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# SCOPE NEWSLETTER

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**NUMBER 56**

**June 2004**

## Phosphorus recycling

### Canada

#### **Developing struvite recovery processes**

*Projects underway at UBC, Vancouver, include studying struvite precipitation parameters and reactor operation, testing of two 5m pilot reactors at sewage treatment plants, and work into struvite recovery from animal manure*

### Greenhouse waters

#### **Phosphorus recovery from vegetable growing**

*Beaker tests show that phosphorus can be recovered from waste waters from vegetable growing greenhouses.*

## Nutrients and ecosystems

### Marine iron

#### **Fertilising the sea**

*Dumping iron sulphate into the ocean offers the potential to stimulate primary production and provide a carbon dioxide sink*

### Five lakes

#### **LEEDS phosphorus chlorophyll model**

*Development and testing of the Lake Eutrophication Effect Dose Sensitivity (LEEDS) model shows progress in modelling how phosphorus moves between different forms and compartments, but difficulty in predicting chlorophyll levels.*

### Water body fertilisation

#### **Impact on fish production**

*Additional information on the impact of water body fertilization on fish production, in response to SCOPE Newsletter n°53*

## Conference

### Aquatech 28 Sept. – 1 Oct.

#### **Nutrient management: European experiences and perspectives**

## International Conference

### **STRUVITE: its role in phosphorus recovery and reuse**

**Cranfield University, England,**

**17-18 June 2004**

**Thursday 17<sup>th</sup> June 09:30 -17h00**

**Beneficial reuse of struvite :  
fertiliser value and acceptance**

**Practical Issues associated with P recovery :  
reactor design and operation experience**

**Friday 18<sup>th</sup> June 9h00-17h00**

**Struvite Chemistry & Crystallisation :  
modelling, supersaturation kinetics, interactions  
with other ions**

**Struvite recovery from sources  
other than sewage.**

#### **Venue**

Cranfield University is situated north of London and midway between Oxford and Cambridge. It is close to thriving Milton Keynes, a new town with one of the largest covered shopping centres in Europe, and the historic riverside town of Bedford.

#### **Registration**

The conference registration fee includes: a copy of the proceedings, the coffee breaks, lunch on Thursday and Friday. It also includes the banquet dinner on the Thursday night. Additional places are available for the dinner for accompanying persons.

#### **Participant Fees**

Full delegate                      UK£295  
Student participant              UK£200  
Accompanying Dinner          UK£40  
Accommodation inc. Breakfast – from approx UK£40/night

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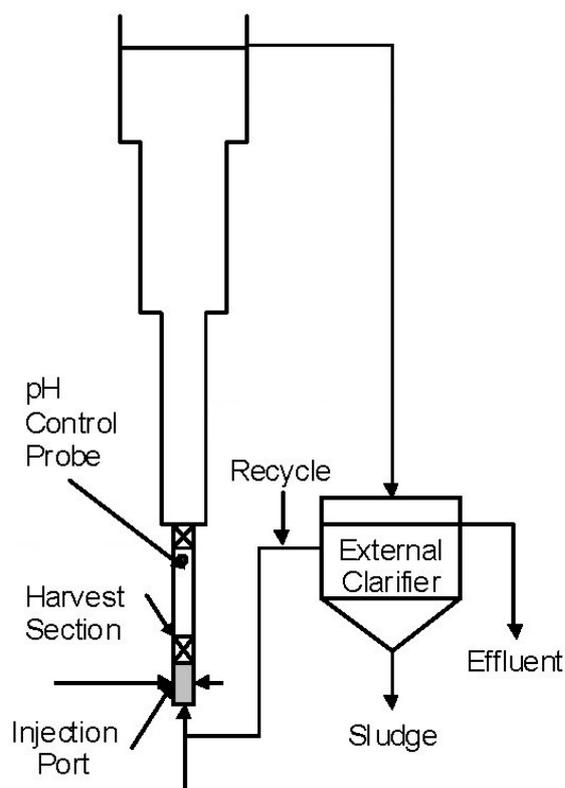
<http://www.cranfield.ac.uk/sims/water/struvite/>

## Phosphorus recycling

### Canada

#### Developing struvite recovery processes

The Civil Engineering Dept., University of British Columbia, has developed since 1999 a R&D programme addressing struvite recovery from sewage and animal wastes. Two initial papers have been published (reviewed here) presenting research into struvite precipitation parameters (in particular, supersaturation ratio), the design of two 5m high 24-28 litre volume precipitation reactors, and initial test runs with pure chemical solutions. A third paper (currently pending publication) presents test runs using the reactors with real wastewater (digester supernatant at Penticton City sewage works, British Columbia, operating biological P-removal). Other projects are also now underway: follow-up work at Penticton, pilot tests at Richmond sewage works (Vancouver), development of struvite recovery from animal wastes.



The two papers published to date present a **proprietary reactor design based on a fluidised bed reactor** with a separate external clarifier (see figure). The reactor was constructed from clear PVC and acrylic pipe, with a stainless steel injection port at the base. The wider sections in the upper reactor resulted in lower upward fluid velocities, allowing settling of precipitated solids (similar principle to previous reactor designs such as [Battistoni et al.](#) and update in SCOPE Newsletter n°49 me to add link, [Mitani et al.](#) (Kurita process), [Nawamura et al.](#), [Ueno et al.](#) (Unitika process) ...)

The **step changes in reactor diameter** (rather than the progressive conical slopes used in the other reactor designs cited above) resulted in turbulent mixing at each transition level.

The lower three reactor sections were fluidised, with the top (widest) section acting as a settling area. An external clarifier was used to trap any fine particles washed over the top of the reactor.

#### Synthetic waste water

In the initial work described in these 2 published papers to date, pure chemical solutions of magnesium (MgCl), phosphate (diammonium hydrogen phosphate 50-90 mgP/l), ammonium chloride and caustic (NaOH for pH adjustment) were used at concentrations comparable to those found in real wastewaters. The reactors were operated for a number of months.

These papers also present 24-hour paddle-stirred laboratory beaker tests carried out to **establish struvite supersaturation factors**, in order to define reactor parameters.

#### pH and magnesium

The studies showed that key reactor control parameters, to achieve reliable phosphate precipitation rates, were pH and Mg/P ratio. With a high level of magnesium addition, over 90% of phosphorus removal from solution could be achieved even at a near neutral pH (pH 7.3). At a Mg/P ratio of 1.4 however, the pH had to be raised to 7.8.

A disadvantage of using high Mg/P ratios is that excess soluble magnesium in the reactor outflow,

returning to the sewage works, could cause nuisance struvite precipitation elsewhere in the works.

### Operating issues

When struvite supersaturation in the reactor was high, plugging problems were encountered in the injection zone. A window of good operating conditional solubility levels was identified. Within these parameters, **no significant loss of fines** from the top of the reactor was encountered. These parameters were similar for lower or higher influent phosphorus concentrations within the range used (see above).

“**Crystal residence time**” (CRT) was defined and identified as a key operating factor, essential for influencing the size and physical characteristics of the precipitated struvite, and thus for the feasibility of its recovery for reuse applications. This differs from previous authors (in particular Battistoni *et al.* see above) who have emphasised hydraulic residence time in the reactor. The Crystal Residence Time is calculated on the basis of bed volume x harvesting rate.

### Recovered phosphate

Both the size and the hardness of the precipitated struvite were very slow to stabilise and both were still increasing after several months of pilot reactor operation. Both these factors are important for the reusability of the recovered phosphate from the reactor (drying, handling ...). With a CRT of 10 days, the average size of the recovered struvite particles was >3mm diameter, and 81 to >90% of the influent phosphorus removed solution was effectively transferred to the harvested struvite (that is, limited loss of fines).

The struvite particles recovered were very hard, facilitating handling. SEM examination showed that they were formed of many tightly aggregated small orthorhombic (wedge shaped) crystals, each covered in minute finer crystals. The authors suggest that the excellent crystal agglomeration achieved in these studies (resulting in the production of relatively large, hard struvite particles and a limited loss of fines) may be the consequence of the high Mg/P ratio and low pH used. According to Bouropoulos and Koutsoukos 2000 (see this SCOPE Newsletter) such conditions give rise to struvite with a low zeta

potential, thus readily agglomerated. It remains to be seen whether this can also be achieved in real wastewater where other mineral ions and soluble organics with varying charges may give rise to interference.

“*Pilot-scale study of phosphorus recovery through struvite crystallization — examining the process feasibility*” *J. Environ. Eng. Sci.* vol. 2, n°. 5, September 2003, pages 315-324

“*Pilot-scale study of phosphorus recovery through struvite crystallization — II: Applying in-reactor supersaturation ratio as a process control parameter*” *J. Environ. Eng. Sci.* vol. 2, n°. 6, November 2003, pages 473-483

A. Adnan, F. Koch, D. Mavinic, University of British Columbia, Dept. Civil Engineering – Environmental Engineering Group, Vancouver, BC V6T 1Z4, Canada.

Journal web site: <http://jees.nrc.ca/>

List of phosphorus recovery theses at UBC:

[http://www.civil.ubc.ca/home/env\\_lab/thesis2003.html](http://www.civil.ubc.ca/home/env_lab/thesis2003.html)

UBC News Article:

<http://www.publicaffairs.ubc.ca/ubcreports/2003/03feb06/sewage.html>

Contacts: [dsm@civil.ubc.ca](mailto:dsm@civil.ubc.ca) and [koch@civil.ubc.ca](mailto:koch@civil.ubc.ca)

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### Greenhouse waters

#### Phosphorus recovery from vegetable growing

Greenhouse vegetable production uses significant quantities of water and fertilisers, with an estimated 20-25% of nutrients in the feed water remaining unused by crops and thus present in outflow waters. Vegetable growers are reluctant to recycle outflow waters in the greenhouse for fear of spreading diseases, so that the nutrient rich discharge waters pose a potential pollution problem.

The authors carried out beaker-scale phosphate precipitation experiments in real greenhouse discharge waters, testing different levels of magnesium addition and pH increase. After addition of the relevant reagents (MgCl<sub>2</sub>, NaOH) the beakers were stirred for one hour at 20rpm at room temperature, then allowed to settle for one hour, followed by analysis of the precipitant and the

supernatant. Mg/Ca molar ratios of 0.3 – 3.6 and pH's in the range 7.5 – 9.5 were tested.

A typical greenhouse vegetable production uses annually 7-8,000 m<sup>3</sup>/ha of water and 8.5-9.5 tonnes/ha of fertilisers. The greenhouse waters used for the experiments, from vegetable production glasshouses in British Columbia, Canada, and showed average pH of 6.65, phosphate (P-PO<sup>4</sup>) 63 mg/l, calcium 432 mg/l, magnesium 76 mg/l, potassium 174 mg/l.

### Phosphorus precipitation efficiency

**90% or higher phosphorus precipitation was achieved when the pH was 8.3 or higher**, irrespective of the Mg/Ca molar ratio in the range studied. At lower pH, the phosphorus precipitation efficiency was reduced at higher Mg/Ca ratios.

Calcium content of the precipitated phosphate produce was reduced at higher Mg/Ca ratios, at all pH levels, with pronounced effects when Mg/Ca > 1. Also, the phosphorus content of the precipitate was lower with higher Mg/Ca ratios. Potassium content of the precipitate never exceeded 1%, showing that K-struvite was not a significant product. Analysis of molar ratios suggested that hydroxyapatite (HAP) was the main phosphate formed

**The authors conclude that phosphate precipitation would be an efficient route for removing phosphate from greenhouse waste waters and recovering for recycling.** Further work on the design and operation of a crystallisation reactor to achieve this has also been carried out and is pending publication.

*“Phosphate recovery from greenhouse wastewater”  
Journal of Environmental Science and Health, Part B. vol B38, n°4, pages 501-509, 2003*

<http://www.dekker.com/servlet/product/productid/PFC>

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## Nutrients and ecosystems

### Marine iron

#### Fertilising the sea

As reported in *SCOPE Newsletter n°52*, scientists are looking at using iron fertilisation of the ocean to stimulate algal growth (primary production), and thus generate a sink for carbon dioxide, to help address greenhouse gas accumulation in the atmosphere.

The most recently published results of the ongoing **Southern Ocean iron fertilisation experiments** (SOFeX and SOIREE) suggest that the addition of one iron atom can remove 10,000 to 100,000 carbon atoms from the atmosphere, as phytoplankton develop and then the biomass largely sinks to the ocean floor as decaying phytoplankton, dead fish or excrement. Estimates suggest that iron fertilisation of the Southern Ocean, around the South Pole, which is classified as high-nitrogen, low-silicate waters, could absorb 15% of the atmospheric carbon dioxide build up resulting from man's activities. These results are based on experimental addition of 1.7 tonnes of iron sulphate to the Southern Ocean in 2002, with robot carbon flux monitoring.

**The world's oceans are often iron limited**, as they depend on inputs of the metal from iron rich soils in dry areas on land, and inputs have diminished since the last Ice Age.

Work is also currently underway to try to assess the ecological impact of such artificial generation of algal blooms to try and see whether there are negative impacts on ecosystem balance or on certain species.

**More details of the methods used in this work can be found in *SCOPE Newsletter n°52*.**

*J. Bishop, T. Wood, R. Davis, J. Sherman, Science 304, page 417, 2004*

<http://www.sciencemag.org/cgi/doi/10.1126/science.1087717>

*Q. Schiermeier, Nature, 421 pages 109-110, 2003*

<http://www.nature.com/nsu/040419/040419-7.html>

### Five lakes

#### **LEEDS phosphorus chlorophyll model**

This paper presents further development of the Eutrophication Effect Dose Sensitivity (LEEDS) lake phosphorus and chlorophyll model. This predicts the distribution of phosphorus between different compartments (water, sediment, biota) and forms (soluble, colloidal, particulate) and also levels of chlorophyll, on the basis of simple and readily available data on lake hydraulics, climate, and phosphorus input loadings.

The model was tested/calibrated for six very different lakes: Lake Erken (Sweden), Lake Batorino, Lake Miatro and Lake Naroch (all in Belarus), Lake Balaton – second basin (Hungary), Lake Kinnaret (Israel).

Inter-relations between phosphorus in soluble, colloidal and particulate forms in, separately, surface and deep water, in biota with short and long turnover times, and in active (shallow) sediments and in passive (deep) sediments.

Phosphorus input to the lake system is modelled, taking into account (by estimation based on the annual total) seasonal variation and a spring peak phosphorus load resulting from high phosphorus transports during spring floods and snow melt. Other additions from previous versions of the model include seasonal variation in phosphorus outflow, phosphorus carried out of the lake system in phytoplankton biomass, influence of concentration gradients on mixing, refinements regarding sedimentation and sinking of organic material.

The model as revised provides good predictive fits with observed total phosphorus concentrations in the lakes' waters for five lakes for which graphs are provided (not Lake Miatro).

#### **Difficulties predicting algal development**

For chlorophyll concentrations, the authors also consider that the model performs acceptably except for Lake Kinnaret where chlorophyll levels (algal

development) is known to be related to internal storage of phosphorus by algae, and to be disconnected from inflow phosphorus loadings. The model's predictions of average chlorophyll over the whole year are indeed close to observed values for all five lakes, but the predictions do not however reflect reality for peak chlorophyll levels (algal blooms).

For three of the lakes, the model predicts algal blooms over 2-3 months at 2x – 4x higher chlorophyll levels than those in fact observed. For the other two lakes, (Lake Balaton et Lake Kinnaret), significant algal blooms were in fact observed but there were not predicted by the model (observed peak chlorophyll levels 2x – 3x higher than predicted by the model).

This work shows both the interest and the considerable difficulty in developing models able to accurately predict chlorophyll levels (algal blooms) response to phosphorus loadings.

*“Development of a lake eutrophication model”,  
Ecological Modelling 171(2004), pages 35-63  
[www.sciencedirect.com/science/journal/03043800](http://www.sciencedirect.com/science/journal/03043800)*

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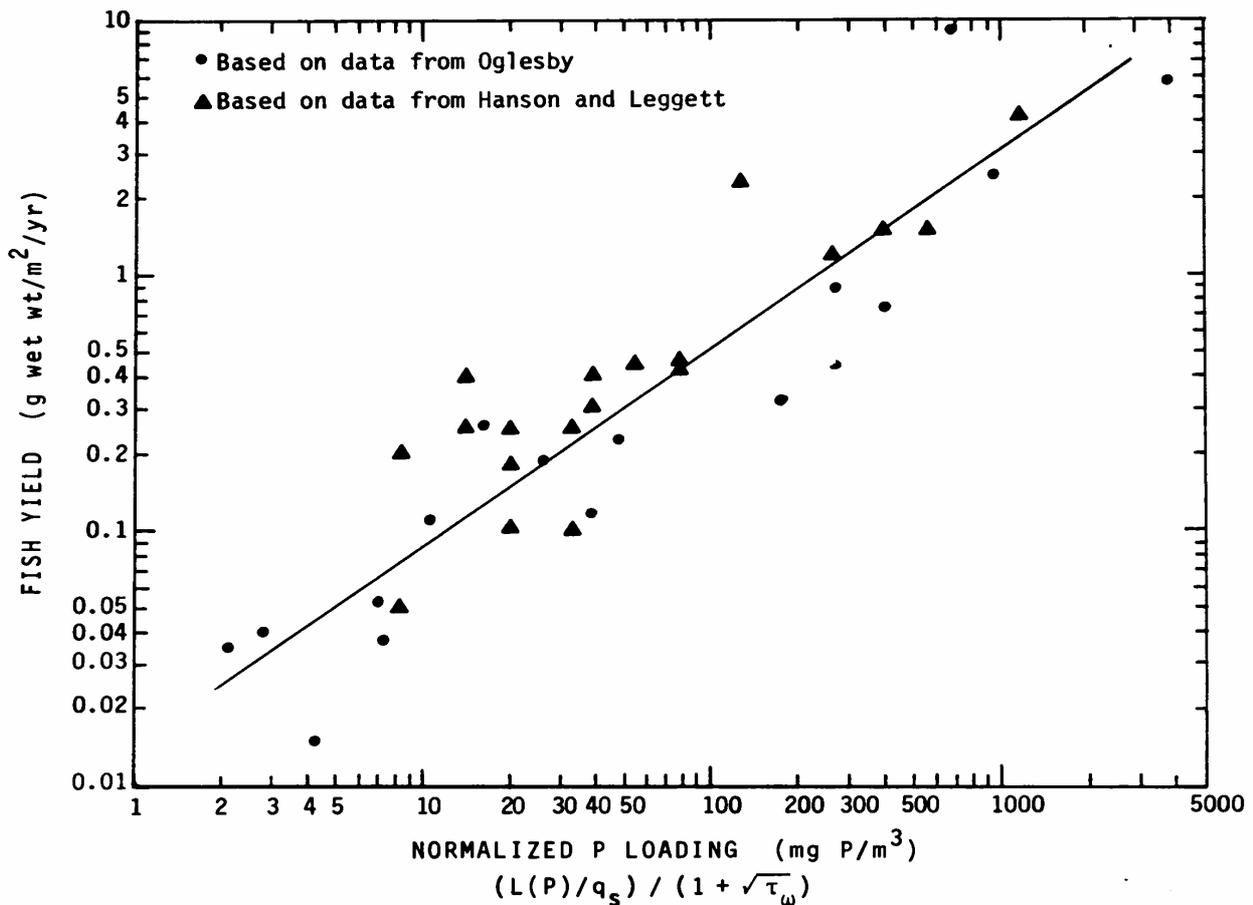
## Water body fertilisation

### Impact on fish production

Additional information on the impact of water body fertilization on fish production, in response to SCOPE Newsletter n°53

SCOPE Newsletter *n°53* presented a summary of several papers published in the proceedings of the first international conference on nutrients in salmonid ecosystems, American Fisheries Society, Bethesda, MD USA. The impact of fertilization of waterbodies on fish production and characteristics has long been of interest to the authors. A decade ago they reported a summary quantification of how fertilization of waterbodies improves fish production

in terms of total fish biomass; this relationship is shown in the graph below. As Lee and Jones (1991) discussed, moderate levels of fertilization can improve fish production of lakes, impoundments and ponds. However, fertilization, especially at high levels, can be adverse to the production of desirable forms of fish. In highly fertilized waterbodies that stratify, the oxygen demand in the hypolimnia (created by the decomposition of algae that had grown in the surface waters and settled to the bottom) can be sufficient to deplete the oxygen there. Since desirable coldwater fish (such as the salmonids, trout, etc.) normally inhabit the hypolimnion during the summer in temperate waterbodies, these more desirable fish cannot survive in highly eutrophic waterbodies because of a lack of oxygen in the cooler hypolimnetic waters..



**Graph : Relationship between Normalized P Load and Fish Yield** (From Lee and Jones, 1991)

$L(P)$  = Areal annual phosphorus loading ( mg P/m<sup>2</sup>/yr)       $m^2$  = surface area of the waterbody  
 $q_s$  = waterbody mean depth/hydraulic residence time; mean depth is the waterbody volume divided by its surface area  
 $I_0$  = hydraulic residence time (waterbody filling time)

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## SCOPE NEWSLETTER

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Thus, while there may be increased overall fish production in highly eutrophic waterbodies as shown in the graph below, the populations of rough fish, such as carp, which can tolerate lower dissolved oxygen levels, often dominate the increased fish production characteristic of excessively fertile waterbodies. The relationship shown in the graph applies to waterbodies with surplus nitrogen available for algal growth.

The abscissa in the graph is the Vollenweider normalized phosphorus loading term, which is the phosphorus load normalized by the waterbody's mean depth and hydraulic residence time. This term is approximately equal to the annual average phosphorus concentration in the waterbody's water column. Additional information on the Vollenweider OECD Eutrophication Study results is available from Jones and Lee (1986).

### References:

Jones, R. A. and Lee, G. F., "Eutrophication Modeling for Water Quality Management: An Update of the Vollenweider-OECD Model," *World Health Organization's Water Quality Bulletin* 11(2):67-74, 118 (1986). Available at:

[http://www.gfredlee.com/voll\\_oecd.html](http://www.gfredlee.com/voll_oecd.html)

Lee, G. F. and Jones, R. A., "Effects of Eutrophication on Fisheries," *Reviews in Aquatic Sciences*, 5:287-305, CRC Press, Boca Raton, FL (1991). Available at

<http://gfredlee.com/pexfert2.htm>

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### Conference:

**During Aquatech, Amsterdam,  
28 September – 1 October 2004**

### **Nutrient management: European experiences and perspectives**

Organised by the European Water Association (EWA), the conference includes the following subtopics:

\* **Wastewater treatment plants and nutrient removal:** Design parameters; implementation of the Urban Wastewater Treatment Directive; decentralised systems; source control; efficiency aspects; experiences in operation and maintenance

\* **Sludge management:** legislative background; agricultural sludge use (incl. quality assurance); nutrient recovery; sludge treatment technology for nutrient management (technical and economic aspects; incineration; sludge management concepts; risk assessment

\* **Diffuse pollution:** impacts on ground water; significance of diffuse nutrient pollution (agriculture; forestry; urban areas; households; traffic); risk assessment; monitoring; effects of nutrient enrichment; agriculture utilization of sewage sludge and groundwater contamination; innovative ways of controlling the risks from diffuse sources; new Groundwater Directive

Email: [Overmann@atv.de](mailto:Overmann@atv.de) Web: [http://www.show-info.nl/aquatech2004/e/bez\\_overig129](http://www.show-info.nl/aquatech2004/e/bez_overig129)

## 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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**CEEP**  
Centre Européen d'Etude  
des Polyphosphates

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# SCOPE NEWSLETTER

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NUMBER 55

May 2004

## Phosphorus recycling

### Belgium

#### **Phosphate recovery from starch wastewaters**

DHV is to install a Crystalactor® system to remove phosphorus from wastewaters from the Amylum Europe starch plant, Aalst, Belgium, recovering the phosphate as recyclable pellets.

### Struvite parameters

#### **Understanding struvite precipitation**

Experimental data for chemical and kinetic parameters for struvite precipitation at conditions comparable to wastewaters. Results show significant variations in crystal surface charge, crystal shape and precipitation rates as a function of pH, different counter ions, magnesium/phosphorus ratios.

### Treviso

#### **Full scale P-recovery process**

Results of operation of the full scale pilot phosphorus recovery plant at Treviso municipal sewage works (March 2001-October 2002) show successful phosphorus precipitation but difficulties with organics and suspended solids.

### Modelling

#### **Calcium phosphate precipitation**

The PHREEQC computer programme was used to thermodynamically model the effects of changes in solution conditions on calcium phosphate precipitation from pure solutions. Experiments show that carbonate concentrations can inhibit or enhance phosphate precipitation, but solution pH is still a dominant factor.

### Spain

#### **An industrial by-product magnesium source for struvite recovery**

Precipitation of struvite from pure chemical solutions and from real sewage treated liquors using a by-product of industrial magnesium oxide production, as magnesium source. The by-product proved effective used at higher dosages, but this

### Italy

#### **Improved REM-NUT for P-recovery**

A new phosphorus-selective ion exchange resin was tested, improving the REM NUT process for nutrient recovery as struvite.

### Poland

#### **Struvite crystal shape**

Laboratory studies and pilot reactor tests show formation of struvite with two different crystal forms (rhomboid and needle), influencing recovery possibilities. The authors suggest that this may depend on free ammonia levels.

### France

#### **Fate of phosphorus in manure treatment**

Three pig manure treatment plants were studied to assess under what conditions phosphates were found in solid or liquid fractions.

### Novaquatis

#### **Struvite precipitation from urine**

Ongoing R&D project addressing source separation of urine and recovery of nutrients, includes two workpackages on struvite precipitation

### North Carolina

#### **Struvite recovery from livestock lagoon liquor**

Operating parameters and reactor design for struvite precipitation were evaluated using first beaker tests, then a laboratory scale continuous mode crystalliser of novel fluidized bed design, and finally a continuous field scale reactor operated at an anaerobic pig slurry lagoon, sized to treat the wastewater flow to irrigation from 1,000 pigs.

## Sewage treatment

### Nutrient removal

#### **EU Commission report into Urban Waste Water Treatment (UWWT) Directive implementation**

EU Commission maintains pressure on Member States to implement adequate nutrient removal from sewage, and publishes Third Report on UWWT Directive 91/271 implementation.

## International Conference

### **STRUVITE: its role in phosphorus recovery and reuse**

Cranfield University, England,  
17-18 June 2004

[See page 2](#)

## International Conference

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17-18 June 2004

**Thursday 17<sup>th</sup> June 09:30 -17h00**

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*Struvite recovery from sources other than sewage.*

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Student participant    UK£200  
Accompanying Dinner   UK£40  
Accommodation inc. Breakfast – from approx UK£40/night

### **Information, registration and full programme details**

Tel: +44 (0)1234 754902 - Fax: +44 (0)1234 751671 - Email: [struvite@cranfield.ac.uk](mailto:struvite@cranfield.ac.uk)

<http://www.cranfield.ac.uk/sims/water/struvite/>

### Phosphorus recycling

#### Belgium

#### Phosphate recovery from starch wastewaters

DHV Water BV (Netherlands) are to install a Crystalactor® unit for phosphate recovery at the Amylum Europe starch and starch derivatives plant, Aalst, Belgium. The unit is located between the existing anaerobic and aerobic wastewater treatment installations.

This system crystallises magnesium phosphates onto sand seed particles in a fluidised bed reactor, induced by a pH increase (50% sodium hydroxide addition). Prior to the reactor, magnesium chloride is dosed, producing high-quality magnesium phosphate pellets which can be recycled into the phosphate industry.

The starch plant has an average wastewater flow of 155 m<sup>3</sup>/hour with up to 80 mg/l of phosphate. The Crystalactor® system will **bring the final effluent phosphate concentration down to 2 mg P/l**. The system is being delivered Autumn 2003 and should be operative by 2004.

The recovered phosphates pellets will be taken by *Thermphos International* (The Netherlands) and **used in their phosphorus production**, thus recycling the phosphates into industrial products. See <http://www.nhm.ac.uk/mineralogy/phos/Nordwijkerhout/Schipper1704.doc>

A Crystalactor® system has been running, recovering phosphates from a sidestream, at Geestmerambacht municipal sewage works since 1994, producing 200-300 tonnes of phosphate pellets per year from a 230,000 pe sewage flow. See: <http://www.naturalhistorymuseum.org.uk/mineralogy/phos/gaastr.htm>

Crystalactor® systems have also been previously installed for phosphorus removal and recovery (as struvite: magnesium ammonium phosphate) at the AVEBE potato starch factory, Veendam (The Netherlands) (150 m<sup>3</sup>/hour) and pilot units (calcium phosphate recovery) at Westerbork municipal sewage

works (12,000 pe) and Heemstede municipal sewage works (35,000 pe). See <http://www.nhm.ac.uk/mineralogy/phos/crystalact.htm>

The Crystalactor® system is also used for a number of other applications ranging from the chemical industry to drinking water purification.

#### Information:

[http://www.dhv.nl/frameset.asp?mainpage=http://www.dhv.nl/Application/PerformanceManagerServlet/English/Groups/site/DHVProjects/Water/Crystalactor\\_unit\\_for\\_Amylum/Crystalactor\\_unit\\_for\\_Amylum.asp](http://www.dhv.nl/frameset.asp?mainpage=http://www.dhv.nl/Application/PerformanceManagerServlet/English/Groups/site/DHVProjects/Water/Crystalactor_unit_for_Amylum/Crystalactor_unit_for_Amylum.asp)

Contact: Karel Gelsing [karel.gelsing@dhv.nl](mailto:karel.gelsing@dhv.nl)

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### Struvite parameters

#### Understanding struvite precipitation

Despite considerable interest in struvite precipitation within different wastewaters, both because of nuisance deposit formation in installations, and as a route for phosphorus recovery for recycling, few studies are available of struvite precipitation and chemistry kinetics. F. Abbona *et al.* publications (1980's – early 1990's) remain references with some more recent applied chemistry studies (see eg. Parsons *et al* in Scope Newsletter n°54, n° 41 at [www.ceep-phosphates.org](http://www.ceep-phosphates.org)).

