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## SCOPE NEWSLETTER

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*SCOPE N°36 - 03/2000 - Sweden*

### **Trends for sewage sludge disposal**

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

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

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

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

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

- ensure that harmful substances from industries and households do not enter the domestic sewage system
- install separate collection of urine (not through the sewerage system), as this contains 60% of phosphorus and 80–90% of nitrogen in domestic wastes. The separate collection enables recycling as fertiliser or other applications.

The separation of household streams, however, would imply far-reaching changes in existing waste water infrastructure which would be very costly.

## ===== Product recovery and phosphate recycling =====

When source separation is not feasible, the paper suggests that sewage sludge can be split into **fractions that can be re-used (nutrients, organic substances for energy, inorganic substances for use in building materials)** and into a small fraction containing the harmful substances which require disposal.

Two existing examples of sludge fractioning processes are cited, both currently functioning in Scandinavia : the Krepro system at Helsingborg, Sweden, and the Cambi system at Hamar, Norway.

The Krepro system uses acids at high temperature. The Cambi system treats sewage sludge before digestion using pressure and steam which releases phosphates and ammonium and making the remaining organic substances more digestible, thus increasing biogas production.

## ===== Possible phosphate recycling pathways =====

**The authors present phosphorus recovery as an important area for resource recovery from sewage sludge fractioning.**

Several different pathways are indicated :

- **anaerobic digestion** of sludge leading to a liquid phase rich in soluble phosphate and ammonium which can be treated to precipitate phosphates. Digestion of untreated sludge will render soluble roughly 50% of the phosphorus in the sludge, higher proportions can be achieved by utilising a sludge pre-treatment such as the Cambi process.
- **dissolving of sludge** in acids or bases. Work carried out in the author's research department indicates that nearly all the phosphate can be rendered soluble by acid at pH2 (for sludges containing iron and aluminium precipitated phosphates)
- **reaction with sulphides**. The same work found that sulphides at neutral pH did not cause phosphate release from the same sludge, but released 80% of phosphates at pH4. Such reactions would pose safety, corrosion and odour problems. Efficiency might be improved by using a two step bacterial process but this has not yet been investigated.
- **heat treatment**, with the aim of developing processes which release phosphates and improve sludge biodegradability at temperatures below 100°C.
- **phosphorus recovery from sludge incineration ash** (see article on work by Erik Levlin of the same research division in this Newsletter)

SCOPE editor's note : **agricultural spreading of sewage sludge in Sweden has recently come under significantly stronger pressure** with the recent recommendation (Autumn 1999) by one member of the committee responsible for defining sludge quality standards that agricultural spreading should be suspended because of the presence of brominated flame retardants in sludges, the risk of their accumulation in soil and possible effects on organisms.

*“Trends in Swedish sludge handling”, Proceedings of the Polish – Swedish Seminar on Sustainable Municipal Sludge and Solid Waste Handling, Royal Institute of Technology, Stockholm August 24th 1999.*

Bengt Hultmann, Division of Water Resources (Civil and Environmental Engineering), Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden.

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## SCOPE NEWSLETTER

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### *SCOPE N°36 - 03/2000 - Recovery and Recycling Phosphorus in sludge incineration ash*

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*Results are presented for preliminary investigations of phosphate and metal contents of sewage sludge incineration ashes and of leaching of these using acids. Different types of ash, various incineration temperatures, different acid concentrations and leachate phosphorus/metal ratios are studied.*

*Phosphate contents of 13 ash samples from 6 literature sources are given, showing phosphate levels mainly varying from 9–27% (one third of the samples over 20% phosphates, but also two samples with very low levels).*

*Investigations of acid leaching of incineration ash were made using three types of ash :*

- *pure sewage sludge incinerated at different temperatures in a laboratory oven (sludge from the Stockholm Himmerfjarden sewage works which uses iron salts for phosphorus removal)*
- *fly ash from the Igelsta incineration plant burning dewatered Himmerfjarden sludge with biofuel (approx 20% sludge / 80% biofuel)*
- *bottom ash from the Högdalen incineration plant burning the same sludge with municipal waste (around 10% sludge / 90% waste)*

*The phosphorus content of the Igelsta and the Högdalen ashes were 0.44–0.45% respectively, with an estimated 80% of this coming from the input sewage sludge component.*

*The experimental results presented show that no phosphate can be dissolved from the ashes without acid digestion, roughly half at 0.5 M hydrochloric acid (HCl) and almost all of the phosphate at 1 M HCl or more (see diagrams below).*

*Matsuo (1996) however indicated that phosphorus can be leached from biological P-removal sludge incineration ash using warm water (see opposite).*

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### **Metal leaching**

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*As well as phosphorus, metals are leached out of the ashes by acid. Metal:phosphorus ratios are*

*generally significantly better (lower) in the raw sludge than in the Högdalen and Igelsta ashes, but this may be due to the metals present in the municipal waste and biofuels which were co-incinerated with these sludges.*

