dying then counting), bacterial production ([3H]leucine incorporation into protein), DOC concentration and mean crustacean zooplankton size (biomass-weighted average size in samples from 80µm net hauls).

Response to nutrients and limiting by zooplankton

Respiration was relatively low in the unfertilised lakes (Paul Lake , and the other lakes before 1993) at around 8.5 μ molO₂/l/day, and was in this case correlated to dissolved organic carbon (DOC) concentrations. Nutrient addition caused an increase of respiration to a range of 12 - 25 μ molO₂/l/day, but with significant differences as a function of variations of crustacean zooplankton sizes.



In Peter Lake, respiration rates appeared to continue to increase with higher nutrient rates, whereas in East and West Long Lakes, respiration rates "platformed" (asymptote), not increasing for nutrient loading increases above 50 µmolP/m²/day. The platform maximum of respiration rates was higher in East Long Lake (at around18 µmolO₂/l/day), with its somewhat smaller average zooplankton size, than in West Long Lake (around 14 µmolP/m²/day). Zooplankton grazer populations thus appeared unable to control algal and bacterial development (as measured by respiration) in the nutrient-loaded lake where they were subject to high predation pressure from high densities of small fish (small-bodied zooplankton size); whereas in the lakes with lower fish predation, respiration "platformed" at levels which were a function of average zoolankton size and not of nutrient loading (larger average zooplankton size, lower "platform" respiration level).

Respiration was also shown to be positively correlated to primary production, phytoplankton biomass (chlorophyll-a) and bacterial production, but to be independent of dissolved organic carbon concentrations in the fertilised lakes.

"Effects of whole-lake manipulations of nutrient loading and food web structure on planktonic respiration". Canadian Journal of Fisheries and Aquatic Science n° 57, pages 487-496, 2000. Figures reproduced with permission of the Journal. M. Pace, J. Cole, Institute of Ecosystem Studies, Millbrook, NY 12545, USA. Email : pacem@ecostudies.org The SCOPE Newsletter is produced by the CENTRE EUROPEEN D'ETUDES DES POLYPHOSPHATES, the phosphate industry's research association and a sector group of CEFIC (the European Chemical Industry Council).

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- Agriculture as a source of phosphorus transfer to water: sorces and pathways. Phil Haygarth, Scope Newsletter N°21 special edition, June 1997 (Reprint).
- Shallow lakes biomanipulation and entroplication. Brian Moss. Scope Newsletter Nº 29 special edition 1998 (44 pages)
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A study of 12 tributaries and the Paimionjoki river Finland show that concentrations of nutrients are correlated with the percentage of land under agriculture, whereas suspended solids are related to the average slope.

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Model calibration using mesocosms

A structural dynamic model of nutrient – algae – zooplankton – fish interactions was calibrated using mesocosm experiments and indicates that differences in species composition of zooplankton populations can significantly modify ecosystem response to management actions.

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Flow conditions and stream eutrophication

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A marine nutrient cycling model explains why nitrates generally limit immediate phytoplankton growth, whereas phosphorus inputs control longer-term productivity.

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Ocean ecosystems primary production is fuelled with limiting nutrients by preferential recycling loops for nutrients.

FEBRUARY 2001

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A comparative study of 1985 and 1995 shows the influence of weather and internal phosphorus loads on Loch Leven's water quality.

STREAM ECOLOGY

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Nutrient diffusing substrata experiments show that benthic algae in the Leet Water, Scotland, are not limited by nutrients in summer, but probably by light or grazing.

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The liquid fraction of pig manure was separated using straw as a filter and struvite was precipitated after anaerobic digestion.

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In agronomic pot trails using the vegetable Komatsuna, struvite recovered from sewage gave fertiliser results comparable to superphosphate fertiliser.

BOOK REVIEW

SHOCKING

The biography of Phosphorus

A book worth reading: "The Shocking History of Phosphorus" – a fascinating telling of the element's animated true story, from its discovery through to its uses today.

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International Phosphorus Transfer Workshop (IPTW) 2001

Connecting Phosphorus Transfer from Agriculture to Impacts in Surface Waters

28 August to 01 September 2001, Plymouth, Devon, England

The SCOPE Newsletter wishes to publicise a 3.5 day workshop focussing on the problems of phosphorus (P) transfer from agricultural land and its effects on water quality. This workshop follows on from those held at Johnstown Castle, Ireland (1995) and Greenmount College, Northern Ireland (1998). The format will comprise 3 'indoor' morning sessions to establish the international science base, combined with 3 afternoon 'field' sessions to discuss examples of local problems in South West England. The final workshop session will focus on considering issues relating to scaling up, and options for mitigation based on discussions from the preceding sessions. It is intended that this workshop will be multidisciplinary and therefore agronomists, aquatic ecologists, chemists, hydrologists and soil scientists are all encouraged to participate.

Information (poster and paper submission, registration) : Jo Chisholm, IGER North Wyke, Okehampton, Devon, EX20 2SB, UK. Tel + 44 1837 883503 Fax: +44 1837 82139 email: <u>IPTW.2001@bbsrc.ac.uk</u>, web page <u>http://www.iger.bbsrc.ac.uk/igerweb/Nwnew/IPTW/IPTW2001.htm</u>

5th International Conference :

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Towards coastal zone management that ensures coexistence between people and nature in the 21st century : an opportunity for defining new environmental protection policy for the new century

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Enclosed coastal sea regions are susceptible to poor sewage dispersion and other environmental pollution and require special conservation efforts. However, most such areas across the world are continuing to be degraded.

Information : Masahiko Inatsugi International EMECS Center, Kobe, Japan

> Email: 2001@emecs.or.jp web page <u>http://ww.emecs.or.jp</u>/

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NUTRIENT MANAGEMENT

FINLAND

Land use and nutrient loads

Data for the concentrations of nutrients (20 sampling surveys for total phosphate TP, soluble reactive phosphate SRP, total nitrogen, ammonium nitrogen and nitrate+nitrite nitrogen) and of suspended solids were analysed at the outlets of 12 tributaries of middle and lower reaches of the Paimionjoki river, in the South-West tip of Finland, as well as at 22 sites in the main river, principally just up- and downstream of the tributary outlets. The river basin has a total area of 1088 km² and the 12 tributaries have basins with areas in the range 9 - 137 km² (accounting for around 66% of the total middle-lower Paimionjoki river catchment area).

Concentrations were analysed rather than total nutrient loads in the river, because reliable flow data were not available site by site. Most of the river flow, and most of the nutrient transport, occurs during the spring snowmelt, with occasional snowmelt in winter and some transport with autumn storms. During summer dry periods, there is near zero flow in the river. The 20 sampling surveys were usually carried out during wet periods, so that the average flow at the sampling times was twice that of the period concerned (1989-1994)

The river's catchment is mainly intensively cropped agricultural land (particularly spring cereals and rape), with 50% of the remaining land being forests. The agricultural topsoil is mostly clayey, with some fine sands and silts. Five municipalities discharge purified sewage into the river, but the largest source is the municipality of Paimio which discharges at the mouth of the river where it enters the Baltic. These municipalities have nutrient removal installed and, upriver of the Paimio discharge, 85% of anthropogenic phosphate discharges come from field cultivation, 8% from animal husbandry and only 5% from sewage discharges (population around 8,000).

Topsoil phosphorus status in the tributary catchments varied from 7.3 to 13.9 mg/l (acid ammonium acetate extraction). The % land use under agriculture (% fields) and the average field slope was estimated for each tributary catchment using National Land Survey data. The % fields in the 12 catchments varied from 23 - 62% (overall average 44%) and the average slope from 0.6% - 1.2% (overall average 0.8%).

The concentrations of the different forms of nutrients and suspended solids were compared with three different variables : tributary catchment area, % fields and average field slope. These three variables were not correlated with each other.

