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Field tests of struvite as a fertiliser

Preliminary results of field tests of struvite provide mixed results.

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Phosphorus recovery feasibility

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USA

Seeding struvite precipitation

Beaker experiments using pure chemical solutions looked at how different seed materials and mixing energies modified struvite precipitation efficiencies.

Canada

P-recovery from greenhouse wastewaters

Beaker tests show feasibility of phosphorus recovery, as calcium phosphates, from pepper-growing greenhouse wastewaters, high in calcium, magnesium and potassium.

Manures

Phosphorus release and recovery from pig manures

Research underway into simultaneous removal of nitrogen and phosphorus from pig manures looks at forms of phosphorus, precipitation potential, and acidification of manures via animal feed regimes.

Germany

Tobermorite for P- recovery

A tobermorite-rich industrial waste by-product was used as a carrier for experimental calcium phosphate precipitation from adjusted sewage liquor.

Regulatory

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Europe puts further pressure for sewage treatment on France, Ireland, Luxembourg, Portugal, Spain

The European Commission has engaged further action against Portugal and Luxembourg for failure to adequately implement European sewage treatment legislation, and the European Court has rendered judgements or opinions against France, Ireland and Spain.

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Comparing nutrients and sediments to biological impairment

29 Pennsylvania watersheds showed clear differences between attainment of water quality objectives for nitrogen, phosphorus and sediments, and biological impairment.

Lake Apopka

Incipient recovery following phosphorus load reduction

Phosphorus load reduction and lake restoration actions appear to be starting to give positive results for Lake Apopka, Florida, contradicting pessimistic predictions that the lake's restoration was not feasible.

Patuxent River

Quantifying nutrient sources

Sources of nutrient inputs to the Patuxent river were quantified for different forms of phosphorus and nitrogen.

Alberta

Nitrogen and phosphorus limitation

Nutrient limitation of periphyton (surface growing algae) was tested at river sites up- and downstream of sewage treatment works and paper mill effluent discharges.

CEEP
Centre Européen d'Etudes des Polyphosphates

cefic

Phosphate recycling

Struvite

Field tests of struvite as a fertiliser

A promising route for the recovery of phosphate for recycling from sewage and animal wastes is as struvite (magnesium ammonium phosphate). A variety of work suggests that struvite is an effective agricultural and horticultural fertiliser – see summary in Scope Newsletters n°43, 57. 2004 saw the first results of a multi-year field test intended to assess the effectiveness of struvite as a fertiliser using modern agronomic practices in the field.

Potato (*Solanum tuberosum*) was used as the test crop, since this crop is known to be ineffective in utilising available phosphorus in soil. Three batches of synthetic struvite (*Budit 370*) from Buddenheim Spain were used. This was more readily available in the significant quantities needed and in a homogenous form, than struvite recovered from waste streams.

Two sets of fertiliser gradients (one for struvite, one for TSP = Triple Super Phosphate) were established on a field that had not received P or K fertilisers for some 20 years, but had been regularly cropped over that period. Each set of gradients comprised three independent gradients, each with 8 plots. For each fertiliser, application was before planting, and was adjusted to give soil P indexes (Defra) from 3 to 9 (8 different P levels). Each plot also received 600 kg/ha of sulphate potash to provide potassium (K). Potatoes were planted on 31st March 2004, in test fields at Wellesbourne, near Warwick, England (52°12'N, 01°36'W, 49m above sea level). Seed tubers were sampled before planting; shoots, roots and tubers were sampled (3 plants from each plot) at tuber initiation as indicated by flowering; tubers were sampled at commercial maturity. Samples were assessed for dry weight and mineral content (N, P, K, Mg, Ca, Cu, Fe, Mn).

Good initial response to struvite

At tuber initiation, for both struvite and TSP treated plots, the potatoes showed a statistically significant response to differing phosphorus levels for dry weight of shoots, roots and tubers and for mineral contents of plant tissues. **At this stage, plant dry weight and mineral contents were higher for plots treated with struvite than for those treated with TSP** (for the same phosphorus levels), except for potassium contents which were significantly lower in the struvite plots.

At commercial maturity however, yields were not significantly higher with increasing phosphorus levels for the struvite treated plots, whereas the TSP plots showed statistically significant increases of yield with increasing phosphorus levels.