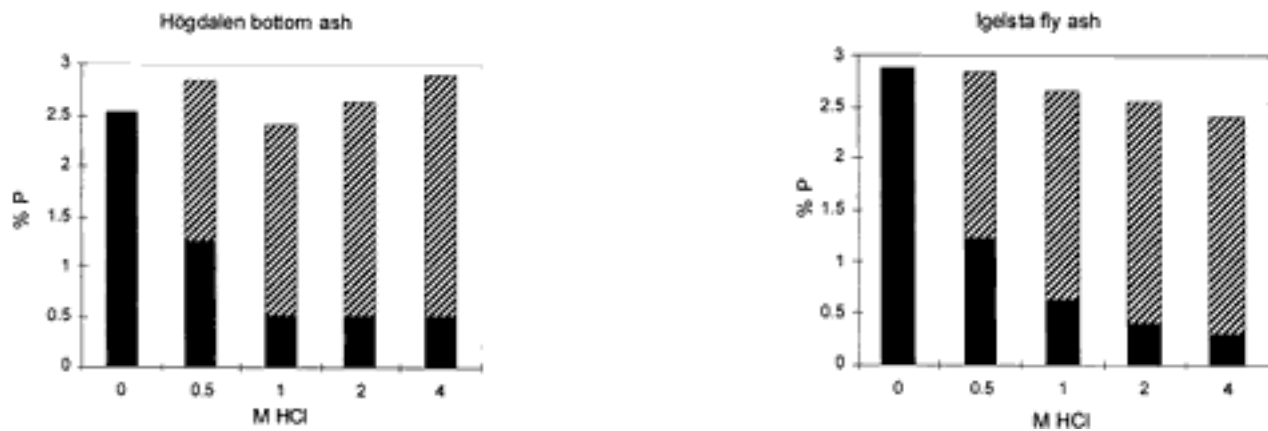
*The paper also explores the volatility of the different metals in these ashes. The author suggests that metal contamination of the recovered phosphorus could be avoided by evaporating them during incineration and recovering the phosphorus from the bottom ash.*

*The paper also summarises possible routes for using sludges or incineration ash in the manufacture of bricks or ceramic materials.*

*Percentage phosphorus in ash from Högdalen and Igelsta after leaching and dissolved phosphorus versus acidity in M HCl of the leaching liquid.*

■ P in ash after leaching

■ Dissolved P



*“Trends in Swedish sludge handling”, Proceedings of the Polish – Swedish Seminar on Sustainable Municipal Sludge and Solid Waste Handling, Royal Institute of Technology, Stockholm August 24th 1999.*

*Bengt Hultmann, Division of Water Resources (Civil and Environmental Engineering), Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden.*

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## SCOPE NEWSLETTER

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### *SCOPE N°36 - 03/2000 - Biological P-removal ash* **Availability of Phosphorus for Recovery**

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**The study used sludge produced by a laboratory scale Enhanced Biological Phosphorus Removal plant (28 litres/day influent) running on synthetic waste water. The sludge was evaporated, dried and then incinerated in an electric muffle furnace for 2 hours at 670°C.**

The bio-P plant removed nearly all the phosphorus from the influent (15–18 mg total P/l), giving a sludge which the authors indicate contained 5–10% P. The P content of the sludge incineration ash is not indicated, but would appear to be roughly 32% (total ash P = approx. 320 mg/l according to graph p410, in a suspension of 40 mg in 40 ml water).

#### **Phosphorus elution**

Phosphorus elution was tested by suspending the ash in water, at a given temperature for a certain time, then filtering to separate eluted from non dissolved phosphorus.

**The authors state that a large part of the phosphorus in the ash is released in a relatively short time using hot water.** The graphs given indicate that around 80% of ash total P is eluted after 4 days using water at 86°C. No results are given for shorter time scales, but it is possible that most of the release might occur in a much shorter period.

Release at a comparable level (around 80%) occurs using lower temperature water at 53°C after around 10 days.

Water at 30°C or 5°C only achieves low P elution rates (less than one third) even after 12 days.

Varying concentrations of ash in suspension were tested (from 0.5 g ash/l to 5 g ash/l) showing reduced proportions of P eluted in the presence of higher concentrations of ash (probably as a result of higher phosphorus concentrations developing in the water).

#### **Orthophosphate**

Interestingly, almost all the eluted phosphorus appeared to be in the form of dissolved orthophosphate at 86°C, whereas there was little orthophosphate released at 53°C or lower (eluted phosphorus is assumed to then be inorganic polyphosphate).

The authors indicate that at 86°C the phosphorus is initially eluted as polyphosphates but rapidly hydrolyses to orthophosphates.

### **Magnesium and potassium**

Sodium and calcium were not significantly eluted during the different experiments, whereas magnesium and potassium are released.

The ratios of release of these elements to phosphorus release were (water at 40°C):

$$DMg/DP = 0.19 \text{ mol/mol}$$

$$DK/DP = 0.19 \text{ mol/mol}$$

### **Implications of iron addition**

The authors then made a tentative release test on ash produced in a full-scale biological P-removal sewage plant. Phosphorus elution was insignificant. The ash was coloured redish because of the presence of iron. It was therefore decided to test the implications of the presence of iron in the sludge on P elution from the sludge incineration ash.

This was done by adding ferric chloride solution to the laboratory bio-P plant sludge, before incineration, to give iron contents in the sludge of zero, 0.75 and 3 % Fe dry weight.