The two papers summarised here present detailed experimental work measuring, in closely controlled laboratory conditions, the induction time and precipitation rate of struvite from

- (A) **pure phosphate, magnesium and ammonium solutions** (plus sodium chloride for ionic strength) and
- (B) **synthetic wastewater** containing also organic carbon and certain counter ions (carbonate, sulphate).

In all cases unstable supersaturated solutions were used. The studies were carried out at pH8.5 or 9.0, comparable to pH susceptible to occur in waste waters by CO<sub>2</sub> degassing or to be developed in a phosphorus recovery reactor.

The studies used continuously stirred 0.25 litre beakers, water bath regulated to 25°C, held underneath a surface flow of water-vapour saturated nitrogen to avoid CO<sub>2</sub> intrusion and/or escape from the supersaturated solutions. pH and reagent concentration were automatically adjusted throughout the experiments by auto-titrators linked to pH and ion probes. pH was thus controlled to an accuracy of 0.05.

### Pure solution struvite chemistry

The first series of experiments (paper A) used magnesium chloride and ammonium phosphate solutions. Salt (NaCl) was used to adjust ionic strength to 0.015 molar. Precipitation of struvite resulted in a drop in pH, triggering reagent addition by the autotitrators.

Measurement of induction times as a function of supersaturation rates, enabled a **stability diagram** of the structure to be developed (log K for equilibrium of all reactions). In all cases, the only precipitant being formed was struvite. The **surface energy of the precipitating struvite** was calculated from the induction measurements as a function of the solution supersaturation. Newberyite (MgHPO<sub>4</sub>) was not formed at the experimental conditions examined. The struvite formed as **long needle like crystals**, as reported previously by various other authors. The precipitation rate showed a second order dependence on supersaturation, suggesting a surface diffusion mechanism.

**The precipitated struvite crystals showed a strong negative charge** which increased at higher pH but which was dependent on magnesium concentration. At low magnesium concentrations, the charge of the struvite particles was in fact slightly positive, and it became increasingly negative with increasing magnesium concentrations. Aggregation of precipitant particles may be favoured at higher magnesium concentrations.

At high pH 10.5, flocculation occurred. Small variations in pH caused significant changes in particle zeta potential, and this is likely to destabilise suspensions by aggregation.

### Organics and counter ions

The second paper (B) presents further experiments carried out under the same closely controlled conditions and experimental method, but this time in the **presence also of soluble organic molecules** (glucose at 100gCOD/l) and different counter ions: carbonate (NaHCO<sub>3</sub>), nitrate (NaNO<sub>3</sub>), sulphate (either by using magnesium sulphate as the magnesium source or from Na<sub>2</sub>SO<sub>4</sub>). Salt was used to ensure ionic strength. Phosphate : ammonium : magnesium ratios of 1:1:1 were used, and pH was adjusted using NaOH. Again, equilibrium log k was calculated for all reactions in the systems.

**Precipitation again showed to be a second order function of supersaturation rates.** The kinetics of spontaneous struvite precipitation showed, as expected, to be faster at pH9 than at pH 8.5. Further, the kinetics were faster for magnesium sulphate as magnesium source than for magnesium chloride.

**Very different shapes of struvite crystals were found**, with long needle like structures at pH8.5 and oblong rhomboid crystals at pH9 – see also on the question of struvite crystal shape summary of the report by Suschka *et al* in this Newsletter.

(A) “Nucleation and crystal growth of struvite in aqueous media. New perspectives in phosphorus recovery”. Paper presented at the WASIC Conference (Workshop on Advance in Sensing in Industrial Crystallization), June 18-20, 2003, Istanbul, Turkey.

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(B) “Spontaneous precipitation of struvite from aqueous solutions”, *Journal of Crystal Growth*, 213 (2000) pages 381-388 [www.elsevier.nl/locate/jcrysgr](http://www.elsevier.nl/locate/jcrysgr)

### Treviso

#### Full scale P-recovery process

The full scale pilot phosphate recovery installation at Treviso municipal sewage works is presented in previous articles and in [Scope Newsletter n° 49](#). The unit is fed with liquor from the dewatering line from the anaerobic sludge digester at a now 70,000 pe biological nutrient removal sewage plant and aims to precipitate phosphorus by aeration only (CO<sub>2</sub> stripping leading to a pH increase) in robustly designed fluidised bed configuration. The published report covers results obtained in the plant from start up in March 2001 through to October 2002, as well as further preparatory bench ageing and supersaturation tests.

Previous work by Battistoni *et al.* used smaller semi-pilot installations and bench tests, using anaerobic supernatants from Ancona sewage works to model phosphorus precipitation kinetics and parameters.

Because of problems in the operation of the sewage plant itself (start up of new installations, water leakage into sewers resulting in diluted influent), it was necessary to add soluble phosphate to the digester supernatant to levels in the range 25-250 mgP-PO<sub>4</sub>/l.

#### Phosphorus removal

**A reasonably high level of phosphorus removal from the inflow liquor was achieved** in the phosphorus precipitation unit (average 54% removal of total phosphorus) and visible growth of the sand particles used as a seed in the fluidised bed reactor was seen.

Hydraulic conditions established in the fluidised bed reactor enabled the bed to remain homogenous and suspended, but **the bed showed a loss of sand** over the period. It was not clear whether this was the result of fixing of sand into the fluidised bed's gravel base, or of loss of sand carried out of the top of the reactor.

At the same time the density of the bed material decreased progressively during the operating period,

presumably because **organic material** is adhering to the seed sand as well as precipitated phosphates. This affected performance, as the lighter particles were then carried out of the top of the reactor and lost. An elevated level of nucleation instead of particle growth in the phosphate formation also resulted in the generation of fine particles, again partly lost over the top of the reactor in the outflow. A modification to the Dortmund settling device at the top of the reactor failed to resolve this. The presence of organics in the precipitant particles was also shown by chemical analysis.

Phosphate content of the bed material reached 8.1% and nitrogen content 0.4% by the end of the reported period.

#### Suspended solids problems

The authors note that the results obtained so far in this pilot plant start up phase do not enable the theoretical and previous experimental results to be confirmed. Further work will look at growing the self-nucleating particles rather than using sand as a seed, thus increasing the potential P-content of the precipitated material and removing problems relating to sand release from the reactor which can pose problems for pumps downstream. Further work will look at systems to prevent carry over of small and light particles from the reactor (outflow at reactor top), for example a system to capture foams and froth.

Finally the **limitation of suspended solids** in the digester dewatering liquor used as feed appears as very important.

*“Phosphate crystallisation process for P-recovery applied at Treviso Municipal Wastewater Treatment Plant (Italy)”, report 2003*

F. Cecchi – University of Verona, Paolo Battistoni, Raffaella Boccadoro – Marche Polytechnical University, Italy [p.battistoni@univpm.it](mailto:p.battistoni@univpm.it)

Available for download at [www.nhm.ac.uk/mineralogy/phos/](http://www.nhm.ac.uk/mineralogy/phos/)

### Modelling

#### Calcium phosphate precipitation

The authors' 2002 paper used computer modelling to study the speciation and saturation index for the precipitation of calcium phosphates from pure chemical solutions under different conditions of ionic strength and temperature comparable to those found in wastewaters.

The **theoretical thermodynamic calculations** were carried out using the computer programme PHREEQC for precipitation of calcium phosphate as hydroxyapatite (HAP). Variable inputs were concentrations of phosphate,  $H^+$ , soluble calcium ion, total ionic strength (assumed addition of  $KNO_3$ ). Temperature ranges of 5-30 °C were considered.

Phosphate concentrations of 1-200 mgP/l were considered, and soluble calcium concentrations 1-10 x molar Ca:P ratio. The saturation index showed to increase logarithmically with phosphate and calcium concentrations, and polynomially with pH in the range 7-11. The saturation index, as can be expected, also decreases logarithmically with total ionic strength.

The authors conclude that adjusting soluble calcium concentrations and solution pH values should be two effective tools for controlling calcium phosphate precipitation, and in particular for enabling phosphates to be precipitated from wastewaters as HAP for recovery and recycling.

#### Effects of carbonate

Previous work by the same authors (2001) briefly reported in [Scope Newsletter n°41](#) showed that **calcium phosphate precipitation is significantly inhibited by dissolved carbonate**, particularly at pH below around 9. The authors suggested, on the basis of solution speciation calculations, that this is because of the formation of ion pairs between carbonate and calcium ions thus decreasing the concentrations of calcium ions, and so the thermodynamic forces for calcium phosphate precipitation.

This 2002 work used phosphate concentration of 20 mgP/l in solutions of total ionic strength comparable to

wastewaters at 0.02 mol/l, with carbonate concentrations up to 5 mmol/l.

In the absence of carbonate, at pH 8, phosphate precipitation showed firstly a rapid precipitation of around 10% of phosphates in around 10 minutes, then an "S" curve with a low rate of acceleration for around 4.5 hours, then a faster rate, achieving around 50% precipitation after 6 hours, then only very slow further precipitation. The acceleration at 4.5-6 hours is considered to be due to the formation of a new calcium phosphate species.

With 2.5 mmol/l carbonate addition at pH 8, initial phosphate precipitation was faster (around 20% in the first 10 minutes), but the time to the acceleration phase was delayed to around 7 hours. After 10 hours, around 50% of phosphate had been precipitated, comparable to the no-carbonate experiment after 7 hours.

With 5 mmol/l carbonate at pH 8, phosphate precipitation was significantly inhibited, with around 10% precipitation after 10 minutes, but only 20% after 12 hours.

At pH 9 also, the most efficient phosphate precipitation was recorded at 2.5 mmol/l carbonate, but again the precipitation was strongly inhibited at 5 mmol/l carbonate.

At pH 10 and 11, carbonate at 5 mmol/l inhibited phosphate precipitation only very marginally (by 1-2%).

Analysis of the precipitate, showed that at pH 9, 10 and 11 the phosphorus/calcium ratio of the precipitate was significantly lower for 5 mmol/l carbonate addition, compared to 2.5 or zero. This effect was more marked and the P/Ca ratio was also lower at all pH, when the pH was higher. P/Ca ratio of the precipitate was unchanged with carbonate addition (at around 0.8) at pH 8.

The authors conclude that the formation of ion pairs between carbonate and calcium ions decreases the concentrations of soluble calcium ions, thus the thermodynamic forces for calcium phosphate precipitation; calcium carbonate and calcium phosphate co-precipitate, thus enhancing the

precipitation of phosphate at certain solution conditions, resulting the decrease of the relative phosphate content in the precipitate, especially at higher pH values and higher calcium additions. Increasing solution pH value and the calcium addition properly are two approaches to overcome the inhibition of carbonate on the precipitation of phosphate.

*“Effects of solution conditions on the precipitation of phosphate for recovery a thermodynamic evaluation”*. *Chemosphere* 48, pages 1029-1034 (2002).

[www.sciencedirect.com/science/journal/00456535](http://www.sciencedirect.com/science/journal/00456535)

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Download PHREEQC:

[http://wwwbr.cr.usgs.gov/projects/GWC\\_coupled/phreeqc/](http://wwwbr.cr.usgs.gov/projects/GWC_coupled/phreeqc/)

*“The effect of carbonate on the precipitation of calcium phosphate”*, *Environmental Technology*, vol. 22, pages 207-215 (2002). [www.environtech.co.uk](http://www.environtech.co.uk)

Y. Song, H. Hahn, E. Hofmann, as above.

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## Spain

### An industrial by-product magnesium source for struvite recovery

One of the possible economic obstacles to phosphorus recovery from sewage for recycling via struvite precipitation (magnesium ammonium phosphate  $MgNH_4PO_4$ ), is the cost of adding magnesium which is generally present at significantly lower molar concentrations than phosphates. This paper examines the feasibility of using a by product of the Spanish magnesite mining and magnesium oxide (MgO) production industry, in effect low-grade MgO of low economic value.

Precipitation was tested in 1 litre beakers, stirred for up to 4 hours, using pure solutions of phosphate – magnesium and ammonium and using real wastewater,

with results for the industrial by-product being compared to those for pure MgO.

The wastewater liquor used was filtrate from dewatering of digested sludge from the Arroyo del Soto municipal wastewater treatment plant, Madrid, Spain, which uses and anaerobic/aerobic (A/O) biological phosphorus removal configuration.

The byproduct was analysed and showed to contain 68% (as MgO) of magnesium compounds with 10% (as CaO) of calcium compounds and significant traces (>2.5%) of iron oxide, sulphate and silicon compounds. Its particle size as supplied was 18% >0.1mm.

### Preliminary experiments

**First struvite was precipitated from pure chemical solutions** of 1:1:1 molar phosphate, ammonium and magnesium ions (initial concentration 200 mgP/l) by raising the pH to 9 with NaOH.

**Then, the industrial by-product was tested in synthetic solutions** containing molar ratios of phosphate, ammonium and magnesium comparable to real wastewater, by adding up to 1.5, 2.0 and 2.6 x molar ratio to phosphate. Pure MgO was tested similarly for comparison. NaOH was not added (except for prior pH adjustment of the synthetic solutions to pH 7.5 similar to real wastewater) because the by-product or MgO caused a pH increase sufficient for struvite precipitation.

With pure MgO, the variation in Mg/P ratio from 1.5 to 2.6 did not improve precipitation efficiency, whereas the byproduct (particle size as delivered) required the highest Mg/P ratio as well as prolonged stirring time to achieve a phosphate precipitation efficiency of 80% (2 hours stirring) – 95% (4 hours).

X-ray diffraction analysis suggests that this is because **only a part of the magnesium ions in the by-product are “available”** to react and form struvite (periclase = MgO), with part being held as magnesite ( $MgCO_3$ ) and dolomite ( $CaCO_3/MgCO_3$ ), insoluble at the pH of the experiments.

Correspondingly, the phosphate content of the struvite precipitated in the experiments using the by-product was somewhat lower than when pure magnesium sources were used (9.8% - 10%, compared to 11 - 12.9%) because of the presence of other substances (in particular magnesite and dolomite from the by-product, which do not intervene in the reaction).

### Real wastewater

**Experiments were then carried out using real wastewater liquor**, previously aerated to increase its pH. In this case, three forms of the industrial by-product were tested: by-product as supplied ; ground to particle size <0.04mm ; and the fraction (47,5%) with particle size <0.04mm after sieving, and compared with pure MgO. Magnesium/phosphate ratios of 1.5 - 3.6 were tested.

**Finally, further experiments were carried out using the sieved <0.04mm by-product to confirm optimal magnesium/phosphate dosages.**

These experiments confirmed the effectiveness of the by-product in real wastewater at Mg/P ratios of 2.0 to 2.5. The sieved by-product (<0.04mm) was also effective at an Mg/P ratio of 1.6. In all cases, the precipitate contained >9% phosphorus and >3% nitrogen, important criteria for its value as a fertiliser.

**The authors conclude that the by-product can be an effective magnesium source for struvite precipitation**, for recovery of phosphorus from wastewaters in the form of a useful fertiliser. Higher Mg/P dosage ratios are necessary than with pure chemicals as a magnesium source, but this could be balanced because of the low cost of the by-product compared to the purchase of such chemicals. The sieving of the by-product to achieve particle size <0.04mm improved its effectiveness significantly, but only 47% of the product as supplied passes through a sieve of this size, so most of the supplied product would be wasted.

*“Use of a by-product of magnesium oxide production to precipitate phosphorus and nitrogen as struvite from wastewater treatment liquors”, Journal of Agricultural and Food Chemistry, vol. 52, n°2, pages 294-299, 2004.*  
<http://pubs.acs.org/journals/jafcau/>

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### Italy

#### Improved REM-NUT for P-recovery

The REM NUT process uses ion exchange to remove phosphorus and nitrogen from sewage works effluent. Resin regeneration then gives relatively clean and concentrated phosphate and ammonium solutions, which can be used to precipitate struvite, enabling nutrient recovery for recycling.

The REM NUT process was originally designed to remove all phosphorus and nitrogen from sewage works effluent as a third stage nutrient removal alternative to chemical or biological nutrient removal systems (see previous articles in *Water Research vol.13* and *vol. 20 issue 6*). This required an ammonium ion exchange line of 6-8x the capacity of the phosphate exchange line, reflecting the higher concentration of ammonium in wastewater effluent. Phosphate, as well as magnesium, addition was then necessary to precipitate the removed ammonium as struvite (magnesium ammonium phosphate with 1:1:1 molar ratio).

In 2001 the process configuration was revised to target phosphorus recovery (rather than removal of all effluent ammonium), with the ammonium ion exchange line being now of the same capacity as the phosphate line. This reduced investment costs, avoided phosphorus addition and reduced magnesium consumption requirements, thus reducing costs.

#### Interference problems

This work was presented at the 2<sup>nd</sup> International *Conference* on Phosphorus Recovery and Recycling, Noordwijkerhout, 2001 (see *conference paper, article* in *Environmental Technology* vol. 22, 2001, and summary including diagram in *SCOPE Newsletter*

[n°41](#)). A key problem identified however was the poor selectivity of the ion exchange resin available for phosphate and interference of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ .

Also at the 2<sup>nd</sup> Phosphorus Recovery and Recycling [Conference](#) 2001, A. Sengupta [presented](#) a new ion exchange resin developed at Lehigh University, PA, USA, with specific selectivity for phosphates. This new resin is based on the commercial weak base anion exchanger *Dowex M-4195 Dow Chemical USA*, converted to a copper form and with chelation of the metal species.

The 2003 paper reports results of extensive laboratory testing of application of this resin for phosphates removal from a tap water + phosphates solution and in a 0.1 m<sup>3</sup>/hour pilot REM NUT plant at the Grottaglie-Montieasi municipal sewage treatment works, South East Italy. The pilot plant was operated continuously using real sewage works effluent for 3 months.

### Laboratory results

The preliminary laboratory experiments, using a **tap water + phosphates solution** at concentrations comparable to waste water effluent, showed that under such conditions flow rates of up to 20 bed volumes(BV)/hour allowed phosphorus levels to be brought below 0.1 mgP/l and that up to 400 BV could be treated before resin regeneration. 95% of phosphate ions removed from solution were recovered during regeneration in <1 hour using 3 BV of slightly acidified (pH 4.3) brine (0.6 M NaCl). The regenerated phosphate solution thus had a >100x higher phosphate concentration than the original solution treated. The resin loading capacity was 15gP/litre.

### Performance

The pilot plant using real wastewater effluent showed significantly lower resin performance: 150BV between regenerations to achieve 0.1 mgP/l in the effluent and a resin loading capacity of only 1.2gP/l (**<10% of that found with tap water phosphate solutions in the laboratory**). However, no resin fouling or copper loss were noted after 3 months operation.

The authors conclude that the results are moderately encouraging as to resin performance in real wastewaters and that further work is needed to obtain a better understanding of the factors affecting this.

*“REM NUT ion exchange plus struvite precipitation process”*, *Environmental Technology*, [www.envirotechnol.co.uk](http://www.envirotechnol.co.uk) vol.22, pages 1313-1324, 2001. L. Liberti, D. Petruzzelli, L. De Florio. [Direct link to article](#).

*“A new phosphate-selective sorbent for the Rem Nut® process. Laboratory investigation and field experience at a medium size wastewater treatment plant”*, *Water Science and Technology* <http://www.iwaponline.com/wst/toc.htm> vol. 48,

N°1, pages 179-187, 2003

<http://www.iwaponline.com/wst/04801/wst048010179.htm>

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[www.sciencedirect.com/science/journal/00431354](http://www.sciencedirect.com/science/journal/00431354)

### Poland

#### Struvite crystal shape

Laboratory beaker precipitation tests and experiments using two pilot reactors (continuous flow fluidised bed, 10 and 100 litre capacity) were carried out using sludge digester supernatant from Zabrze and Komorowice municipal waste water treatment plants (wwtps), Poland. Magnesium was added and a combination of aeration and/or reagent addition used to increase pH, to obtain struvite precipitation.

The sewage sludge digester supernatants had the following characteristics. Zabrze wwtp is a Bardenpho type biological phosphorus removal plant, using also some iron dosing. Soluble phosphorus (P-PO<sub>4</sub>) in the sludge filtrate was 130-170 mg/l and ammonium N-NH<sub>4</sub> 800-1450 mg/l. Komorowice wwtp operates partial biological phosphorus removal, and the sludge centrate used had P-PO<sub>4</sub> at 65-106 mg/l and ammonium 990-1600 mg/l.

**Simple aeration in the laboratory resulted in pH increases** in these substrates from around 7.6-7.8 up to 8.6-8.8.

Laboratory preliminary tests in 3 litre beakers showed that 80% of soluble phosphorus could be precipitated from the wastewater by aeration combined with soluble magnesium addition to a 1/1 Mg/P ratio, and 90% at a 1.5/1 ratio, after 4 hours mixing.

#### Pilot reactors

The first reactor (see diagram) was 1m high and volume 10 litres. Partial recycling of the effluent flow to the reactor base enabled upflow rates in the reactor to be controlled for bed fluidisation. The reactor had a 50° slope conical base, then a vertical sided settling zone above the fluidised bed.

The second reactor, volume 100 litres, was a 1.8m high cone of slope 20°, with no recycling flow, again using a continuous flow fluidised bed design.

The two reactors were operated at the sewage works, with the first reactor at Zabrze and the second at Komorowice, for 85 and 67 days respectively continuous operation time.

#### Crystal shape

A number of experimental results and many photos of precipitated struvite crystals are provided in the published report. The crystals show two distinct shapes: wedge shaped (rhomboid) and long needle shaped. This confirms work by previous authors who have found one or other of these crystal forms:

- \* **needle shaped:** Schultze-Rettmer 2001, Stratful 2001, Abbona 1984, Hirose 1996
- \* **rhomboid:** Parsons 2001

Of previous authors, Hirasawa has suggested that the shape is dependent on Mg/P ratio (rhomboid for Mg/P=1, needle shaped for Mg/P=4), Durrant 1999 suggested that the needle like form resulted from supersaturation with magnesium and nitrogen ammonia ions.

**The authors of this report suggest that the change in crystal shape could be related to levels of free ammonia** (NH<sub>3</sub> – as opposed to soluble nitrogen ammonium NH<sub>4</sub> ions) – with high levels of free ammonia resulting in the needle shaped crystal form. This is based both on the results of the different experiments and operating conditions tested by the authors (details experimental results published in the report), and with comparison of the operating conditions and crystal forms produced in the work of previous authors (see above).

Free ammonia will occur as a function of high soluble ammonium ion concentration if the pH is raised, but not under significant aeration which will drive the ammonia away with the air flow.

The authors emphasise that the form of struvite crystal being precipitated may be a key factor in successful phosphate recovery, in particular in influencing the **formation or not of “fines”** (susceptible to be lost from the reactor), the reaction speed of the precipitation, and in the mechanisms of aggregation of the crystals to form larger particles (which will then

settle in the reactor and can be recovered, and readily handled and recycled).

The pilot reactors in this work were operated to optimise production of larger particles, rather than complete removal of soluble phosphorus. After only 2 weeks of operation, aggregation of crystals into particles was noted in the reactors, with granules of around 1mm diameter being successfully formed.

*“Study of the effects of the reactor hydraulics on struvite precipitation at municipal sewage works”, Polish Academy of Sciences/ University of Bielsko-Biala research report, published at <http://www.nhm.ac.uk/mineralogy/P-recovery/> - direct link:*

<http://www.nhm.ac.uk/mineralogy/phos/Suschka2003rep.pdf> J. Suschka\*, E. Kowalski, S. Poplawski

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### France

#### **Fate of phosphorus in manure treatment**

In France's main pig producing area, Brittany, limits to nitrogen loads in manure spreading (because of increasing nitrate levels in aquifers) are causing farmers to install aerobic/anaerobic treatment plants to achieve nitrification/denitrification of manure, transferring nitrogen content to atmospheric N<sub>2</sub>. Thirty such farm-scale treatment plants were already in operation in the area in 1999, with many more planned.

Such plants transfer phosphorus, and also potassium as well as metals such as copper and zinc, to the liquid plant effluent and/or to a solid fraction whose form can vary from liquid sludge to a dried, transportable compost or equivalent.

**This study presents mass balances for suspended solids, nitrogen, phosphorus, copper and zinc** for three such full-scale operational farm treatment plants, of similar size (7,200 – 7,800 – 8,300 weaned pigs per year, that is treatment capacities of 16-19 m<sup>3</sup>/day of slurry). The general principle of the three plants was similar: a reception/mixing/holding tank, followed by a

reactor tank subject to alternate aeration and anoxic (non aerated) periods (for nitrification/ denitrification respectively). However, **the configuration of the three plants varied significantly** in aspects such as: prior separation or not of the solid fraction before treatment, presence or not of a decanter, aeration/anoxic period lengths ...

#### **Liquid phosphates**

Only 25-30% of the initial manure phosphorus content was in the solid fraction, after the initial solid/liquid separation, using a screw press auger. This is significantly different from the figures given by Coillard 1998 (see *SCOPE Newsletter n°26*) who indicated 85-90% of pig manure phosphorus was in the solid fraction, after solid/liquid separation using centrifuges. This is because **much of the phosphate in pig manure is contained in small, dense particles**, which do not make up a large mass, but which are highly concentrated in phosphorus. These particles are separated from the liquid in a centrifuge, but not in a screw press auger. This is explained in a paper presented by the authors at the ISAAFPW Conference 2003 (see references).

The three plants studied each transferred around 60% of the total inflow phosphorus to the solid fraction after treatment, with an additional 20-30% (depending on the plant) being also in a solid form, but as suspended solids in the liquid effluent or sludge.

The levels of phosphorus in the liquid effluent from these plants were sufficient, according to the authors, to raise concerns about their possible contribution to eutrophication, given the ready availability and susceptibility to run-off of phosphorus applied to fields in such effluent, particularly if application rates are calculated on the basis of the (low) residual nitrogen content in these liquids.

**The authors suggest that the phosphorus can be orientated towards either the solid or the liquid fraction from a plant**, by modifying the aerobic (tends to fix phosphorus in organic solids) or anoxic (tends to cause phosphorus release to solution) final phase of the treatment.

In this case, plant operators could choose to either optimise phosphorus transfer to solids, where these are in a transportable form (dry compost or similar) which can be moved away from the farm area, or concentrate phosphorus in the liquid fraction then operate a phosphorus recovery process. They suggest that phosphorus could be recovered either by struvite precipitation (magnesium ammonium phosphate) or possibly as potassium struvite (potassium magnesium phosphate) where inadequate ammonium was available following the nitrification/denitrification treatment.

*“Fate of phosphorus from biological aerobic treatment of pig slurry. By-products characterization and recovery”*  
*Environmental Technology*, vol. 24, pages 1323-1330.

<http://www.envirotechnol.co.uk/>

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A preparatory version of this paper was presented at the  
2<sup>nd</sup> International Conference on Phosphorus Recovery and  
Recycling, Noordwijkerhout 2001,

<http://www.nhm.ac.uk/mineralogy/P-recovery/> and is  
available at:

<http://www.nhm.ac.uk/mineralogy/phos/Nordwijkerhout/Daumer.doc>

*“The effect of pig diet and solid/liquid separation of pig slurry on phosphorus fractionation”*. Proceedings of the  
9th International symposium on animal, agricultural and  
food processing wastes (ISAAFPW), Research Triangle  
Park, NC, USA, 2003 pages 463-471

<http://www.asae.org/meetings/index.html>

Direct link:

<http://asae.frymulti.com/request2.asp?JID=1&AID=15284&CID=fpw2003&T=3>

M-L Daumer, F. Beline, M. Sperandio - as above.

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### Novaquatis

#### Struvite precipitation from urine

The Novaquatis research package underway at EAWAG Switzerland is looking at routes and technologies for recovery of nutrients from human excrements in wastewater. Urine typically contains 80% of nitrogen, 50% of phosphorus and 90% of potassium in human excrements. Source separation toilets save 80% of water use and would enable recovery of nutrients from urine by struvite precipitation.

Two workpackages in this overall R&D project are looking specifically at struvite precipitation.

A PhD thesis (March 2002-December 2005) is addressing biological and chemical interactions affecting phosphorus precipitation in high strength media.

A second workpackage is researching the thermodynamic and kinetic properties of struvite precipitation in real and artificial urine, in particular looking at the effects of inorganic complexes present in urine. First results suggest that organic complexing agents do not influence struvite solubility, and that struvite precipitation rates are controlled by surface reaction.

Novaquatis web site:

<http://www.internal.eawag.ch/~maurer/Nova/nova.htm>

### North Carolina

#### Struvite recovery from livestock lagoon liquor

Keith E. Bower's thesis, published by North Carolina State University 2002, presents three years of work investigating parameters and testing reactor design for phosphorus precipitation as struvite from anaerobic livestock slurry lagoon effluents. The published thesis includes an initial literature review, results of laboratory beaker tests, reactor modelling, design and laboratory tests of a continuous mode struvite crystalliser, and finally design and operation of a field-scale reactor at a hog farm sized to treat the wastewater flow to irrigation from 1,000 pigs (11 litre bed volume) and achieving peak total phosphorus and orthophosphate phosphorus removal of 82% and 87%, respectively. All of the experimental work used real pig manure lagoon liquors.

A preliminary literature review concluded that struvite precipitation offered the potential to remove phosphorus from North Carolina pig manure lagoon effluent in a recoverable form. It also provided thermodynamic and kinetic information regarding struvite precipitation, necessary for reactor design.

#### Initial beaker tests

**Initial parameter testing experiments were carried out using lagoon effluents from two local pig farms:** one covered, ambient temperature in-ground digester (pH 7.8, total phosphorus [TP] 62 ppm, total ammoniacal nitrogen [TAN] 30 ppm, magnesium [Mg] 30 ppm); one anaerobic lagoon (pH 7.6, TP 47 ppm, TAN 1087 ppm, Mg 19 ppm).