Phosphorus run-off, field area and slope

Most of the phosphorus in the tributary outlets was in particulate form $(190 - 440 \ \mu gTP/l \ but \ only \ 13 - 42 \ \mu gP-SRP/l)$ and levels of total phosphorus (TP) correlated

closely to levels of suspended solids. TP, soluble reactive phosphorus (SRP) and suspended solids (not significantly) all increased with higher field %. Total phosphorus and suspended solids, but not SRP, were higher in tributaries having high field slopes. Suspended solids was the only variable which correlated only with slope. The only variable explaining variations in total nitrogen and NO_X-N was field percentage, whereas NH₄-N correlated only with catchment area.

Suspended solids and TP levels in the main river channel showed similar patterns to those in the tributaries, with relatively low levels at the uppermost sampling site (area with low field percentage, around 35%), rising in the middle reaches (high field percentage at 56%) and falling again in most of the lower river (lower field percentage, 40%).

The authors note that in all the tributaries the main sources of nutrient loading were cultivated fields and forests and that the load from agricultural land in Southern Finland is around ten times that from forests (Rekolainen, 1989).

The relation between field slope and suspended solids and total phosphorus levels is in accordance with field scale measurements reported in the literature. Soluble phosphorus concentrations are however harder to predict, as run-off is related to soil phosphorus status and waters also receive inputs from animal husbandry.

Catchment size effect

The literature indicates that total phosphorus loading per hectare from agricultural land tends to decrease with increasing catchment area, whereas the loading per hectare remains constant for forested catchments of different sizes (Walling 1977, Prairie and Kalff 1986). The data presented in this paper, however, do not show such an effect : total phosphorus and suspended solids levels appear independent of, whereas soluble reactive phosphorus increases, with catchment size.

Also in contrast with the literature, the authors note that their data – in particular the increase in SRP concentrations with catchment size - suggest that SRP is released from particulate forms (in TP) in the river. They estimate that in the main river channel 2.6% of particulate phosphorus (TP – SRP) was released to SRP.

The authors tentatively conclude that although erosion control in sloping fields may be useful to decrease water turbidity and total phosphorus run-off, this may not significantly reduce soluble reactive phosphorus levels, and thus the nutrient concentrations actually available for algae.

"Relationship between catchment characteristics and nutrient concentrations in an agricultural river system". Wat. Res. vol. 34, n° 15, pages 3709-3716, 2000.

P. Ekholm, K. Kallio, S. Salo, O-P. Pietilainen, S. Rekolainen, Y. Laine , M. Joukola, Finnish Environment Institute, PO Box 140, 00251, Finland.

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EUTROPHICATION

Model calibration using mesocosms

Four 4m diameter, 0.85m deep artificial ponds were used as mesocosms in 8 - 10 week experiments to measure material balances and interactions between nutrients, algae, zooplankton and planktivorous fish and thus to calibrate and verify a structural dynamic model of shallow, eutrophic aquatic ecosystems. The model considered two types of algae (blue green and non blue green), three different groups of zooplankton (rotatoria, cladocera and copepoda) and a single species and size of fish (crucian carp carassius sp.).

Eutrophied lakes often fail to respond to reductions in nutrient inputs or the recovery process tend to be very slow. Biomanipulation, by measures such as removing fish populations, are often used to try to accelerate lake restoration. The authors indicate that manv biomanipulation projects have failed to have the anticipated results and that one reason may be unexpected changes in algal and zooplankton (grazers of algae) species composition. A model which could help predict species composition changes could thus be a useful tool for surface water management.

A number of structural dynamic models have been calibrated using biomanipulation and observations of lakes (eg. Janse *et al.* 1992, Nielsen 1994, Jayaweera and Asaeda 1996), but these data are highly variable because of ecosystem complexity. Rose *et al.* 1988, on the other hand, calibrated a multispecies algae – zooplankton model using laboratory scale "microcosm" systems. The authors indicate that the "mesocosm", an intermediate scale artificial system, is a more realistic proxy of real lake ecosystems, and also offers a large enough scale to include fish.

Modelled interactions

The authors defined a complete mixing, one box model of carbon, nitrogen and phosphorus flow dynamics in the water column and included two different types of algae (blue green and non blue green), three different types of algae-grazing zooplankton (rotatoria, cladocera and copepoda) and one type of planktivorous fish. Carbon, nitrogen and phosphorus masses in each of these biota compartments, in detritus, soluble form and sediments thus appear as variables. Other factors included light and temperature. The model defines the equations for flows between these different compartments, as a function of growth, respiration, non predatory mortality, and the different predation interactions.

Mesocosm observations were obtained from four outdoor, shallow, artificial ponds of just over 4.0 m³, situated in the Shizuoka Prefecture (around 200 km from Tokyo), Japan. These were filled with well water and with 0.4m depth of highly eutrophied sediment, then subjected to filtered daylight and to natural rainfall. The ponds were stabilised for around 5 months, then fish (crucian carp *Carassius sp.*

of 8-10 cm) were introduced to two of the four ponds. Experiments were carried out from 30th July to 13 October 1997, then from 4th November 1997 to 12th January 1998.

During the stabilisation period the ponds were nitrogen limited, so the experiments were started by adding ammonium sulphate as a nitrogen source over a number of days. At weekly intervals, samples were taken and the levels of carbon, nitrogen and phosphorus in the different compartments (algae, zooplankton, soluble in water ...) were assessed (either by direct measurement or using conversion ratios from measured data), as were algal and zooplankton populations. Fish weight was measured at the start and end of the experiments in which they were present.

Mesocosm results

In the different mesocosm experiments, different zooplankton groups became dominant. This enabled model parameters defining the dynamics of different algal and zooplankton types to be stepwise calibrated using three of the experiments. The model was then validated by comparison with the results of two other experiments.

The parameters concerning the no-fish situations showed a relatively good correlation with the validation experiments (Pearson's coefficient around 0.9) whereas in the mesocosm with fish the correlation was poorer (around 0.6), showing that the system with fish was more difficult to model. This was maybe because of the variation in fish species and size in real ecosystems.

The model was also used to simulate biomanipulation by fish removal. This suggested with a rotataria dominated zooplankton population, higher fish biomass levels led to lower algal growth rates, but higher final algal biomass. With a cladocera dominated zooplankton (eg. *Daphnia*) the algal growth rate was not greatly affected by increased fish levels, but the final algal biomass decreased significantly. The authors conclude that this shows that zooplankton species composition considerably influences the effects of biomanipulation actions.

The authors note however that their model shows some limitations, in particular the simplification of the algae into just two types (blue green and other). Also, the model was parametered on the basis of the mesocosm results, where *Ankistrodesmus* was generally the dominant non blue green algal species, whereas in eutrophied water bodies blooms of diatoms and of colonial blue greens (eg. *Microcystis*) are problematic. Certain blue greens are inedible, or are toxic for most zooplankton, but not for some rotatoria, and the model does not take this effect into account in predicting zooplankton species balance. They also note that the model does not take account of macrophytes which can play an important role in zooplankton growth.

"Modelling the structural dynamics of a shallow and eutrophic water ecosystem based on mesocosm observations". Ecological Modelling 128, pages 221-243, 2000.

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NEW ZEALAND

Flow conditions ans stream eutrophication

Data concerning dissolved nutrient concentrations (SRP, phosphorus; SIN, nitrogen), mean and maximum chlorophyll concentrations (indicative of levels of algal development, mg chl.a/m²), dominant algae (taxa) and the mean time between spate flow events with flows >3x the median (days of accrual d_a) were collected from 30 sites on 25 New Zealand streams and rivers.

Data was collected monthly for 13 - 19 months. All the streams and rivers studied flowed from upland watersheds (but not greatly affected by snowmelt), and were without significant point pollution sources, shading, lake or spring inflows. They represented nonetheless a variety of catchment land use and climate patterns.

The mean monthly chlorophyll levels at the different sites (mean of the 13-19 monthly measurement for each site) varied from 0.73 to 81 mg chL_a/m^2 , with site maxima ranging from 9.1 to 396 mg/m².