Questions about potassium

The experiments results are thus contradictory: better crop response to struvite than TSP at the tuber initiation stage, but failure of struvite to be an effective fertiliser by the commercial yield stage of potato development. **The authors suggest that these contradictory results may be related to potassium deficiency in the struvite treated plot** – this is suggested by the observed lower potassium levels in the plant tissues for the struvite plots at both the tuber initiation and maturity stages. Indeed, the TSP plots had received in 2003 a potassium fertiliser application (when used for experimental cropping of *Brassica*) whereas the struvite plots had not. Potassium deficiency would not however have been expected as all plots received, as indicated above, a sulphate potash application equivalent to 300 kg/ha K_2O = DEFRA soil index 2 for K). The authors are currently investigating the effects struvite might have on the availability of potassium in the soil.

Further field experiments are planned in 2005 – 2007 (funded by the UK government Department of the Environment and Agriculture, Defra) and this question of potassium availability will be addressed.

"Is struvite a valuable phosphate source for agriculture", Project report – Entrust 675382.006, March 2005, available at http://www.nhm.ac.uk/research-curation/departments/mineralogy/research-groups/phosphate-recovery/

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The Netherlands

Phosphorus recovery feasibility

The phosphorus recovery feasibility study carried out by the Netherlands national Water Industry Research Organisation STOWA looks at the practical and economic aspects of precipitating phosphates in a recyclable form in enhanced biological phosphorus removal (EBPR) sewage works, in particular in side-streams in BCFS type sewage treatment facilities. The study includes laboratory tests of precipitation from real sewage works liquors using aluminium, calcium and magnesium addition (the latter precipitating struvite), and provides an economic assessment of possible full-scale installation.

The Deventer urban waste water treatment plant (uwwtp), treating 185,000 pe, was used for the study. 12 such BCFS enhanced biological nutrient removal sewage plants are operating today in the Netherlands, enabling discharge levels of <1 mgP/l to be achieved by the biological process. These plants are equipped with a "Dortmund" stripper tank, removing phosphorus from the P-rich return side stream in the biological phosphorus removal cycle.

The phosphorus concentration (total P) in the liquor in this side stream is reasonably stable at around 30 mgP/l (measured concentrations: 23 – 29 mgP/l), with **approximately 40-45% of total inflow phosphate passing through this sidestream and thus potentially available for recovery here**.

Laboratory precipitation tests

Using real side-stream stripper liquor from the Deventer uwwtp, laboratory experiments were carried out (2 litre beaker scale) into precipitation by addition of: $Ca(OH)_2$; $ALCl_3$ and MgO. Initial pH was around 7. Conditions were set as follows:

$Ca(OH)_2$	Ca:P ratio = 1.5:1	pH8
$ALCl_3$	Al:P ratio = 1.5:1	pH7
MgO	Mg:P ratio = 1:1	pH9.5

In fact, acid addition was necessary in the case of $Ca(OH)_2$ to maintain the pH around 8 but in practice pH adjustment would not be necessary. For the $ALCl_3$ experiments the pH stayed between 6 and 7 without adjustment. For the MgO experiments, NaOH addition was necessary to ensure that the pH stayed around 9.

Residual soluble phosphorus concentrations were taken down to around 12-17 mg ortho-P/l residual (55% phosphorus removal), 1-2 (97%) and 6-13 (70%) respectively for the calcium, aluminium and struvite precipitation experiments.

Liquor buffering capacity

Approximately one quarter of the precipitate generated was calcite (calcium carbonate) in the case of both calcium and magnesium addition (but not with aluminium addition). This effect, and the significant addition of sodium hydroxide necessary to maintain pH9 chosen for struvite precipitation led the team to investigate **aeration** to reduce the stripper liquor buffering capacity.

Experiments showed that ¼ hour of aeration (20 l/hour of air per litre liquor) reduced dissolved $C0_2$ by 73% and total alkalinity (HCO_3^- + CO_2) by 10%, raising pH from 7.2 to 7.7.

The use of aluminium chloride, on the other hand, was estimated to be liable to result in a too low pH in the stripper return liquor. This problem, it is expected, could be avoided by using a different aluminium compound (a cheaply available industry aluminium by-product, but this needs to be tested).