49% and 73% respectively of the TP was present as soluble orthophosphate, and thus potentially available for struvite precipitation.

Magnesium bicarbonate and ammonia were used to provide magnesium ions and increase the pH for struvite precipitation. Beakers were stirred for 20 minutes then stood overnight.

As expected, phosphate precipitation increased with magnesium addition and/or ammonia addition.

#### Magnesium availability

Literature data showed that magnesium solubility is higher in solutions containing species which will lose protons when the pH increases and before the pH reaches 10, for example ammonium. This effect can be accentuated by bubbling CO<sub>2</sub> through the solution and this was experimentally demonstrated. **Ammonia addition was also shown to be effective in precipitating struvite**, at addition rates as low as 40 ppm, with the advantage of adding no "foreign" ion not already present in the liquor.

**Calcined magnesium carbonate was identified as an optimal magnesium source** when rendered soluble by CO<sub>2</sub> addition. This magnesium product is readily available (used as a livestock feed supplement). CO<sub>2</sub> could in theory be collected from lagoon digester biogas.

#### Reactor design

From the beaker experiment results, it was concluded that the struvite precipitation reaction was sufficiently rapid for a continuous mode fluidised bed reactor to be effective. Reactor design needs to prevent the loss of fine particles with the fluid flow out of the top of the reactor, so a cone shaped reactor was used.

Reactor operation was modelled using three hypothesis: **MLMB** = mixed liquid, mixed bed (liquid perfectly mixed and particle sizes mixed throughout the bed); **PLMB** = plug flow (liquid moves up the reactor linearly without mixing vertically), mixed bed; **PLCB** = plug flow, classified bed (that is, the particles in the bed are stratified by size).

#### Laboratory test reactor

The laboratory scale test reactor was a 40 cm high, transparent plastic cone, with 1.27 cm internal diameter at the base (reactant and fluid injection zone), 10.2 cm at the top (the bed top generally stayed at around two-thirds of the cone height, thus forming a bed occupying about 0.45 litres). Liquid throughput rate used in the reactor was 34 – 57 litres/hour.

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## SCOPE NEWSLETTER

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**Fifty different reactor runs of 1.5 – 5 hours duration were carried out in the lab**, using real lagoon liquors as indicated above, and testing ammonia addition rates of 0 – 200 ppm TAN, magnesium addition rates of 0 – 60 ppm Mg, with and without seeding. Results are presented in detail in the published thesis available online, including statistical analysis.

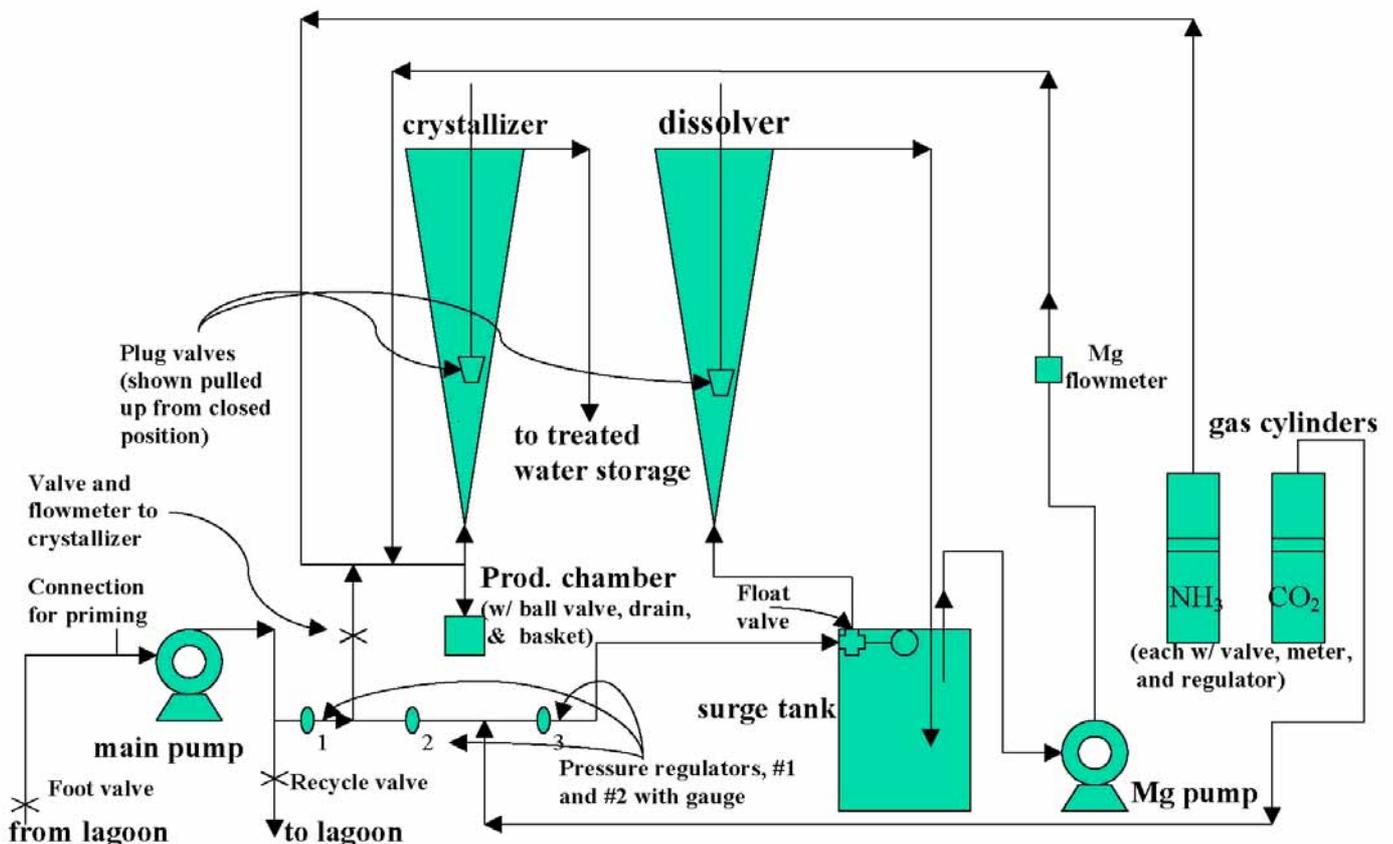
Reductions in total phosphorus (TP) and orthophosphate phosphorus (OP) of 58% and 74% were achieved in the second set of runs.

The PLMB reactor operation model (see above) showed to best fit to the reactor behaviour. Results also suggested a surface-area specific rate constant in the range of 10-15 dm/hour.

### Field scale reactor

The successfully tested laboratory reactor design was scaled up to 455 litres/hour, to accommodate irrigation water throughput, corresponding with 1,000 hogs averaging 58 kg each. Channelling of fluid flow (instead of mixing) had been observed in the lab scale reactor, and to reduce this effect the field scale reactor was built with a more gradual upward increase in diameter (steeper cone sides): height 152 cm; internal top and bottom diameters 25.4 cm and 3.8 cm (the bed top generally stayed at around two-thirds of the cone height, thus forming a bed occupying about 11 litres). Two identical cones were used: one as the struvite precipitation fluid bed crystalliser, the other for dissolving magnesium oxide (magnesium chloride was used in later runs to achieve the control on Mg concentration needed for factorial experiments). Ammonia was injected into the base of the reactor from a pressurised supply, alongside the magnesium solution

### Scheme of field reactor (U.S. patent application no. 10/659,239)



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## SCOPE NEWSLETTER

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Fifteen initial runs of 0.5 – 30 hours were carried out achieving OP reductions of 22-58% when ammonia injection was operating. Three further runs were then carried out, each testing 18 different operating parameters combinations (in a randomised order). In these runs, TP and OP removal averaged 70 and 77% when ammonia and magnesium were added, and 82% and 87% at optimum conditions.

The author concludes that the reactor performed at least as well in the field as had been initially envisaged at the start of the work. Phosphorus removal was higher than for theoretical calculations of struvite precipitation (other phosphate compounds were maybe also being precipitated to a small extent). The system “shows promise for application in treating North Carolina livestock waste lagoon effluent and removing most phosphorus”.

*“Development of a struvite crystallizer for reducing phosphorus in effluent from livestock waste lagoons”, PhD Dissertation, North Carolina State University, Biological and Agricultural Engineering.*

K. Bowers [keithebowers@yahoo.com](mailto:keithebowers@yahoo.com)

Full text available online (174 pages) at:  
<http://www.lib.ncsu.edu/theses/available/etd-11042002-164459/>

## Sewage treatment

### Nutrient removal

### EU Commission report into Urban Waste Water Treatment (UWWT) Directive implementation

The EU Commission’s previous reports into implementation of the 1991/271UWWT Directive underlined the failure of many Member States to have introduced adequate sewage treatment collection and treatment within the required deadlines, and particularly the failure to implement nutrient removal by 1/1/1998 as required by the Directive for any agglomeration of 10,000 person equivalents or more discharging into waters potentially susceptible to

eutrophication (“Sensitive Areas”). As indicated in [Scope Newsletter n°45](#) the Commission ran an active media campaign in 2001-2002 (“*Name and shame*”) denouncing the non implementation of the Directive, and in particular the failure of Member States to adequately designate Sensitive Areas. The European Parliament also voted a *motion* on 14<sup>th</sup> March 2002 underlining the importance of implementation of this Directive.

The Commission’s third report into implementation of this Directive, [COM\(2004\)248](#), covering the period up to 2003, is therefore of considerable political significance. This report confirms the continuing failure of Member States to implement in particular the nutrient removal requirements of this Directive.

**As of 1<sup>st</sup> January 2002, some 42% (by organic load) of wastewater from the 5,500 agglomerations identified by Member States as discharging into “Sensitive Areas”, was still not subject to adequate treatment (nutrient removal). 91% of the wastewater from these agglomerations was being effectively collected by 2002.**

### Failure to designate “Sensitive Areas”

The Commission particularly criticises the failure of certain Member States to correctly designate as “Sensitive Areas” water bodies which are in fact subject to eutrophication or potentially so. The Commission employed ERM Consultants from 1998-2000 to verify the Sensitive Area designation by Member States and [this audit](#) revealed a number of shortcomings. These had already been emphasised in the IEEP report for CEEP (see [SCOPE Newsletter n°34](#)) and in *Scope Newsletter n°s 52, 45 and 46*.

As well as inland waters inadequately taken into account by Member States, the Commission emphasises that major coastal areas including the Baltic Sea, the Adriatic and the North Sea (from Northern France to Sweden) are in effect “Sensitive”.

The Commission indicates that certain Member States (in particular Spain, for the Ebro and Guadalquivir rivers) and Italy (for the Po) have failed to plan nutrient removal for agglomerations in the (upstream)

catchment of Sensitive Areas. The Commission points out that since nutrients are carried downstream, designation of part of a catchment must inevitably mean effective designation (and nutrient removal requirements) for all agglomerations upstream of this area.

The Commission indicates that the legal actions it has brought against certain Member States has been effective in leading to improvements in Sensitive Area designation and that most member states now plan to achieve conformity with the nutrient removal requirements of the Directive by 2005 – 2008.

**Germany and The Netherlands have achieved respectively 90% and 79% total removal of phosphorus from sewage** (in conformity with the Directive) and 74% and 66% removal of nitrogen (not conform). These States have designated some time ago their whole territory as Sensitive Areas

### **Inadequate sewage treatment**

Particularly poor performing Member States, according to the Commission's report, include **Belgium**, where a number of large agglomerations (including Brussels, Liège) do not even have adequate sewage collection systems, and only 22% of sewage flowing into Sensitive Areas is treated adequately (the whole of Belgium has now been classified as a Sensitive Area).

**Greece** achieves only 10% adequate treatment of discharges into Sensitive Areas.

**Spain** has still not adequately designated Sensitive Areas (the Commission has identified 44 areas which should be but have not yet been designated). Spain also failed to provide performance monitoring results regarding treatment, but the Commission estimates that only 25% of wastewater flowing into Spain's Sensitive Areas (as designated to date) is treated adequately.

**France** is also pinpointed as not having adequately identified a number of Sensitive Areas, and is currently facing legal action from the Commission on this issue. France also failed to provide adequate monitoring data. The Commission estimates that only 36% of

wastewater flowing into French Sensitive Areas (as designated to date) is treated adequately.

**Italy**, as indicated above, is criticised for inadequate designation of Sensitive Areas and all catchments of the Po and the Adriatic will need to be designated. Cities currently without adequate sewage treatment or appropriate nutrient removal include Milano (under construction), Venice, Rimini, Ravenna, Cagliari, Como, Trieste and Florence.

### **Legal pressure**

The Commission is backing up its report with **legal actions against Member States**, announcing actions against 8 Member States (Commission [Press Release](#) 13<sup>th</sup> January 2004, ref. IP/04/39). The legal actions are against **Belgium, France, Germany, Greece, Ireland, The Netherlands, Portugal and Spain** for non-compliance with different EU water regulations including dangerous substances discharged to water, drinking water, beach pollution, shellfish waters, the nitrates directive.

In particular, **France is being referred to the European Court of Justice** for failure to provide information concerning implementation of the Urban Waste Water Directive, and in particular concerning designation of Sensitive Areas. **Spain** has received a final written warning for contravening this Directive and the Bathing Water Directive in the region of Valencia with inadequate sewage treatment leading to beach water pollution.

On 25<sup>th</sup> March 2004, the [conclusions](#) of the Advocate General to the European Court of Justice to the European Court suggested that **France should indeed be condemned for failure to designate as Sensitive areas which are subject to eutrophication** in the Seine-Normandy, Artois-Picardie and Rhône-Mediterranean-Corsica basin authority areas, and consequently for failure to ensure adequate treatment of sewage in these areas. This follows condemnation of France in the European Court in a separate procedure for failure to take account of nitrates contribution to eutrophication (see [SCOPE Newsletter n°46](#)).

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## SCOPE NEWSLETTER

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### Sweden and Finland

However, the Commission is also pointing to Member States usually reputed for the quality of their water treatment, and has sent Final Written Warnings to both **Sweden and Finland**, indicating that they are failing to ensure adequate nitrogen removal in sewage works discharging in the Baltic Sea (Commission [Press Release](#) 2<sup>nd</sup> April 2004, refs. IP/04/449).

The Commission has also published a [summary](#) of **recent European legal judgements** regarding environmental issues, which provides information on a number of different legal actions brought by the Commission against Member States for non compliance with different EU Directives concerning water quality and sewage treatment.

*EU Commission Third Report into implementation of the Urban Wastewater Treatment Directive 91/271, document refs. COM(2004)248 : [http://europa.eu.int/eur-lex/en/com/rpt/2004/com2004\\_0248en01.pdf](http://europa.eu.int/eur-lex/en/com/rpt/2004/com2004_0248en01.pdf)*

*EU Parliament Resolution March 2002:*

[http://www.europarl.eu.int/plenary/default\\_en.htm](http://www.europarl.eu.int/plenary/default_en.htm) then go to "Texts adopted by Parliament" -> "By date" -> March 14<sup>th</sup> 2002 or by number A5-0459 or P5\_TA(2002)0122

[http://www3.europarl.eu.int/omk/omnsapir.so/calendar?AP=P=PDF&TYPE=PV2&FILE=P5\\_TA\(20020314\)0122en.pdf&LANGUE=EN](http://www3.europarl.eu.int/omk/omnsapir.so/calendar?AP=P=PDF&TYPE=PV2&FILE=P5_TA(20020314)0122en.pdf&LANGUE=EN)

*EU sewage treatment "name and shame" press release*

[http://europa.eu.int/comm/environment/nsf/city\\_sewage.htm](http://europa.eu.int/comm/environment/nsf/city_sewage.htm)

*Commission permanent update page summarising infringement procedures:*

[http://europa.eu.int/comm/secretariat\\_general/sgb/droit\\_com/infractions](http://europa.eu.int/comm/secretariat_general/sgb/droit_com/infractions)

*Commission summary of leading cases in European Environment law*

[http://europa.eu.int/comm/environment/law/leading\\_cases\\_en.pdf](http://europa.eu.int/comm/environment/law/leading_cases_en.pdf)

*Advocate General to the European Court conclusions concerning France's failure to adequately designate "Sensitive Areas", refs. C-280/02 Opinion 2004-03-25:*

<http://www.curia.eu.int/jurisp/cgi-bin/form.pl?lang=en&Submit=Submit&docrequire=alldocs&numaff=c-280/02>

## 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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**The SCOPE Newsletter is circulated, free of charge electronically : to receive it or to unsubscribe:**

<http://www.ceep-phosphates.org/subscribe.htm>



# CEEP

Centre Européen d'Etude  
des Polyphosphates

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# SCOPE NEWSLETTER

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NUMBER 54

March 2004

## Special : P-recovery seminar summary

### Seminar

#### **German Environment Agency (UBA) p2**

A seminar organised by Germany's Federal Environment Agency UBA and the Aachen Institute for Water Management RWTH addressed a wide range of issues concerning phosphate resources, plant and crop needs, phosphorus fate in the landscape and technical perspectives for P recovery and P recycling.

## Phosphorus recycling

### Phosphate removal

#### **P-release in biological P-removal p6**

10-25% of phosphorus in sludges from biological P-removal plants can be released during digestion, generating a significant return of soluble phosphates to the sewage works head and reducing P-removal effectiveness. The authors suggest that this release can be kept below 10% by appropriate sludge management.

### Scaling

#### **Preventing struvite precipitation p8**

Struvite precipitation offers a route for recycling phosphorus from sewage, but can also cause significant scaling problems in waste water treatment works. The effects on struvite precipitation of 4 anti-scaling products and chelating agents were tested.

### The Netherlands

#### **Biological P-removal for sustainability p9**

Summary text for front page  
Integrated design of biological phosphorus and nitrogen removal sewage works can minimise energy production and CO<sub>2</sub> emissions, enable phosphorus recovery, and enable strict discharge limits to be met.

## Nutrients and ecosystems

### Sweden

#### **Variations in benthic algae**

A study of benthic algae in Lake Erken, Sweden, showed considerable variability in algal biomass at many different sites over the areas of the lake, apparently not related to the local nutrient status.

## Call for Papers:

**STRUVITE:  
its role in phosphorus recovery  
and reuse**

**International Conference  
Cranfield University, England,**

**17-18 June 2004**

**Authors are invited to submit an extended abstract  
(up to 2 pages) by 30<sup>th</sup> March 2004.**

**Travel and conference costs for selected speakers  
will be covered by the organisers**

### **Selection of papers:**

\* The conference covers themes from struvite precipitation chemistry, through experience of struvite recovery units operating in sewage and animal waste streams, to the value of struvite as a fertiliser (see conference flier)

\* Extended abstracts must be submitted by email to [struvite@cranfield.ac.uk](mailto:struvite@cranfield.ac.uk) by 30<sup>th</sup> March 2004: maximum 2 pages including figures etc. References of previous published papers should be included.

\* Papers will be selected by the Conference Organisers for acceptance for presentation at the conference and for selected papers for travel and conference cost coverage. Priority will be given to papers presenting practical experimental or pilot scale experience and results.

\* Authors will be informed by 30<sup>th</sup> April as to whether their paper has been accepted and whether cost contribution is possible

\* Papers selected to be presented at the Conference should be submitted as full manuscripts (max 8 pages) in "Water Science and Technology" format by 30<sup>th</sup> May. These will be reviewed and selected papers will be published in this Journal.

### **Further information:**

<http://www.cranfield.ac.uk/sims/water/struvite/>

*Special :*  
P-recovery seminar summary

### Seminar

#### German Environment Agency (UBA)

The German Federal Environment Agency UBA seminar on phosphorus recovery for recycling in February 2003 brought together around one hundred experts, regulators and water industry operators (SCOPE Newsletter n° 52). The Conference led to the announcement by UBA of phosphorus recovery as a national objective (see <http://www.nhm.ac.uk/mineralogy/P-recovery/UBApressrelease.doc>).

The 2001 Annual Report of the German Federal Environment Agency (UBA) stated: "In the context of new orientations for waste management, it is planned to initiate cycling for phosphorus. Phosphorus containing wastes include sewage sludge, animal and poultry wastes, slaughter wastes, human and food wastes. After separative incineration, the phosphate content from these wastes can be recovered for recycling. Today, phosphate fertilisers are exclusively manufactured from mineral phosphate rock. Inevitably, this raw material will progressively become scarcer and more expensive globally. The element phosphorus is an essential plant nutrient which cannot be substituted by any other element, and is therefore vitally important for crop production. Therefore, technology development should rapidly be launched to recover phosphorus from domestic phosphate-rich waste streams in order to produce fertilisers which offer both hygiene safety and plant availability and efficiency of nutrients."

**The Berlin 2003 seminar presentations have been published and include 18 papers, mainly in German.**

The first papers look at availability of phosphorus resources and use of phosphorus by plants.

**E. Schnug** gave a detailed balance of the pathways for P in soils, the short- and long-term availability of fertilizers, and the amounts of P needing to be added to soils in Germany, questioning whether soils need over the long term the levels of phosphate addition they are currently receiving.

**D. Pradt** (Agricultural Industry Federation, Frankfurt) indicated that existing known mineral rock reserves amount to around 12 billion tonnes, with estimated as yet unexplored reserves of a further 22 billion tonnes, compared to consumption (2001) of around 126 million tonnes. The agricultural mineral fertiliser industry uses 80-90% of world phosphate production. Resources are thus finite but not rare, but 75-80% of (known – unexplored) reserves are held by only three countries: Morocco, Jordan and South Africa. Sources of recovered phosphates must fulfil criteria of quality, logistic availability and public acceptance, and if these conditions are met, may be used by the fertiliser industry.

**W. Römer** (Georg-August University, Göttingen) presented experiments into plant uptake of phosphorus from soils treated with sewage sludges containing different iron:phosphorus (Fe:P) ratios. He concluded that Fe:P ratios > 1.4:1 resulted in significantly reduced plant phosphorus uptake and even would fix and render unavailable for plants both existing soil phosphorus or phosphorus added in fertilisers.

**H-G. Frede and M. Bach** (Giessen University) presented a simplified balance of agricultural phosphorus flows in Germany (2000). This can be interestingly compared with the complete P-balance (all uses, including domestic and agriculture) prepared for The Netherlands by Fong, presented by Van Ruiten 1998 (See <http://www.nhm.ac.uk/mineralogy/phos/manure.htm>) The authors show that Germany imports 196,000 tonnes of phosphorus per year (tP/y) into agriculture, plus inputs of 61,000 tP/y from domestically grown animal food crops. Net excess phosphorus from German agriculture is 166,000 tP/y, susceptible in time to be lost from soil to surface waters. *SCOPE Newsletter authors note:* this agricultural excess can be compared for example with an estimated use of phosphorus in dishwasher detergents in Germany of 20,000 tP/y (derived from AISE 1999 data).

#### P-recovery techniques

A number of authors presented different proposed **systems for extracting phosphorus from waste streams in a recyclable form.**

**Ruckert et al.** (Fraunhofer Institute) presented a process for treating manures to produce biogas

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## SCOPE NEWSLETTER

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(methane), compostable solids and then (after ultra-filtration and reverse osmosis) precipitation of phosphorus as struvite (magnesium ammonium phosphate MAP). This process has previously been described in English at the [Second International Conference on Phosphorus Recycling](#) (Noordwijkerhout, 2001) and a full-scale pilot plant is now operational in Belgium (see [SCOPE Newsletter n° 52](#) page 4).

**U. Brüß** (A3 GmbH, Gelsenkirchen) proposed struvite MAP precipitation from manures after biogas production, settling/solid separation, ultra-filtration, with membrane clarification and reverse osmosis as final steps after the phosphate precipitation.

**G. Kley et al.** (German Federal Office for Materials Research and Testing – Bundesamt für Materialforschung und –prüfung – BAM, Berlin) discussed possibilities for P recovery for recycling from sewage sludges and manures by thermal processes. The authors present analyses of ash from incineration of different sewage sludges (Schirmer, 1998) showing phosphate contents ( $P_2O_5$ ) varying from 9.9 – 19.3% (that is 3.7 - 7.1 % P) and from animal manure incineration of 27.7%  $P_2O_5$  (10.2% P) (Feistel). The sewage sludge ashes show iron levels of up to 20% ( $Fe_2O_3$ ), copper up to 0.012% (Cu) and zinc up to 0.039% (Zn) which could prove to be obstacles to recycling in the phosphate industry (see [Schipper et al.](#) at the [Second International Conference on Phosphorus Recycling](#) Noordwijkerhout, 2001) <http://www.nhm.ac.uk/mineralogy/phos/Nordwijkerhout/Schipper1704.doc> The authors suggest thermal treatment with alkaline earth chlorides to evaporate the heavy metals from the ash. They also suggest thermal treatment with sulphate of meat and bone meal ash to improve the availability of phosphate to plants.

**J. Rogasik et al.** (German Federal Office for Land Economy - Bundesforschungsanstalt für Landwirtschaft, Braunschweig) also gave figures for the P content of incineration ashes from animal manures and sewage sludge, as 18.6% and 3.6%P respectively (I. Rosyadi, 2003, unpublished). Rosyadi also showed that the plant availability of phosphorus can be improved by inoculation of *Thiobacillus* and elemental sulphur.

**K. Fricke** (Braunschweig Technical University) and **W. Bidlingmaier** (Bauhaus University Weimar) indicated that effective usability of phosphate rock resources depends on the ratio between phosphorus and cadmium, and that P-recovery from organic wastes offers the benefit of providing a P-resource with low cadmium levels. They presented an assessment of arisings of different phosphorus-containing wastes for Germany, taking into account realistically feasible levels of collection, giving the following **annual arisings potentially available for recovery for P-recycling**:

(in tonnes P/year):

* organic part domestic refuse,	
food wastes	6,425
* garden/park wastes (woody)	717
* garden park wastes – other	3,466
* sewage sludges	31,185
* slaughter house wastes	5,460
* food wastes, wine industry, fruit, paper wastes, etc	1,120
* wood bark	945
TOTAL	49.316

Certain slaughter house wastes subject to specific regulations requiring their hygienic disposal are not included. The authors reach a total of 49,316 tonnes P/year. SCOPE Newsletter authors' note: the above figures do not include phosphorus arisings in agriculture: crop wastes, animal manures from livestock and poultry production.

**N. Jardin** (Ruhrband, Essen) presented detailed information concerning phosphorus flows into and through sewage treatment works and implications for phosphorus recovery (see also his [previous paper in English](#) at the [Second International Conference on Phosphorus Recycling](#) Noordwijkerhout, 2001). For 2002, he estimated (UBA Umweltbundesamt 1999 "[Nährstoffbilanzierung des Flussgebiete Deutschlands](#)" 75/99 ) the average domestic phosphate load to sewage works as 1.9 gP/person/day, of which detergents (dishwasher) around 0.3gP/person/day. The phosphorus loads from households to municipal sewage works in Germany were thus around 51,500 tonnesP/year (74.2 million persons connected to sewage works), to which an additional 40% (+19,600 tP/y) from industry were added, giving a total of 72,100 tP/y reaching municipal sewage works.

A 1999 survey suggested that 92% of the German population was then connected to sewage works, with phosphorus being removed to below 1 mgP/l (annual average) for 79% of waste waters being treated. Consequently, phosphorus emissions from German sewage works to surface waters had been reduced by 80% (1983-1985 to 1993-1997), down to 11,350 tP/y (that is 16% of sewage works inflow phosphorus as estimated above).

Jardin provides (reference UBA as above, 1999) a **breakdown of phosphorus inputs to the environment in Germany for 1993-1997:**

	(in tonnes P/year):
* municipal sewage works	11,350
* industrial discharges	1,250
* storm and sewage overflow	2,570
* erosion, drainage water, underground water, and other diffuse sources	22,070
<b>TOTAL</b>	<b>37.240</b>

**Jardin then presented material flow balances for phosphorus in different types of sewage works configuration.** In a conventional sewage works (without nutrient removal) he suggested that the inflow phosphorus will go 11% to primary sludge, 37% to secondary sludge, leaving 52% in discharge water. Where simultaneous chemical P-stripping is installed, 11% of inflow phosphorus continues to go to primary sludge, but now 79% goes to secondary sludge (37% in organic form, 42% as insoluble precipitate), leaving only 11% in discharge. Where biological P-removal with chemical “finishing” is installed, the same figures were given, but with only 5% in insoluble form in the secondary sludge.

Jardin concluded that **around 90% of input phosphorus in sewage works is potentially available for recovery from sewage sludge or from sewage sludge incineration ash**, that is around 64,000 tonnesP/year for Germany – corresponding to some 43% of national mineral phosphate fertiliser use.

**T. Buer and D. Montag** (RWTH Aachen) took a somewhat different premise, suggesting that only the phosphorus removed in sewage works but not transferred to primary or excess secondary sludge, that is 33-67% of inflow P, would be available for phosphorus recovery processes operating within the sewage works. They discussed configurations for

integrating P-recovery into sewage works using chemical or biological P-removal, and presented a number of possible technical processes for phosphorus recovery for recycling (including cost estimations for each): calcium phosphate precipitation, ***BioCon process*** (P-recovery from sludge incineration ash), struvite precipitation from sludge filtrate. A more detailed paper is available at: [http://www.isa.rwth-aachen.de/docs/wiss\\_Anh\\_KTBL\\_Buer.pdf](http://www.isa.rwth-aachen.de/docs/wiss_Anh_KTBL_Buer.pdf)

### **P-recovery in Berlin**

**Heinzmann and Engel** (Berlin Wasserbetriebe BWB) presented a **detailed study of P-recovery feasibility at Berlin’s two largest sewage works** (Wassmannsdorf 169,000 m<sup>3</sup>/day and Ruhleben 208,000 m<sup>3</sup>/day) and a pilot experiment at WWTP Wassmannsdorf. These works achieve <0.5 mgP/l discharge by carefully designed and controlled biological P-removal only.