The 3% iron in the sludge was equivalent to a sludge molar Fe:P ratio of less than 0.25.

The ash from the 0.75% iron sludge slowed slightly reduced P elution at 85°C, whereas the 3% iron sludge ash showed very low P elution.

The authors suggest, given the molar ratios present, that this may be due to the **formation of heterogenous iron polyphosphate complexes** during incineration.

## **===== Incineration Temperature =====**

Under incineration at 1000°C (instead of 650°C) the laboratory bio-P plant sludge was vitrified. P elution was reduced in this case by around half (using water at 40°C).

*"Release of Phosphorus from ash produced by incinerating waste activated sludge from Enhanced Biological Phosphorus Removal", Wat. Sci. Tech., vol.34 n° 1-2, pages 407-415, 1996.*

Y. Matsuo, Dept. Civil Engineering, Faculty of Science and Engineering, Chuo University, Kasuga, 1-13-27, Bunkyo-ku, Tokyo 1121, Japan.

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### *SCOPE N°36 - 03/2000 - Sewage Sludge* **Citric acid P-extraction**

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**This paper presents experimental work carried out to assess the feasibility of extraction of heavy metals from sewage sludges, in order to facilitate appropriate re-use, for example in composting. Results show that 80–90% of sludge phosphorus is also extracted using citric acid at pH 3-4.**

Lab scale experiments used sewage sludge from the Almere municipal sewage treatment works, Holland. This is a low-loaded activated sludge plant producing secondary sludge which is dewatered in decanting centrifuges after addition of inorganic flocculants.

This dewatered sludge contains 7.9 g/kg iron, 21.5 g/kg aluminium and 22.3 g/kg phosphorus (of dry matter). The heavy metal concentrations exceed legal standards (for fertilisers) for cadmium (2 mg/kg), copper (472 mg/kg) and zinc (425 mg/kg), with a total metal content of 1.96 mol/kg dry matter (heavy metals and competing metals).

Elution experiments were performed by diluting sludge to 5g/l in 500 ml containers. Extraction was measured after five time periods from 0.04 to 11 days.

### **===== Organic acids =====**

**Two different organic acids were tested (citric and oxalic) as well as nitric acid** (in order to distinguish pH effects from complexing effects).

Citric and oxalic acid both proved more effective at eluting metals at relatively mild pH's than nitric acid. Oxalic acid, however, tended to be removed by precipitation of calcium oxalate, resulting in a lower effectiveness than for citric acid.

The extraction of different metals by citric acid at different pH's was studied over varying temperatures and reaction times. Results are presented for elution of copper, zinc, calcium and iron.

The authors conclude that a pH < 4 is necessary in order to avoid degradation of citric acid (so that the elution acid can be reused several times). 50% of citric acid is degraded after 30 days at pH 3 but after

only 8 days at pH 6.

## =====**80–90% extraction of phosphorus**=====

The authors indicated that 80–90 % of total phosphorus in the sludge is also eluted out at the same time as metals (the exact conditions for these figures are not given).

They conclude that “*extraction with citric acid could be an attractive option to recover the economic cost of phosphate*”.

Following elution, metals and phosphorus would need to be removed from the extracting liquid, both to avoid accumulation of metals in the elution process, and to permit phosphorus recovery. The authors suggest this would be possible by chemical sulphide precipitation for the metals or ion exchange.

Because citric acid is readily biodegradable under aerobic and anaerobic conditions, traces remaining in the sludge are not a problem for further processing or agricultural recycling.

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*"Removal of heavy metals from sewage sludge by extraction with organic acids". Wat. Sci. Tech. Vol. 40 n° 1 pages 129-136, 1999.*

A. Veeken, H. Hamelers, Dept. Agricultural Env. and Systems Technology, Wageningen Agricultural University, PO Box 8129, 6700 EV Wageningen, Holland.

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## SCOPE NEWSLETTER

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*SCOPE N°36 - 03/2000 - Japan*

### *P-recovery as calcium phosphates*

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*Laboratory experiments used calcium silicate hydrate seeds in a 50–250 ml/hour fixed and expanded bed reactors to precipitate calcium phosphates from secondary effluents and sidestreams of different sewage works. Around 70% P-recovery efficiency was achieved at a pH of 8 without prior decarbonation, producing a recovered phosphate material with a 17% phosphorus content.*

*The seed material used was produced by mixing siliceous and calcareous raw materials, followed by autoclaving. This produced, under suitable conditions, nearly spherical calcium silicate hydrate (tobermorite) particles with card-house or needle shaped crystal growths on the surfaces. For the experimental work, 1.7–2.4 mm diameter seed particles were used. The shape of the surface tobermorite crystals did not appear to affect calcium phosphate precipitation efficiency.*

### **==== Experiments with secondary effluent =====**

*Initial experiments used a 50 ml/h reactor consisting of a sidearm test tube, and sand-filtered sewage works secondary effluent. The reactor was tested with both a fixed bed and a 25% expanded bed using an upstream circulator. The 50 ml/hour flow rate gave a reactor residence time of around one hour. Several runs of up to 400 days duration were carried out.*