The stream flow regime, as indicated by the average time between spate flows (da), explained more variation in both average and maximum chlorophyll levels than did nutrient concentrations. This confirms earlier work (Biggs and Close, 1999).

The average time d_a between spate flows (flood events where the flow exceeded 3x the median) explained 40% of the variation in mean chlorophyll levels, and a quadratic function of d_a explained 62% of the variation in maximum recorded chlorophyll levels. Log-log correlations with nutrient concentration were significantly lower than with d_a .

r ²	values for correlations with log mean chlorophyll levels :				
	d_a	->	0.397		
	SIN (nitrogen)	->	0.122		
	SRP (phosphorus)	->	0.226		
r ²	values for correlations with log maximum recorded chlorophyll levels :				
	$(d_a)^2$	->	0.618		
	SIN (nitrogen)	->	0.325		

Multiple regression models of algal biomass as a function of both days of accrual and nutrients were used to construct 'Vollenweider' type nutrient loading nomographs for streams. These can be used to predict oligotrophic, mesotrophic and eutrophic conditions as a function of nutrient concentrations for different flow regimes. These are the first eutrophication models to be developed for gravel bed streams.

The frequency of algal blooms (chl_{-a} >60 or 200 mg/m²) was also best explained by the average time between spate flows, with nutrient concentrations showing a relatively low correlation. Nomographs were also developed to predict the frequency of algal blooms. The results indicated that in streams with little variation in the flow regimes, a small increase in nutrient concentrations may greatly increase the frequency of algal proliferation incidents, whereas in streams with more frequent spates dissolved nutrients have little effect as algae are regularly flushed away.

Significant differences in algal taxa were not noted between sites with varying nutrient concentrations and successional patterns are difficult to predict.

Management strategies, in particular flow variation

For streams with little flow variation ($d_a > 50$ days), the author suggests that to prevent algal biomass reaching 200 mg chl._a/m² (boundary suggested by Dodds *et al.*, 1998), **nutrient concentrations must be held very low** (approximately 20 mg/m³ SIN and 2 mg/m³ SRP). These levels are coherent with other published work using trough experiments.

However, shading by bank vegetation or sand-silt stream beds can significantly reduce algal development (the streams in this study all had no shading and gravel beds).

The author concludes that although the target nutrient concentrations suggested for streams and rivers with infrequent spates may be too low to be practically achievable in catchments with agricultural activities, any reduction in nutrient loading should lower the frequency of algal blooms. This can be achieved, for example, by creating strips of buffer vegetation between fields and river banks. Where streams or rivers are dammed or flows modified by weirs, **artificial variation of the flow regime will generally be the most effective way to avoid algal development**.

"Eutrophication of streams and rivers: dissolved nutrientchlorophyll relationships for benthic algae". Journal of the North American Benthological Society, 19(1) pages 17-31, 2000.

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AQUATIC ECOSYSTEMS

MARINE NUTRIENTS

Nitrogen or phosphorus limitation?

The author develops a simple model of nitrogen and phosphorus cycles, including a representation of the competition between nitrogen-fixing (eg. cyanobacteria) and other phytoplankton (algae), in order to look at how marine waters react to external nutrient inputs. The model proves to be convergent and robust, and is used to explain why, on the one hand, the limiting nutrient in coastal waters often appears to be available nitrogen (nitrate inputs cause algal development), but on the other hand longer-term primary marine productivity is controlled by phosphorus.

The model treats the marine environment as a simple twobox system : surface waters and deep waters. The phosphorus cycle is modelled using six simple pathways : 1) external inputs of phosphorus to surface waters; 2) biological assimilation of available soluble phosphorus by phytoplankton in surface waters; 3) subsequent release of phosphorus back into surface waters by grazing, phytoplankton death, cell breakdown and bacterial degradation; 4) release of phosphorus into deep waters following the sinking of organic matter; 5) slow mixing of surface and deep waters by currents and diffusion; 6) loss of phosphorus to the ocean floor by sedimentation.

The nitrogen model is somewhat more complex because of the additional possibility for certain phytoplankton to "fix" dissolved nitrogen N_2 into organic forms and for denitrifying bacteria to convert nitrate back to N_2 .

Marine phytoplankton which are able to fix nitrogen have a competitive advantage when reactive nitrogen is scarce, but are at a disadvantage when it is abundant, because of the high energy requirement necessary for nitrogen fixation. This is modelled by giving the nitrogen fixing phytoplankton a lower growth rate. Both sorts of phytoplankton are given the same mortality rate (20% per day).

Convergent model

The model thus has six variables : surface and deep water concentrations of soluble phosphorus, surface and deep water concentrations of reactive nitrogen, and surface populations of nitrogen fixing and non nitrogen fixing phytoplankton.

Six equations (one for each variable) include representations of the pathways indicated above for the phosphorus and nitrogen cycles : 1) riverine and atmospheric inputs of nutrients to the ocean; 2) phytoplankton nutrient uptake (growth); 3) release of nutrients by death and decomposition; 4) sedimentation; 5) mixing of deep and surface waters; 6) phytoplankton N_2 uptake (N_2 -fixation), and (7) loss of reactive nitrogen by denitrification.

Nitrogen fixation homeostasis

The solution of theequations for the 6 variables is shown to converge to a stable steady state from a wide variety of initial variable values.

Sensitivity analyses show that the convergent nature of the model is not dependent upon tuning the parameter values. In fact, the model is homeostatic because of its inherent behaviour as regards nitrogen fixation. If reactive nitrogen concentrations increase, non N_2 -fixing phytoplankton will after some time out-compete N_2 -fixers, thus reducing nitrogen fixation. If they decrease, nitrogen fixers will develop, increasing nitrogen fixation, thus again counteracting the change.

P and N inputs

In any steady state, reactive nitrogen will be more limiting than phosphorus, in order to compensate for the nitrogen fixing phytoplankton's inherent competitive disadvantage (lower growth rate or higher energy requirements), because they would otherwise be progressively outcompeted, thus reducing nitrogen fixation, until a reactive nitrogen limited system appeared.

This explains biologists' observations that nitrate additions to bottle samples taken from nutrient-poor marine surface water generally results in phytoplankton growth whereas phosphate additions do not.

Increased phosphorus loads, on the other hand, will generate a deficit of reactive nitrogen and enable nitrogen fixing phytoplankton to develop. This will mean an increased overall total input of nitrogen to the system, matching the increased phosphorus input. This will enable, over the longer-term, an increase in primary productivity.

Other authors have suggested that the low reactive nitrogen levels in marine waters may be due to deficits of trace metals, in particular iron, necessary for nitrogen fixing phytoplankton. This model suggests that the reactive nitrogen deficit is structural and persistent, even without such factors.

Management implications

The author concludes that nitrate removal from sewage may be useful to address local "end of pipe" eutrophication problems, but that as a general rule it is phosphorus inputs to marine systems which will control algal growth. This means that phosphorus removal from sewage, rather than nitrate removal, should be the priority where eutrophication problems over areas such as enclosed seas (such as the Baltic) and restricted circulation coastal bays are at issue, but also that it is phosphorus inputs to marine systems which are likely to limit fishery productivity. The model indicates that P inputs may control eutrophication in the long term even where bioassays show lack of N is restricting immediate phytoplankton growth. However these conclusions are likely to apply only where (1) N₂-

fixers (could) exist in the receiving system, and (2) residence time of water in the receiving system is sufficiently long to allow this feedback mechanism to become effective before the water has left the system.

"The relative influences of nitrogen and phosphorus on oceanic primary production". Nature, vol. 400, pages 525-531, 5th August 1999.

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OCEAN ECOLOGY

Preferential nutrient recycling

The uptake of carbon dioxide by oceans is driven by new primary production by phytoplankton, with subsequent settling of organic matter to deep waters providing a "sink" for atmospheric CO₂. The authors' observations in the Baltic Sea and other observations suggest that this process is not necessarily limited by inorganic nutrient availability: preferential recycling mechanisms, and the varying carbon:nutrient ratios of organic matter at different stages of the planktonic food web, may mean that nutrients remain available for phytoplankton primary production causing enhanced carbon fixation.