Material flow balances for phosphorus at both of these sewage works were carried out and showed very similar results: 5% of inflow P goes to filter sand, aerosols, etc, 11% to primary sludge, 81% to bio-P secondary sludge, and just 3% to discharge water.

Wassmannsdorf sewage treatment works has suffered major struvite incrustation problems in sludge centrifuges (see <http://www.nhm.ac.uk/mineralogy/phos/Nordwijkerhout/Heinzmann1704.doc>), so that P-removal for recovery offers significant potential advantages in terms of operating cost savings and problem prevention. Analysis of the material flow balance suggested that the optimal site for P-recovery would be at the outflow of the anaerobic sludge digesters.

**A pilot struvite precipitation installation has therefore been installed**, with an aeration reactor in which magnesium chloride is dosed (and aeration drives off carbon dioxide, resulting in a pH increase). This also enabled dosage of cationic flocculation agents (prior to the sludge centrifuges) to be reduced.

However, the struvite was then mixed in with digested sludge in the centrifuges. Analysis showed that 95% of the struvite crystals were of length >63µm. One hydrocyclone was therefore installed between the struvite reactor and the centrifuges in order to selectively recover the larger, denser struvite crystals but not the organic sludge. Trials

were also carried out with a recycling of the outflow of the hydrocyclone back to the precipitation reactor. The hydrocyclone separation resulted in a precipitation product, after washing, with 17% phosphate = 6.3% phosphorus (P) and a very low organic content, but with significant levels of other precipitation products. Impurity levels (heavy metals, AOX ...) were tested and found to be very low (lead, chromium, nickel, AOX < 100 ppm, copper and zinc < 300 ppm).

**A full translation of this paper**

(Heinzmann and Engel) is available at

<http://www.nhm.ac.uk/mineralogy/P-recovery/>

### Phostrip and P-recovery

**E. Kaschka**, Posch & Partners Innsbrück Austria, <http://www.pap.co.at/english.html>, presented experience of integrating phosphorus recovery into the “Phostrip” biological nutrient removal process. This process is based on the inclusion of a phosphorus “stripper” in the return stream recycling sludge from the final settling tank back into the biological nutrient removal system. This stripper is an anaerobic (up to 14 hours) tank (plus pre-stripper tank), which ensures both thickening of the sludge and release from the sludge of biologically removed phosphorus (stored within bio-P micro-organisms cells) into a soluble form. The lowering of the micro-organism cellular P-content in the return sludge improves the efficiency of the biological phosphorus removal process.

The authors presented a detailed phosphorus flow balance for two municipal sewage works operating “Phostrip” process biological nutrient removal: Hoffkirchen Austria (6.3 kgP/day inflow) and Darmstadt-Eberstadt Germany (69kg P/day inflow). Both plants achieved over 90% P-removal. Phosphorus concentrations in the P-stripper outflow water were respectively 80-110 and 25-30 mgP/l, but with experience showing that concentrations at Darmstadt- Eberstadt could be increased by increasing the anaerobic residence time in the stripper. The authors conclude that the Phostrip system provides, in the P-stripper outflow, a cost-effective site for phosphorus recovery.

Experiments at Darmstadt-Eberstadt are reported (Hillenbrand *et al.* 1999) where lime slurry was added to the P-stripper supernatant outflow to precipitate calcium phosphates (pH raised to 9 –

9.5). After static settling, the product reached around 25% dry solid content, so that further dewatering (filter press) was necessary to achieve a produce with 40% dry solid with low organic content and 19-20% phosphorus which hardened to a cake (Barti 2003). This product was not considered to be of value for direct use as a fertiliser, because of the low solubility of the calcium phosphates, but had value as a soil improver, or as a raw material for the cement industry, or particularly as an additive in the calcium carbonate industry.

Phosphorus can also be recovered from the P-stripper outflow stream as calcium phosphate pellets using a fluidised bed reactor as at Geestmerambacht sewage works (see S. Gaastra’s papers at the First International Conference on P-recovery <http://www.nhm.ac.uk/mineralogy/phos/gaastr.htm>), or in theory by precipitation as aluminium phosphate or as magnesium ammonium phosphate (struvite = MAP).

Cost elements for Phostrip system operation at four different municipal sewage works in Austria were presented (Wallen, Schlalchen, Braunau, Hofkirchen). Estimated costs for P-removal by chemical precipitation (iron addition) were compared to those for biological P-removal (Phostrip) with either filtration or phosphorus recovery (as calcium phosphate cake). For all sludge handling/disposal cost scenarios (50€/tonne upwards), the biological P-removal options were cheaper than chemical P-removal plus polymer flocculation. Phosphorus recovery costs were comparable or marginally higher than Phostrip+filtration costs, depending on costs of filter materials.

**A full translation of this paper** (Kaskchka)

is available at

<http://www.nhm.ac.uk/mineralogy/P-recovery/>

**A. Giesen and R. de Boer**, DHV Amersfoort <http://www.dhv.com>, The Netherlands, presented experience in phosphorus recovery using the “Crystallactor” process. Plants using this fluidised bed precipitation process have been constructed and operated for removal/recovery of heavy metals, fluorides from industrial liquors, for the softening of drinking and process water, and for the recovery of phosphates from municipal sewage works liquors (see in particular S. Gaastra papers indicated above) and from food-industry waste waters (see P.

Piekema paper at the Second International Conference on P-Recovery (<http://www.nhm.ac.uk/mineralogy/phos/Nordwijkerhout/Piekema.pdf>). This process can produce compact pellets (0.8-1.0mm) with 90-98% phosphate content and low (1-5%) water content after simple draining. Experience at Westerbork and Geestmerambacht municipal sewage works, The Netherlands is summarised (calcium phosphate precipitation), as well as struvite (MAP) precipitation in a potato processing plant waste stream. In recent pilot plant experiments for a chemical industry waste stream, potassium magnesium phosphate precipitation was tested, but magnesium phosphate precipitation proved more effective. In ongoing tests reported with a food industry waste stream, calcium phosphate and magnesium phosphate precipitation are being compared (in all cases, using the Crystallactor process). The authors indicated that magnesium phosphate precipitation can be achieved under high loading and is not perturbed by carbonate concentrations (which are a problem for the Geestmerambacht sewage works calcium phosphate Crystallactor operation).

**C. Cornel and D. Schaum**, Technical University Darmstadt, Germany, presented various processes proposed for recovering phosphates from sewage sludge or from sewage sludge incineration ash. The Kemira Kemwater Krepro process is presented, including detailed mass balance and cost information (see SCOPE Newsletter n°41 page 32, <http://www.ceep-phosphates.org/scope/articles/scope41/Scope41.pdf>

The authors also briefly present the **Seaborne process** for recovering different values from organic sludge, for which a pilot plant is operational at Owschlag and a full-scale plant is being constructed at Stadt Plön (both Schleswig-Holstein) – see below, and the Aqua Reci (Feralco AB <http://www.feralco.com/feralco/ferintr1.nsf>) process for wet oxidation of sewage sludge. The authors indicated that sewage sludge incineration ash can contain 4-8% phosphorus (P) but that heavy metal or other contaminants can be an obstacle to the use of this as an industrial raw material. They conclude that under present conditions, phosphorus recovery by these routes is unlikely to be economically feasible.

**N. Vesterager**, Seaborne Environmental Research Laboratory GmbH, Owschlag, Germany, presented

the Seaborne process, which treats organic materials (such as sewage sludge) to produce biogas by fermentation (methane), heavy metal removal (by sulphide precipitation), and nitrogen and phosphate values as ammonium phosphate for fertiliser. The process can be adapted to recover magnesium or calcium phosphate.

**D. Donnert**, Karlsruhe Research Centre KZH, Germany, presented experimental phosphate precipitation from waste waters using Calcite and Tobermorite as seed materials. The interaction of phosphorus with the two materials led to fixation onto the seed material surface, and the precipitation of calcium phosphate with calcium from the Calcite improves the process for this material. The authors suggest that this process can be used to recover phosphates from waste waters with relatively low phosphorus concentrations in the range 5-10 mgP/l, as well as from liquors with higher concentrations (>200 mgP/l). Phosphorus precipitation is inhibited by the presence of organics in the water, particularly for the Calcite seed material. See also <http://www.nhm.ac.uk/mineralogy/P-recovery/projects.htm>

In a final paper, **Jürgen Hahn, of the German Federal Environment Office (Umweltbundesamt UBA)** announced the development of phosphorus recovery for recycling as an objective, suggesting that technical process R&D could be funded from existing taxes on waste waters. A translation of this paper is available at: <http://www.nhm.ac.uk/mineralogy/P-recovery/UBApressrelease.doc>

### Phosphorus recycling

#### Phosphate removal

#### P-release in biological P-removal

Biological phosphorus removal processes (EBPR) in sewage treatment function through a series of anaerobic, anoxic and then aerated phases. In the presence of readily available fatty acids, micro-organisms subject to such conditions, take up significant levels of phosphates during the final aerobic phase, enabling high levels of P-removal to be achieved. However, if this phosphorus-enriched

EBPR sludge then becomes anaerobic, the micro-organisms will tend to re-release phosphorus, as soluble phosphates. This is an issue in sludge holding tanks, sludge thickening, and particularly in anaerobic sludge digestion.

The authors used a laboratory scale experimental anaerobic sludge digester (17 litre, 35°C, 20 day solid retention time) to assess **rates of and conditions for soluble phosphate release from EBPR sludge**. The sludge was generated by a 1.3m<sup>3</sup> pilot EBPR plant fed with real sewage, and was thickened by centrifuge before digestion. The digester was fed with various combinations of EBPR sludge (from the biological P-removal part of the pilot plant), primary sludge from the pilot plant (from the primary settling tank, upstream of the EBPR part of the plant), pre-fermented primary sludge (after anaerobic treatment at 20°C for 6 days), and EBPR sludge from the pilot plant operated with additional phosphate in its influent (resulting in EBPR sludge with a higher P content).

Phosphate concentrations in the EBPR sludge reached 300g totalP/m<sup>3</sup> and 400g when the pilot plant influent was dosed with additional phosphate (P/COD = 3-3.5% and 4-4.5% respectively). The P/COD ratio was reduced to 1.7-2% using the mixed primary + EBPR sludge (just over 50% primary sludge) and to 2-2.3% using mixed pre-fermented primary + EBPR sludge (similar ratio).

### Modelling P-release

A mathematical model was developed of phosphorus release mechanisms under different sludge conditions, taking into account in particular effects of concentrations of iron, calcium, aluminium, magnesium ions on phosphate precipitation:

\* **struvite (magnesium ammonium phosphate)** is precipitated according to the release of magnesium ions by hydrolysis of organic polyphosphates in the sludge and other degradation of organic solids. A ratio of 0.25 gMg/gP is frequently found.

\* **calcium ions** largely originate in sludge from release from detergent zeolites (sodium aluminium silicates). These zeolites are used in detergents to sequester calcium ions from the wash water.

\* **detergent zeolites** in the sludge also provide aluminium ions when they are partly degraded. Aluminium release was found to be constant in the

digester at 0.52%/day. Almost all aluminium in fresh sewage sludge is known to come from by detergent zeolites (Jardin and Pöpel 1994, Wild *et al.* 1996).

\* **iron** is only available for fixation of phosphorus after deduction of that needed for available sulphur

The model allows prediction of phosphorus release rates at different plant operating conditions, for different process configurations, water hardness, concentrations of detergent zeolites, phosphorus, etc.

### Return of phosphates to sewage works head

The authors found that 10-25% of phosphorus in EBPR sludge was released as soluble phosphate when EBPR sludge alone was digested, levels which would represent a considerable obstacle to efficient operation of biological phosphorus removal on return to the sewage works input. When mixed sludge was digested, however, even with pre-fermented primary sludge, release of soluble phosphates could be kept below 10% (equivalent to 20% of the EBPR sludge P-content, if it is assumed negligible release from the primary sludge).

This does not take into account the risk of return of insoluble phosphates to the sewage works head, which will also occur if the separation of solids from the digester supernatant is insufficient. If such insoluble phosphates are not easily soluble, they should not affect the biological P-removal process.

The authors note that a further problem area can be the thickening step prior to sludge digestion, as this can be long enough for anaerobic conditions to develop and phosphates to be released, but too short for these to be precipitated. This is particularly true if EBPR and primary sludges are mixed for thickening, because the available fatty acids in the primary sludge will accelerate phosphate release.

*"Prediction of recycle phosphorus loads from anaerobic digestion" Wat. Res. Vol. 13, n°9, pages 2300-2308, 1997.*

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### Scaling

#### Preventing struvite precipitation

Struvite (magnesium ammonium phosphate = MAP) scale formation has been reported as causing problems in municipal waste water treatment works (wwtp), in severe cases obliging replacement of lengths of piping or affecting pumps, aerators, centrifuges. The hard deposits formed can often only be removed by chipping them away by hand, or by using corrosive acid to dissolve them, leading to significant operating costs.

Struvite precipitation particularly occurs where aeration causes CO<sub>2</sub> to be driven off, leading to a pH increase. Ohlinger (1999) showed that increased energy input to sludge liquors, creating turbulence, led to CO<sub>2</sub> off-gassing, increased pH, and so struvite precipitation.

Whilst struvite precipitation offers a potential route for recovering phosphorus from sewage for recycling (P-recovery), it is thus, on the other hand, often a significant operating problem.

**Beaker tests** using sludge liquor were used to assess the effectiveness of 4 commercial anti-scaling additives and of 3 chelating agents in preventing struvite precipitation. The most effective product (the chelating agent EDTA) was also tested to establish whether it could be used to dissolve away existing struvite deposits.

Anaerobically digested sludge liquor from the centrate line of **Coleshill Sludge Destruction Plant, Warwickshire, England** (Severn Trent Water) was acidified to prevent struvite formation in storage or transport, then centrifuged to remove suspended solids. Phosphorus, calcium and magnesium concentrations were in the ranges 0.5 to 3 mMol. To test struvite precipitation, magnesium was added up to around 3mM/l, then the liquor was stirred for 5x8 hours at 150rpm using a stainless steel impeller with a surface of just over 12,000mm<sup>2</sup>. After 8 hours of stirring, the liquor was replaced. Between each 8-hour run, the impeller was dried and weighed (to assess deposits). After the 5<sup>th</sup> and final 8-hour run the impeller was placed in nitric acid to dissolve the struvite deposit, and phosphorus, magnesium and calcium concentrations measured to

determine the total mass of struvite deposited. Each experiment was repeated in triplicate.

#### Effect of pH

The acidified liquor's starting pH was below 7, rising to 8.5 after 8 hours stirring. Struvite mainly precipitated on the points of the impeller most subject to turbulence. The mass of struvite deposit clearly increased, linearly, with each 8-hour run, with slightly higher masses of deposit at higher supersaturation ratios

#### Inefficient commercial products

The effects on struvite precipitation of 4 commercial anti-scaling agents, dosed at around 30 mg/l, and of 3 chelating agents (acetyl acetone = AcAc, NTA, EDTA), dosed at around 8mM/l, were compared to a control (no chemical addition).

**Only one of the four anti-scaling products had any significant impact on struvite precipitation.** This one product led to an approx. 50% reduction in struvite deposits, but further work would be needed to establish whether this could be achieved at dosages economic for real liquors. Of the chelating agents, AcAc had no discernible effect, NTA a limited effect, but EDTA was very effective (more effective than the one effective anti-scaling agent). The authors suggest that the effect of EDTA may be achieved by chelating magnesium ions out of solution, thus removing them from availability for struvite precipitation.

Further work was carried out using EDTA at different dosage concentrations, suggesting that a molar dosage of 2 EDTA : 1 magnesium was effective in controlling struvite precipitation (95% reduction). Surprisingly, EDTA, even at molar ratios <2:1, also proved able to cause significant dissolving of previously formed struvite deposits after 8 hours, with the dissolution rate being related to the EDTA concentration.

*"Chemical control of struvite precipitation", Journal of Environmental Engineering, vol. 129, issue 5, May 2003, pages 419-426 <http://ojps.aip.org/eeo>*

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See also summaries of: "Struvite formation, control and recovery" and "Struvite formation and the fouling properties of different materials" in *Water Research*, see SCOPE Newsletter n°50 at [www.ceep-phosphates.org](http://www.ceep-phosphates.org)

### The Netherlands

#### Biological P-removal for sustainability

A combination of specific design of the mainstream biological nutrient removal configuration of municipal waste water treatment works, integrated with ammonium removal and phosphorus recovery from the return sidestream and sludge digestion (for methane production) enables overall environmental impact of sewage treatment to be minimised, in particular energy consumption, greenhouse gas emissions and phosphorus recovery for recycling.

The proposed biological nutrient removal system is based on the "BCFS<sup>®</sup>" (Biological and Chemical phosphorus and nitrogen removal system), developed from the standard UCT biological nutrient removal configuration. The implementation of this system in the upgrading of existing sewage works is described in [SCOPE Newsletter n°32](#) (Van Loosdrecht *et al.* 1998).

The standard configuration for biological nutrient removal plants is a mainstream series of anaerobic, anoxic then aerobic compartments, enabling respectively selection of phosphorus-accumulating micro-organisms, reduction of nitrates (to remove nitrogen), then phosphorus uptake by these organisms (in the presence of readily available organic carbons) in the anoxic (denitrifying dephosphatation) and aerobic zones. The BCFS configuration includes a "contact" zone between the anaerobic and anoxic zones, fed with nitrate-containing return sludge, to remove hydrolysis products and repress filamentous bacteria development; and a "mixed aeration" tank between the anoxic and aerobic zones. This mixed tank is aerated only if necessary and ensures simultaneous nitrification and denitrification to minimise effluent nitrogen levels. A sludge sidestream from the initial

anaerobic zone, rich in soluble phosphates, is used to enable phosphorus recovery for recycling.

This BCFS configuration selects denitrifying P-removal bacteria, which can use nitrate as an oxygen source instead of air in the aerobic P-removal zone, thus reducing by up to 50% the demand for readily available carbon necessary for nitrogen and phosphorus removal. The carbon thus economised is available for methane production in sludge digestion, thus providing net energy savings. Also, aeration energy requirements are reduced.

#### Struvite recovery

In order to optimise plant design for sustainability, whilst using known and tested technologies, the authors suggest that phosphorus recovery and ammonium removal should be installed downstream of the sludge digester (methane production) in the above configuration. Phosphorus recovery can be achieved using struvite precipitation (by magnesium addition), and ammonium removal using the CANON process ("Completely autotrophic N-removal over nitrite" - a biofilm reactor supporting simultaneous nitrification and ANAMMOX nitrogen removal).

Approximately 50% of the influent COD to the sludge digester is converted to methane, the rest remaining in sludge requiring disposal.

The inclusion of a pre-settling tank on the plant inflow allows the volume of the biological nutrient removal reactors to be reduced by around 50%.

The authors model inputs, outputs and operating parameters for an 8,500 m<sup>3</sup>/day inflow sewage treatment plant (inflow COD = 625 g/m<sup>3</sup>/day, TKN = 60 mgN/m<sup>3</sup>, P = 9.5 gP/m<sup>3</sup>). Effluent concentrations are 30 gCOD(inert)/m<sup>3</sup>, <5 - 9 gN/m<sup>3</sup> and <0.5 - 0.6gP/m<sup>3</sup>. The model suggests that 28% of influent COD can be converted into methane via sludge digestion, and 49% of total plant inflow phosphorus can be recovered as struvite, almost without additional costs.

#### Greenhouse emissions

Net energy use and CO<sub>2</sub> emissions are significantly lower than for a conventional sewage works. Energy use for aeration is reduced by 35-44%. Also, increased COD retention in sludge transferred to digestion, allows an increase in methane production

of 154-271%. The net energy balance for the plant then becomes positive: more energy is produced in methane than is consumed in the treatment processes and operation.

The authors suggest that such integrated sewage treatment systems, optimised for sustainability, could be compared favourably to proposed separate urine collection and treatment systems.

*“Contribution of P-bacteria in biological nutrient removal processes to overall effects on the environment”, Water Science and Technology Vol. 44 No 1 pages 67-76, 2001 <http://www.iwaponline.com/wst/toc.htm>  
X-D. Hao<sup>1,2</sup>, J.J. Hiejnen<sup>2</sup>, Y. Qian<sup>1,2</sup>, M.C.M. van Loosdrecht<sup>2</sup>.*

*“A proposed sustainable BNR plant with the emphasis on recovery of COD and phosphate”, Water Science and Technology Vol. 48 No 1 pages 77-85, 2003  
X.-D. Hao<sup>1,2</sup> and M.C.M. van Loosdrecht<sup>2</sup>.  
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## Nutrients and ecosystems

### Sweden

#### Variations in benthic algae

Lake Erken in Sweden (59°50'N) is a 24 km<sup>2</sup>, mean depth 9m, dimictic, alkaline and naturally slightly eutrophic lake with a mainly rocky or stony shoreline. Algae growing on submerged rocks floor,) were sampled by SCUBA diving.

Samples were collected on 9 dates in May-October 1996 and on four dates May-July 1997, in each case at several sites and a variety of depths: the sampling used different horizontal scales (cm, dm, 10m, km), compared both within and between seasons and successive years, and at depths of 0, 1 and 4 m. Samples were analysed for algal biomass/surface area, parameters such as nutrient:carbon ratios, and algal taxonomical composition. Over the same

periods water physico-chemical parameters were monitored in the pelagial, as well as parameters such as light and wind speed, and also specific samples of water were taken for nutrient analysis directly at the sampling sites.

Nutrient status of the collected algal samples was assessed on the basis of both nutrient:carbon ratios (C:N:P) and APA (alkaline phosphatase activity). Severe phosphate limitation was considered as corresponding to C:P > 369 and N:P > 32 on an atom:atom basis, or APA > 0.2 nmMUP $\mu$ g/Chl<sub>a</sub>/min; nitrogen limitation as C:N > 11. No nutrient limitation was assessed to correspond to C:N:P ratios of around 158:18:1.

Average (median) epilithon algal biomass for all sampling sites and periods was 8  $\mu$ gChl<sub>a</sub>/cm<sup>2</sup>, 1580  $\mu$ gC/cm<sup>2</sup> and 5 mm<sup>3</sup>/cm<sup>2</sup> biovolume. Average (median) nutrient ratios were C:N:P = 210:24:1, indicating an overall slight phosphorus limitation, but with high levels of variation both in space and time.

### Patchiness

There was considerable horizontal variation in both algal biomass and nutrient status, with both small and large horizontal scales accounting for large variations. There was also considerable variation with depth (lowest biomass at 0m depth) and with time (within-season variation was very high, but there was an overall increase in biomass in the Autumn after a summer minimum). *“Patchiness in the nutrient status of algae was not coupled to the patchiness of biomass, indicating that internal nutrients and biomass were regulated by different factors”.*

Local variation of nutrient ratios was much less than for biomass, suggesting that herbivore grazing could be an important factor in the biomass variability. Epilithon algae were obviously not nutrient regulated over the whole lake in the same way at the same time: at one site, algae seemed to have adequate supplies of both nitrogen and phosphorus; at other sites there were nutrient limit spots occurring only centimetres away from spots without apparent limitation. Nitrogen and phosphorus limitation appeared to occur independently of each other. Contrary to expectation, algae growing near local sources of nutrients (residential areas, bird roosts) did not show high nitrogen or phosphorus levels.

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The authors conclude that “variation in algal nutrient status was not coupled to that in algal biomass, indicating that different factors were responsible. Neither could we detect direct control of biomass by internal nutrients ... their effects may be overridden by biomass removal, turbulence or grazing”.

This shows the importance of sampling design in such studies, in order to limit the inaccuracies resulting from the wide variations, including over distances of 10cm, of algal biomass and nutrient status. Wind and water currents (including wave

effects), light limitation and groundwater effects are identified as key factors requiring further investigation.

“Spatial and temporal variation in the biomass and nutrient status of epilithic algae in Lake Erken, Sweden”.  
*Freshwater Biology*, n°47, pages 1191-1215, 2002.

<http://www.blackwellpublishing.com/journals/fwb/> and  
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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).

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

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

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# SCOPE NEWSLETTER

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**This special edition of the SCOPE Newsletter is devoted to positive nutrient management: fertilisation of lake, river and marine ecosystems**

## Maricult

### Maricult project overview

#### Fertilising the sea

Significant efficiency improvements in harvesting of marine resources could be achieved by artificial nutrient addition to coastal zones, and by harvesting algae, zooplankton or shellfish instead of carnivorous fish.

### Coastal bay

#### Nutrient addition and shellfish growth

Spring-summer nutrient addition to an enclosed coastal bay on the Norway coast resulted in significant increases in blue mussel and scallop growth.

### Marine mesocosm

#### Zooplankton response to nutrients

An 18 day mesocosm nutrient addition study in Norwegian marine waters showed a rapid but temporary increase in small zooplankton (ciliates) and a more stable increase in meso-zooplankton (copepods).

### Environmental impacts

#### Impacts of nutrient increases on marine ecosystems

The impact of nutrient addition on marine ecosystem balance was studied using both mesocosms and field monitoring of Hopavagen lagoon, whilst a further study assessed impacts of increased nutrient levels in the coastal North Sea.

## Salmonid ecosystem conference

### Conference overview

#### Nutrients sustain productivity and biodiversity

A first international conference on nutrients in salmonid ecosystems, 24-26 April 2001, looked at the importance of nutrients in sustaining ecosystem productivity and biodiversity, the potential for restoration of salmonid ecosystems and salmonid populations by artificial nutrient addition (fertilisation with phosphate and nitrogen) and at the conditions for and management of such initiatives

### Struvite fertiliser

#### Using struvite to add nutrients to salmon streams

Struvite (magnesium ammonium phosphate) and struvite/urea slow-release fertilizer combinations were tested in trough and field experiments to aid in rehabilitating nutrient poor Pacific Northwest streams, in order to restore salmonid populations.

### Keogh and Salmon Rivers

#### Nutrient addition to trout and salmon rivers

Over a decade, phosphorus and nitrogen addition to two British Columbia rivers resulted in increased weights and populations of trout and salmon.

### Big Silver Creek, Adam River

#### Nutrient addition increases trout productivity

Fertiliser was added for four years to two nutrient-impooverished coastal rivers, showing 4x increase in abundance of resident trout species in both rivers.

### Arrow Lakes Reservoir

#### Lake fertilisation to restore native salmon

A 5-year experimental programme of fertiliser addition (N and P) to the Arrow Lakes Reservoir, British Columbia, was started in 1999 with the aim of restoring populations of the native non-migratory kokanee salmon, following anthropogenic oligotrophication. The first two years' results show encouraging signs of ecological productivity and salmon spawning fecundity.

### Redfish Lake Idaho

#### Nutrient supplementation for salmon restoration

A 4-year nutrient addition programme in Redfish Lake resulted in increases of *Daphnia* zooplankton, a key salmonid food species, and showed an increase in the local Snake River Sockeye salmon population densities and a near tripling in salmon overwintering survival. Comparison with a control, unfertilised, lake suggests that some of this improvement could be due to climatic conditions, but that the nutrient addition was nonetheless effective.

### MARICULT

#### Fertilising the sea

Only 1% of world human food energy is currently supplied from fisheries and aquaculture (5% of protein needs). The MARICULT programme looked at how marine food production could be increased, whilst respecting ecosystem balance, through artificial fertilisation of coastal waters and changes in cultivation approaches.

The ultimate aim of the EU co-funded MARICULT programme was to find routes to increase sustainable production of feed, raw materials and energy from the ocean. The general strategy is both to **increase primary marine production, by creating artificial upwellings or by fertilisation (nutrient inputs)**, and to harvest at a lower trophic level (algae or zooplankton/ shellfish, instead of carnivorous fish).

Terrestrial agriculture largely harvest the lowest trophic level (vegetable crops = primary production). Where animals are produced, some 80-90% of the energy value stored in the vegetable material used as feed is lost. Fisheries, both natural and aquaculture, mostly harvest at least 2 or 3 trophic levels higher, and at each level much of the energy captured in primary production is lost.

#### Trophic levels in fisheries :

Level 1	algae
Level 2	zooplankton (eg. krill), shellfish
Level 3	fish: eg. herring
Level 4	fish: eg halibut, turbot
Level 5	fish: eg. tuna ; squid

Because fish production is harvested on average maybe 2 trophic levels higher than terrestrial agricultural products, the 1% of human food energy currently supplied from fisheries may correspond to around the same primary production as that of agriculture.

All articles concerning Maricult project summarised in this Newsletter are published in **Hydrobiologia** 484, [www.wkap.nl](http://www.wkap.nl)

Abstract: use search function at:  
<http://www.kluweronline.com/issn/0018-8158/contents>

Maricult web site [www.maricult.org/](http://www.maricult.org/)

#### Food chain structure

Various projects in MARICULT looked at **food web reaction to increased nutrient supply**. This confirmed that a balanced N:P:Si input generally resulted in a positive increase in primary production. Although pico-cyanobacteria dominated European summer coastal waters, these are in fact tiny cellular blue-greens which are not problematic. In euphotic waters, zooplankton graze around one half of primary production. Little energy or materials from bacteria are taken up by grazers, so that the base of the food web is essentially linear, with zooplankton depending directly on algae (primary production) for food.

**This increased primary productivity is fairly reliably related to overall increased fishery productivity** (at higher trophic levels), but the effects in a given region or on a given fish species are less predictable, because of fish movements and species interactions.

#### Artificial fertilisation

Marine water fertilisation can be achieved either by adding nutrients or by generating artificial upwellings (upward water movements, which can bring nutrient-rich deep waters up to the light, enabling primary production near the water surface).