*A variety of calcium ion sources were tested, including calcium chloride and seawater, to give a calcium ion concentration of 40–80 mg/l. Seawater proved a less effective calcium ion source (at comparable calcium concentrations), possibly because of sodium inhibition of phosphate precipitation.*

*Removal of soluble phosphate from the effluent treated varied from 80% at pH 9 to 70% at pH 8.5.*

*The authors suggest that optimal operating conditions would be around pH 8.5, allowing reliable soluble phosphate removal from 2 mg/l down to 0.6 mg/l, with a reactor residence time of 30–40 minutes.*

### **==== P-rich sludge sidestreams =====**

*Further experiments then used sludge treatment sidestreams with soluble phosphate contents of 10–50 mg/l in expanded bed reactors of 250 ml/h flow rate. The bed was expanded 12.5% by an upstream circulator. Bed size was 250 mg of seed crystal, giving once again a reactor residence time of around one hour. In certain runs, calcium chloride was added to dose calcium ion concentrations to 80 mg/l in the reactor (higher calcium concentrations did not improve performance) and sodium hydroxide to control pH at different levels in the range pH8–pH9. In other runs, hydrated lime addition was used.*

*Several runs of up to four months in different conditions were carried out.*

*For these higher effluent phosphate concentrations, soluble phosphate removal rates of 80% were achieved at a pH of 8, considered by the authors to be the optimal operating pH for treating such effluents. In this case, around 60% of the total phosphorus in the treated effluent was trapped on the bed crystals.*

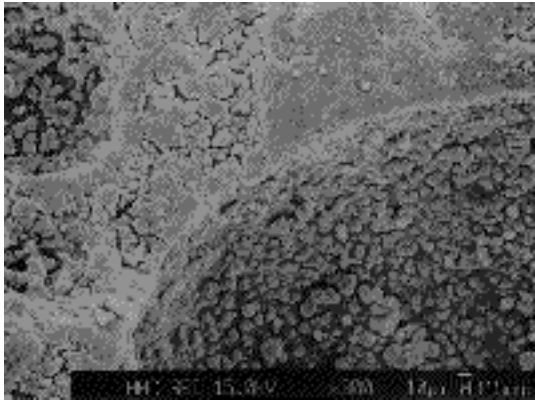
## **==== Quality of recovered phosphate product =====**

*The citrate solubility of the precipitated phosphates were assessed. Complete solubility in 2% citric acid indicated that these are partially formed hydroxyapatite crystals, and that the recovered material could be used as a slow release fertiliser. When 50 mg soluble phosphate concentration effluents are treated with a one hour reactor residence time, the phosphorus content of the bed material reached around 16% after six months' operation, approaching that expected of commercial mixed phosphate fertilisers.*

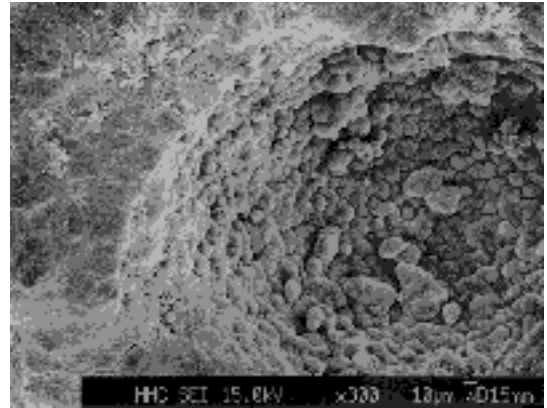
*In addition, the heavy metal content of the recovered phosphate material is relatively low (after 126 days) : 3.4 mg/kg arsenic, 0.5 mg/kg cadmium (both around half the level in the initial seed material) and 0.021 mg/kg mercury (the same as in the initial seed material). These levels are one to two orders lower than recommended maximum values for use in fertilisers in Japan.*

## **==== Crystallisation process and reliability =====**

*The authors suggest, on the basis of surface analysis, that the seed material is first covered with a calcium-excess calcium phosphate of unknown structure, then by poorly-crystallised hydroxyapatite and finally by fine granular hydroxyapatite crystal layers.*



SEM after 1 day of operation



SEM after 7 days of operation

*The authors indicate no problems with seed material deterioration even after several month long runs, and no problems with biofilms or slime, even in the presence of significant concentrations of organic matter in the effluents (200–400 mg/l COD in the sidestream effluent treated).*

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*"Phosphorus removal with calcium silicate hydrates as seeding crystals in sidestreams". Proceedings of the 54th Annual Conference of the Japan Society of Civil Engineers (part 7), pages 336-339, 1999 (in Japanese).*

*K. Moriyama, Kyushu Kyoritsu University, Faculty of Engineering – Civil Engineering Section, MN807-8585, 1–8 Jiyugaoka, Yahata Nishi-Ku, Kitakyushu City, Japan. Email : [moriyama@kyukyo-u.ac.jp](mailto:moriyama@kyukyo-u.ac.jp)). Seed crystal materials are produced by Mitsubishi Materials Corporation - Email : [to-kojma@mmc.co.jp](mailto:to-kojma@mmc.co.jp).*

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*SCOPE N°36 - 03/2000 - Wastewater chemistry*

### **Struvite precipitation kinetics**

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**Nucleation of struvite (magnesium ammonium phosphate) was studied using pure solutions in the laboratory and precipitation onto different surfaces under varying mixing conditions was then studied in the supernatant of storage lagoons of an anaerobically digested sludge at the Sacramento Regional Wastewater Treatment Plant (685,000 m<sup>3</sup>/day), Northern California.**

**This work follows a previous paper in which a solubility constant for struvite was experimentally determined and confirmed in the sewage sludge supernatants.**

#### **===== Nucleation times =====**

Struvite nucleation was studied using pure reagent solutions with different equimolar concentrations of struvite constituents in Pyrex beakers in the lab. Supersaturation was varied by adjusting the pH in the range 6.3-7.9. Mixing energy was altered by adjusting stir speeds. Nucleation was detected by light scintillation.