Primary production by phytoplankton growth produces, through death and decay, particulate organic matter (POM), some of which will sink down from ocean surface layers into deep waters and to sediments, providing a "carbon sink" mechanism for absorbing and long-term sequestering atmospheric "greenhouse gas" carbon dioxide. It has been generally considered that the rate of primary production, and thus of this carbon pump, is limited in the ocean by dissolved inorganic nitrogen or phosphorus, necessary as nutrients for phytoplankton growth.

The carbon:nutrient ratio of oceanic phytoplankton biomass is generally considered to be relatively homogenous at around 106:16:1 C:N:P (that is 6.6:1 C:N) constituting the "Redfield" ratios. However, several investigations suggest that **dissolved inorganic carbon** (DIC) decreases to a larger extend than the corresponding inorganic nutrients nitrate or phosphate. This means that for example the ratio between changes in DIC and changes in dissolved nitrate is higher than the C:N ratio in POM and that primary production may be higher than predicted with respect to inorganic nutrient concentrations and the Redfield ratio.

Decoupling of primary production from nutrient concentrations

The authors cite studies in the North Atlantic (Chipman *et al.*, 1993, Sambrotto *et al.*, 1993) and in Southern Oceans (Karl *et al*, 1991, de Baar *et al*, 1997, Dehairs *et al*, 1997)

where DIC uptake: N uptake ratios significantly exceed the Redfield ratio, despite the ratios measured in the organic matter (POM) remaining close to this ratio.

Analysis of the BATS (US Joint Global Ocean Flux Study Bermuda-Atlantic time-series) data also indicates that **biological uptake of DIC**, occurs even when nutrient concentrations are below the detection limit.

The authors' own data from the Baltic Sea (Thomas and Schneider, 1999, Osterroht and Thomas, J. of Mar. Sys. 25, 33-46, 2000) show that DIC uptake is not related to nitrate uptake, or even to nitrate availability, occurring even when dissolved nitrogen is exhausted. As a consequence, the estimate of Baltic primary production based on nitrate supply (including atmospheric and river inputs and aquatic nitrogen fixation) only accounts for 65% of a carbon-based estimate. This is confirmed by the high oxygen levels (supersaturation) in the Baltic from March to September (indicative of net primary production), despite dissolved inorganic nitrogen being exhausted throughout the months of July – September. The Baltic data also confirm that C:N ratios in the organic material (POM) remain at the Redfield ratio.

These analyses are supported by data concerning the seasonal development of carbon:nitrogen ratios in the Northeast Atlantic (Körtzinger *et al.*, *Deep-Sea Res. I*, 48, 661-668, 2001) and by mesocosm experiments (Banse, 1994) which both indicate that primary production continues to occur even when dissolved nitrogen is exhausted.

In the Sargasso Sea, also, nutrient recycling may explain the discrepancy between levels of production and low nutrient levels (Bates *et al.*, 1996).

The Baltic provides particularly informative data because of the specific behaviour of the intermediate-depth layer of water lying below the (euphotic) surface layer and above the deep water (from around 25m to 65-80m depth). This intermediate layer becomes trapped by thermal stratification during the spring and summer, with no significant exchange of dissolved carbon or nitrogen, and no atmospheric exchange of CO₂. Dissolved nitrate in this layer is reliably around 4-5 μ M at the end of the winter mixing of the sea, but by the summer is completely exhausted. At the same time, however, DIC actually increases, indicating that remineralisation (bacterial breakdown) of organic matter is indeed taking place. The authors suggest that the explanation for this difference between behaviours of nitrate and DIC is that POM (organic matter) sinking into this layer has a significantly higher C:N ratio than the Redfield ratio, because nitrogen is effectively being recycled in the surface water layer (in primary production). This is coherent with other work showing that C:N ratios and nitrogen contents of POM increase with depth.

Preferential nutrient recycling

Droop (1973) suggested a mechanism which might explain preferential nutrient recycling during phytoplankton

growth: cell growth is possible if the carbon:nutrient ratio can be maintained in internal cell organs, and so can be achieved by releasing carbon-enriched organic material (Fogg, 1983). This may explain high C:N ratios observed in the surface waters of the Baltic (Olesen and Lundsgaard, 1995; Matthäus *et al.*, 1998) and in other regions during the productive season.

External mechanisms can also enable preferential nutrient recycling. Studies of algal decay have shown that **organic nitrogen is recycled faster than carbon** (Azam, 1998). Bacteria have a lower C:N ratio than phytoplankton, so that they tend to "leave" carbon-rich particles as a residue of degradation of dead phytoplankton, and these particles will tend to sink. At the same time, if bacteria are grazed by zooplankton, these will excrete nitrogen-rich compounds in order to maintain their own C:N ratio which is higher than that of bacteria. The excreted nitrogen-rich compounds are thus kept in the productive system and enable further carbon fixation by phytoplankton, though they are not considered and detected as inorganic nutrients.

The consequence of these nutrient "recycling" mechanisms is that **net production and in particular** CO_2 fixation is limited by a internal cellular deficiencies of essential components (for example total nitrogen) or by light, (physiological limitation), rather than by inorganic nutrients in the water (systemic limitation). In the Baltic Sea, the contribution of nutrient recycling is estimated as 50% of production. The authors suggest that carbon based estimations of production, rather than nutrient based estimates, should be used to assess the biological CO_2 pump in both regional and global contexts.

"Preferential recycling of nutrients – the ocean's way to increase new production and to pass nutrient limitation?" Limnol. Oceanogr. 44(8), pages 1999-2004, year 1999. H. Thomas, Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstrasse 55, D-20146 Hamburg, Germany. V. Ittekkot, now at: Centre for Tropical Marine Ecology, Fahrenheitstrasse 6, D-28539 Bremen, Germany. C. Osterroht, Institute of Marine Sciences, Düsternbrooker Weg 20, D-24105 Kiel, Germany. B. Schneider, Baltic Sea Research Institute (IOW), Seestrasse 15, D-18119 Warnemünde, Germany.

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SCOTLAND

Lake response to nutrient loadings

Comparisons of the years 1985 and 1995, for Loch Leven, Scotland, show that a >50% reduction in external phosphorus loads did not result in lower levels of phytoplankton development in the lake (chlorophyll concentrations). Total diffuse loads of phosphorus to the lake were estimated at 4.71 tonnes total phosphorus

(tP) in 1995 compared to 8.5 tP in 1985, mainly because of lower rainfall leading to reduced run-off flow (890 mm rainfall in 1995 compared to 1250 in 1985). Point phosphorus sources showed an even more significant reduction (3.28 tP in 1995 compared to 11.6 tP in 1985), through sewage works upgrading and because phosphorus releases from a wool mill had been stopped (6.29 tP in 1985). These reductions in external phosphorus loadings were, however, counteracted by the difference in temperatures between 1985 and 1995, resulting in high levels of phosphorus release from sediments in 1995 (internal loading).

Loch Leven is situated at a latitude of 56° 12' North and a longitude of 3° 22' W in East Scotland. The lake has a surface area of 13.3 km², an average depth of around 4m and a flushing rate of 2.25 volumes/year (1995). The 145 km² catchment has a population of around 12,000 (of whom just under 9,000 are connected to sewage works) and is 75% agricultural, including rough grazing and arable crops, with the remainder mainly being made up of upland moor, coniferous forest and heathland.

1,300 water samples

Sampling methods and sites for 1995 were essentially the same as those used in 1985 by the same authors. Sixteen sites were sampled in seven influents to the lake, while some smaller influents (which had been sampled in 1985 but then proved to only carry in a total of less than 4% of lake phosphorus inputs) were not sampled but instead estimated using 1985 data adjusted with 1995 rainfall. At each site, duplicate water samples were collected every 8 days, giving over 1,300 samples for analysis. For each sample, total phosphorus, total soluble phosphorus and soluble reactive phosphorus were analysed (as well as dissolved silica and nitrate-nitrogen, not reported in this paper).