**The large, natural upwelling areas of the world's oceans are known to be highly productive**, through both the nutrients carried in the deep waters, and through locally shortened food webs. MARICULT included modelling the creation of artificial upwellings in Norwegian fjords by using submerged freshwater outlets, concluding that this had potential to increase algal productivity (primary production) by a factor of 3-4x by carrying upwards nutrients from deep waters, as well as reducing uptake of toxics by mussels and shellfish.

**There is little doubt that the productivity of marine waters can be enhanced by artificial nutrient input (fertilisation)**, however it is not predictable what the results will be in the food web. Jellyfish, lower-order carnivore fish, benthic animals or invertebrate predator populations may develop, rather than commercially attractive fish species. It will not therefore generally be economically feasible to fertilise by nutrient addition to then harvest carnivore fish. On the other hand, in semi-closed coastal waters, production yields following nutrient addition may be both predictable and efficient for

larger algae and for shellfish such as blue mussels and scallops, as demonstrated by Reitan *et al.* 2002, Oie *et al.* 2002.

### Harvesting herbivores and algae

The authors suggest that considerable potential is offered by a **move towards harvesting algae and herbivores instead of carnivorous fish** (avoiding the factor of 10 losses in each step up the food chain).

Herbivore copepods and krill are abundant in some regions of world oceans. Because fish stocks are already under threat (from fishing), it is important to ensure that such harvest is not adding to the pressure by reducing fish food availability, but it is likely that in many cases the abundance of these invertebrate herbivores is limited by food availability (in fact, nutrient limitation of primary production), so that harvesting would not significantly effect population densities available as food for fish stocks. These organisms, once harvested, could perhaps be processed to use in human foodstuffs, or could be used to supply fish farming, being much more efficient than using low-order carnivorous fish as food in aquaculture.

**Another potential for more efficient marine harvesting lies with benthic shellfish, such as the blue mussel.** These are very efficient filter feeders on both algae (primary production) and even on bacteria and organic particles. Management could include the productive use of waste nutrients from anthropogenic activities such as fish or terrestrial farming to fertilise areas for production of such shellfish. Nutrients from fish farms in Norway could potentially be converted into around 2 million tonnes/year of blue mussels. Again, blue mussel biomass could provide an efficient input to aquaculture (fish food).

**The use of both artificial nutrient addition and run-off to fertilise blue mussel production was demonstrated experimentally in the MARICULT programme.**

Finally, macro-algae themselves are a poorly exploited primary biomass. Only their polysaccharides are currently used industrially. They provide a potentially rich and efficient source of [n-3]-rich lipids and can potentially be converted into fish food for aquaculture, bulk chemicals, fuels. Macro-algae cultivation can also contribute to bio-remediation of deteriorated coastal waters.

The authors note that all of these paths towards improved use of potential marine resources **necessitate limiting pollution of marine waters**, particularly by heavy metals and by bio-accumulative organic toxic chemicals.

“MARICULT research programme: background, status and main conclusions”, *Hydrobiologia* 484, pages 1-10, September 2002. Abstract: use search function at: <http://www.kluweronline.com/issn/0018-8158/contents>

**Maricult project home page:**  
<http://www.maricult.org/>

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### Coastal bay

#### Nutrient addition and shellfish growth

Hopavagen Bay, on the central Norway coast (69° 35' N, 09° 30' E), is an enclosed water of 370,000 m<sup>3</sup>, mean depth 18m, connected to the open North Sea by a shallow, narrow channel (1m deep at low tide). Algal biomass production and growth of blue mussels (*Mytilus edulis*) and scallops (*Pecten maximus*) were analysed at various depths over three years (1997-1999), with nutrients (nitrogen, silicon and phosphorus) being added during the second two years. A control site on the open coast was also monitored for comparison (no nutrient addition).

Nutrients were added in 1998 at a rate estimated to be twice the natural supply (0.4µgP/l/day, N:Si:P ratio 15:5:4.1) and in 1999 at 3x the natural supply (0.8 µgP/l/day, ratio 16:8:1). No nutrients were added in 1997. The natural supply was taken to be the average sedimentation rate for phosphorus in summer = 0.4µgP/l/day. **Nutrients were added automatically in the rising tide as water flowed into the bay** (that is usually twice per day), from early May to mid October. The three nutrients were added through separate dosing channels to avoid reactions leading to precipitation.

**Primary production** was estimated by collecting weekly algal biomass samples from the central area of the bay and assessing chlorophyll<sub>a</sub> (mixed samples from the surface waters 0-10m depth). Samples were also taken from the open coastal

waters, by sampling just outside the bay inlet at rising tide.

**Blue mussels** were transported from a commercial farm in May in each year and cultivated on net trays in selected locations (four sites within the Bay, one control site in the open coastal waters outside the Bay). Individual mussels' shell length was measured monthly to assess growth, and all the mussels were harvested in November so that biomass could be measured (wet weight, dry weight, ash free dry weight of the tissue).

**Juvenile scallops** from a scallop farm were placed in baskets in July at the same four sites within the Bay and the control site outside the Bay. Scallop shell height and survival rate were measured monthly, and all scallops were harvested in November with wet weight, dry weight and ash-free dry weight being determined.

### Consumption of nutrients

No difference in water dissolved nitrogen or phosphorus concentrations could be detected, showing that **the added nutrients were being fully consumed by the ecosystem** (but increases in dissolved silicon levels were detected). The 1998 (lower) nutrient addition only slightly increased monitored algal biomass in the Bay and not primary production, whereas the 1999 (higher) nutrient additions resulted in respectively a 50% increase in mean summer algal biomass and a doubling of primary production.

### Increases in mussel productivity

Shell growth of mussels in 1998 was not significantly higher than in 1997. **For 1999, however, the shell length of mussels at 2m depth was significantly increased both compared to previous years and to the control site** (no nutrient addition, open coastal water). Also, a significantly higher meat content of mussels (proportion of mass being organic rather than shell) was recorded for the higher nutrient addition year of 1999 in the Bay (compared to previous years and to unfertilised waters outside the Bay: 5-65% increase). These effects were not however apparent in mussels at 10m depth, in effect below the level in which light enables algal primary production to increase in response to nutrient inputs.

**The authors conclude that growth of blue mussels in these coastal waters is limited by nutrient availability in summer, and that nutrient addition (fertilisation) tripling natural nutrient levels (estimated as phosphorus supply) can positively enhance shellfish growth and productivity.**

### Increases in scallop productivity

The scallops in the Bay showed a significantly higher growth rate in both 1998 and 1999 (fertiliser addition years) than in 1997 (no fertiliser). In 1998 (fertilisation to twice natural nutrient supply), the **scallops achieved significantly larger sizes** (shell height) at the two sites in the more enclosed part of the Bay, whereas in 1999 (fertilisation to three times natural nutrient supply) scallops at all sites in the Bay were significantly larger than at the control station outside the Bay. Biomass measured by wet weight, dry weight and tissue weight (ash free) were significantly higher for scallops from sites within the Bay (fertilised sites) both for 1998 and 1999. End-of-season scallop biomass was some 20-50% higher for all sites within the Bay (fertilised) than for outside the Bay (not fertilised) in 1999.

Scallop growth was lower at 15m depth than at 5m or 10m depth, probably as a consequence of both lower temperatures and lower concentrations of food particles in the water.

**The authors conclude that fertiliser addition had a positive effect on scallop growth in this marine environment.**

*“Effect of nutrient supply on growth of blue mussels (*Mytilus edulis*) in a landlocked bay” and “Response on scallop culture to enhanced nutrient supply by experimental fertilisation of a landlocked bay”, *Hydrobiologia* 484, 2002, pages 99-109 and 111-120 respectively [www.wkap.nl](http://www.wkap.nl)*

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## Marine mesocosm

### Zooplankton response to nutrients

Seven 38m<sup>3</sup> (12m depth) floating mesocosms were studied for 18 days (19 August – 4 September) in the Hopavagen coastal lagoon, just south of Trondheimsfjord, central Norway. The mesocosms were filled with ambient sea water. Nutrients were added to the mesocosms in different concentrations, ranging from zero (control) to 2.16 µMolN/l/day. Phosphorus and silicon were also added, in Redfield ratio proportional doses relative to the nitrogen addition (16N:16Si:1P).

Phytoplankton and zooplankton were sampled in each mesocosm every second day. Chlorophyll<sub>a</sub> concentration, algal species, and zooplankton species were counted, length estimates made for copepod species, and zooplankton biomass calculated. Egg production experiments using *Acartia sp.* and *Temora longicornis* from samples, and also mortality rates, were assessed.

#### Primary production

**Algal populations responded quickly to nutrient addition, after only 5-7 days. Diatoms, dinoflagellates and small flagellates all increased with nutrient addition, in particular diatoms** (despite a very low initial diatom biomass in the mesocosm water). Dominant blooming species were *Rhizosolenia fragilissima*, *Skeletonema costatum* and unidentified centric diatoms. It was noted that the mesocosms with higher nutrient addition levels tended to show a higher proportion of chlorophyll<sub>a</sub> as larger particles (20-200µm), indicative of possibly less readily digestible algal species.

#### Zooplankton response

**Smaller zooplankton (ciliates) responded within one week to the nutrient addition**, but this response was only shortlived, with populations returning to initial levels by the end of the 18 day experiment. Ciliate populations were dominated by *Tontonia* and *Strombidium* species. *Tontonia* reached up to 15.4 individuals/millilitre (ml), mean length 30µm. *Strombidium* numbers were greater, but their biomass was lower because of their generally small size (mean length 14µm).

After 18 days, the biomass of mesozooplankton was higher in all mesocosms to which nutrients were

added, but with response levelling off for the higher nutrient dosages (whereas phytoplankton response continued to increase with higher nutrient addition, almost linearly).

Crustaceans dominated zooplankton biomass, with calanoid copepods dominating zooplankton biomass throughout the experiments, and cyclopoid copepods dominating in numbers from days 7-13. The calanoid response to nutrient addition was due to population increases in *Acartia clausi* and *A. longiremis*, and *Centropages hamatus* and *C. typicus*. *Pseudocalanus* species were largely present in the lagoon in the autumn, but did not develop in the mesocosms, possibly because of their lower egg production rate (sac spawners).

Egg production rates for *Acartia* were enhanced at increased food levels, but there were no linear correlation to nutrient addition or chlorophyll levels. *Temora* did not produce any eggs, possibly because the experiments were run in the late summer, near the end of the species' reproductive period.

**Overall, zooplankton response was prolonged, with a doubling of biomass in response to nutrient additions.** Copepod population response shown was higher than that reported in previous distinct copepod cohort experiments.

#### Food levels

The proportion of large diatom phytoplankton was higher in the most fertilised mesocosms, and the difficulties in ingesting these for zooplankton may partly explain the non-linear response of zooplankton populations.

The authors indicate that the different species-specific responses are not readily explained, but that the experiments clearly show that nutrient enhancement in natural waters effects relative species composition of both smaller and meso- zooplankton. They conclude that the fertilisation has a positive effect on copepod community biomass, in the absence of predation from fish or larger jelly plankton. Ciliates were not able to maintain higher populations after the initial population increase. It is not clear whether the evolution of ciliate response is due to predation, food deprivation or other internal community effects.

“Micro- and mesozooplankton response to enhanced nutrient input – a mesocosm study” *Hydrobiologia* 484, 2002. Pages 75-87, Abstract: use search function at : <http://www.kluweronline.com/issn/0018-8158/contents>

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### Environmental impacts

#### Impacts of nutrient increases on marine ecosystems

Response of algae and of littoral (shore) macrofauna to nutrient addition (fertilisation) of marine waters was studied using, on the one hand (Kraufvelin *et al*), eight 17m<sup>2</sup> concrete mesocosms, and on the other hand (Bokn *et al*), monitoring of 2 sites in Hopavagen lagoon before and during nutrient addition (plus 2 control sites outside the lagoon). A third study (Colijn *et al*), based on literature analysis, examines the impacts of increased nutrient concentrations in the coastal North Sea.

The nutrient addition to Hopavagen is described in "Nutrient addition and shellfish growth" in this Newsletter, and was a three year study: 1997 – no nutrient addition, 1998 addition of nutrients to the whole enclosed lagoon to 2x natural levels, 1999 addition to 3x natural levels. Macroalgae and slow moving or sessile large fauna were monitored at 2 tidal (and upper subtidal) zone rocky shore sites on the shore of the Hoavagen lagoon, and also at similar 2 control sites in the Verrafjorden lagoon a few a few kilometres further South along the coast. Non-destructive square sampling and seaweed washing for invertebrates was carried out at each site in October 1997, April, May, August, October 1998 and July, October 1999.

#### Mesocosm results

The **eight mesocosms** are situated at the Solbergstrand Research Station (Oslofjord, Norway 59° 37'N, 10° 40' E). They are concrete bottomed, 17 m<sup>2</sup> area and 1.35m deep with steps to mimic tidal levels on a rocky shore, with a tidal amplitude of 36cm similar to the Oslofjord, and artificial waves. They are fed with fjord water with a residence time of around 2 hours. Littoral ecosystems were established in the mesocosms some 2 years prior to the reported experiments, by transferring rocks with associated macroalgae and fauna from the Oslofjord.

**Nutrients were added to the mesocosms starting in spring 1998**, at 16:1 molar N:P ratio and 1, 2, 4, 8, 16 and 32 M dissolved inorganic nitrogen, in addition to natural levels (plus 2 mesocosms without nutrient addition as controls). Community structure, biomass, plant nutrient content, metabolism rates, were examined with intensive monitoring campaigns spring summer and autumn each year.

In the mesocosm studies, the effects of nutrient addition on the ecosystem community were "*few and only marginal during the first year of nutrient addition*", with some effects becoming somewhat clearer during the second year, in particular growth of periphyton (algae on rock surfaces) and of fast-growing macroalgae such as *Ulva lactuca* on artificial rock substrates. Fauna communities showed only marginal changes. Contrary to expectations, "*no obvious eutrophication response was observed*".

Even after two and a half years of nutrient addition, the **only significant changes in mesocosm fauna** which could be detected were an increase in *Littorina littorea* (common periwinkle) and maybe in *Jaera sp.* (small isopods).

#### Response to lagoon fertilisation

**Similar results appeared in the study of shore sites in the fertilised Hopavagen lagoon.** No major responses occurred in macroalgae coverage. An increase in filamentous algae (brown *Ectocarpus* and green *Cladophora*) occurred at one of the two Hopavagen sites (but still with cover <10%) but not at the other Hpavagen site.

**Overall, both studies "demonstrate only minor responses to increased nutrient levels within the littoral community (both plants and animals)",** although it is possible that the time scales of these studies is too short to show up changes.

The authors suggest that wave exposure may limit the impacts of increased nutrient concentrations on the structure of marine littoral communities, or maybe that such communities are biologically stable and able to counteract nutrient changes by internal regulation mechanisms such as grazing.

#### Impacts of nutrients in the North Sea

**Colijn *et al.*** assess the impact of anthropogenic changes in nutrient concentrations in the coastal North Sea over the last few decades on biomass, phytoplankton (algae), bottom living animals, zooplankton, shrimp and fish productivity.

Nutrients carried by rivers into the North Sea increased from 202,000 tonnes N/year and 15,000 tonnes P in 1950 to 918,000 tonnes N and 100,000 tonnes P in 1980. Since then, **sewage treatment has led to a significant decrease in phosphorus inputs**, whereas nitrogen inputs have not significantly decreased (because of agricultural releases). This has led to significant changes in the N:P ratio.

Vidal *et al.*, 1999 (see SCOPE Newsletter n°45, page7) inventoried some 170 published papers concerning eutrophication in the North Sea, and the authors identified 100 recent publications.

Their assessment of the published literature suggests that the large-scale anthropogenic fertilisation of the North Sea has “*without doubt*” led to various changes, but that it is not clear whether these are positive or negative for society. Clear conclusions are not possible because of difficulties in distinguishing nutrient effects from natural variations.

Primary production and chlorophyll (indicator for algae) appear to be mostly related to dissolved inorganic nitrogen concentrations. Increased N:P ratios may result in undesirable proliferation or blooms of algae such as *Phaeocystis* or may stimulate algal toxic production.

**The authors conclude that although there has been an increase in shrimp and fish productivity in the North Sea, it is not possible to conclude that this is the consequence of the increased nutrient levels.**

*“Littoral macrofauna (secondary) responses to experimental nutrient addition to rocky shore mesocosms and a coastal lagoon”*

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*“Are rocky shore ecosystems affected by nutrient-enriched seawater? Some preliminary results from a mesocosm experiment”*

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*“Effects of the large-scale uncontrolled fertilisation process along the continental coastal North Sea”.*

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*All in Hydrobiologia 484, 2002, respectively pages 149-166, 167-175 and 133-148 [www.wkap.nl](http://www.wkap.nl)*

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## Salmonid ecosystem conference

### Nutrients sustain productivity and biodiversity

Studies and field work has been carried out in a number of countries looking at the potential to restore salmonid populations in lakes, rivers and streams by artificial addition of phosphorus and nitrogen, in order to balance anthropogenic oligotrophication (reductions in nutrient loads) and to help fish populations recover from other pressures, such as overfishing or habitat destruction (dam construction, loss of wetlands and spawning grounds). Several studies and programmes in Canada, Scandinavia and the USA were presented in *SCOPE Newsletter n°27* and in *SCOPE Newsletter n° 38* “Cultural oligotrophication” was summarised.

This symposium was the first international conference to bring together and present the variety of work being developed worldwide in this area, representing some 25 years of groundbreaking ideas and investigative research.

The conference attracted some 400 people and its published proceedings include 21 papers and 290 pages, published by the *American Fisheries Society*. Papers include presentations of a number of field experiences of fertilisation of nutrient-impooverished streams, lakes and rivers. These show that very significant positive effects are achieved on fisheries productivity and salmonid population restoration, whilst appropriate management enables ecosystem equilibrium to be maintained. Other papers specifically address ecosystem response, fertilisation methods, and management/stakeholder issues including considerations for defining relevant environmental protection policies and regulations.

**Symposium proceedings “Nutrients in salmonid ecosystems: sustaining production and biodiversity”**, American Fisheries Society Symposium n°34. Editor: John G. Stockner 2003. Available at

<http://www.fisheries.org/publications/catbooks/x54034.shtml>

Abstracts of all papers available at:

[http://www.gpafs.org/confnutr/NCfinalprogram\\_abstracts.pdf](http://www.gpafs.org/confnutr/NCfinalprogram_abstracts.pdf)

## Keynote paper

The keynote paper from *John Stockner* and *Ken Ashley* summarised the main **mechanisms of anthropogenic oligotrophication (nutrient impoverishment) of surface waters**: dams and weirs (impoundments) which retain organic matter and act as a phosphorus “trap”, drainage of wetlands, logging and clearance of forests, reductions in fish stocks, nutrient removal in discharges. This leads to declining fishery productivity as an “inevitable” consequence of changes in the food web. Nutrient addition, as well as increasing fish productivity, will increase CO<sub>2</sub> assimilation through increased primary production.

**In the case of migratory fish, such as salmonids (salmon, trout, char ...), oligotrophication adds a negative feedback loop to reducing fish stocks.** Adult salmon travel up rivers and streams to their spawning ground, and then die. Their carcasses are not lost or waste however, because they effectively carry significant amounts of nutrients upstream from the ocean, releasing them near the spawning grounds to fertilise the waters in which their offspring will shortly hatch as fry.

Murota provides **estimates of the quantities of nutrients being carried upstream by salmonids.** Five species of Pacific salmon in British Columbia (B.C.), Canada, are estimated to carry upstream some 2,300-2,500 kgN of nitrogen per year, and 273-295 kgP of phosphorus. Total phosphorus carried by Atlantic and Pacific salmon is estimated at 1,500-3,000 tonnesP/year. This may appear small compared to phosphorus removed from the oceans in commercial fisheries (112,000-300,000 tonnesP/year) or even as guano by seabirds (annual deposits to land estimated at 9,000-60,000 tonnesP/year), but the nutrients carried by salmonids are deposited in streams and lakes in a dispersed way, exactly where they are needed to fertilise the ecosystem for fish reproduction, whereas marine fishery nutrients mostly end up concentrated in discharges from coastal food factories or from sewerage systems in big cities, and seabird guano deposits are also concentrated along the coast.

### Outlook

The introduction to the published proceedings concludes with the need to restore nutrient supply to streams and rivers where the loss or decline of salmonid migration has caused the loss of this nutrient input, and to facilitate fishery and ecosystem recovery through nutrient addition and habitat restoration. *“Hopefully you will find these proceedings informative and use the information to help protect and restore critical salmonid habitat, so that the nutrient shadow now so attenuated can be restored to its fullest extent to the benefit of aquatic and terrestrial ecosystems that are so vitally dependent upon it”.*

*Symposium proceedings “Nutrients in salmonid ecosystems: sustaining production and biodiversity”, American Fisheries Society Symposium n°34, 24-26 April 2001, Eugene, Oregon, Canada, 21 papers, 290 pages. American Fisheries Society, Bethesda, Maryland, MD 20814 USA, 2003. Editor: John G. Stockner, Fisheries Centre, University of British Columbia, Vancouver, B.C., Canada and Eco-Logic [stockner@telus.net](mailto:stockner@telus.net), 2614 Mathers Avenue, West Vancouver, British Columbia, Canada. ISBN: 1-888569-44-1. Available price US\$60.00 at <http://www.fisheries.org/publications/catbooks/x54034.shtml>*

*Abstracts of all papers available at: [http://www.gpafs.org/confnutr/NCfinalprogram\\_abstracts.pdf](http://www.gpafs.org/confnutr/NCfinalprogram_abstracts.pdf)*

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### Struvite fertiliser

#### Using struvite to add nutrients to salmon streams

The decline in Northwest Pacific salmonid populations results from a number of factors, including overfishing, loss of freshwater and marine habitats and wetlands, dam building and water pollution. A decrease in spawning populations results in fewer carcasses of dead post-spawn adults, and reduced nutrient input from these decaying carcasses to the upper stream spawning grounds.

This **reduced nutrient input reduces food availability for young fish and fry**, reducing their survival rates, and accelerating the population decline. Fertiliser addition (input of phosphate and nitrogen) has been shown to successfully counter this negative feedback (Perrin *et al.* 1987, Slaney and Ward 1993, Bilby *et al.* 1996, Ashley and Slaney 1997). Liquid fertilisers have successfully been used, but are

expensive because application has to be reviewed frequently, or complex drip-feed systems have to be installed.

This paper reports tests of slow-release fertiliser briquettes, offering the possibility of a once-a-year or once-a-season application. Struvite and urea combinations compacted into “briquettes” with different binder products were tested in both trough and field experiments to assess dissolution rates for stream fertilisation and practical use characteristics. Ideally, briquettes for such application should be large enough to resist carrying downstream or burial in sediments, should dissolve progressively over a period of around four months (the Spring growth season, which is the key to salmonid fry development). Phosphate should be food-grade and free of heavy metal contaminants. Binders used should be natural or biodegradable.

#### Struvite manufacturers

Pons (1995, refs. below) tested various products showing that one from **IMC Vigoro** (Water Haven, Florida) based on struvite (magnesium ammonium phosphate = MAP) bound with Daratak® XB-3631 (a complex polymer) was the most suitable product. Chemical and physical factors affecting the bioavailability of phosphate in struvite in this product were determined in Sterling (1997, refs. below) and Sterling *et al.* (2000, refs. below). The product was successfully tested in streams in British Columbia (B.C.), Canada by Mouldley and Ashley (1996, refs. below).

IMC Vigoro discontinued manufacture of this product in 1997 and another fertiliser company, **Lesco Inc.** (Rocky River, Ohio) manufactured the **struvite briquettes** used in this study, producing a range of 26 struvite or struvite plus urea briquettes with different binders for the purposes of the study. Because urea dissolves rapidly, its presence significantly accelerated the physical breakdown of the briquettes when used.

#### Trough studies

Indoor troughs at a trout hatchery at Abbotsford, B.C., Canada, were used to test the dissolution rates of twenty-six different briquettes supplied by **Lesco Inc.**, each containing around 9g of compressed fertiliser, with different binders.

The briquettes were hung on wires in a water velocity of approx. 0.3 m/s at water temperature approx.

13°C, both factors being stabilised. Dissolution was assessed by removing sample briquettes, drying, then calculating weight loss, with samples being removed at 1, 2, 3, 4, 6 and 8 weeks.

Many of the samples tested, with a variety of binders including molasses, polymers, hydrated lime, different vegetable oils, dissolved too rapidly. The best briquettes tested used either no binder, or canola vegetable oil, with a 75% struvite 25% urea combination. The briquettes without binder gave the most regular and consistent nutrient release.

### Field trials

Field experiments (water velocity approx 0.15 m/s; temperature range from 3.6-9.5°C) showed reliable dissolution for these no-binder briquettes dropped onto the stream bed, with results comparable to those obtained in simultaneous trough experiments, at 4.6-6.6% dissolution per week, giving 53-64% dissolution after 8 weeks.

**The 9g (of struvite fertiliser) briquettes thus proved suitable to provide nutrients (phosphate and nitrogen) for a 4-month period to the stream,** during the spring and summer growth seasons. Struvite plus urea with no binder, or only vegetable oil, proved the best solution, capable of providing efficient nutrient supply to stream water over a 4 month period, as briquettes with other binders dissolved too slowly. Spring-time application has been shown to efficiently increase forage and salmonid production in streams. They were not carried downstream by stream flows usual for the time of year, and were adapted to distribution by hand or from the air via helicopter. Briquettes functioned best if added to stretches of stream with a bed of small stones (gravel) of similar size to the briquettes. The briquettes became similar in colour to the stones, after a few weeks, reducing the risk of human interference.

*“Evaluations of slow-release fertilizer for rehabilitating oligotrophic streams”, in symposium proceedings “Nutrients in salmonid ecosystems: sustaining production and biodiversity”, American Fisheries Society Symposium n°34, 24-26 April 2001, pages 237-243. Available from <http://www.fisheries.org/publications/catbooks/x54034.shtml>*

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<http://www.saumon-fqsa.qc.ca/>

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## Keogh and Salmon Rivers

### Nutrient addition to trout and salmon rivers

Test field studies of nutrient addition to the Keogh River (127°W, 50°N, British Columbia (BC) Canada, on Vancouver Island, near Port Hardy), with first a pilot experiment within the uppermost reach of the river in 1981, were followed by whole river treatment for 4 years 1983-1986. Following the positive impact on salmonid fisheries obtained, a long-term fertilisation programme of the Grilse Creek tributary of the Salmon River (situated approx 130 km south of the Keogh River) was launched in 1989 and carried out through the 1990's. Further work was also carried out in the Keogh River 1997-2000 combining fertilisation with habitat structure restoration.

The 32 km long Keogh River has annual average rainfall of 173 cm, water temperature of 12°-16°C in Spring-Summer, and mean annual flow at discharge of 5.3 m<sup>3</sup>/s. Spring-Summer nutrient concentrations are very low, with total dissolved phosphorus < 5 mgP/l and nitrate-N < 15 mgN/l.

The Keogh River supports runs of Pink salmon *Oncorhynchus gorbuscha*, Coho salmon *O. kisutch* and trout *O. mykiss*. Non-migratory salmonids Cutthroat trout *O. clarki* and Dolly carden char *Salvelinus malma* are also present. Steelhead trout migrate to the sea as smolts aged 2-4 years, whereas most Coho salmon migrate in their first year.

#### Experimental studies

The initial **experimental nutrient additions in the mid-1980s raised phosphorus up to target concentrations of 10-15 µg P/l** in the river water along the whole river, in Spring and Summer, however these loading rates were found to be excessive and were subsequently reduced to 5 µgP/l.

Data from sampling of fish population densities and fish sizes for the five years with nutrient addition (1 year pilot trial in upper reach, 4 years whole river treatment) were compared to 5 years without nutrient addition. **Average weight of first year Coho salmon and Steelhead trout increased respectively by 1.4x and 2.0x with nutrient addition (fertilisation)** and weights of parr (ages 1-3, before migration) increased

by +30% - +130% despite similar densities of fry (newly hatched young) each year. Steelhead smolts (young migrating seawards) showed a tendency to migrate earlier (mainly at age 2 instead of 3 years), so that the average size of migrating smolts did not increase. **Catches of adult fish returning to the river to breed and corresponding to the years with nutrient addition (age 5 years approximately) increased comparably, whereas there was no such increase in nearby untreated rivers.**

#### Long-term field application

On the basis of the positive test results above, nutrient addition to the Grilse Creek tributary of the Salmon River was started in 1989, continuing through the 1990's, with nutrient addition targets fixed at around one third of those used for the Keogh River. The objective was to accelerate salmonid population recovery following installation of a fish-run at a dam which had been preventing migration from the Salmon River into Gilse Creek, and to offset oligotrophication (nutrient impoverishment) resulting from intensive logging in the catchment.

The Salmon River is used by Pacific salmon (*Oncorhynchus sp.*), dolly varden char, Steelhead trout, Cutthroat trout and rainbow trout *O. mykiss*. Water temperatures in the Grilse Creek are 7-10°C in May and 13-19°C in July, with flows of 3-0.m<sup>3</sup>/s in Spring-Summer.

**Fertilisation of the salmon river also proved efficient in improving salmonid populations for a relatively low cost over long stretches of river.** Age 1+ parr showed average weight increases of 2-3x in treated sections, and salmonid population standing biomass increased from 1.5-30 kg/ha to 40-130 kg/ha., and smolt fish populations migrating seaward from 1,500/year to 8,000/year, also showing a shift from mainly 3 years age to 2 years at migration.

**The Salmon River results thus confirmed those from the Keogh River experiments, showing that nutrient addition can produce long-term, sustainable increases in salmonid fishery productivity and assist restoration of trout and salmon populations.**

#### Restoration and fertilisation

Further works, using a combination of slow-release fertiliser addition (see Sterling in this Newsletter) and habitat structure restoration (adding boulders and logs in the stream to create shelter habitats, wetland

restoration) was carried out in the Keogh River, starting in certain sections in 1997 and covering the whole river by 2000. Fish population sampling was carried out and compared to results from the nearby, untreated, Waukwaas River.