Struvite nucleation was found to be reaction controlled, with nucleation times strongly dependent on struvite supersaturation and mixing energy having only a minor effect.

#### **===== Struvite precipitation =====**

Struvite accumulation was studied in the sewage works (anaerobically digested) sludge supernatant by suspending duplicated or triplicated surfaces in three selected locations in the lagoons : an undisturbed zone, a moderately mixed zone near a brush aerator operating 12 hours/day, and a high energy zone covered by splashing from the brush aerator when in operation.

To measure struvite growth rates, stainless steel flat surfaces of 2250 mm<sup>2</sup> were used. PVC and acrylic plastic surfaces were used to examine the effects of surface roughness on struvite accumulation rates.

**Struvite accumulation occurred in all three zones in the sludge supernatant, but accumulation rates**

and crystal habit varied significantly according to the location. The struvite in the undisturbed zone formed long crystals, whereas that in the high energy zone was less elongated and more tightly packed.

Growth rates for the three zones were 1.8 g/m<sup>2</sup>/day in the undisturbed zone, 4 g/m<sup>2</sup>/day in the medium energy area and 22.4 g/m<sup>2</sup>/day in the high energy zone. After an initial induction period, in which a first layer of struvite crystals was established on the surface, constant growth rates were observed for each zone.

The pH and total inorganic carbon content of the supernatant were measured at the three different zones. Carbonate concentration was around one order of magnitude higher than for equilibrium with atmospheric CO<sub>2</sub> because of biological CO<sub>2</sub> production in the sludge digesters and in the lagoon. The splashing of supernatant into the air above the aerator may have caused CO<sub>2</sub> release and thus a higher pH (confirmed by measurements) in the supernatant in the mixed and splash zones.

Calculated theoretical struvite growth rate differences between the three zones (+3.3% between undisturbed and moderately mixed zones ; +4.2% between moderately mixed and splash zones) were very significantly lower than actual growth differences (+125%, +460%)

### ===== Different surfaces =====

Experiments in the lagoon supernatants showed that acrylic surfaces had a lower accumulation rate than PVC, and PVC in turn significantly lower than stainless steel. On the two plastic surfaces, most of the accumulation was not on the smooth surfaces, but in fact on rough surface edges where the surface samples had been sawn. However, even when only these rough edge surfaces were taken into account, the struvite accumulation rate/mm<sup>2</sup> was still lower on the plastics than on stainless steel.

In a further experiment, roughened stainless steels surfaces were compared with unmodified surfaces. The roughened surfaces had higher initial struvite accumulation rates, but rates were similar once an initial struvite coating had covered both surfaces.

### ===== Concentration or kinetic parameters ? =====

The authors conclude that **struvite nucleation and the initial deposit of a first struvite layer on a new surface (induction) are mainly reaction-controlled (dependent upon supersaturation and thus pH)**, with only a small transport influence. Induction is strongly influenced by the relative surface roughness of different materials.

**Struvite crystal growth is essentially transport-controlled** and is primarily influenced by mixing energy intensities, with a low sensitivity to temperature variation. At higher mixing intensities, control shifts to surface integration processes, and becomes more temperature sensitive.

## ===== Solubility constant =====

In previous work, the solubility constant of struvite had been measured using laboratory formation and dissolution equilibrium experiments, then confirmed in the same sludge supernatants used for the above work.

Formation experiments were carried out using solutions of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $(\text{NH}_4)\text{H}_2\text{PO}_4$  in duplicated, pH adjusted with sodium hydroxide, in sealed 400 ml glass beakers at  $25^\circ\text{C}$  which were opened at 38 and 105 days. pH was measured on opening. The filtered precipitate was dried at  $40^\circ\text{C}$  in order to avoid loss of water of crystallisation (which occurs at  $60^\circ\text{C}$  according to Ando et al., 1968).

Dissolution experiments were carried out using struvite manufactured in the laboratory using the above method, and struvite collected from deposits formed during operation of the Sacramento sewage works (after identification of the material as struvite using powder X-ray diffraction analysis). The experimental conditions (time, temperature, equipment) were the same as those of the formation experiments.

**Formation equilibrium was shown at pH 6.25-6.34 for phosphate concentrations of 20.6-21.6 mmol/l, or pH 7-7.12 for phosphate concentrations of 6.46-7.1 mmol/l.** Dissolution equilibrium was shown at pH 8.06-8.34 for phosphate concentrations of 1.65 –1.94 mmol/l.