Recovered phosphate product

The phosphate precipitated in all cases showed metal and **contaminant levels compatible with industrial use as a raw material**, except for levels of organics which would require reduction by process modifications and/or adjustment of the industrial re-use circuit to eliminate these.

Economic assessment

The authors indicate that although the market value of the recovered phosphate is not high, **this P-recovery route may offer net cost advantages because of reductions in iron dosing and in sludge production**. In particular, phosphate recovery may be advantageous where a nearby outlet for the recovered phosphate exists, as at **Thermphos International, Vlissingen**, The Netherlands.

The economic assessment of phosphate recovery based on the Deventer uwwtp suggests that **P-recovery via calcium phosphate precipitation could offer net savings of 0 (breakeven) – 0.3€ / p.e.** (per person equivalent connected to the wwtp). Aluminium dosing for P-recovery would result in a small net cost, mainly because of higher chemical purchasing costs: this could possibly be avoided by using an aluminium industry by-product. Struvite precipitation also shows a net cost, because of chemical consumption for pH adjustment (NaOH): this could possibly be avoided by aeration of the stripper liquor to reduce its buffering capacity.

There are currently two BCFS urban waste water treatment plants operating in the Netherlands with P-strippers (Deventer, Holten 40,000 pe), plus one under construction (Echten). Ten other uwwtps in the Netherlands offer configurations which could readily be equipped with P-strippers.

Further investigation is recommended *into the organic matter content of the precipitate, the composition of the precipitates, the availability of other aluminium sources, the yields of the separators, thickeners and filter presses used to extract the precipitates, the use of innovative precipitation seeding techniques.*

"Onderzoek fosfaat-terugwinnung uit stripperwater BCFS rwzi Deventer", B. Reitsma, H. Kuipers et al., STOWA, Postbus 8090, 3503 RB Utrecht, The Netherlands. Contact: F.Brandse@reestenwieden.nl

STOWA report 2005-01, ISBN 90.5773.000.6 stowa@stowa.nl www.stowa.nl

USA

Seeding struvite precipitation

Beaker experiments using synthetic wastewater (magnesium sulphate, calcium chloride, ammonium chloride, ammonium phosphate) were used to assess how different seed materials and mixing energies affected struvite precipitation (10 minutes at pH 9.0).

Quartz (sand), granite chips (both acid-washed and then dried) and ground struvite crystals were tested as seed materials, with in each case two sizes of seed (<75µm, 75-150 µm).

The synthetic wastewater had molar concentrations of magnesium 2.6, ammonium 29 and phosphate 0.87 (31 mgP/l). In all experiments, the solution was adjusted to pH 9 by sodium hydroxide addition, then mixed for ten minutes (by air bubbles at 200, 300 or 400 ml/minute of air for 60ml ml of solution in 125 ml funnels), then allowed to settle for 30 minutes. When seeded, 0.5g of seed material was used. The pH of 9 was used as identified from literature as optimum for obtaining rapid struvite precipitation and minimal precipitation of other magnesium compounds (magnesite).

Effectiveness of seeding

For each of the three mixing energies, seeding showed to very significantly increase the phosphate precipitation efficiency (from 8-14% P-removal without seeding to 23-83% with seeding). Granite was not a very effective seed at low mixing, but sand and even more so struvite were very effective at all mixing energies.

The better performance as a seeding material of struvite, the authors suggest, is probably due to its lower specific gravity: more particles (and so surface area) for the given mass of added seed, easier to maintain in suspension by mixing.

The medium mixing energy was optimum for the smaller seed particles, and the high energy mixing for the larger seeds, but the difference was not significant for sand or struvite as seeds

Particularly for the smaller seed particles, phosphorus removal efficiency was improved by 5-15% if the supernatant was filtered as well as settled (**that is, some phosphate was forming fine precipitate particles which were not settling by gravity**). This was shown for all three mixing energies.

Phosphate precipitation was generally higher with the larger seed size, except for sand and struvite at medium mixing energy when it was very similar. The reason for this is not very clear, as it would be expected that larger seed particles would offer smaller surface area for precipitation. It is possible that the better P-removal with the larger particles is because of loss of "fines" (non settling of small seed particles whose specific gravity has become lower as they are coated with precipitate) – see as regards filtration above.