Stream flows were measured at three continuous gauging sites and by instantaneous measurements when the 8-day samples were taken. In order to correct for short episodes of high flow (which could either be missed by the 8-day measurements or lead to over-estimations of phosphorus loadings by coinciding with a measurement time), the flow estimates were corrected using the continuous flow data to adjust the instantaneous measurements (the variations in flow between the different influents to the lake were demonstrated to correlate closely). In 1995, for example, two of the instantaneous samples coincided with short spells of very high flow. If, for these dates, it was assumed that this level of flow continued for 8 days until the next sample was taken, figures for phosphorus loading for one influent alone would be one tonne higher than if the flow peak was assumed to be short-lived as indicated by continuous flow monitoring at other sites.

Finally, discharge from the monitored influents accounted for 123 km^2 of the total lake catchment of 145 km^2 .

Loading from the remaining catchment area was estimated by comparison to the similar Pow Burn catchment (which was monitored) and direct rainfall input to the lake itself was also estimated.

Point and diffuse sources

Point sources included three sewage works (serving 7000, 1225 and 500 persons), a woollen mill (whose effluent was analysed throughout 1995 to confirm that phosphorus discharge had indeed been stopped) and fish-rearing ponds. Inputs from these sources were assessed both from discharge monitoring and by monitoring the receiving streams both upstream and downstream of the discharges.

One specific diffuse source of phosphorus to Loch Leven is from geese. Around 6,000 pinkfooted (*Anser* brachyrhynchus) and 1,000 greylag (*A. anser*) overwintered on the lake in 1985, contributing 0.37 tonnes of phosphorus. Because this quantity is not significant (<2%of external loadings) it was assumed to have not changed in 1995.

Total phosphorus concentrations in the influent streams unaffected by point sources (or upstream of these) varied from below 10 μ gP/l at the most upstream monitoring points, and 30-50 μ gP/l in streams receiving run-off from areas with little agriculture, to >80 μ gP/l in streams with more intensely agricultural catchments.

Phosphorus source	1985 (tonnesP/year)	1995	1985 (tonnesP/year)	1995
	total phosphorus		SRP	
woollen mill	6.29	0	4.52	0
sewage works	5.32	3.09	3.62	2.60
geese	0.37	0.37	0.18	0.18
fish ponds	-	0.19	-	0.08
diffuse run-off from land	8.13	4.34	3.52	2.13
TOTAL external load	20.11	7.99	8.14	4.99

The external phosphorus loading results show a very significant (near 75%) decrease in point sources, both because of the stopping of phosphorus discharge from the woollen mill industrial point-source and because of upgrading of sewage works, but also a near 50% reduction in phosphorus run-off from land, related to lower rainfall and so lower influent flows.

Differences in weather patterns

Rainfall in 1995 was 890 mm, significantly lower than for 1985 (1,250 mm), resulting in a lower lake flushing rate (2.25 lake volumes in 1995 compared to 2.53 in 1985). Furthermore, the rainfall in 1995 did not show the same distribution over the year as in 1985 : in 1995 the main flow period (resulting in a significant part of the total annual diffuse phosphorus loading) occurred in late January – early February, whereas the highest flows in 1985 were in the early Autumn and in December.

The key difference in the weather patterns, however, was probably the much hotter summer in 1995, when UK summer temperatures were higher than for any year since the 17^{th} century.

The authors suggest that the hot summer of 1995 led to a warming of the lake sediments and thus to the release of soluble phosphorus (internal loading). This is reflected in a significant peak in soluble reactive phosphorus (SRP) concentrations in August-September 1995, giving an annual mean SRP concentration of 19 μ gSRP/l for this year (compared to only 9 μ gSRP/l annual mean in 1985). At the same time, nitrate-nitrogen concentrations fell very low (consumption by algae and denitrifying bacteria) and

considerable algal development occurred.

Algal blooms

The annual mean chlorophyll_a concentration thus reached 34 mg/l in 1995 (compared to only 21 mg/l in 1985), with a very high peak in August. The 1995 algal development was dominated by *Anabaena spiroides* which had not been observed in the lake over the previous 30 years.

In 1985 the annual mean chlorophyll_a concentration related to the measured annual mean total phosphorus concentration in the lake's water according to the "OECD model" and the measured mean total phosphorus concentration (63 µg total P/l) corresponded to expected values calculated from the external loadings and the flushing rates. In 1995, on the other hand, measured mean total phosphorus levels were higher than would have been expected (79 µg total P/l, compared to a calculated value similar to that of 1985) and chlorophyll_a concentrations were higher even than would have been expected by applying the "OECD model" to the measured total phosphorus concentrations. This may be partly explained by an overestimation of chlorophyll_a concentrations in 1995 caused by the accumulation of floating gas-vacuolate cyanobacteria near the lake outflow where samples were taken (these algal species were scarcely present in 1985).

The authors conclude that the hot summer of 1995 and the resulting internal phosphorus loadings (sediment release) effectively negated the predicted effects of a marked reduction in both total and bioavailable external phosphorus loadings between 1985 and 1995. Even after the >50% reduction in external phosphorus loadings

achieved over these ten years, these still exceed the ideal levels for a lake of around 4m depth (OECD 1982), showing that reversing eutrophication trends in Loch Leven going to be a real challenge.

"Poor water quality in Loch Leven (Scotland) in 1995 in spite of reduced phosphorus loadings since 1985: the influences of catchment management and inter-annual weather variation". Hydrobiologia 403, pages 135-151, 1999. © Kluwer Academic Publishers – with kind permission – www.wkap.nl

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STREAM ECOLOGY

Factors limiting algal growth

The Leet Water is a tributary of the River Tweed in Berwickshire, Eastern Scotland (latitude $55\infty45^{\circ}$ N). It has a catchment of around 113 km² and an annual flow range from 0.1-2.4 m³/s in 1996 and 0.1-3.4 m³/s in 1997. The catchment has no upland headwaters and is mainly intensive arable land and is known to suffer from a variety of problems including high soluble phosphate (mean soluble P was 0.78 mg/l in 1996 and 0.20 mg/l in 1997), large diurnal variations in pH and dissolved oxygen, impoverished invertebrate communities and profuse algal and macrophyte growth By depleting dissolved oxygen through nocturnal respiration, high standing stocks of algae can negatively affect sensitive fish and invertebrates and fish mortality in the Leet is common in prolonged warm, dry spells.

An important objective of a recent catchment action plan was to establish whether point source phosphate reductions were having a discernible effect on the trophic status of the watercourse, the effect on algal growth being of greatest concern. If algae are not limited by nutrients, then attempts to control growth by reducing point or diffuse sources will be ineffectual. Therefore there is the need to assess the extent to which the availability of nutrients limits the growth of algae during the summer months. Phosphate concentrations in the stream are highest during the summer months, when dilution is normally at a minimum.

A study was conducted over the summer of 1999 using nutrient-diffusing substrata (NDS) to determine the likely impacts of nutrient additions on algal growth in the Leet Water and in one of its oligotrophic tributaries, the Gala Water (catchment area around 207 km², annual flow range from 0.36-36.7m³/s in 1996 and 0.47-51.97m³/s in 1997, mean soluble P was 0.04mg/l in 1996 and 0.02 mg/l in 1997). Algal response to nutrient enrichment was assessed through analysis of chlorophyll-*a* (an index of algal biomass) extracted from algae scraped from the surface of nutrient diffusing ceramic clay pots after 33 and 34 days

immersion in the waters Leet and Gala respectively. The clay pots were filled with nitrate-N, phosphate-P, N + P, or no nutrients as controls, immobilised by agar.

The experimental approach was validated by measurement of nutrient release rates from P⁻ and N⁻enriched NDS clay pots.

No nutrient limitation

In the Leet water, chlorophyll concentrations on the clay pots did not differ significantly between treatments except for one site where nitrogen was limiting (P <0.05). It therefore appears that algal growth in the Leet Water is limited by other factors than phosphorus, possibly light availability and grazing.