**A solubility constant for struvite of  $\text{pKSO} = 13.26$  was established,** comparable to 13.15 proposed by Taylor et al. 1963 and 13.12 by Burns and Finlayson 1982.

The authors conclude that the solubility of struvite is lowest at pH 10.5-11, decreasing nearly linearly from pH 5 up to around pH 9. In particular, the authors predict significantly lower solubility at pH's 7-10 than do previous authors (Snoeyink and Jenkins curve, 1980).

A number of samples of sewage works sludge supernatants and digester supernatants were collected. Their conditional struvite solubility product was calculated and compared with the predicted curves. **The authors' curve correctly predicted struvite precipitation problems in the sludge lagoon supernatants** (whereas these were not predicted by the Snoeyink and Jenkins curve), corresponding to field observations of scaling on pipes and equipment in these lagoons.

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*"Kinetics effects on preferential struvite accumulation in wastewater", Journal of Env. Engineering, August 1999, pages 730-737. "Predicting struvite formation in digestion", Wat. Res., vol. 32 n° 12 pages 3607-3614, 1998.*

K. Ohlinger, Civil and Environmental Engineering, University of Alabama, Tuscaloosa, AL 35487-0205. T. Young, E. Schroeder, Civil and Env. Engineering, University of California, Davis One Shields Avenue, Davis, CA 95616, USA.

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## SCOPE NEWSLETTER

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*SCOPE N°36 - 03/2000 - European Union*  
**Phosphorus discharges dropping**

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“Environment in the European Union at the turn of the Century” is the latest report from Europe’s green watchdog, the European Environmental Agency. This report, published in June 1999, indicates that cleaner rivers due to the application of waste water treatment legislation, and in particular reduced point phosphorus discharges, are one of the few environmental success stories.

This is against a background of **general environmental deterioration resulting from increased energy use and growth in transports**. Problems particularly emphasised are the “snail-like” progress of **nature protection measures**, waste, increased production and use of chemicals, noise, pollution and landscape fragmentation.

The report particularly underlines the continuing pressure on the environment from greenhouse emissions and increasing chemicals and waste. Considerable uncertainties are identified regarding areas where data is inadequate (soil loss, biodiversity, pesticides) or where issues are currently emerging (human health related questions such as hazardous substances or genetically modified organisms).

The report does identify some environmental success stories, in particular acid rain, ozone depletion substances and reduced pollution of water by organic and nutrient pollution from point sources.

### ===== **Marked reductions in phosphorus from sewage works**

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The number of heavily polluted rivers has been reduced significantly, mainly as **a result of improved waste water treatment** (industries and sewage). The proportion of heavily polluted rivers in Western Europe has fallen from around 25% in 1975–80 to around 5% in 1992–98, in particular as a result of application of the urban waste water treatment Directive.

Over the past 15 years, many northern European countries have achieved 50-80% reductions in organic matter discharges and **60-80% reductions in phosphorus discharges from urban waste water treatment plants**.

Full implementation of the urban waste water treatment Directive 91/271 should **further reduce phosphorus discharges from sewage by 21% across Europe in the near future.**

## ===== Sources of phosphorus =====

The report indicates the proportion of phosphorus reaching surface waters from various sources : **agriculture is indicated to contribute 43% in the UK, 46% in Germany, 50% in Switzerland and 38% in Denmark.** In Norway, fish farms alone contribute around one half of the phosphorus discharged.

Over the North Sea catchment area, total phosphorus discharge to surface waters is estimated at 2.7 kg/hectare, with roughly half coming from sewage, somewhat more than a third from agriculture and the remainder from industrial and background sources.

## ===== Phosphorus levels declining in rivers and lakes =====

The phosphorus concentration in European Union rivers has been decreasing since the mid-1980's, with roughly a 25% reduction over a decade. The reductions have been most pronounced in the most polluted rivers. Similar improvements have been achieved in lakes, although the water quality in many cases is still poor and below that of good ecological status.

**Regarding nitrates, on the other hand, the report emphasises the extent of nitrate contamination problems in drinking water extractions** (although data across Europe and comparisons of changes over time are not available) and indicates that nitrate levels in surface waters have not decreased, despite the reduced application of nitrogen fertilisers.

Overall, regarding the effectiveness of policies for water quality, the report suggests that control of discharges has been relatively effective for point sources (treatment of urban and industrial waste waters), although there is room for improvement in most Member States.

Construction and upgrading of sewage works in Accession Countries would result in considerable reductions in pollutant discharges. The application of the urban waste water treatment Directive 91/271 in these countries would reduce phosphorus and nitrogen loadings to the Baltic and Black Seas by 15–30%.

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*"Environment in the European Union at the turn of the Century", European Environmental Agency 1999. ISBN 92-828-6888-5.*

Available from EEA Information Centre, Kongens Nytorv 6, 1050 Copenhagen K, Denmark. Available in several languages. Price 21 Euros.