The authors conclude that ground struvite crystals of size 75-150 µm offered the best performance as seed material amongst those tested.

"Struvite precipitation: impacts of seeding materials and mixing strength", WEFTEC 2003 www.weftec.org

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Canada

P-recovery from greenhouse wastewaters

Eleven sets of 500 ml beakers were used to test phosphorus removal effectiveness, by phosphate precipitation, from greenhouse wastewaters with magnesium and ammonium addition and pH adjustment. This follows previous work already published using the same methods (see Yi & Lo, 2003 summarised in *SCOPE Newsletter n°56*, initial experiments using water from the same greenhouse). The wastewater had initial pH around 6.5 and 31-284 mg/l phosphate concentration (11-102 mgP/l) and relatively high levels of calcium (average 11.5 x phosphate mol/mol), magnesium (5.7 x phosphate mol/mol), potassium (8.5 7 x phosphate mol/mol), and also nitrate and sulphate.

The wastewater was from the South Alder Greenhouse, Delta, British Columbia, Canada, used for pepper growing, from the nutrient-rich stream collected from the cropping field in the greenhouse in a storage tank before partial use by recirculation to the crops.

For the experiments, **ammonium was added up to 1.5 – 10 x the phosphate concentration (mol/mol), pH was adjusted to 7-9** (6 different pH levels were tested for each of the eleven sets of tests). 500 ml of wastewater was stirred for one hour, then settled for one hour, before filtering off the precipitate.

Three different batches of greenhouse wastewater were used for the tests, giving three different groups of experiments. The main difference between these three batches was a variation in calcium concentrations: 7.6, 9.6 and 12 mmol/l.

P-removal efficiency

At the lower calcium concentration, phosphate precipitation was very sensitive to pH, with >90% removal of phosphate from solution at pH >8.4, falling to 30% removal at pH 7.6. With increasing calcium concentration, the P-removal became less sensitive to pH, with 60% P-removal at pH 7.3 for medium and at pH 7.0 for high calcium.

In all the tests, regardless of calcium concentration, the P-removal was as high or higher than that reported in the previous work by the same authors – see above. P-removal was not related to N/P or Ca/Mg ratios, nor to total ionic strength. The main factors affecting phosphorus precipitation appeared to be the calcium concentration and the pH.

As in the previous study cited, without ammonium addition, the precipitate appeared to be principally calcium phosphates. With high N/P ratios (up to N/P = 19), ammonium content of the precipitates reached 11% at pH 7.8 (ammonium tends to be present more as an available ion at relatively low pH, but ammonia NH_3 at higher pH, not available for reaction with phosphate).

"The effects of magnesium and ammonium additions on phosphate recovery from greenhouse wastewater", Journal of Environmental Science and Health, vol. 40, n°2, pages 363-374, March 2005
http://www.tandf.co.uk/journals/titles/03601234.asp

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Manures

Phosphorus release and recovery from pig manures

A research project underway at the French agricultural research institute Cemagref is looking at the different forms of phosphorus in pig manures, at routes for rendering this phosphorus soluble, and at possibilities of precipitation (eg. as struvite or calcium phosphate). Work to date shows the complexity of phosphorus forms, difficulty in achieving Enhanced Biological Phosphorus Release, but positive potential for phosphate precipitation for recovery once the phosphorus is available in a soluble form.

Only a very small proportion of the phosphorus present in the raw manure is initially present in soluble forms, around 10-15% when the manure is stored for several months. Phosphorus extractability experiments were carried out on raw manure and after addition of phosphorus in various organic and inorganic forms to enable method calibration.

Enhanced Biological Phosphorus Removal (EPBR) was tested as a route for releasing solid forms of phosphorus to soluble forms in the manures. A 100-litres useful volume pilot reactor was used with aerobic/anaerobic cycles of around 12 hours. A series of such tests was also carried out with pH regulated at 8.3 and at 7.2, plus a test at pH 8.3 with nitrification inhibited in a 4 litre pilot reactor. These tests showed that **the biological process could not reliably ensure release of phosphorus into a soluble form**, suitable for recovery for recycling via precipitation, even if nitrification processes are involved in the changes in concentrations of soluble phosphorus, calcium and magnesium.

Acidification of the manure, on the other hand, increased the level of soluble phosphorus forms, potentially available for recovery by precipitation.

