SCOPE NEWSLETTER

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 17th June 09:30 -17h00

Beneficial reuse of struvite :
fertiliser value and acceptance

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

Friday 18th 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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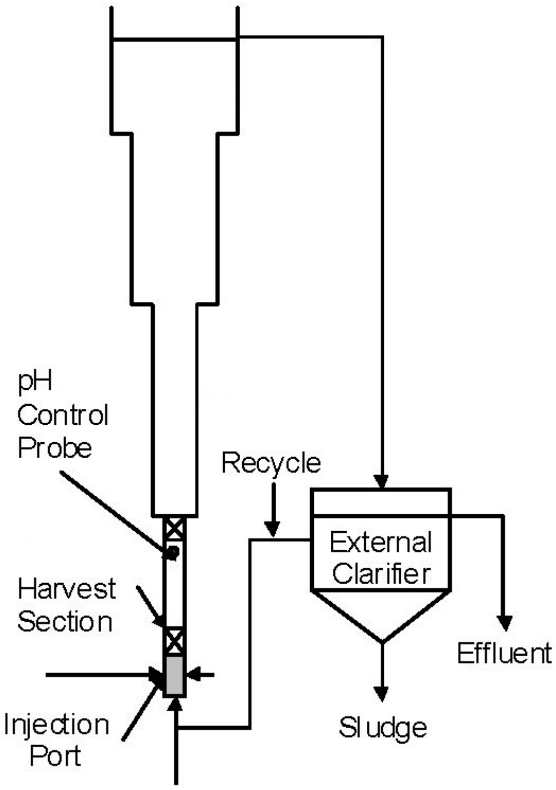
Phosphorus recycling

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 Bouropolous 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

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Journal web site: http://jees.nrc.ca/
List of phosphorus recovery theses at UBC: 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 *and* *koch@civil.ubc.ca*

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 ($MgCl_2$, 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^3/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 ($P-PO^4$) 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 know 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

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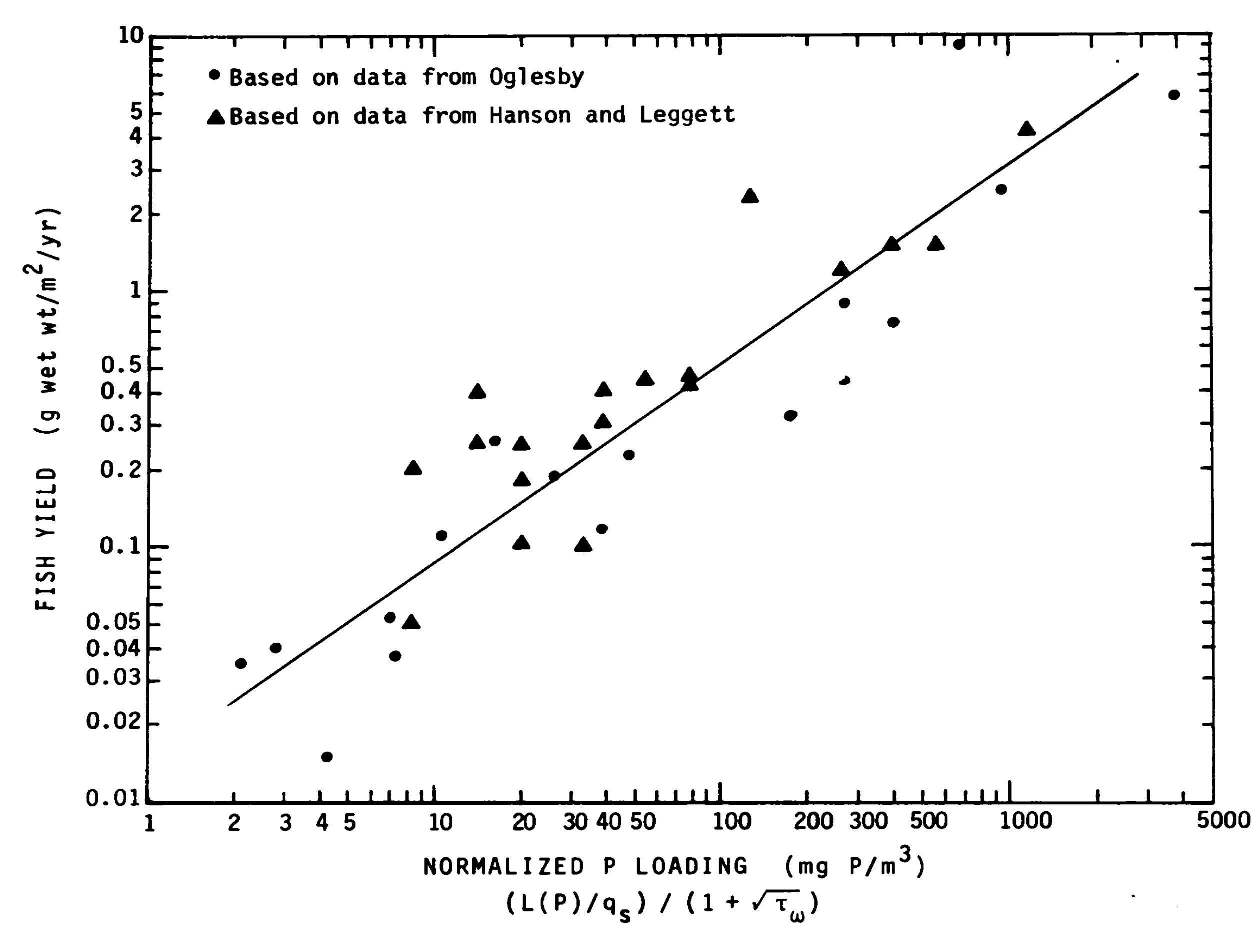
Water body fertilisation
Impact on fish production

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^2/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_ω = hydraulic residence time (waterbody filling time

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

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

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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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