Email: [information.centre@eaa.eu.int](mailto:information.centre@eaa.eu.int)

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*SCOPE N°36 - 03/2000 - Lower Rhine river*  
**Silicate limitation of algal development**

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**The production of phytoplankton was analysed in the three main branches and sedimentation areas of the lower Rhine river in Holland. A model based on carbon and silicate metabolism derived from sampling programme data which followed the water flow as it moved downstream.**

Data were based on samples taken on five dates in 1988, one each month from April to August. Water was collected from the surface of the river at several points across its width. **The same body of water was sampled over a 96 hour period**, as it moved down the three branches of the river, the speed of movement being calculated on the basis of the average flow rate. The samples were analysed for photosynthesis (carbon absorption at different light intensities), for dry weight of suspended matter and chlorophyll-a. Sky irradiance was obtained from local weather stations and the vertical light attenuation of the water was measured at the sampling stations.

### **===== Phytoplankton development model =====**

A **plug-flow model of phytoplankton development** was constructed on the basis of :

- photosynthetic production and silicate uptake
- loss factors of algal biomass : respiration, grazing and sedimentation

The photosynthetic production was modelled on the basis of the sample data (measured photosynthetic rate of samples, sky irradiance data) and by application of reduction factors related to light attenuation in the water column (for all algal species) and to silicate limitation (applied to diatoms only).

### **===== Silicate limitation =====**

It was assumed that phytoplankton growth was not limited by nitrogen or phosphorus, as average concentrations of soluble nitrogen and phosphorus in the lower Rhine were 5 mgN/l and 0.3 mgP/l respectively (1988), **whereas silicate in the river water was sometimes depleted in summer.**

The dissolved silicate concentration was modelled as affecting diatom growth, algal silicate uptake and algal cellular Si/C ratio (standard Si/C ratio = 0.6 mgSi/mgC, minimum 0.3).

The fraction of diatoms in the algal population was derived from cell counts taken on the five sampling dates, varying from 53–86% diatoms at the most upstream point and changing little as the water moved downstream.

Silicate was assumed to be not released from algae except after settling to the river bed, and a literature derived estimate of 10 mgSi/m<sup>2</sup>/h was used for release from the sediment.

**Dissolved silicate concentrations at the upstream sampling point were observed to be lower during algal blooms** (May, July and August) and to decrease as the water moved down the Rhine.

### ===== Algal grazing and biomass loss =====

Respiration losses, as a function of water temperature, were based on literature values from Janse and Aldenberg 1990 and Westlake 1980.

Settling rates, again based on literature values from shallow lakes from Janse and Aldenberg 1990, were taken to be 3% per day for 5m deep water, which may be an underestimation for the sedimentation areas of the lower Rhine.

For zooplankton grazing of algae, the Janse and Aldenberg lake-derived functions were also applied, despite the fact that in **much of the lower Rhine rotifers are the dominant grazer with crustaceans reaching substantial numbers in the lowest reaches.**

### ===== Modelling results and conclusions =====

In periods without algal blooms (April, June), chlorophyll-a concentrations increased linearly as the water moved down the river. For the other months, **an initial increase was followed by a substantial decrease further downstream, thought to be the result of accelerated zooplankton grazing** (cf. Ruyter van Steveninck et al 1990).

**The model correctly predicted significant phytoplankton losses due to zooplankton grazing during algal bloom conditions.** Simulated zooplankton densities were in the range of 0.1–0.2 mgC/l, not far removed from the maximum zooplankton densities observed in the Rhine of 0.3 mgC/l (van Zanten and de Ruyter van Steveninck 1991).

**The model predicted changes in dissolved silicate concentrations along the river matching with observations** and diurnal variations agreeing with literature data.

The model indicates that the daily photosynthetic production rate can reach 50% of the algal biomass, enabling significant algal production even within the relatively short residence times resulting from river flow.

The model suggests that silicate limitation can decrease this algal production rate by a factor of 0.4–0.5, a reduction factor comparable to that observed in dilute plankton systems such as in Narragansett Bay (Kremer and Nixon, 1978). This is in agreement with certain field observations, such as the halving of phytoplankton photosynthetic capacity after dissolved silicate depletion in the Rhine (de Ruyter van Steveninck et al. 1992), or the observation of dead or poor condition diatoms at stations with low silicate concentrations (Bijkerk, in de Ruyter van Steveninck et al. as above).

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*"A model of phytoplankton production in the lower Rhine verified by observed changes in silicate concentration". Journal of Plankton Research, vol. 15, n° 6, pp 659-682, 1993.*

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## SCOPE NEWSLETTER

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*SCOPE N°36 - 03/2000 - Lake Ecology*

### **Dissolved Organic Carbon and nutrient response**

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**The term dystrophic was first used for lakes with high Dissolved Organic Carbon (DOC) by Theinemann in 1921. This overview paper presents the different ways in which varying DOC levels modify lake response to many environmental and anthropogenic factors. The authors suggest that the widely used lake nutrient level - algal productivity paradigm should be extended to take into account DOC concentrations.**

Although DOC varies considerably in forms and properties, its overall ecosystem significance can be approximated by measuring light absorption, which varies as a function of coloured DOC. The authors suggest using light absorption at a wavelength of 320 nm which is a reasonably good approximator, even if the 320 nm absorption / DOC ratio can vary over an order of magnitude.