In the Gala Water, on the other hand, algal chlorophyll production was significantly higher on the pots with added phosphorus, confirming that in this oligotrophic ecosystem phosphorus was a limiting nutrient. It is not clear why the nitrogen-only diffusing pots gave lower chlorophyll levels than the control pots in the Gala Water.

In the Leet Water *Cladophora* was most abundant alga, occurring at all sites, followed by *Stigeoclonium*, *Gongrosira* (a crustose form only identified at site 1), and *Enteromorpha*. In the Gala Water only *Cladophora* could be identified, however various gelatinous taxa where also present, especially on nutrient-enriched substrata.

Managing light availability and algae grazers

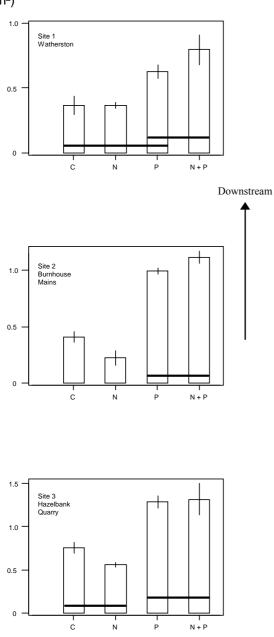
Since phosphorus availability is not limiting the growth of algae in the Leet Water during the summer months, work is needed to establish by how much the phosphorus loading in the river would need to decrease for nutrient limitation to occur. This work is currently in progress. A strategy involving manipulation of riparian areas to restrict light levels, and mechanisms to enhance recruitment of invertebrate grazers and increase their abundance will probably also need to be developed, if further studies suggest that light availability and grazing do indeed limit algal growth in the Leet.

Degraded stream channels with poorly developed riparian habitat exacerbate deleterious effects of residual nutrients via decreased riparian uptake, increased retention time due to siltation and wider channels, and by allowing full sunlight to reach the stream (Barling and Moore, 1994, cited by Miltner and Rankin, 1998). Conversely, high quality habitats with mature, intact riparian zones may ameliorate potential adverse impacts of nutrients by terrestrial assimilation (with export via leaf litter), by reducing sunlight and by reducing clay and silt loads to which nutrients are often adsorbed (Klotz, 1988, cited by Miltner and Rankin, 1988).

Developing streamside vegetation would increase shading of the water, and act as a buffer against diffuse sources of nutrients. The creation of artificial riffles would aid grazer recruitment upstream, with the Lambden Burn tributary as a possible source, by improving the substratum of the Leet Water sufficiently to allow invertebrate grazers to gain a

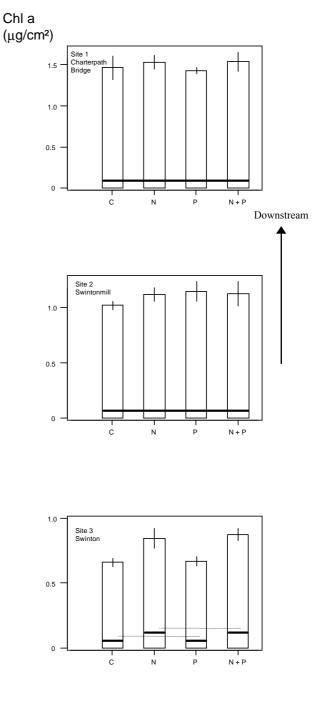
foothold. The effectiveness of an artificial riffle previously installed downstream of the town of Swinton on the Leet will need to be assessed at some point in the future. The aforementioned proposals would act to regulate algal biomass over the medium to long term.





Treatment

Fig. 1. Mean (\pm SE) chlorophyll-a concentration (mg/cm²) on nutrientdiffusing substrata (34-d) after retrieval from the oligotrophic Gala Water (a tributary of Leet Water). C = control, N = nitrate added, P = phosphate added, N + P = nitrate and phosphate added. Horizontal bars link treatments with chlorophyll concentrations that were not significantly different (post hoc t-tests: P<0.05).



Treatment

Fig. 2 Mean (\pm SE) chlorophyll a concentration (mg/cm²) on nutrientdiffusing substrata (33-d) after retrieval from the Leet Water. C = control, N = nitrate added, P = phosphate added, N + P = nitrate and phosphate added. Horizontal bars link treatments with chlorophyll concentrations that were not significantly different (post hoc t-tests: P<0.05).

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PHOSPHORUS RECOVERY AND RECYCLING

RUSSIAN-DUTCH PROJECT

Struvite recovery from pig manures

An integrated treatment system for liquid manure wastes, including several different treatment systems, was tested at the lab scale using flushing effluents from two pig farms in the Moscow and Saint Petersburg regions. More than 100 billion litres/year of such dilute effluents (2-4% total solids) are produced in Russia from medium-large intensive livestock units using flushing techniques for cleaning.

The project looked at different possible phases for the treatment of such wastes:

- use of straw filtration to separate solid and liquid fractions
- anaerobic digestion to reduce the organic load using Upflow anaerobic sludge bed (UASB) reactor
- use of zeolite to remove ammonia from the anaerobic reactor effluent
- removal of ammonia and phosphates from the anaerobic reactor effluent by struvite precipitation
- use of a nitrifying biofilter to treat the anaerobic reactor effluents
- denitrification of aerobic effluents in a UASB reactor

The straw filter at Saint Petersburg contained 15 kg of straw in a $0.52m^2$ cross-section filter. The Moscow set-up filter was around 5x smaller but with similar proportions. After 4 hours, the straw in the Saint Petersburg reactor was removing 97% of suspended solids, 45% of total nitrogen and 75% of total phosphorus from the raw manure flushing effluent. This reflects the relatively high proportion of phosphorus in pig manure which is found in the solid fraction (see SCOPE n° 26, page 6). 60% suspended solids removal was achieved at the Moscow site, where the raw manure flushing effluent was substantially more dilute.

When straw treatment was combined with a UASB reactor (2.6 litre lab scale) organic load (COD) and phosphate removal improved, but ammonia concentrations on the other hand increased significantly, presumably by anaerobic decomposition of proteins in the reactor. Whitish deposits were noted on the reactor walls and in the biogassludge separation device, attributed to the formation either calcite or phosphates, but not analysed.

Ammonia removal

The natural zeolite Urals laumantite (particle size 1-2 mm) was found to remove ammonia efficiently from the anaerobic UASB reactor effluent (effluent concentrations 218-319 mg (N-NH₃⁺)/litre). One volume of zeolite could treat 10 volumes of effluent and achieve, after 4 hours, ammonia concentrations down to 1.5 mg(N-NH₃⁺)/litre.

However, analysis of the saturated zeolite showed it to

contain only 5.3 g total nitrogen per kg, too low a nitrogen content for it to find applications as a fertiliser. One possible solution might be to use nitric acid to regenerate the zeolite for multiple uses and to produce liquid ammonia nitrate fertiliser, but this was not tested.

Struvite precipitation

As well as ammonia, the anaerobic UASB reactor effluent contained 45-59 mg (P-PO₄²⁻)/litre. Phosphate precipitation was tested using pH increases caused by natural ageing, air stripping of CO₂ and by addition of sodium hydroxide. This effluent already had a pH of 7.7 - 8.0 but this could be raised to nearly 8.6 by natural ageing over 3 days and to 9.0 by air stripping for 2 hours.

23% and 7% removal of phosphates and ammonia were achieved by natural ageing; 66% removal of phosphates and 29% removal of ammonia were achieved by air stripping (with 30 minutes being sufficient to achieve most of this reduction). Sodium hydroxide addition resulted in 56% phosphate removal and 41% ammonia removal. Some of the ammonia removal figure would be losses related to the pH increases in all three cases.

Denitrification in an UASB reactor, using COD from the raw manure as a source of organic feed, also proved to be an effective method for treating the nitrified aerobic reactor effluent.