Pig farmers are currently looking at trying to reduce the pH of manures, via changes in pig feeds, in order to reduce ammoniac emissions as required by environmental legislation. The continuation of this work will therefore explore the dissolution of phosphorus forms in the manure by acidification.

Precipitation products were modelled using adjusted Minteq software. This suggested that precipitation of phosphate as struvite (magnesium ammonium phosphate) and hydroxyapatite (calcium phosphate) are feasible by magnesium addition, but that dolomite (calcium magnesium carbonate) is also likely to precipitate.

« Etude de l'évolution des formes du phosphore au cours du stockage et du traitement biologique aérobie du lisier de porcs – faisabilité d'une élimination conjointe de l'azote et du phosphore »

Study of changes in the form of phosphorus during storage and biological treatment of pig manures – feasibility of simultaneous elimination of phosphorus and nitrogen.

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Germany

Tobermorite for P- recovery

Two consecutive experiments, each of 3-6 moths duration, were carried out using a 35cm high, 144 ml bed volume laboratory scale upflow reactor. In each case, the reactor was initially loaded with 80-90g of a filter / seed material, grain size 0.6-1.3 mm. This material is a by product of the construction industry and consists mainly of tobermorite ($Ca_5Si_6O_{16}(OH)_2*4H_2O$)..

The reactor was fed with sewage treatment works secondary treatment effluent, to which sodium phosphate solution was added to give a phosphorus concentration of around 10 mgP/l.

Every 2-3 days, phosphorus concentrations in the reactor inflow and outflow, pH and dissolved organic carbon were measured. At the end of each experiment, the phosphorus, carbon and impurities contents of the filter material were assessed, and its surface characteristics were examined (chemical components, specific surface area).

Phosphorus removal efficiency

Both experiments showed, for a hydraulic residence time in the reactor of one hour, that phosphorus removal remained effective (>75%, outflow phosphorus concentration <2mgP/l) for around 4 months (3000 bed volumes throughput). With only 0.5 hours hydraulic residence time, efficiency began to fall 3-4x earlier.

The pH of the inflow liquor was in the range 7.5 – 9. pH in the reactor outflow was >9 for the first 100-150 bed volumes, then fell to 7.7 – 8.4.

The phosphate precipitation is considered to result from the dissolution of tobermorite in the filter material, producing quartz (SiO_2) and $Ca(OH)_2$. The latter causes the pH to increase and provides available calcium ions, thus facilitating the precipitation of calcium phosphates. Phosphorus removal efficiency remained effective for so long as the pH in the reactor outflow remained significantly higher than the inflow (approx 3000 bed volumes), showing that tobermorite was continuing to dissolve. **Phosphorus removal efficiency fell off when tobermorite was no longer available to dissolve**, i.e. the calcium phosphate coating on the surface impeded a further dissolution of tobermorite.

Process effectiveness

At the end of the experiments, when tobermorite was no longer dissolving, the filter material contained 7 – 13% phosphorus (TP): that is around 20-30% phosphate. Water content (<5% after allowing to dry for 24 hours), organic carbon content (2%) were fully compatible with use of the recovered filter material as a raw material in the phosphate industry.

Copper content of the recovered filter material (20-40 mgCu/kg) was low (copper has been fingered as a potential problem contaminant in sewage-recovered phosphates, see Schipper et al. (2001), but iron (1.5% iron oxide) and zinc (1240 mgZn/kg) were potentially problematic (higher than target levels indicated by Schipper in above). The iron and zinc levels, however, may be related to specifics of the sewage liquor being treated (iron dosing in sewage treatment plant, seperative sewerage network).

In both experiments **a significant biofilm developed in the reactor outflow area** (5-15 mm thickness), considerably more than in the inflow area.

The authors conclude that these experiments confirm previous work from Japan (Moriyama *et al.*, 2001) using a special pellet spherical tobermorite as a material for phosphorus recovery for recycling. **The use of the industrial byproduct resolves the high costs of pure tobermorite** (> US$ 1,000/ton, see Moriyama *et al.*, above). The recovered material was compatible with industrial reuse for P-recycling. Further work is necessary to better understand the accumulation of certain metal contaminants in the recovered material, and to ensure that biofilm development does not pose long-term reactor operating problems. The authors also suggest testing calcium addition by the use of calcite, in order to extend filter bed material effective life by supplementing/replacing the calcium release from tobermorite decomposition.