The use of this “proxy” for the real quantities and properties of DOC is comparable to the widespread use of “total phosphorus” concentrations as a proxy indicator of eutrophication status (chlorophyll concentration). Both these proxies **show a clear statistical relationship but do not reflect the varying characteristics of any given waterbody.**

### ===== Importance of DOC =====

Variations between the concentration and forms of DOC in different lakes will very significantly modify response to factors such as nutrient loadings, organic toxins, metals, acid precipitation, increased UV radiation (resulting from deterioration of the ozone layer) or climate change. **The authors group these effects into four areas :**

Processes influenced by DOC in fresh water :

#### 1. Attenuation of solar radiation

- reduces primary productivity
- attenuates damaging UVR radiation
- decreases mixing in small lakes

- alters depth distribution of algae and grazers
- alters water colour

## 2. Indicator of watershed characteristics and of local and global processes :

- reflects watershed drainage, morphology, vegetation
- drought decreases DOC
- forest fires increase DOC
- acidification decreases DOC
- global warming modifies DOC

## 3. Modification of response to toxicants and to nutrients

- increases acidity but reduces impact of acidity on biota
- reduces metal toxicity, binds methylmercury
- reduces toxicity or bio-availability of organic toxins
- alters availability of P; Fe and modifies carbon cycle, thus modifying nutrient response

## 4. Problem for drinking water supply

- reduces effectiveness of disinfectants
- generates toxic chemicals with chlorine or ozone disinfectants

## ===== DOC and nutrient response =====

**Lake response to nutrients is modified by DOC** both directly, through reduced availability of phosphorus (Stewart and Wetzel 1982, Francko 1986) and iron (Jackson and Hecky 1980), but also, to a large degree, indirectly through effects on primary production, water temperature, mixing ...

Carpenter et al. 1998 estimated that increasing refractory DOC from 5 to 17 mg/l will **reduce primary production and chlorophyll concentrations** (because of reduced light penetration) to an extent comparable to a reduction in phosphorus loading from 5 to 0.5 mgP/l. Field evidence of this is derived from work by Christensen et al. 1996, where Long Lake, Wisconsin, USA, was artificially divided to separate sources of organic carbon. DOC in the East Basin almost doubled from 7.5 to 14.1 mg/l over 2 years, suppressing increases in primary production even when the lake was enriched with N and P.

## ===== Evidence from Alaskan glacial lakes =====

The pronounced deglaciation chronosequence has left behind in Glacier Bay, Alaska, a series of lakes varying in age from 10 to over 1,000 years, in a pristine environment with low lake productivity. The younger lakes have only sparse vegetation in their watersheds, are fed by groundwater and have

extremely low DOC.

As the lakes become older, vegetation, and then peat, develop in the watershed, often leading to high levels of DOC in the older lakes. Consequently, the depth penetration of 320 nm light decreases with lake age. Phosphorus concentrations, on the other hand, remain relatively constant.

Light and UVR penetration data from a subset of 32 of these lakes show pronounced directional changes in coloured DOC, indicative that the low DOC levels in the younger lakes make them very vulnerable to environmental modifications.

To summarise, the authors indicate that **higher DOC levels render lake ecosystems significantly more capable of adjusting to changes in environmental factors**, to anthropogenic stressors or to nutrient loadings. DOC also provides a valuable indication of how lakes interact with their watershed and local climate.

The authors conclude that **the reinstatement of a DOC axis in the nutrient – productivity paradigm will provide a more reliable conceptual framework for understanding lake ecology** and for addressing lake management.

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*"Dissolved organic carbon and nutrients as regulators of lake ecosystems : resurrection of a more integrated paradigm".  
Limnol. Oceanogr. 44 (3, part 2), 1999, pages 795-803.*

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## SCOPE NEWSLETTER

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*SCOPE N°36 - 03/2000 - Texas Reservoirs*  
**Nutrient limitation of algal growth**

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**Nutrient limited algal growth in two Texas reservoirs was studied by a combination of nutrient addition experiments and statistical modelling. Algal growth proved frequently and strongly nutrient limited, with N being more often stimulatory than P. Half saturation constants for nitrogen were in the range 20–200 µg/l, relatively high compared to literature values.**

The two reservoirs studied were Eagle Mountain Lake (32°52' N) and Cedar Creek Lake (32°14' N). Their areas are respectively 3,638 and 13,950 ha ; mean depths both 6.1m ; residence times 198 and 275 days. Their dissolved inorganic N:P ratios were respectively 3.33 and 2.62 by weight ; and total N (excluding dissolved organic N) : total P loading ratios 5.04 and 4.29.

On eighteen separate dates in January - June 1994, samples were collected from several sites in the two reservoirs and mixed together to make a composite sample for each reservoir.

### ===== **Bottle bioassay experiments** =====

In order to permit development under non-crowded conditions, the algal population concentrations in the samples were “diluted” by a factor of 9 by adding 0.2µm filtered sample water. Development of algal density was measured (using chlorophyll concentration) over 4 days, following addition of 0, 10, 100, 200 and 1000 µg/l of soluble P or soluble N, trace elements only, or 1000 µg/l of both P and N plus trace elements (3 duplicates for each test). Light and temperature were maintained at conditions typical of the mixed layers of the reservoir at the relevant time of year.

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