Nutrient addition or habitat restoration alone gave 1.9-2.5x increases in Steelhead parr densities, and both treatments together gave 3.8x increases. Both Steelhead trout and Coho salmon smolt yields were significantly increased, though with some annual variations. **Nutrient addition showed to be a key variable for salmonid restoration with the restoration of habitats buffering any negative environmental factors.**

*“Experimental nutrient addition to the Keogh River and application to the Salmon River in Coastal British Columbia”*. Pages 111-126 in J.G.Stockner, editor, 2003: *Nutrients in salmonid ecosystems: sustaining production and biodiversity*. American Fisheries Society, Symposium <http://www.fisheries.org/publications/catbooks/x54034.shtml>

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### Big Silver Creek, Adam River

#### Nutrient addition increases trout productivity

Adam River is situated 50°W, 126°N and flow into Johnstone Strait, Vancouver, Canada, with an mean summer flow of 14-15 m<sup>3</sup>/s. Big Silver Creek is also situated in Vancouver, at 49°N, 122°W, and flows into Harrison Lake, with a mean flow of 50-60 m<sup>3</sup>/s in Spring falling to 10 m<sup>3</sup>/s in summer.

In both rivers, **fish migration is naturally limited by falls** respectively 4 and 6 km upstream from the river mouths. Above the falls, both rivers have Rainbow trout (*Oncorhynchus mykiss*) populations, and Adam River also has introduced Brown trout (*Salmo trutta*). In both rivers, prior to fertilisation, most of the Rainbow trout were small (<20 cm length) with densities of 10-20 individuals/ha (35-45 ind./km). Additional salmonid species are found in small numbers downstream of the falls in both rivers.

**Both watersheds have seen intensive logging, with little old forest growth remaining in place**, but well established secondary growth and riparian vegetation. Both rivers are very oligotrophic (nutrient poor) with Total Phosphorus 3-5 µgTP/l, but include good potential fish habitats, which is consistent with the observation of reasonable fish population densities but low fish sizes.

#### Fertiliser addition

**Liquid agricultural-grade ammonium polyphosphate fertiliser was added to each river from June to September over the four years 1994-1997**, with addition levels defined to raise Dissolved Inorganic Phosphorus concentrations in the river water to 5µgDIP/l. In the Adam River, additional nitrogen (liquid urea ammonium nitrate) was added to bring nitrogen concentrations up to 5µgN/l.

For both rivers, sections downstream of the fertiliser addition were compared with a control section of river upstream of the addition point.

#### Ecosystem impacts

Physical and biological monitoring started in 1992, two years before the fertiliser addition, enabling impacts of fertilisation to be compared both to previous years and to the control river sections.

Periphyton (algae growing on the river bed) showed around 4x increases in the fertilised sections of both rivers. Populations of benthic (river bed) invertebrates also increased, by a factor of around 2x.

River water nutrient concentrations, however, did not show increases downstream of the fertiliser addition points, showing complete uptake of the added nutrients by primary production (plants).

**Fish populations in both rivers responded very positively to the fertilisation**, though response was in some cases slow, probably as a result of the low initial nutrient levels. Size of age-0 fish approximately doubled, and density of >20cm Rainbow trout multiplied by 4x. Big Silver Creek also showed a large increase in 10-20cm Mountain whitefish (*Prosopium williamsoni*), from 8 to 48/ha, and Adam River a smaller increase in Brown trout.

**The authors estimate that the positive effects of the fertiliser addition extended some 8-11 km downstream of the point of addition**, estimated on the basis of changes in periphyton biomass.

*“Experimental enrichment of two oligotrophic rivers in South Coastal British Columbia”*. Pages 149-162. in J.G.Stockner, editor, 2003: *Nutrients in salmonid ecosystems: sustaining production and biodiversity*. American Fisheries Society, Symposium 34, Bethesda, Maryland. Available from <http://www.fisheries.org/publications/catbooks/x54034.shtml>

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### Arrow Lakes Reservoir

#### Lake fertilisation to restore native salmon

The Arrow Lakes Reservoir is 240km long and on average 1.8km wide, average depth 83m, in the Columbia River catchment. The Reservoir contributes 16% of Columbia River's total flow, and with an area of 465km<sup>2</sup> is the largest lakes to have undergone experimental fertilisation.

The lake has been anthropogenically oligotrophised (nutrient deprived) by the **construction of a dam** in the Columbia River downstream (Grand Coulee 1942) and at the reservoir outlet (Keenleyside 1967), preventing upstream migration of salmonids to spawn and thus removing this source of marine nutrient input (decaying carcasses of post-spawning adults); and by construction of dams upstream (Mica 1973, Revelstoke 1983), which act as nutrient traps, preventing nutrients being carried downstream.

Further ecosystem changes resulted from the introduction of *Mysis relicta* in 1968, a small crustacean which is a very efficient competitor to the zooplankton species preferred as food by the Kokanee salmon.

Before dam construction, anadromous runs of chinook salmon *O. tshawytscha*, sockeye salmon *O. nerka* and steelhead trout *O. mykiss* were found in the Arrow Lakes and further upstream.

Kokanee salmon (*Oncorhynchus nerka*) is a native, landlocked (non migratory) sockeye salmon, and is a keystone species to the lake ecosystem, supporting large piscivorous sport fish such as Rainbow trout (*Oncorhynchus mykiss*), white sturgeon (*Acipenser transmontanus*) and bull trout (*Salvelinus confluentus*). Spawning populations had fallen from 600-800,000 in the 1980's to 97,000 in 1997.

#### Nutrient addition

**In order to try to restore the salmonid populations, a five-year lake nutrient addition programme was started in 1999**. 1060 tonnes of agricultural grade liquid fertiliser were added to the upper end of the lake in both 1999 and 2000, by pumping off the side of a regularly operating ferry. A blend of ammonium polyphosphate and urea ammonium nitrate was used to deliver 52.8 tonnes-P and 233 tonnes-N each year. Somewhat higher

nitrogen levels were added during the summer to reduce risks of blue-green algal development.

Some increases in algal biomass were noted in the two first fertilisation years, and **significant increases in zooplankton biomass**, in particular *Daphnia* which are a key food for kokanee salmon and of *Mysis relicta*. In response to this, populations of *Mysis relicta* increased significantly, but this did not prevent very positive improvements in kokanee salmon populations, with a change appearing in population trends in 1999, the first fertilisation year. Prior to 1999, populations had been decreasing, whereas **in 1999 and 2000 escapements increased by 3x and 4x respectively. Also, the mean sizes of kokanee in 1999 and 2000 were the highest on record**, the size of mature spawning fish increased, and fecundity in spawning channels also increased (from below 300 to 400-460 eggs per female).

The authors conclude that, as the five year nutrient addition programme progresses, results from the first two years suggest that **the reservoir is responding positively to fertilisation**, with more efficient carbon flows in the ecosystem: increased primary productivity is passed through the system to result in an increase in kokanee salmon fish size, numbers and spawning fertility.

“Restoration of Kokanee salmon in the Arrow Lakes Reservoir, British Columbia: preliminary results of a fertilization experiment”. Pages 177-196. in J.G. Stockner, editor, 2003: *Nutrients in salmonid ecosystems: sustaining production and biodiversity*. American Fisheries Society, Symposium 34, Bethesda, Maryland. Available from <http://www.fisheries.org/publications/catbooks/x54034.shtml>

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## Redfish Lake Idaho

### Nutrient supplementation for salmon restoration

Redfish Lake is one of five pre-Alpine lakes in the Sawtooth Valley, in Southern Idaho, in the headwaters of the Salmon River (44° N, 115°W), which itself flows into the Snake River and this in turn into the Columbia River – see article “Keogh and Salmon Rivers” in this Newsletter. Redfish Lake is situated at 1996m altitude, with a surface of just over 6 km<sup>2</sup>, a mean depth of 44m and a residence time of 3 years. The smaller Stanley Lake was monitored for reference, being chosen because it was not receiving nutrient addition or fish stocking.

Snake River sockeye salmon *Oncorhynchus nerka* once bred in several lake systems in the Snake River system, but are now reduced to a relic population in Redfish Lake. Declining populations in the Lake led the Shoshone-Bannock Tribes to petition authorities to list the salmon under the US Endangered Species Act, which was obtained in 1991, leading to initiation of a project to conserve and restore the population, starting with breeding and restocking. It was feared that the stocking may exceed the Lake’s carrying capacity for the salmon, so during 1995-1998 nutrients were added to Redfish Lake.

Redfish Lake has three distinct forms of *O. nerka*: anadromous Sockeye salmon, which live in the Lake freshwater for 1-2 years, then migrates in May to the Pacific Ocean, where it resides for 2 years before returning in October to spawn on the Lake shores; residual Sockeye salmon, genetically similar to the anadromous form but which reside in the freshwater Lake for their whole life cycle; Kokanee salmon, which spend their whole life cycle in Redfish Lake but spawn in August in Fishhook Creek, a major tributary of the Lake.

Other native salmonid species found in the lake system include Steelhead/Rainbow trout *O. mykiss*, Chinook salmon *O. tshawytscha*, Westslope Cutthroat trout *O. clarki lewisi*, Bull trout *Salvelinus confluentus*. Two introduced salmonids are found in Stanley Lake: Brook trout *S. fontinalis* and Lake trout *S. namaycush*.

### Fertiliser addition

**Liquid ammonium phosphate and ammonium nitrate were added weekly to Redfish Lake throughout the growing season in 1995-1998**, at approximately 45:1 N:P molar ratio (the high N:P ratio being intended to avoid nuisance blue-green algae). Consent authorised fertiliser addition unless transparency fell below 8m Secchi depth, chlorophyll<sub>a</sub> exceeded 3-6µg/l or total phosphorus exceeded 15µg/l: these conditions were always respected during the five years and nutrient addition proceeded uninterrupted.

Phytoplankton increased and primary production was positively correlated to nutrient addition, but phytoplankton communities remained typical of oligotrophic conditions, dominated by small readily-grazable microflagellates.

Although it was not possible to establish clear links between primary production and food chain effects, it was noted that **total zooplankton biomass increased by 31%** (compared to stable levels in the unfertilised Stanley Lake) and *Daphnia* (key salmonid food) increased by 225%. **Salmon populations also showed improvements with fertilisation: *O. nerka* density increased by 26% and overwinter survival by 192%.**

It was also noted that there were no apparent declines in water quality with fertilisation, and that numbers of salmon spawning on the Lake's beaches (residual salmon) did not increase (fertilisation did not appear to be leading to a reduced tendency to migrate).

**The authors conclude that nutrient addition is a useful tool for supporting salmonid populations during restocking programmes**, without any apparent negative effects, and that further research is necessary into the role of microbial food webs in the use and transfer to fish populations of primary productivity.

*"Redfish Lake Sockeye salmon: nutrient supplementation as a means of restoration". Pages 197-211. in J.G.Stockner, editor, 2003: Nutrients in salmonid ecosystems: sustaining production and biodiversity. American Fisheries Society, Symposium 34, Bethesda, Maryland. Available from <http://www.fisheries.org/publications/catbooks/x54034.shtml>*

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## SCOPE NEWSLETTER

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# SCOPE NEWSLETTER

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**NUMBER 52**

**July 2003**

## Public Policy

**Europe** p2

### **EU Commission presses for water quality**

*The EU Commission is maintaining legal pressure on Member States to implement EU water quality legislation, and in particular Directives requiring nutrient removal from sewage works and control of agricultural nutrient releases. A UNESCO report meanwhile suggests that Belgium has the most polluted rivers in the world, through the absence of adequate sewage treatment and agricultural manures.*

## Phosphorus recycling

**Belgium** p4

### **Struvite recovery from manure**

*A full-scale pilot struvite recovery plant is operational in Belgium, with a capacity of 15,000 tonnes/year of manure (1,500 tonnes of struvite per year)*

**Kawasaki City Japan** p4

### **P-recovery from sewage-sludge incineration ash**

*Kawasaki City has developed a technology for recovering phosphorus and aluminium contained in the ashes of sewage sludge.*

**Japan** p5

### **Published patent**

*Furnace extraction of phosphorus from sewage sludge incineration or carbonisation ash*

**Analysis** p7

### **Total phosphorus in manures**

*Total phosphorus content of animal manures is an important issue in nutrient management, but methods of assessing this currently used are both problematic and unreliable. This paper suggests a more simple analysis procedure.*

**Bio P-removal** p8

### **Magnesium makes bio P-removal reliable**

*Soluble magnesium addition renders biological P-removal from sewage more efficient and reliable, which may offer relevant opportunities for the design of struvite recovery processes.*

**Conference announcement** p17

### **Sustainable land application**

## Water quality

**Estonia** p8

### **Modelled and observed river nutrient loads**

*First results of a GIS modelling study of nutrient loads to the Emajõgi and Võhandu rivers (Lake Peipsi) show results close to observed nutrient loads for three 5-year modelling periods between 1985 and 1999*

**Germany** p10

### **Impacts of nutrient removal on river quality**

*An analysis of effects of sewage nutrient removal on the Ruhr River shows that significant further investment is still needed, that this should improve ammonia-nitrogen levels relevant for drinking water extraction and nitrogen discharges to the North Sea, but that neither the considerable reductions in phosphorus loadings already achieved nor the small remaining reductions will probably prevent algal blooms*

**Ontario** p11

### **Combined effects of light and nutrients in a P-limited lake**

*A 12 week enclosure experiment assessed the combined effects of different levels of light and of nutrient addition (P, N) on phytoplankton and total biomass and their carbon:nutrient ratio.*

**Coastal waters nutrient over-enrichment** p12

### **“Estuaries” special issue: 18 papers from NAS Symposium**

*Most of the USA’s coastal waters have been degraded by nutrient over-enrichment, with nitrogen releases causing the most damage. Point source nutrient releases have been effectively addressed, in particular by sewage treatment, in many cases, but nitrogen emissions continue to be a major issue, and a generalised and increasing problem worldwide.*

**Southern Ocean** p15

### **Iron limitation of marine algae**

*Iron addition to Southern Ocean waters proved to significantly stimulate phytoplankton development, showing that iron limitation effectively controls marine algal growth in these waters in summer.*

**Conference announcement** p17

### **Eutrophication of waters from diffuse sources.**

### Public Policy

#### Europe

### EU Commission presses for water quality

In SCOPE Newsletter n°46 <http://www.ceep-phosphates.org/scope/articles/scope46/SCOPE46.pdf> we reported EU Commission action against Austria, Belgium, France, Greece, Italy, Luxembourg, The Netherlands, Portugal, Spain and Sweden for inadequate implementation of EU water quality Directives, in particular the Urban Wastewater Treatment Directive 91/271 .

In January 2003 and April 2003 the Commission announced **further actions against 10 Member States**, this time Belgium, Denmark, France, Germany, Ireland, Italy, The Netherlands, Portugal, Sweden and the UK.

#### Obligation to treat urban sewage

**Belgium and France are both facing actions concerning inadequate implementation of the *Urban Wastewater Treatment Directive 91/271***, adding to actions already underway against Greece, Spain and Sweden – see *SCOPE Newsletter n°46*). For Belgium, this concerns “*the lack of a general implementation in the Brussels and Wallonia regions*”. And for failure to adequately designate “sensitive areas”. France has failed to provide information about implementation of this Directive, in particular designation of sensitive areas.

**Belgium, meanwhile, is flagged up as having the dirtiest water in the world** according to a report published by UNESCO in March 2003, the UN’s first *World Water Development Report*, ranking below India, Jordan and nine African states who appear as the other nations with dirtiest water. The OECD is quoted as saying that “*raw sewage still pours untreated into Belgium’s rivers where it mixes with manure from intensive livestock farms*”. Brussels, Belgium and Europe’s capital, hopes to complete its sewage works ... in 2005.

### Nutrient removal

**The *EU Urban Wastewater Treatment Directive 91/271* required sewage to be collected and treated**, with nutrient removal in all conurbations of 10,000 pe = around 6,000 population discharging into “sensitive areas”, defined as any water potentially subject to eutrophication by 1998, **with “appropriate treatment” also for smaller conurbations**. Many Member States are well behind this schedule, but the EU Commission and the EU Parliament have both stated their determination to obtain implementation of this Directive, including in the new Member States (Accession States have signed agreements to implement by 2010-2015). This should essentially resolve the issue of nutrients in sewage.

The European Court of Justice also declared (April 2002) that **Italy has failed to fulfil its obligations under Directive 91/271** by not adequately treating water flowing into rivers upstream of the Po Delta and Adriatic coast, which are classified as nutrient “sensitive areas”, in particular with the absence of sewage treatment for the city of Milan. The Court considered that, although Milan is not itself in a “sensitive area”, the rivers into which it discharges flow into such areas, and so Milan is subject to “sensitive area” nutrient removal requirements.

**Belgium, Denmark, Germany, Ireland and Sweden are accused of failing to adequately implement the *Bathing Water Directive 76/160***, both for failure to ensure that bathing water respected the standards set by the Directive and for inadequate sampling.

Portugal and France face action concerning failure to implement the *Drinking Water Directive 80/778*, The Netherlands under the *Dangerous Substances in Water Directive 76/464*, the UK under the *Freshwater Fish Directive 78/659* and Ireland under the *Groundwater Directive 75/440*.

### Nitrates

**Germany, UK and France face action concerning failure to implement the *Nitrates Directive 91/676***. For Germany and the UK this concerns implementation, in particular inadequate designation of “nitrate vulnerable zones”. France

has already lost a European Court of Justice case concerning nitrate pollution of surface waters in Brittany used for drinking water supply. The EU Commission is now taking further action under the Nitrates Directive, because of the absence of an effective action plan to reduce nitrate pollution in Brittany. If France fails to comply, the Commission may then refer again to the Court and request that fines be imposed.

**These numerous and varied actions show the continuing determination of the EU Commission to obtain implementation of EU water quality legislation by Member States**, in particular to resolve the issue of nutrients in sewage and (Nitrates Directive) to limit the impact of nutrients from agriculture.

The EU has also now published **Guidelines for implementing the *Water Framework Directive 2000/60***, including instructions as to how to implement aspects regarding: analysis of pressures and impacts, identification of water bodies, identification of “heavily modified” water bodies (not subject to the obligation to reach “good water quality” by 2015), ecological assessment of transitional and coastal waters, selection of network and process, monitoring, public participation, GIS, assessment of rivers and lakes, planning process on wetlands. The Water Framework Directive takes the various existing water quality Directives, in particular the urban Wastewater Treatment Directive, as the minimal starting point for implementing water quality and management on a catchment basis.

### **Sewage sludge spreading**

**Switzerland** has now banned the spreading of sewage sludge on farmland, with effect from 1<sup>st</sup> May 2003. The ban initially concerns land used for growing vegetables and animal fodder, and will be extended to all farmland in 2006. Some 60% of Swiss sewage sludge is already treated, and the regulation is expected to result in a further 80,000 tonnes per year being incinerated.

UN World Water Development Report  
<http://www.un.org/Pubs/whatsnew/e03107.htm>

EU Press Release 4 April 2003 “Commission pursues legal action against France and the United Kingdom over EU water laws” IP/03/494  
[http://europa.eu.int/rapid/start/cgi/guesten.ksh?p\\_action.gettxt=gt&doc=IP/03/494|0|RAPID&lg=EN&display](http://europa.eu.int/rapid/start/cgi/guesten.ksh?p_action.gettxt=gt&doc=IP/03/494|0|RAPID&lg=EN&display)

Switzerland sewage sludge spreading ban:  
<http://www.umwelt-schweiz.ch/buwal/de/news/artikel/20030325/00985/index.html>

EU Press release 21/1/2003” Commission pursues legal action against eight Member States over EU water laws” IP/03/84  
[http://europa.eu.int/rapid/start/cgi/guesten.ksh?p\\_action.gettxt=gt&doc=IP/03/84|0|RAPID&lg=EN&display](http://europa.eu.int/rapid/start/cgi/guesten.ksh?p_action.gettxt=gt&doc=IP/03/84|0|RAPID&lg=EN&display)

EU Court of Justice decision against Italy concerning protection of nutrient sensitive areas, 25 April 2002  
<http://www.curia.eu.int/en/actu/communiqués/cp02/aff/cp0237en.htm>

EU Water Framework Directive:  
[http://europa.eu.int/eur-lex/pri/en/oj/dat/2000/l\\_327/l\\_32720001222en00010072.pdf](http://europa.eu.int/eur-lex/pri/en/oj/dat/2000/l_327/l_32720001222en00010072.pdf)

## Phosphorus recycling

### Belgium

#### Struvite recovery from manure

The Fraunhofer Institute for Chemical Technology (ICT), Germany, has developed a process to treat pig manures involving a methane-producing digestion stage followed by solid/liquid separation. The solid fraction is used for compost production, whilst the liquid fraction is **membrane treated** allowing a **high-quality phosphate solution** to be produced, from which struvite can be precipitated, for resale as a fertiliser.

The process was presented at the *Second International Conference on Phosphorus Recovery* in March 2001 and a full-scale pilot is now operational in Peer, Belgium, operational since January 2003, treating 15,000 tonnes of pig manure per year (photo below). Around 100 kg of struvite (magnesium ammonium phosphate = MAP) are recovered from 1 tonne of manure.

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Photo with permission: Mark Adriaensens



### Kawasaki City Japan

#### P-recovery from sewage-sludge incineration ash

Japan is totally reliant upon imports for phosphorus ores, 80% of which are used in the production of agricultural fertilizers. Kawasaki City collects sewage sludge from four sewage treatment facilities in the city, and disposes of it through incineration. Approximately 14 tons/day of ashes are then produced from the sludge. The ashes are rich in phosphorus, the content of which is expected to increase as sewage disposal technologies are improved. Thus, it is of great importance with respect to the recycling of natural resources to recover phosphorus from sewage ashes.

Kawasaki City has therefore investigated methods for recovering phosphorus from sewage ashes and found that, **if an alkaline solution is added to sewage ashes, phosphorus and aluminium can be selectively eluted** to the solution. Phosphorus and aluminium can be separated from the solution through solvent extraction.

**The extracted phosphorus will be used as a material for fertilisers**, and the aluminium as a material for flocculants used in the removal of phosphorus from sewage.

#### Experimental results

We added nitric acid to sewage-sludge ashes in order to separate contained phosphorus and aluminium in the solution. The contents of these elements moved to the solution were compared with those separated in

an alkaline solution of sodium hydrate. The sewage-sludge ashes were added to water, then mixed with the acid or alkali for one hour at room temperature in order to perform element extraction. The table shows the contents of each filtrate: the concentration of P and Al eluted to the alkaline solution was half that in the acid solution. However, unlike in the acid solution, **heavy-metal elements did not move into the alkaline solution**, while Al and P were selectively extracted.

[Al and P contents in acid and alkaline solutions](#)

	Al (mg/L)	P (mg/L)
Acid solution	3,000	5,100
Alkaline solution	1,900	2,200

**Methods were then investigated for eluting only aluminium from the alkaline solution** containing P and Al. Among various solvents, di-(2-ethylhexyl) phosphate (D2EHPA), a phosphate ester, was identified. Because D2EHPA forms an emulsion in alkaline solutions, the solvent cannot be separated from water under normal conditions. If the pH is too low, the extraction of aluminium becomes very difficult. To ensure successful separation, the pH of the solution was adjusted, and aluminium was eluted to a D2EHPA/kerosine solution, so that the solvent formed a clear layer readily separable from the (aqueous) alkaline solution. The solvent fraction was then reverse-eluted with sulphuric acid and then this solution was allowed to stand. Aluminium was then successfully collected in the form of aluminium sulphate.

**Meanwhile, phosphorus was precipitated from the alkaline solution in the form of hydroxyapatite (calcium phosphate)** by first removing sulphate ions through the addition of calcium chloride, and then adding calcium hydroxide to control the pH.

**Developed process**

The final process developed is thus as follows. An alkaline solution is added to the sewage-sludge ashes in order to leach phosphorus and aluminium. Then the solvent di-(2-ethylhexyl) phosphate (D2EHPA) is added to this alkaline solution and aluminium is transferred (eluted) into the organic solvent fraction. The organic solvent fraction is then separated from the alkaline (aqueous) solution, and sulphuric acid is added to the solvent fraction in order to recover

aluminium in the form of aluminium sulphate. A calcium source is added to the alkaline aqueous fraction in order to recover phosphorus in the form of calcium phosphate.

**The D2EHPA solvent and sulphuric acid can be recycled in the process.** The recovered aluminium can be used as a flocculent in waste water treatment.

**Recovered phosphorus**

**The recovered phosphorus compound was 100% citric-acid soluble**, and contained phosphoric acid by 37%. With respect to toxic heavy metals specified by the Fertilizer Control Law, the contents of Cd and As were below the standards, while Ni, Cr, Pb, and Hg were not detected in the available chemical analyses. Thus, the recovered phosphorus compound was of sufficient quality for use in plant-friendly fertilizers, and is an alternative to phosphorus ores.

Assuming that the daily production of 14 tons of sewage ashes contains approximately 6.1% phosphorus, 2.2 tons/day of hydroxyapatite (calcium phosphate) and 0.9 tons/day of aluminium sulphate will be recovered from the ashes. Kawasaki City is pushing forward with a recycling plan utilising sewage-sludge ashes.

*Information from and article in "Water 21" December 2001*

<http://www.iwapublishing.com/template.cfm?name=iwapwater21> by Yutaka Suzuki (Public Works Research Institute, Japan) [ysuzuki@pwri.go.jp](mailto:ysuzuki@pwri.go.jp) and further detail provided by: Takahiko Nishimura, Kawasaki City [kobayashi-ko@city.kawasaki.jp](mailto:kobayashi-ko@city.kawasaki.jp) ; [53gikai@city.kawasaki.jp](mailto:53gikai@city.kawasaki.jp) February 2003

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**Japan**

**Published patent**

US Patent 6,022,514 published 8<sup>th</sup> February 2000 presents methods for recovering phosphorus from sewage sludge by heating either sludge incineration ash with a carbon source or carbonised sludge (after heat treatment at 400-700°C) in a furnace (1,000 --1,250 °C).

The patent authors indicate that sewage sludge incineration ash can contain a significant amount of phosphorus: **13% P<sub>2</sub>O<sub>5</sub> for polymer coagulated sludge to 22% P<sub>2</sub>O<sub>5</sub> for sludge from sewage works using lime for phosphorus removal.** After

phosphorus recovery by the patent proposed method, the  $P_2O_5$  content of the ash is reduced to 4.4 – 7.2 %<sup>(1)</sup>, a level which the authors indicate is compatible with use of the material in the cement industry.

(1) The *patent text* refers to phosphorus content but the tables and the numbers quoted suggest that this is in fact expressed as % weight  $P_2O_5$ .

The authors cite previous Japanese Unexamined Patent Publications (n<sup>o</sup>s 7-251141 and 9-77506) which present **methods for recovering phosphorus from sewage sludge incineration ash by acid treatment** (to dissolve the phosphorus into phosphoric acid) followed

by organic solvent extraction (to separate the phosphoric acid from the process acid), and n<sup>o</sup> 9-145038 in which sludge incineration ash is melted at around 1,400°C with an added carbon source allowing phosphorus to be vaporised and recovered. The presented patent aims to avoid the complexities of solvent extraction and the very high temperatures (and so energy consumption) of the latter method.

The *presented patent* involves using either sewage sludge incineration ash or carbonisation of the sludge after drying at 400 – 700 °C. The ash or carbonisation product is then heated in an oxygen-free furnace at 1,000 – 1,250 °C, either with a carbon source (in the case of incineration ash) or using the carbonised sludge organics as an internal carbon source (in the case of the carbonised sludge).

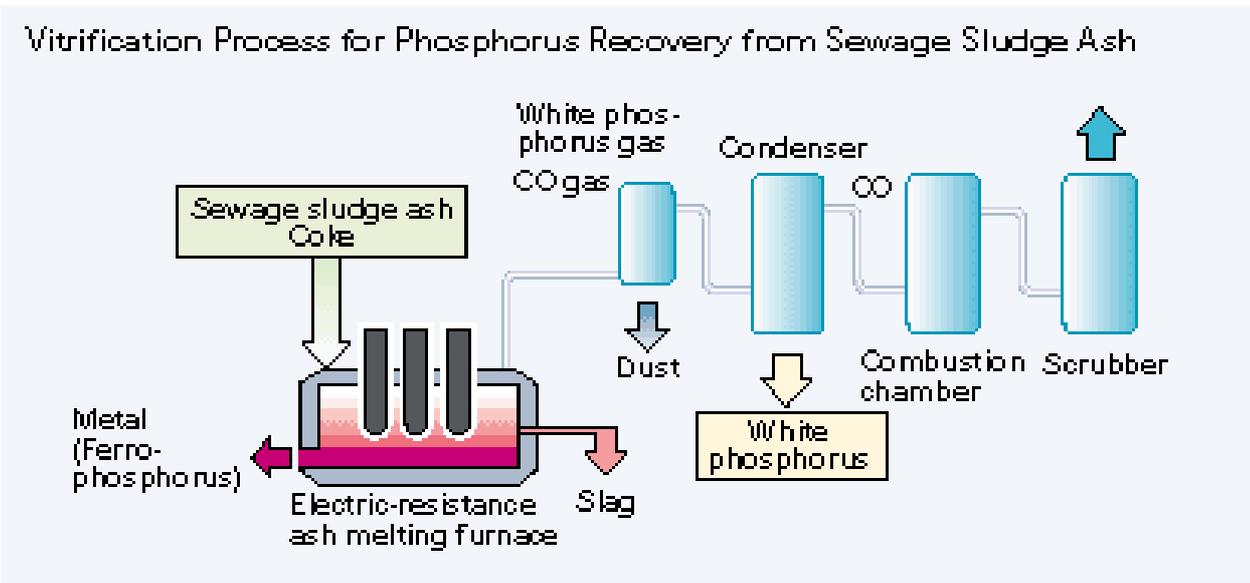
This furnace treatment causes vaporised phosphorus to be released which can be recovered either as elemental phosphorus by condensation in water, or as phosphoric acid by oxidation to phosphorus pentoxide which is then brought into contact with water (these are the classic pathways for harvesting phosphorus from the industrial furnaces using mined phosphate rock).