The authors conclude that a combination of the treatment processes studied, plus additional "finishing" nitrogen and phosphorus removal, would be necessary to achieve discharge effluent qualities good enough for release into surface waters.

"Intergrated mechanical, biological and physico-chemical treatment of liquid manure streams". Water Science and Technology, vol. 41, n°12, pages 175-182, 2000 S. Kalyuzhnyl¹, V. Skylar¹, J. Rodriguez-Martinez¹, I. Archipchenko², I. Barnoulina², O. Orlova², A. Epov³, V. Nekrasova⁴, A. Nozhevnikova⁴, A. Kovlaev⁵, P. Derikx⁶, A. Klapwijk⁷.

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POT TRIALS

Fertiliser value of recovered struvite

The results of two series of agronomic pot trials are presented. Both use 5 plants per pot of the green vegetable Komatsuna in phosphorus-poor sandy soil from the Chiba area of Japan. Soil pH was 5.8, so 0.5 mg of calcium carbonate per pot (500g dry soil weight) was added. The first pot trial compared the fertiliser value of 1 - 1.4 mm grain size recovered struvite with that of calcium superphosphate fertiliser, at 100, 200, 300 and 400 mg P_2O_5 per pot (500 g dry weight of soil), and a low phosphate control. The second trial compared three different grain sizes of recovered struvite with calcium superphosphate, with a citric acid soluble phosphate and with a no phosphate control.

In the first trial, three series of pots (each including levels of 100, 200, 300 and 400 mg $P_2O_5/500g$ soil) were compared with a control :

Thus, nitrogen and potassium were effectively both dosed

(mg)	phosphate	nitrogen (as ammonium sulphate)	potassium (as potassium chloride)	magnesium (as magnesium sulphate)
1)	100 – 400 as struvite	made up to 100 (as a function of the amount in the struvite)	100 (in struvite)	57 – 228
2)	100 – 400 as superphosphate	100	100	zero addition
3)	100 – 400 as superphosphate	100	100 added to give same levels as in (1)	57 – 228
control	25 as superphosphate	25	25	zero addition

at 100 mg/500g soil, except in the control where they were both dosed at only at 25 mg.

Sprout and growth rates

The sprout rate was similar for all the pots, but dropped slightly for the very high phosphate application rates of both struvite and superphosphate. The authors conclude that no decrease of sprout rate is observed even for overdosing of struvite as a fertiliser.

Growth rates for the control pot were 17.4 g, whereas for all the other pots they were in the range 24.4 - 29.1g. Growth rates for struvite were the same or better than those for superphosphate without magnesium addition, whereas those for superphosphate plus magnesium were marginally higher (+5 to +8%).

The 4x lower nitrogen and potassium dosing in the control pot make comparisons between struvite and no fertilisation impossible, but these trials do indicate that struvite offers fertiliser effectiveness comparable to calcium superphosphate in the tested conditions.

Struvite granule size

In a second pot trial experiment, in which soil acidity was corrected to a higher extent by the addition of 12g/pot (500g dry weight of soil) of calcium carbonate, three different granule sizes of struvite were compared to calcium superphosphate, fused phosphate (a citric acid soluble but not water soluble phosphate) and to a no phosphate control.

The three phosphate sources were each dosed at 5% and 10% of the soil phosphate adsorption (soil P adsorption was 3070, so that 10% gave 720 mgP₂O₅/500g pot). Nitrogen was dosed as ammonium sulphate at 140 mg/pot for all pots (including the control) except for the struvite

pots (for which the struvite contained respectively 70 and 140g of nitrogen per pot at 5% and 10% doses, and therefore 70g was added to the 5% struvite pots only). Potassium at 100g K₂O and 27 mg of a micro-element fertiliser were dosed in all pots (including the control). Magnesium was dosed as magnesium sulphate at levels equivalent to that present in the 5% or 10% struvite respectively (zero in the control).

The struvite granule sizes used (for both the 5% and 10% doses) were : <0.5, 1 to 1.4 and 1.7 to 2.4 mm diameter.

The results showed no significant growth in the nophosphate pot, and 7 to 23 g/pot growth in the phosphate fertilised pots.

At the 5% phosphate dose, the best growth of all occurred with the small granule struvite ; the medium granule struvite gave growth similar to the calcium superphosphate ; large granule struvite slightly lower. Even the large granule struvite resulted in growth around 2x greater than for the fused phosphate.

At the 10% dose, the growths with struvite were reduced somewhat, so that at this dosage small granule struvite gave results similar to calcium superphosphate, and medium and large granule struvite somewhat lower growth – but still better than fused phosphate. For calcium superphosphate and fused phosphate, on the other hand, the 10% dosage gave better growth than at 5%. This suggests that the lower growths with the different struvite granules at 10% (as compared to 5%) may be because of nitrogen not phosphorus availability (70g of nitrogen as ammonium sulphate was added to the 5% struvite pots, and none to the 10% struvite pots, whilst 140g was added to all the calcium superphosphate and fused phosphate pots).

This interpretation is confirmed by the nutrient uptake

results : phosphorus uptake was higher or comparable for the 5% struvite pots (compared to the 10% struvite dosed pots), whereas nitrogen uptake was slightly (small granule struvite) or significantly lower (medium and large granules).

Magnesium uptake was similar for all pots other than the control (which received no magnesium) and no inhibition of sprouting occurred with either lower or higher phosphate doses for any of the products tested.

Agricultural value

The paper also gives a chemical analysis of the recovered struvite used, which shows nitrogen, phosphorus and magnesium contents close to the theoretical values for struvite, K_2O at 262 ppm, iron at 35 ppm, zinc 56.5 ppm, copper 2 ppm, lead 59 ppm, arsenic 68 ppm, mercury and

cadmium non detectable.

The author concludes that fine granule struvite has a fertiliser efficiency comparable to calcium superphosphate and ammonium sulphate, without increasing soil conductivity, and that the sewage-recovered struvite tested has metal concentrations which are very low and fully compatible with agricultural application.

"Application of phosphorus recovered from sewage plants". Environmental Conservation Engineering vol. 27, n° 6, pages 418-422, 1998 (in Japanese).

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BOOK REVIEW

SHOCKING

The biography of phosphorus

Phosphorus was discovered by alchemists 300 years ago, through the delightful practice of distilling festered human urine. Its name is derived from the ancient Greek words *phos* (for light) and *phorus* (bringing), because of its luminescent properties. Through the centuries, phosphorus has had a chequered history and has been used as a poison, medicine, for making matches, fire bombs, nerve gases, and more recently in fertilisers, human and animal food additives, detergents and in a wide variety industrial chemicals.

The discovery of phosphorus remains surrounded in mystery, but almost certainly occurred in Hamburg, Germany, in 1669. The alchemist Henning Brandt was investigating the "golden stream" (urine) in the hope of finding the "philosopher's stone" which could turn other materials to gold. At a very high temperature, he produced a white liquid which, when solidified in a closed vessel, would continue to shimmer with a moving, cold, pale green light. Brandt kept his discovery secret for 6 years, but finally concluded that it would not create gold for him and began to show its magic luminescent properties to others. However, he continued to keep secret his method of producing phosphorus, and indeed soon sold this secret to another alchemist, Kraft, who used the phosphorus to give lucrative stage shows around Europe's courts.

As a result, other alchemists, in particular Kunckel, also investigated urine and discovered how to produce phosphorus. In addition, Kunckel discovered that phosphorus could be extracted from a wide variety of animal and plant materials.

It is interesting to note that although human urine contains around 1.4gP/day, Brandt's method for extracting the element was so inefficient that he needed 5,500 litres of urine to produce around 120g of phosphorus. The process, as published by Hooke in 1726, had a certain charm in that the urine was left to "steep ... till it putrify and breed worms, as it will do in 14 or 15 days". With hindsight, this attention was quite unnecessary and would in no way increase the level of phosphorus nor facilitate its extraction using heat reduction!