Where the carbonisation pathway is used, the exhaust gas from the carbonisation process is combustible (containing hydrogen, methane and other hydrocarbons) and can be used to supply energy to heat the carbonisation process. The carbonised sludge at 400 – 700 °C can then be fed directly to the phosphorus recovery furnace, thus reducing the energy input necessary to heat this to 1,000 – 1,250 °C.

**The published patent text includes brief presentations and results for four experimental tests** each using 100g – 200 kg of dried sewage sludge or sewage sludge incineration ash. For two of these, the phosphorus concentration of the phosphoric acid produced is indicated, at 17 and 12.5 %.

US Published Patents can be consulted on the web at <http://www.uspto.gov/patft/index.html> (request "patent number search" then enter "6,022,514" in the "query" box or use NKK in text search).

Further information in NKK Press Release <http://www.jfe-holdings.co.jp/en/release/nkk/40-7/art02.html>



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## Analysis

### Total phosphorus in manures

Manures are rich sources of phosphorus, containing complex mixtures of organic and inorganic, soluble and insoluble phosphorus compounds. Much of the organic phosphorus can be associated with plant cellular material which is resistant to digestion processes, having already come through the animals own simple or more complex (ruminant) digestion processes.

However, to **measure the total phosphorus in the manure** it is necessary to break down all the forms present to soluble inorganic phosphate, which can be then measured known techniques. The standard method for doing this at present is aqua-regis digestion of the manure, followed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy).

The aqua-regis digestion requires mixing with 15.5 molar nitric and 10.3 molar hydrochloric acid in a 1:3 ratio, then boiling for 3 hours under reflux. This is potentially hazardous, and requires constant operator supervision. As well as these practical difficulties, the method is known to give erratic phosphorus recovery rates, added to which the ICP-OES method is also documented as giving unreliable results at low phosphorus concentrations.

#### Autoclave digestion and reagent use

**The authors developed and tested a simpler process** for assessing the total phosphorus in manures. This was then tested and results obtained compared with those using the aqua-regis method, both for known and for randomly labelled replicate samples of four different types of manure: broiler chicken litter, layer chicken manure, cow manure, pig slurry and a certified reference material consisting of ground hay.

The new method involved adding potassium persulphate and sulphuric acid to the manure sample, digesting in an autoclave at 776mm mercury pressure 120°C for one and a half hours, then determination of soluble phosphorus using the molybdate-blue reagent addition method.

Different concentrations of sulphuric acid were tested for the digestion phase, suggesting that the lowest concentration used (2 molar sulphuric acid, giving a sample pH of 1.8) was largely adequate. Tests for different levels of persulphate addition for the digestion phase showed that 0.3g addition of persulphate to 40ml liquid samples was adequate for the manures, 0.6g persulphate was necessary for the hay sample (undigested plant material).

**The total phosphorus analysis results using the new persulphate method were significantly higher than for the traditional aqua-regis method for all the manure samples** (similar for the hay sample). For the hay, the results of both methods were lower than the certified phosphorus content of this material – the authors suggest that this may be because of silica content in the grass interfering with the molybdate-blue reagent reaction.

The authors conclude, from the randomised sample analysis results, that the new persulphate/molybdate-blue method **gives reliable and accurate estimations of total phosphorus** in manures, though further work is necessary regarding results for hay. The new method is considerably simpler, not requiring constant operator surveillance during the digestion phase (3 hours in the existing aqua-regis method) and using considerably less hazardous chemicals.

*“A rapid and simple technique for digestion and determination of total phosphorus in animal manures and herbage”, Commun. Soil Sci. Plant Anal. N°33 (9&10), pages 1577-1587, 2002.*

<http://www.dekker.com/servlet/product/productid/CSS>

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## Bio P-removal

### Magnesium makes bio P-removal reliable

The authors tested the effects of adding soluble calcium (30-90 mg Ca/l) or magnesium (10-20 mg Mg/l) to a bench-scale biological sewage phosphorus removal plant (EBPR) over periods of 50 – 220 days. Influent phosphate (total) varied from 7.7 to 11 mgP/l.

Calcium addition improved bio-P removal performance only slightly (mean P-removal increased from 85 to 90%) and did not resolve problems of performance fluctuation (standard deviation of P-removal reduced only from 20% to 15%, inadequate to ensure reliable effluent P concentrations below 1 mgP/l).

On the other hand, **magnesium addition considerably improved both average P-removal (from 85% to 97%) and above all P-removal reliability** (standard deviation reduced to 4%, enabling 80% P-removal to be achieved nearly all the time).

The authors carried out various analyses (EDXS, STEM) which clearly show that the additional magnesium is being retained in the biological production of polyphosphate granules, within the context of the biological P-removal process. The intracellular polyphosphate granules were based on calcium (Ca), magnesium (Mg) or potassium (K) or combinations of these different cations. Analysis showed that in all the experiments (Ca addition, Mg addition, no cation addition), Mg and Mg+K based granules were the most

common types. During the magnesium addition experiments, more than 50% of the polyphosphate granules were Mg+K based and the calcium content of the granules was significantly lower.

### Magnesium uptake and release

The authors refer to previous research which shows that soluble magnesium and potassium are both taken up and released during soluble phosphate uptake and release in bio-P processes, whereas calcium-based polyphosphate granules are more stable with calcium not being released during soluble phosphate release phases.

This work suggests interesting roads to explore in the **design of processes for the recovery of phosphate for recycling as struvite** (magnesium ammonium phosphate MAP). Magnesium addition could be used to both improve the efficiency and stability of the bio-P phosphorus removal process, and then be “re-used” on release of soluble phosphorus to contribute to struvite precipitation (which usually requires in any case the addition of soluble magnesium).

*“Stability of enhanced biological phosphorus removal and composition of polyphosphate granules”. Water Research vol. 35, n° 13, pages 3190-3196, 2001.*

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## Water quality

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### Estonia

#### Modelled and observed river nutrient loads

Lake Peipsi is a 3,555 km<sup>2</sup> shallow lake (maximum: depth 15 metres) with a 44,000 km<sup>2</sup> catchment shared by Russia, Estonia and Latvia. Population in the catchment is sparse, with only two cities exceeding 100,000 inhabitants (Pskov

in Russia 198,700 and Tartu in Estonia 100,500 inhabitants). Dominant land cover is deciduous, coniferous and mixed forest, interspersed with farmland.

Nutrient emissions to the Estonian part of the lake catchment were modelled for three five-year periods covering 1985-1999. Emissions were modelled for diffuse sources (mainly agricultural activity) and for

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point sources (mainly sewage works and industry, discharging directly into surface waters).

Diffuse emissions were estimated from data covering fertiliser use, livestock numbers and nutrient excretion coefficients per type of animal, crop yields for each crop type, coefficients for nutrient export per mass yield for different crops, land cover, population numbers and connection to different types of sewage works.

Hydrological flows between and residence times in various storage compartments were also modelled using generic maps of soil types, land cover, aquifer and meteorological data, resulting in estimates of direct runoff, shallow groundwater and deep groundwater.

### Point and diffuse emissions

These different models were then combined to **model nutrient transfer and retention** through the hydrological system (soil, groundwater, channel network).

The modelling gives the **estimates of total point and diffuse emissions** (soil surface surpluses) shown in the table below, with the city of Tartu being alone responsible for around one third of point emissions.

Measurements of water nutrient concentrations and of discharge rates (water flows) were available for a number of sampling points from previous studies (Tallinn Technical University). From these, **nutrient loads being carried by the water were calculated,**

by interpolating measured nutrient concentrations to give daily results and multiplying by measured daily discharge.

**Modelled phosphorus and nitrogen loads** for the Emajõgi River at Tartu, the main Estonian tributary to the Peipsi lake (average discharge 68 m<sup>3</sup>/s), coincided reasonably well with observed loads, Simulated loads for the Võhandu River at Räpina, a smaller river (mean discharge 8 m<sup>3</sup>/s) proved higher than observed loads for the period after 1990. The better model performance for the larger Emajõgi catchment probably results from “averaging out” of temporal and local variations in nutrient discharges, related in particular to seasonal spate flows. In general, the decrease of riverine nutrient loads due to the collapse of agricultural economy in Estonia after the independence could be simulated by the model.

**The study provides evidence of the validity of GIS-based modelling of nutrient emissions and loads.**

*“Modelling nutrient fluxes from diffuse and point emissions to river loads: the Estonian part of the transboundary Lake Peipsi/ Chudskoe drainage basin (Russia / Estonia / Latvia)”, Session 9-2, IWA Conference on Diffuse Pollution 30 September – 4 October 2002, Amsterdam*

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<u>Annual emissions:</u>	<u>Point sources</u>		<u>Diffuse sources</u>		<u>Total</u>
<b>Phosphorus (tonnes P)</b>					
1985-1989	309	2%	18 443	98%	18 752
1990-1994	295	3%	8 259	97%	8 554
1995-1999	255	7%	3 209	93%	3 464
<b>Nitrogen (tonnes N)</b>					
1985-1989	1 029	1%	88 800	99%	89 829
1990-1994	990	2%	43 919	98%	44 909
1995-1999	882	3%	29 964	97%	30 846

**Germany**

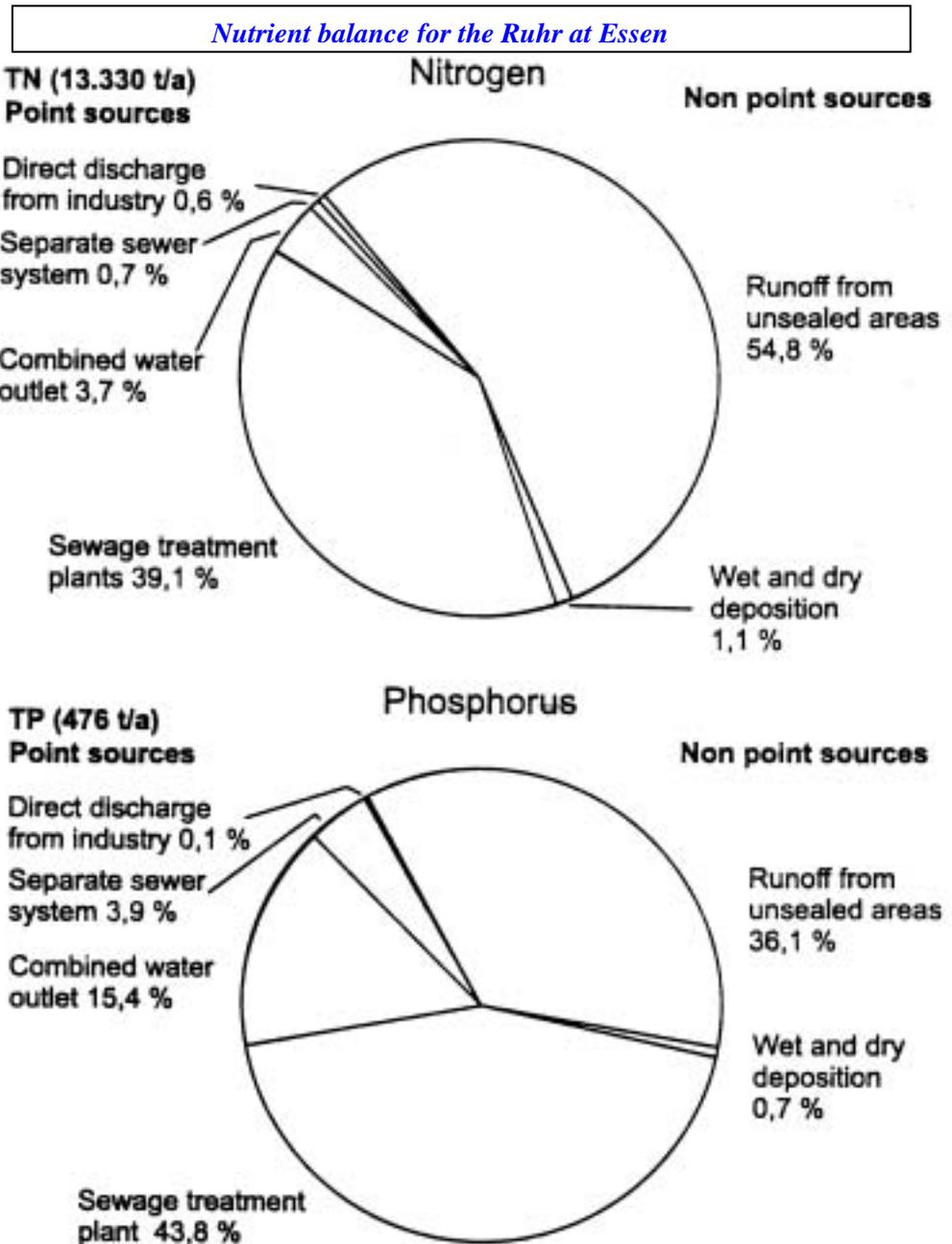
**Impacts of nutrient removal on river quality**

The 217km long Ruhr river drains an industrial and highly populated (2.2 million inhabitants) lowland catchment of 4,500 km<sup>2</sup> in Germany, discharging an average 80 m<sup>3</sup>/s into the Rhine of which it is a tributary (the Rhine then discharges into the North Sea). The river supplies, via artificial groundwater recharge, drinking water for 5 million people and a total of 560 million m<sup>3</sup> per year of water for domestic and industrial (cooling) uses.

By 2001, considerable investments had already been made in the past in sewage collection and treatment, with an **estimated 96% connection of the population to a total of 92 sewage works** (total capacity 3.7 million pe.), plus some 500 stormwater works. At low river flows, 20-30% of the river flow can consist of sewage works discharge.

The middle and lower Ruhr includes 5 dams with residence times in dry weather periods of 1-5 days and these have been and still are subject to algal blooms. **Total phosphorus had been reduced from around 0.8 mgP/l in the 1970's to below 0.2 mgP/l by the mid-late 1990's**, with over this period both the move to P-free laundry detergents in Germany and the implementation of nutrient removal in the river's sewage works (1996 requirements set at: 2 mgP/l in discharges from sewage works of >10,000 pe. And 1mgP/l for those > 100,000 pe.)

**Ammonium-nitrogen concentrations in the river have also been divided to around one third of their 1970's value over this period by investments in sewage treatment (nitrification).** This parameter is considered very important for drinking water extraction (by bank filtration).



Nitrate-nitrogen levels in the river, on the other hand have not significantly decreased over this period (1970's to late 1990's), showing an increase for annual average nitrate concentrations in the 1980's and a return to 1999 to levels near those of 1970-1975, but still a higher level for winter low river flow nitrate concentrations in the late 1990's than in the 1970's. This is attributed by the authors to nitrogen fertiliser use in agriculture.

Investments in sewage treatment over the period 1948 -1999 were estimated to have totalled 2.4 billion €(1995 price index).

### Sources of nutrient loadings

Nutrient balances calculated for the Ruhr showed, predictably, the considerable importance of the sewage works contribution. For phosphorus (total load = 476 tP/year), over 60% came from point sources (44% from sewage works discharges). For nitrogen (total load = 13.330 tN/year), 44% came from point sources.

The authors estimate that, by 1999, EU Urban Wastewater Treatment Directive (91/271) requirements for nutrient removal were met to only 52% with some 1.12 billion € investment remaining necessary to achieve 100% compliance (in particular nitrogen removal and nutrient removal installation, stormwater collection). This is expected to result, by 2006, in further 25% reductions in emissions from sewage works and stormwater releases for nitrogen, and 10% for phosphorus.

This improvement in nitrogen removal is expected to significantly improve the situation for drinking water extraction (ammonia-nitrogen concentrations in the river never exceeding 1 mg/l). Regarding nitrate-nitrogen, the reduction is not expected to improve the Ruhr water quality, given the loadings from non-point sources, but will contribute to the overall wider objective of reducing nitrogen loadings to the North Sea (via the Rhine discharge).

Because the reductions in dissolved phosphorus levels in the river (of the order of 1/10) already achieved over the last two decades have not produced significant effects on algal blooming and eutrophication

symptoms (chlorophyll concentrations), the further expected reduction of -10% is not expected to have significant effects.

*"Nutrient removal in the river basin of the Ruhr – a German case study", Water Science and Technology, vol.44, n°1, pages 15-24, 2001.*

*H. Bode, Executive Technical Director, and R. Klopp, Head of Chemical and Biological Laboratory, Ruhrverband (Ruhr River Association, responsible for water management in the river basin), Kronprinzenstrasse 37, 45128 Essen Germany info@ruhrverband.de*

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## Ontario

### Combined effects of light and nutrients in a P-limited lake

The experiment was carried out from 1st June to 12th August (12 weeks) in Lake 239 of the Experimental Lakes Area, South West Ontario (around 94°W, 49°N, altitude 380m). The lake has been described elsewhere as it has been the subject of extended study (Schindler et al. 1996). The lake is relatively deep (3-30m). Mesocosm enclosures of 25m<sup>3</sup> (8m deep, 2m diameter) made of clear polyethylene and closed at the bottom were used, filled with water pumped from 1.5m depth in the lake from which zooplankton (grazers) were removed by 125µm filtration.

3 different levels of light intensity x 3 levels of nutrient addition (9 combinations) were tested, with 2 replicates for each one. Light levels were 100%, 50% and 25% of natural ambient light, achieved by partial shading. Nutrient addition levels were 1x, 2x and 4x addition of inorganic P at the rate of 5µmolesP/m<sup>2</sup>/day (this being approximately the loading rate of the Experimental Lakes). Inorganic nitrogen was also added with a molar N:P ratio of 75x in order to ensure that the system remained P-limited.

Nutrients were added every 2-3 days and at the same time the water in each enclosure was mixed (throughout the enclosure depth) and 2% of the enclosure volume was replaced by ambient lake water, to simulate lake water renewal. This frequent nutrient addition was considered as

semi-continuous and so close to real nutrient loading conditions.

Every 5-6 days each enclosure was sampled with analysis of water characteristics (dissolved nutrients, chlorophyll<sub>a</sub>) and of particulate C, N and P, seston and algal biomass, nutrient ratios, and of phytoplankton communities. Radioactive labelled carbon was used to assess the fixation of dissolved inorganic carbon (DIC) into biomass and its subsequent release as dissolved organic carbon.

### Nitrogen concentrations

Soluble reactive phosphorus (SRP) levels in the enclosure water were not significantly related to nutrient enrichment levels, and nor was dissolved nitrate (NO<sub>3</sub>-N), whereas NH<sub>4</sub>-N was significantly higher in the high nutrient addition enclosures. **This is indicative that the enclosures remain P-limited in all cases** (phytoplankton sequester all added P). The increase in NH<sub>4</sub>-N in the high nutrient addition enclosures may be related to increased populations of zooplankton in these enclosures (through excretion).

### No effect on chlorophyll or biomass

**The different light intensities and levels of nutrient enrichment showed to have no apparent effect on either chlorophyll<sub>a</sub> (indicator of algal development) nor on total biomass.**

Higher light intensities did result in significantly increased total seston phosphorus (with 60% or more of seston biomass being bacteria). Higher light intensities also increased the C:P ratio in phytoplankton (algae). Both these effects could be expected, as they are indicative of higher primary production with higher light intensity.

**There were no significant correlations between treatments and seston community structure, but nutrient enrichment did result in a significant but moderate increase in the biomass of larger zooplankton.**

The authors explain in introduction that it is increasingly considered necessary to consider the "balance" between energy and nutrient inputs into

systems in assessing possible ecosystem effects, and not just the levels of nutrient inputs.

They suggest that their results support certain aspects of the light:nutrient hypothesis but that further research is required.

**The study results show that in these enclosures the natural lake biocommunity (algae, bacteria, zooplankton grazers) was able to adapt to increases in nutrient enrichment**, both at natural and at reduced light intensities, without showing significant ecosystem modifications (such as algal development).

*"Effects of light and nutrients on plankton stoichiometry and biomass in a P-limited lake"* *Hydrobiologia* 481, pages 101-102, 2000

<http://www.kluweronline.com/issn/0018-8158>

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### Coastal waters nutrient over-enrichment

#### **"Estuaries" special issue: 18 papers from NAS Symposium**

*"Estuaries"*, the bimonthly journal of the Estuarine Research Federation <http://erf.org/>, has published (2002) as a special issue 18 papers from the US National Academy of Science symposium "Nutrient over-enrichment in coastal waters. Global patterns of cause and effect" (2000). These papers cover the question widely including trends in nutrient sources (including atmospheric nitrogen deposition), impacts (on eg. algal blooms, salt marsh ecology, coral reefs), policy and economic issues, positive impacts of nutrient enrichment (fishery productivity), science developments.

Howarth *et al.* set the picture stating that 60% of US coastal rivers and bays have been moderately to severely degraded by nutrient over-enrichment, with increases in both nitrogen and phosphate

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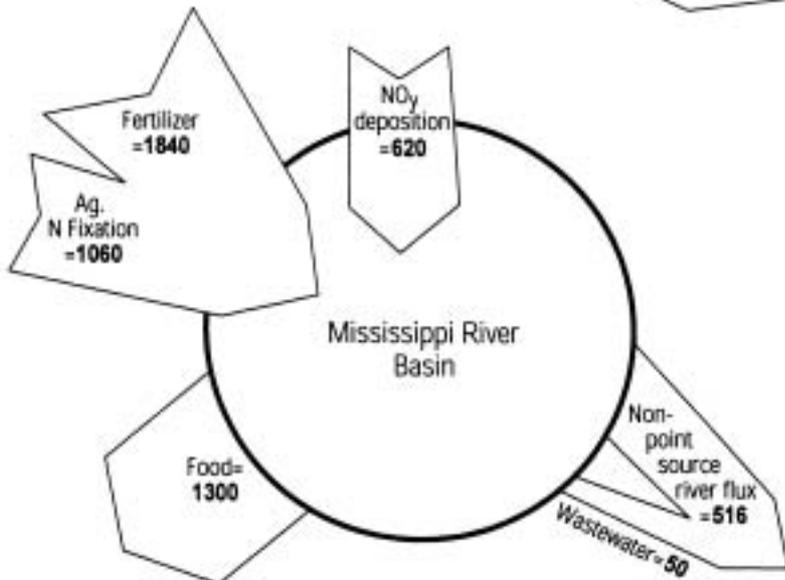
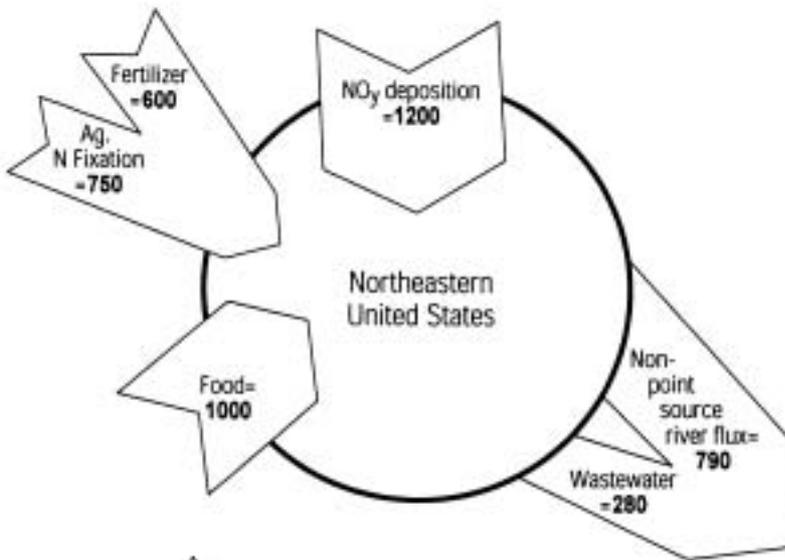
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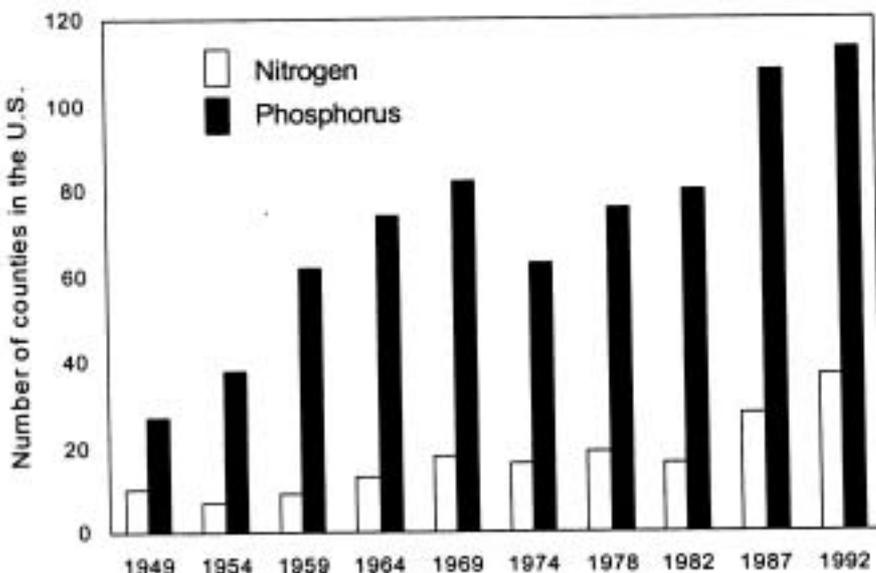
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Number of US counties where manure nutrients exceed potential plant uptake and removal, including pastureland application (in *Howarth et al*, adapted from Kellogg and Lander 1999).



Comparison of anthropogenic nitrogen inputs to nitrogen losses as food and riverine exports (kgN/km<sup>2</sup>/year), for the North Eastern USA and for the Mississippi River basin (modified from NRC2000, based on data in *Howarth et al* 1996).

discharges, but **“for most coastal systems nitrogen additions cause more damage”**. For most waters, nonpoint nutrient inputs are now the most significant, particularly for phosphorus, because of improved sewage treatment. By 1996, sewage was estimated to contribute only 12% of total US nitrogen releases to coastal waters.

Regional nitrogen budgets vary considerably in the USA (see diagram) but with both agriculture and atmospheric deposition playing important roles. **Nitrogen discharges in the US have been increased 4-8 times by human activity**, and are continuing to increase for reasons which vary from one region to another, including both intensification of agriculture and increased atmospheric deposition (related to fossil fuel burning). Phosphate discharges have been generally stable or small increases or decreases over the last 30 years, with increases in phosphate fertiliser use being balanced by reductions in point sources (improved sewage treatment).

Faeth and Greenhalgh explore the synergies between limiting nitrogen discharges and greenhouse gas emissions. **US farmers have dramatically increased fertiliser use since the mid-1960's**: +150% for nitrogen, reaching 11 tonnes by the 1990's, and +25% for phosphorus, reaching a peak of 5.1 million tonnes in 1979 before falling somewhat. US National Research Council analysis (1993) showed that around 40% of N and 60% of P applied in fertiliser in the USA is not taken up in crops.

**Agriculture is responsible, through methane and nitrous oxide emissions only (ignoring agricultural fossil fuel use and changes in soil carbon content), for about 12% of US greenhouse gas emissions.** The paper shows that changes in land use and tillage practices can contribute both to reducing greenhouse gas emissions and to reducing nitrogen discharges, with nitrogen emission reduction policies in some cases giving up to 25% reductions in agricultural greenhouse emissions.

**Anderson et al examine the relationship between nutrient enrichment of coastal waters and harmful algal blooms.** In many cases, algal blooms have been linked with nutrient over-enrichment, and have been reduced when nutrient

discharges have been limited. In other cases, harmful algal blooms (toxic algae, or nuisance algae producing foams, mucilage or other problems) have been linked to changes in the ratios between nutrients (N:P, N,P:Si or N,P:C) but the effects of changes in ratios appear to differ widely in different circumstances. In some cases, nutrient levels do not appear to be a contributing factor to harmful algal blooms. The author concludes that effects are highly species specific, and that the relationship between nutrient loadings and harmful algal blooms remains very poorly understood.

**Turner compared world commercial production of nutrients (in fertilisers, atmospheric releases, other products ...) to the Earth ecosystem's natural production: +0.03% for P, +0.41% for N, +0.73% for C (from Kaiser 2001).** The author indicates that, on a molar basis, world N fertiliser use is 50 times higher than for P. This relatively high N loading results in N:P ratios increasingly higher than the Redfield ratio (biological requirements), leading to disruptions of the diatom – zooplankton – fish food web both more frequently and over wider areas.

**Conley et al. present experience from Denmark where an Action Plan decided in 1987 aimed to reduce total nitrogen loads to surface water by 50% and point source phosphorus sources by 80%.** For municipal sewage works, targets were defined in 1990 to reduce N discharges from 18,000 to 6,600 tN/year and phosphorus from 4,470 to 1,220 tP/year. This corresponds to biological N removal in all plants > 1,000 pe and P removal in all plants > 5,000 pe (down to 1.5 mgP/l). The Action Plan, including a recent extension, is estimated to have cost around 470 million € to the agricultural sector and 1,100 million € for domestic sewage treatment investments.

**This Plan has been successful for point sources, with reductions of 74% for nitrogen from sewage treatment plants and 90% for phosphorus.** By 1999, 81% of total N loads to surface waters came from agricultural sources, 11% from natural background loads, and only 8% from point sources. Diffuse sources of

phosphorus have also become the significant load to coastal waters.

Nixon and Buckley present a somewhat different viewpoint on nutrient enrichment, presenting evidence from a variety of sites, ranging from the Nile delta to Denmark, Scotland and the Baltic, showing that **increased nutrient inputs usually result in increased fish productivity, as increased primary production “feeds” up the food chain.** The authors emphasise that this does not remove the need for concern about nutrient over-enrichment, and that specific issues such as shifts in species of fish (from benthic to pelagic, for example) may occur, but that the economic consequences (positive) of increased fisheries productivity related to nutrient inputs to coastal waters cannot be ignored.

*Estuaries*, <http://estuaries.olemiss.edu/> vol.25, n°4B, August 2002, pages 639-900. Dedicated issue “Nutrient over-enrichment in coastal waters: global patterns of cause and effect”. Containing 18 papers, selected from the 49 papers and 11 oral presentations at the US National Academy of Science Symposium of the same title, Washington D.C., 11<sup>th</sup>-13<sup>th</sup> October 2000, see [http://erf.org/newsletter/W00\\_SCOR.htm](http://erf.org/newsletter/W00_SCOR.htm).

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### Southern Ocean

#### Iron limitation of marine algae

Since the late 1980's, scientists have suggested that iron may be a limiting nutrient in vast areas of the world's oceans, rather than phytoplankton growth being limited by dissolved nitrates and/or phosphates, or sometimes silicon. The “SOIREE” (Southern Ocean Iron Enrichment Experiment) has now provided large scale evidence that this is indeed the case.

**The late Dr John Martin (Moss Landing Laboratory) first succeeded in accurately determining low iron concentrations in the sea – not easy given the pervasive presence of iron in steel in ships, laboratory equipment, wires and so on! - showing that these were indeed low enough to be limiting, and suggested that iron supply to ocean waters could be related to climate change (by limiting phytoplankton CO<sub>2</sub> uptake).**

Experiments onboard ocean research vessels showed that adding iron to seawater could enhance

phytoplankton growth, and two in-situ experiments near the Galapagos islands in 1993 and 1995 then showed the effect in the sea.

The SOIREE experiment was designed to test the theory on a large scale, by adding iron to a 50 square kilometre area of ocean. **In February 1999 (summer), 1.7 tonnes of iron (in around 8.7 tonnes of iron sulphate FeSO<sub>4</sub>·7H<sub>2</sub>O) were added to the 50 km<sup>2</sup> “patch” of seawater over 7 days. The phytoplankton response to the increased iron concentrations was studied over a period of 12 days. The resulting bloom was seen in satellite imagery obtained 42 days after the initial fertilisation.**

The site studied (61°S, 140°E, in the Southern Ocean 2,000 km SW of Tasmania) does not receive iron in dusts from nearby continents. It was selected to be representative of large areas of circumpolar waters with high nitrate – low chlorophyll levels. The site had a mixing depth typical of these waters (50 – 70m), but relatively low horizontal current, resulting in low dispersion of the iron-fertilised patch of water.

#### Nitrogen and phosphorus levels

In the mixed surface layer at the site, nitrate and phosphorus levels were relatively high (around 25 and 1.5 μM respectively), dissolved silicate was somewhat less elevated (around 10μM), dissolved iron levels were low (around 0.08μM) and chlorophyll-*a* concentration was 0.25 mg/m<sup>3</sup>. Phytoplankton were dominated by pico-eukaryotes (50% of chl-*a*) with diatoms also present (20% of chl-*a*). Various physiological and biological observations were indicative of iron limitation.

#### Fertilisation

The waters of the 50 km<sup>2</sup> patch were fertilised by four additions of iron sulphate. The iron was diluted in seawater and added at approx. 15m depth. The four iron additions were calculated to add respectively 3.8 nM FE, 2.6 nM Fe and 2.5 nM Fe to the 50 km<sup>2</sup> patch (total iron added 8.7 tonnes of FeSO<sub>4</sub>·7H<sub>2</sub>O). At the same time, 500g of SF<sub>6</sub> were added to label the fertilised water and enable the movement and dilution of the “patch” to be monitored.

After iron addition, dissolved iron concentrations were comparable to those found in iron-rich zones of the Atlantic polar front, but after 2 days they decreased rapidly, probably as a combined result of

biological uptake and dispersion. Further iron was therefore added on days 3, 5 and 7. When the iron additions were stopped (after day 7), levels decreased to around 1 nM Fe and remained around this levels until the end of monitoring on the site (day 13).

### Algal response

A small but detectable increase in photosynthetic competence ( $F_v/F_m$ ) was measurable immediately after each iron addition, whereas phytoplankton development measured by chlorophyll-*a* levels only began to increase after days 3-4. Chlorophyll-*a* levels increased consistently over days 3-4 to 10-11 to a peak of nearly 120 mg chl-*a*/m<sup>3</sup>. Chlorophyll levels in a controls area of ocean outside the fertilised patch showed no significant increase over the same period.

However, biological indicators of iron limitation (slower rates of iron uptake, decreases in phytoplankton flavodoxin levels) did not decrease until days 5-7.

The rapid phytoplankton development following iron fertilisation resulted in an increase in chlorophyll significantly greater than that of phytoplankton carbon (cellular carbon/chlorophyll ratios halved over the 13-day study). **Overall, net phytoplankton growth more than doubled and phytoplankton carbon tripled.**

The phytoplankton development resulting from the fertilisation caused a species shift in species towards a diatom dominated bloom. This change will facilitate phytoplankton biomass increase, as these larger species are less susceptible to grazing.

**Satellite observations of the patch of ocean 42 days after the first iron fertilisation showed that the bloom was still present, with chlorophyll-*a* concentrations up to 3 mg/m<sup>3</sup> spread over a ribbon-shaped area of 1,100 km<sup>3</sup> of ocean. This suggested that a significant amount of the added iron had been maintained in the surface waters.**

### Carbon sink rate

Despite the increase in chlorophyll levels resulting from the iron fertilisation, carbon loss processes were not observed to increase significantly, although there was some development of small zooplankton grazers. Accumulation of phytoplankton carbon was estimated to account for around two thirds of iron increased primary production, suggesting that **around 800 tonnes of carbon were accumulated as a result of the addition of the 1.7 tonnes of iron Fe.**

However, the bloom continued to develop after the 13 days of monitoring (as indicated by the satellite observations after 42 days) and could thus have continued to contribute considerably to carbon accumulation.

The authors conclude that this experiment provides unequivocal evidence of the role of iron in controlling phytoplankton primary production in the Southern Ocean. It does not however provide proof that iron fertilisation would increase the rate of carbon fixation (CO<sub>2</sub> sink), because increased downward export of carbon particles from the productive surface layer was not assessed.

The authors suggest that the study site is representative of 75% of polar waters in the Australian-Pacific sector of the Southern Ocean in summer. The satellite observations following the study, in March, were at a period when light levels were already 50% lower than peak summer (December) levels, suggesting that algal growth may be iron-limited (rather than light limited) for up to 8 months of the year.

*"A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization". Nature, vol. 407, 12<sup>th</sup> October 2000, pages 695-702 and*  
[http://daac.gsfc.nasa.gov/campaign\\_docs/ocdst/soiree.html](http://daac.gsfc.nasa.gov/campaign_docs/ocdst/soiree.html)

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### Conference announcement

#### Eutrophication of waters from diffuse sources.

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

<http://www.ucd.ie/~dipcon/dipcon.htm>

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### Conference announcement

#### Sustainable Land Application Conference



January 4-8, 2004  
Wyndham Palace Resort and Spa  
Lake Buena Vista

Objectives: Review fundamental and specific reactions of constituents in non-hazardous wastes (manures, biosolids, and effluents)

Improve understanding about contaminant reactions in soils, emphasizing the commonalities of reactions among wastes

Synthesize multi-disciplinary information and characterize the "state-of-the science"

Identify high priority and critical research needs

Promote interdisciplinary approaches to solving societal problems of waste disposal

## 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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# SCOPE NEWSLETTER

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## **A review of the significance of non-point source agricultural phosphorus to surface water<sup>1</sup>**

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<sup>1</sup> A document commissioned by CEEP, CEFIC Sector Group, drawing on an assembly of contemporary knowledge from the literature, including material published previously by the authors.

## Introduction – international perspective

Release of phosphorus (P) from terrestrial environments undermines water quality by contributing to eutrophication in lakes and rivers (Daniel *et al.*, 1998; de Clercq *et al.*, 2001; Watson and Foy, 2001; Withers *et al.*, 2000). Eutrophication arises from a complex interrelationship between nutrient status and ecological circumstances (Haygarth *et al.*, 2000a) that results in accelerated growth of algae or water plants (Pierzynski *et al.*, 2000). There is no internationally accepted ‘critical’ P concentration for water, but the Environment Agency for England and Wales proposed standards of 85 µg total P (TP) l<sup>-1</sup> (annual geometric mean) for standing fresh waters and 200 µg soluble reactive P (SRP) l<sup>-1</sup> (annual mean) for running fresh waters (Environment Agency, 1998). Presence of algae causes significant limitations on water use for drinking and fishing, as well as for industrial and recreational uses (Carpenter *et al.*, 1998). In Europe, 55% of river stations reported annual average dissolved P concentrations in excess of 50 µg P L<sup>-1</sup> over the period 1992-96 (Crouzet *et al.*, 1999). A report on the state of New Zealand’s environment revealed that approximately 10% of shallow lakes were classified as eutrophic (20-50 µg total P L<sup>-1</sup>) or hypereutrophic (>50 µg total P L<sup>-1</sup>) (Cameron *et al.*, 2002). The protection of water quality is, therefore, a major international environmental problem. In recent years, the level of focus and attention on point sources\* has diminished, because of the relative ease by which they have been identified and subsequently controlled. In contrast, and partly due to the success with point sources, the perceived and actual relative importance of non-point source agricultural pollution has increased. In the European Union, the Water Framework Directive (2000/60/EC) is a key legislative driver behind this and aims to restore all waters to ‘good ecological status’ by 2015.

\* See note at end of article concerning the definition of non-point sources

## Generic mechanisms of non-point source phosphorus release from agriculture

The P release from agricultural soils is generally small compared with the amounts of P added to soil as mineral fertiliser and organic manure. These can exceed 25 kg P ha<sup>-1</sup> yr<sup>-1</sup> in many agroecosystems (Cameron *et al.*, 2002; de Clercq *et al.*, 2001; Haygarth *et al.*, 1998; Sibbesen and Runge-Metzger, 1995). Data from a wide range of field and catchment studies have shown that, in most cases, annual total P transfer from soil is less than 1 kg ha<sup>-1</sup>, although higher rates of transfer (2-6 kg P ha<sup>-1</sup> yr<sup>-1</sup>, up to 17 kg P ha<sup>-1</sup> yr<sup>-1</sup>) have been recorded from soil under intensive pastoral or arable farming, especially when animal manure is applied (Gillingham and Thorrold, 2000; Haygarth and Jarvis, 1999; Hooda *et al.*, 2000; McDowell *et al.*, 2001; Nash *et al.*, 2000; Turner and Haygarth, 2000). To help achieve a balanced perspective on non-point source P release from agriculture, it is necessary to consider:

Sources ⇒ mobilisation (by solubilisation and detachment) ⇒ transport.

### Sources

Sources reflect the input of P to the agricultural and soil reservoirs that will represent the long term potential for transfer to the wider environment. This can be natural (indigenous soil P and atmospheric deposition) and anthropogenic (fertilisers and animal feed to the farm, fertilisers and manure to the soil). Phosphorus transfer from land to water cannot occur without ‘sources’ of P, which come from (i) indigenous soil P which relates to soil parent material (i.e. background), (ii) fertilisers, and (iii) imported livestock feed concentrates, which are returned to the land via direct excretion during grazing or, after storage, as spread manure. Haygarth *et al.* (1998) compiled comprehensive P budgets for intensive dairy and extensive upland sheep farming systems in the UK and determined an annual accumulation rate of 26 kg P ha<sup>-1</sup> under dairying compared with only 0.28 kg P ha<sup>-1</sup> under sheep. Withers *et al.* (2001b) determined an average P surplus on arable and grassland farms in the UK of 1000 kg P ha<sup>-1</sup> over the 65 years from 1935 to 2000 (15 kg P ha<sup>-1</sup> yr<sup>-1</sup>). High levels of P accumulation in soil have also been reported under intensive farming systems in other parts of Europe and North America (de Clercq *et al.*, 2001; Sibbesen and Runge-Metzger, 1995; Sims *et al.*, 2000), together with consequent increases in plant available P (Tunney *et al.*, 1997). The accumulation of P in soil from imported feed is particularly important in areas of

intensive livestock production (e.g. pigs, poultry, dairy) where large quantities of manure are applied to land (Sharpley and Tunney, 2000).

### **Mobilisation**

Mobilisation describes the start of the transport process and includes chemical, biological and physical processes that we call as 'solubilisation' and 'detachment'.

#### **Solubilisation**

The term 'solubilisation' refers to the release of molecules or macromolecules of P from soil surfaces and soil biota into soil water, for potential transfer. Levels of P in soil leachate following solubilisation have been shown to be sufficiently high to contribute to eutrophication if transferred to watercourses. Solubilisation reflects long-term management history and there is strong evidence that solubilisation potential increases with soil P status. Several studies have demonstrated that biological processes also play an important role in determining the amounts and forms of P transfer from soil. For example, Turner and Haygarth (2001) found that the process of wetting and drying resulted in accelerated release of soluble organic P from soil biomass. This is confirmed by findings from several studies which revealed that a significant proportion of soluble P and P in subsurface and overland flow from grassland soils is present as organic P (Haygarth and Jarvis, 1997; Heathwaite and Dils, 2000; MacLaren, 1996; Turner and Haygarth, 2000; Turner *et al.*, 2002).

#### **Detachment**

Detachment of soil particles with P attached, often associated with soil erosion, is a physical mechanism for mobilising P from soil into waters (Kronvang, 1990; Sharpley and Smith, 1990). Soil erosion *per se* has been much described (Burnham and Pitman, 1986; Elliot *et al.*, 1991; Evans, 1990; Heathwaite and Burt, 1992; MAFF, 1997; Morgan, 1980; Quinton, 1997) as has the role of particle transfer in P loss (Catt *et al.*, 1994; Kronvang, 1990; Sharpley and Smith, 1990; Zobisch *et al.*, 1994). Various size thresholds have been used to operationally define detachment, with most examples using  $>0.45 \mu\text{m}$ , although in some cases  $>0.4 \mu\text{m}$  or even  $>0.2 \mu\text{m}$  have been used for the threshold between 'dissolved' and 'particulate' P (Haygarth *et al.*, 1997). These filter sizes are somewhat arbitrary as P can occur in a continuum of particulate and colloidal sizes down to near molecular sizes (Aiken and Leenheer, 1993; Buffle *et al.*, 1978; De Haan *et al.*, 1984; Fox and Kemprath, 1971; Hannapel *et al.*, 1963; Mayer and Jarrell, 1995; Nanny *et al.*, 1994).

### **Transport**

Transfers from the hillslope to the stream are mainly controlled by a combination of hydrological factors that include the intensity and duration of rainfall (or irrigation) events, together with the spatial variables of scale and pathways (Haygarth *et al.*, 2000b). Slope (topography) and drainage (substrate permeability) mainly influence P transfer pathways at the field scale. Phosphorus transfer to surface water occurs via overland flow and/or subsurface flow (interflow, drainflow) as base-flow and storm-flow, while transfer to groundwater occurs via a combination of throughflow (percolating water) and preferential flow. Critical transport pathways from hillslope to stream are so called 'incidental transfers' that occur when applications of manure or fertiliser coincide with discharges (Haygarth and Jarvis, 1999), resulting in direct transfers to watercourses without the opportunity for the P molecule to be incorporated into the soil matrix (Preedy *et al.*, 2001). The interaction between the hydrology and the agricultural management practice is clearly important with incidental transfer mechanisms (Haygarth *et al.*, 2000b). Despite the proliferation of anecdotal evidence, there are only a few robust scientific studies providing evidence for incidental mechanisms (Harris *et al.*, 1995; Haygarth and Jarvis, 1997) and an obvious opportunity exists for some scientific criteria to define and manage these occurrences.

## Current state of knowledge of point and non-point sources of P in Europe

Separating the importance of point and non-point source of P in catchments remains difficult and encompasses much uncertainty (de Wit *et al.*, 2002). A wide diversity (from complex process and distributed approaches to simpler less data intensive approaches) of modelling approaches alongside empirical approaches have been developed to assess these, such as:

- Export coefficient approach, which has been used to determine the origin of nutrient loads to the North American lakes (Beaulac and Reckhow, 1982). The approach has been further developed and applied at catchment scale studies (Johnes, 1996) and allows the scaling up from plot scale studies to larger catchment size and to account for complex land-use systems. Export coefficients represent the rate of nutrient loads (mostly  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) that are transported from a particular source.
- Mass balance and material flow analysis, that are simple approaches based on the analysis of nutrient inputs (sources in the catchment) and outputs (river load at basin outlet) enabling large scale nutrient balances to be constructed and nutrient fluxes determined (de Wit *et al.*, 2002; Droic and Koncan, 2002).
- Empirical approaches that use experiments and observations of the sources, mobilisation and transport processes of P are made at various spatial scales. Withers *et al.* (2001a) compared P transfer from soil following application of sewage sludge, fertiliser and manure and observed that the risk of P transfer to watercourses was higher through the addition of inorganic P fertiliser or liquid cattle manure compared to liquid and dewatered sewage sludge. Their results demonstrated that large fertiliser top dressings to agricultural land pose a significant eutrophication risk. The timing and method of addition of P supplements are important, with the incorporation of the P amendment into the soil leading to the lowest P release in runoff (Withers *et al.*, 2001a). The transport of point and non-point sources can be observed through the use of microbiological and chemical tracers, an example of this approach has been the use of boron as a conservative marker for sewage effluent (Jarvie *et al.*, 2002).

A summary table of assembled information on non-point sources of P is presented in Table 1 and detail of case studies is presented in the text below. The percentage values presented in Table 1 are the contribution of non-point source agricultural sources e.g. surplus P transported to drainage network unless stated. Although, in this document, we have tried to confine the examples presented to non-point source agricultural P, it must be emphasised that not all non-point source pollution necessarily comes from agriculture, as other non-point sources may be rural, urban and atmospheric in nature. Where this is not specified, we have followed the original authors definitions and thus the reader is advised that some variation in the exact terminology may exist.

**Table 1. Estimated contribution of non-point\* source phosphorus to river loads in Europe**

Region	Year	P(%)	Reference
Po	Early 1990s	22-25	(de Wit <i>et al.</i> , 2002)
Rhine	Early 1990s	13-21	(de Wit <i>et al.</i> , 2002)
Elbe	Early 1990s	11-16	(de Wit <i>et al.</i> , 2002)
Rhine	1993-1997	42	(Behrendt, 1999)
Elbe	1993-1997	44	(Behrendt, 1999)
Danube	1996	44	(Zessner and van Gils, 2002)
Frome	1998	60	(Hanrahan <i>et al.</i> , 2001)
River Thames	1996	15	(Cooper <i>et al.</i> , 2002)
River Thames <sup>1</sup>	1999	36-53	(Cooper <i>et al.</i> , 2002)
Krka, Slovenia	1996-7	41	(Drovc and Koncan, 2002)
Kennet	1997	2	(Jarvie <i>et al.</i> , 2002)
Kennet <sup>2</sup>	1998-9	29-45	(Jarvie <i>et al.</i> , 2002)
Avon	2000-1	24	(Hilton <i>et al.</i> , 2002)

<sup>1</sup> After P-stripping introduced at Aylesbury sewage treatment works (STW).

<sup>2</sup> Tertiary P treatment installed in summer 1997 Marlborough STW.

\* See note at end of article concerning the definition of non-point sources

### ***The River Frome case study (Hanrahan *et al.*, 2001)***

Non-point and point sources can be spatially combined allowing the relative significance of non-point and point sources to be examined and the impact of differing management options (Hanrahan *et al.*, 2001). This work demonstrated that an export coefficient model in Southern England, could be used to predict total P loading from point and non-point sources in the River Frome catchment on both a seasonal and annual basis. Modelled annual total P from the Frome catchment showed non-point sources associated with land use to be the primary factor accounting for the inputs. A simple sensitivity analysis of the Frome export coefficient model indicated that nutrient export from STWs followed by tilled land were the most sensitive factors controlling the export of P from the Frome catchment (Hanrahan *et al.*, 2001).

### ***Rhine and Elbe case study (Behrendt, 1999)***

The MONERIS (Modelling Nutrient Emissions in River Systems) model was used to estimate the nutrient inputs into the Rhine and Elbe river basins from point and a range of non-point sources. The inputs of P into the Rhine and Elbe were estimated in 1993-1997 to be half that compared to their values in the mid eighties due to the reduction in discharges from municipal wastewater treatment plants. In line with this decrease, the relative contribution of non-point agricultural sources increased from 16 to 42% and 19 to 44% for the Rhine and Elbe basins respectively. Soil eroded from soils and transported to the river systems was the dominant non-point source pathways modelled.

### ***Rhine, Elbe and Po case study (de Wit *et al.*, 2002)***

Agriculture's contribution to the P loads entering the Rhine, Elbe and Po rivers was estimated for the period 1970-1995. Two models differing in complexity were compared and modelled five-year averages river loads were validated with river loads derived from discharge and measurements from a large number of monitoring stations. Non-point source (indirect) loads of P were calculated based on average surpluses at the soil surface upstream of the sampling point and the fraction transferred by the soil and groundwater system to the river network. De Wit *et al.*, (2002) estimated with a mass balance approach that the average contribution of agriculture to the total P load was 13-21 % (Rhine), 11-16% (Elbe), and 22-25% (Po).

### ***Rhine case study (Farmer and Braun, 2002)***

International co-operation through the Rhine Commission has resulted in marked reductions in the discharges of P to the Rhine over the last fifty years. The Rhine catchment states (France, Germany, Switzerland and the Netherlands) established the International Commission for the Protection of the Rhine (ICRP) in Basel on 11<sup>th</sup> July 1950. Since this date a number of internationally agreed measures have successfully reduced the P inputs to the Rhine leading to a reduction in the total P input dropping from 73,738 tonnes yr<sup>-1</sup> in 1985 to 26,793 tonnes yr<sup>-1</sup> in 1996 (Farmer and Braun, 2002). These reductions have been mainly through management of urban and industrial point sources. In 1996 it was estimated that non-point sources contribute 47% to this total P load.

### ***The Thame case study (Cooper et al., 2002)***

Phosphorus stripping was introduced in 1998 at one major STW in the Thame catchment at Aylesbury, UK. Annual catchment budgets were created based on a range of characteristic flow conditions. The annual contribution of point and non-point sources was estimated based on several sets of monitoring data (Cooper *et al.*, 2002). A number of point sources were identified, including 21 STWs and approximately 300 septic tanks. Information on non-point sources was gathered from the Environment Agency and catchment survey data. Non-point source inputs were calculated based on identified inputs to the catchment and the difference between inputs and outputs from the catchment. The STW at Aylesbury contributed half of the total point source discharges prior to the introduction of P-stripping. Following the introduction of P-stripping at Aylesbury STW, STWs were estimated to contribute one half of total P inputs. Significant non-point sources of P, including particulate P transport during winter months were identified. The difference between P leaving the catchment and the input from STW was found to be an inaccurate estimator of the non-point P load; it may be used to estimate the joint influence of non-point sources and in-stream processes (Cooper *et al.*, 2002).

### ***Loch Leven, Scotland (Foy and Bailey-Watts, 1998) taken from Haygarth et al. (2000a)***

Loch Leven in Kinross, Scotland is a eutrophic lake that suffers from problems of reduced water clarity and regular blue-green algal blooms. The Loch Leven catchment is mainly agricultural with minor industrial and sewage based P inputs and drains an area of 13.3 km<sup>2</sup>. Through the removal of P in discharges from a woollen mill and upgrading of existing and new STWs, the annual point source TP inputs were reduced by 40% (Table 2). In addition the soluble inorganic P loading was reduced by 46%, as point source inputs were proportionally richer in molybdate reactive P than non-point source inputs. The presence of significant non-point source P inputs in the catchment (42% in 1985 and 59% in 1995) has resulted in the reduction in point sources not delivering the expected environmental improvements. A large proportion of this agriculturally derived P is believed to enter the Loch in the form of particulate P. Consequently, the Loch Leven Catchment Management Project was set up in 1995 to bring together those organisations with responsibilities for planning and development, rural land use, water quality and pollution prevention, and nature conservation issues within the catchment. Four Working Groups developed a catchment management plan, and implementation of the plan began in 1998.

**Table 2. Inputs of total phosphorus to Loch Leven, Kinross, Scotland in 1985 and 1995, adapted from Foy and Bailey Watts (1998).**

Source	Tonnes total P year <sup>-1</sup>	
	1985	1995
Industry	6.4 (31%)	0.4 (3%)
STWs	5.3 (26%)	3.5 (27%)
Rainfall	0.4 (2%)	0.4 (3%)
Geese	0.4 (2%)	0.4 (3%)
Non-point source	8.1 (39%)	8.1 (64%)
Total	20.6	12.6

### ***Lough Neagh, N. Ireland (Foy and Bailey-Watts, 1998)***

Lough Neagh is a large eutrophic lake in north-east Ireland covers 386 km<sup>2</sup>. The main catchment land uses in 1991 were grassland (77%) and rough grazing (14%). A molybdate reactive P budget was calculated by Foy *et al.* (1982), who estimated that STWs contributed 48% of inputs to the Lough in 1979, 4% was from creameries and the remaining 48% originated from non-point sources. Between 1981 and 1983 P removal was commissioned at ten STWs serving seven major towns (63% of the urban population) in the catchment. The impact of this phosphorus removal on lake TP concentrations was evident, with mean annual values decreasing from about 140 µg L<sup>-1</sup> in 1982 to 100 µg L<sup>-1</sup> in 1988. After 1988, the upward trend resumed as a result of a combination of factors including contributions from non-point sources, including septic tanks (Foy *et al.*, 1995), reflecting an annual increase in molybdate reactive P river loading of between 1.9 and 2.3 kg P km<sup>-1</sup>. The continuing surplus of P in Northern Ireland agriculture since 1995, equivalent to a soil P accumulation rate of around 10 kg P ha<sup>-1</sup>yr<sup>-1</sup>, is thought to be the most likely cause of the increase (Foy and Bailey-Watts, 1998).

### ***Krka case study (Drolc and Koncan, 2002)***

The major inputs of total P into the lower Krka catchment were analysed and a P budget was developed through the use of material flow analysis. Material flow analysis focuses on the stocks and flows of nutrients within the catchment, enabling emissions from point and non-point sources to be compared. The Krka river basin contains a range of land uses with forest covering almost half of the basin. The main sources of P were found to originate from waste water management (52%), with agricultural inputs estimated at 45% of the total P emissions with 41% being classified as P arising from non-point agricultural sources (Drolc and Koncan, 2002).

### ***River Kennet, UK (Jarvie *et al.*, 2002)***

The Kennet is a major tributary to the River Thames, Southeast England, with an estimated catchment area of 1200 km<sup>2</sup>. The system is groundwater fed with approximately 787 mm annual rainfall, with only 34% of this being converted to river flow, due to the high permeability of the catchment. The loads of P through the catchment were studied using in-stream monitoring at a network of river site in combination with analysis of effluent discharges at Marlborough STW to assess the relative importance of point and non-point sources on in-stream P concentrations. In August 1997 tertiary treatment was installed to reduce the P concentration in the effluent at Marlborough STW, which resulted in a significant drop in the SRP concentration in the effluent. Non-point source inputs to the catchment in the summer of 1997, before tertiary treatment was installed was estimated at 2%, whereas in 1998 and 1999 non-point sources contributed 45 and 29% of P inputs, respectively. The results demonstrated that point source treatment was successful in reducing the in-stream soluble reactive P load by an estimated 72%, based on direct measurement of soluble reactive P and the use of boron as a conservative marker for sewage effluent (Jarvie *et al.*, 2002).

### ***Danube case study (Zessner and van Gils, 2002)***

Zessner and van Gils (2002) recently used emission estimates and water quality data to investigate and quantify the sources, pathways and sinks of nutrients in the Danube basin using the Danube Water Quality Model. The approach takes into account retention processes of P which include net storage in the sediments of lakes, flood plains and wetlands. The most important pathways in the Danube basin are for P erosion and runoff (36%, mainly from agriculture) and sewage treatment works (33%) (Lampert and Brunner, 1999). The uncertainties associated with average values of emission estimates from different countries and different years were estimated to be +/- 20% (Zessner and van Gils, 2002). There has been an estimated and observed decrease in both N and P levels in the Danube between 1988 and 1997, due to the reduction in manure discharges in Romania and Bulgaria in the early 90s, following political changes. A challenge will be to ensure that the economic recovery of these countries can proceed without increasing nutrient emissions to the Danube (Zessner and van Gils, 2002). Validation of the results with monitoring data from Reni showed that the model significantly overestimated monitored TP. It was suggested that the TP concentrations were not representative of the river load due to the low sampling frequency (Zessner and Kroiss, 1999).

### **Conclusions**

In general, non-point sources\* of P are at least as an important a source of P as sewage, particularly where point source reduction strategies have been implemented through the use of treatment technologies. There are difficulties and thus uncertainties in providing non-point source estimates, but several European case studies have been used to demonstrate that non-point sources of P contribute between 29 and 60% of the total P load to European catchments.

**\* NOTE: Definition of non-point sources:** *Non-point sources are generally read as being approximately equivalent both to (a) the part of phosphorus coming from all sources other than sewage and industrial wastewaters and (b) to the part of phosphorus coming from agricultural activities and the soil. However, depending on the author/data, non point sources may also include uncollected waste waters (discharged directly to water or via septic tanks) and point sources may include agricultural phosphorus in manure from farmyards and animal production units.*

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