Light of life

Robert Boyle also published in 1680 an account of phosphorus production from urine, and went on to investigate the material's properties, including dissolving it in various oils and in alcohol, and establishing many of its physical and chemical properties.

Because of its characteristic glow and its biological origins, phosphorus became thought of as the "light of life" and so naturally was soon being used as a medicine. This was accentuated when Hensing showed in 1719 that the human brain contains 4gP/kg fresh weight, more than any other organ. Unfortunately, elemental phosphorus, which never occurs in nature, is actually highly toxic, and **its use as a medicine was at best dangerous, sometimes lethal**, and certainly never likely to have any positive effects.

This did not prevent it still being recommended in scientific journals into the 1930's, prescribable in the UK until 1932 and available in over-the-counter products until into the 1950's.

Certain well remembered poisoners, on the other hand, were also well aware of the element's toxic effects, particularly as the poison was not easily detectable, except that sometimes **the victim's bodies would have a ghostly glow in the dark!**

Over the nineteenth century, phosphate compounds also began to be used in medicines, as a way of supplementing the body and the brain's perceived need for phosphorus. These, at least, were not toxic, but would nonetheless be most unlikely to have any positive effect except in the most

improbable case of patients having a dietary deficiency of phosphates.

Only recently have very specific phosphate-containing drugs been developed which are genuinely effective, for example against bone wastage (osteoporosis) in certain medical conditions (bones are made up mostly of calcium phosphates).

The match makers

The phosphorus-based "Lucifer" match was described by the Victorian philosopher Herbert Spencer as "The greatest boon and blessing to come to mankind in the nineteenth century". It is easy to understand why, at a time when heating, cooking and lighting all involved fires or candles, if you try lighting a fire with a tinder box! By 1900, over three trillion phosphorus matches were sold every year.

The first self-igniting matches in the early nineteenth century had used heads of potassium chlorate (KClO₃) and sugar and were ignited by dropping concentrated sulphuric acid onto them, but the latter product was very inconvenient to handle. In 1827, John Walker introduced a self-igniting match based on antimony sulphide (Sb₂S₃) and potassium chlorate, but these were difficult and unreliable until in the 1830's a little white phosphorus was added, to provide an initiator for the flame (protected from oxidation by the other components of the match head, until it was rubbed).

These matches worked very well, indeed rather too well, in that they had a tendency to ignite if rubbed at all, resulting in many accidents. In 1867, for example, the **Archduchess Matilda of Italy was burned to death** after accidentally stepping on a "Lucifer".

This safety issue was resolved when Albright and Wilson in the UK managed to produce commercially the "red" form of elemental phosphorus: unlike white phosphorus, this is stable in air and so could be coated onto the side of the matchbox instead of being included in the match head. The "safety" match thus only ignites if rubbed against the matchbox, not if simply rubbed accidentally.

However, the match factories fast became infamous for exploiting cheap women's and children's labour, working for 60 hours a week or at home for poverty wages, but also for the terrible condition which afflicted the "match girls" who worked in these factories for any length of time: **"phossy jaw".** This phosphorus-caused necrosis would erode teeth and gums, leaving the sufferer in continual pain and with unhealable puss-oozing cavities in the jaw.

Gomorrah

Phosphorus also makes horrifyingly effective war instruments. **Phosphorus bombs** were widely used in World War II. A typical phosphorus bomb weighed around 14 kg, enough to penetrate into buildings when dropped from a height, with a small explosive charge which would scatter burning phosphorus all around. The burning phosphorus sets fire to anything it touches, and even if extinguished with water, will re-ignite as soon as the water evaporates.

In July 1943 phosphorus returned with a vengeance to Hamburg, the city of its discovery. The Allies decided to annihilate the city and its industrial centre. Over 8 nights, some 7,000 tonnes of explosives and 1,900 tonnes of phosphorus were dropped on the city, killing over 37,000 people and reducing it to 40 million tonnes of rubble. On one night, the air flow generated by the rising heat of the burning city fanned flames to a firestorm, an unstoppable raging inferno.

Phosphorus was also the **key ingredient of the nerve gases** developed during the twentieth century, and later in the organophosphorus pesticides which were derived from them. By the end of World War II, the Nazis had manufactured enough of the nerve gas Tabun to exterminate all human life on earth. Fortunately, Hitler wrongly believed that the Allies also had such terrible arms at their disposal and so never used this stockpile. Truly, phosphorus could be "the devil's element".

Essential for life

Over the last half of the twentieth century, many new applications for phosphates have developed, supplied by mining natural deposits of phosphate-rich rock, although the largest use continues to be in agricultural fertilisers and in farm animal feedstuffs. Today phosphorus products are used in agrochemicals, detergents, medicines, food additives, metal treatment, flame retardants and in a whole range of specialist industrial chemicals.

The author emphasises that **phosphorus compounds are essential for the human body (bones, teeth, nerve cells, DNA, muscle and respiratory functions utilise, on average, 2.2 g/day)** and equally for plants. Because of this, and because phosphorus is a limited resource, its stewardship will be a key issue for society's and the planet's future. Recent initiatives towards phosphorus recovery for recycling from sewage and animal wastes are referred to.

Overall, the 300 page book is a most informative, but also extremely interesting read, packed with entertaining stories.

"The Shocking History of Phosphorus – a Biography of the Devil's Element". 2000. ISBN 0-333-76638-5. John Elmsley. MacMillan Publishers, 25 Eccleston Place, London SW1W 9NF, UK.

Why not transform phosphorus burdens in sewage and manures into a valuable raw material ?

Phosphates can be recovered from sewage (either in liquid phases in treatment works, or from biosolids or incineration ash), from manures, and from food industry and other waste streams. Where agricultural reuse of biosolids is not possible, phosphates can be recycled into the fertiliser or the technical phosphate industries.

This conference will provide a forum for the water, animal waste and waste treatment industries to meet the phosphate industries and regulators, in order to assess the economic, environmental, technical and regulatory issues of phosphate recycling. It will bring together scientists and engineers working at the forefront of R&D technologies for calcium phosphate and struvite precipitation processes and for other recovery pathways.

Second international conference on Recovery of Phosphates from sewage and animal wastes 12-13 March 2001 (site visit 14 March 2001)

Golden Tulip Leeuwenhorst conference hotel, Noordwijkerhout, Holland On the coast 25 minutes South-West from Amsterdam International Airport (Schiphol)

<u>Monday 12th March 2001 : 9h30 – 18h30</u> Recovery from sewage : where and why? Technical and economic feasibility of recovery: case studies

Workshops

- implications for the quantity quality and disposal of sewage sludge
- struvite deposit issues and implications of P-recovery for EBNR operation optimisation and bio-P sludge handling
- European and national regulatory issues relating to Precovery and re-use
- possibilities for recovering P from sludges (including iron containing) and from ash
- calcuim phosphate precipitation chemistry and reactor design
- struvite precipitation chemistry and reactor design





<u>Tuesday 13th March 2001 : 8h30 – 17h30</u> Presentations of P-recovery reator operating experiences from Italy, Japan, The Netherlands, Sweden, Australia, Uk Workshops

- economic feasibility of phosphate recovery from sewage
- P-recovery from animal wastes, food factory wastes and other streams
- innovative processes to combine P-removal with Precovery

Conclusions: Priority areas for phosphate recovery R&D and joint development

Wednesday 14th March 2001 : 9h30 – 12h00

Site visit : *operational* Crystallactor® calcium phosphate recovery installation at Geestmerambacht sewage works



Full conference registration : 615 Dutch florins (conference and meals for two days, hotel 2 nights, site visit). **Day rate : 310 Dutch Florins** (for one day including meals)

The Chartered Institution of Water and Environmental Management

Full programme at : http://www.nhm.ac.uk/mineralogy/phos/index.htm

To receive further information, please return the form by fax, post or email : CEEP Phosphate recovery conference – c/o Lidy Groot Conference Events - P.O. Box 83005 1080 AA Amsterdam - The Netherlands - Fax: +31 20 6758236 - Email: phosphates@lgce.nl

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