"Phosphate elimination and recovery from wastewater by active filtration using crushed gas concrete", Environmental Technology, vol. 26, pages 219-229, 2005. www.environtechnol.co.uk

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References:

Moriyama, K., Kojima, T., Minawa, Y., Matsumoto, S., Nakamachi, K. (2001): Development of artificial seed crystal for crystallization of calcium phosphate. Env. Technol. 22(11): 1245-1252.

Schipper, W., Klapwijk, B., Potjer, B., Rulkens, W., Temmink, H., Kiestra, F., Lijmbach, D. (2001): Phosphate recycling in the phosphorus industry. 2nd international conference on the recovery of phosphorus from sewage and animal waste. Nordwijkerhout, The Netherlands, 12-13 March 2001.

Regulatory

Europe

Europe puts further pressure for sewage treatment on France, Ireland, Luxembourg, Portugal, Spain

The EU Commission is continuing pressure on Member States to obtain adequate treatment of urban and agricultural waste waters. Portugal and Luxembourg have been respectively sent final written warnings and referrals to the European Court of Justice, whilst the Court has delivered opinions and final judgements against France, Ireland and Spain. This follows a spate of European Commission actions against Member States already taken earlier this year and a key European Court decision against France regarding the definition of eutrophication Sensitive Areas under EU Directive 91/271 (see SCOPE Newsletter n°59).

Portugal

Following the final warning sent to Portugal by the European Commission in January 2005 for **failure to implement nutrient removal (tertiary treatment) in 18 agglomerations** discharging sewage into "Sensitive Areas" (>10,000 p.e., deadline end 1998), the Commission has now sent a further final warning for **failure to implement adequate secondary sewage treatment in 17 agglomerations** (>15,000 p.e.). These include Alverca, Armação de Pêra/Albufeira, Bacia do Rio Uima (Fiães S. Jorge), Carvoeiro, Costa da Caparica/Trafaria, Costa Oeste (Lisboa), Covilhã, Fundão/Alcaria, Lisboa e Vale do Tejo (Lisboa), Matosinhos, Milfontes, Nazaré/Famalicão, Peso da Régua, Ponta Delgada, Póvoa do Varzim/Vila do Conde, Vila Franca de Xira and Vila Real. The final warning is the last stage before referral of a Member State to the European Court of Justice.

Luxembourg

The European Commission has referred Luxembourg to the European Court of Justice for **failure to ensure nutrient removal** from sewage works in its territory (the State has classified its whole area as a "Sensitive Area").

France

The European Court of Justice has reached judgement (case C-191/04) on a referral brought by the European Commission in April 2004 for **failure to communicate information** concerning implementation of the EU Urban Waste Water Treatment Directive 91/271 (in this case, surveillance of sewage sludges).

This follows the condemnation of France on 23rd September 2004 for failure in implementation of this same Directive by **inadequate definition of eutrophication Sensitive Areas** (case C-280/02) and on 28th October 2004 for failure to respect the EU Drinking Water Directive 80/778 because of nitrate levels in drinking water in Brittany (case C-505/03).

Ireland

The European Court reached judgement in June 2005 (case C-282/02) against Ireland for inadequate implementation of the EU dangerous substances Directive 1976/464, regarding dangerous substances discharged into waters, in effect because of **inadequate water treatment**. This follows written warnings to Ireland regarding inadequate implementation of sewage treatment and of the EU Nitrates Directive 1991/676 (see SCOPE Newsletter n°59).

Spain

Two Opinions issued by European Court advocate generals (cases C-121/03 and C-416/02) recommend condemnation of Spain for **failing to prevent water pollution from pig farms** in the Almeria, Vera and Gerona areas.

European Court Judgements and opinions, access via case number at http://www.curia.eu.int *See C-191/04, C-280/02 and C-505/03 concerning France, C-282/02 concerning Ireland, C121/03 and C-416/02 concerning Spain.*

European Commission press releases at: http://europa.eu.int/rapid/setLanguage.do?language=en *see IP/05/911 and IP/05/912 regarding Portugal and Luxembourg.*

Nutrients in ecosystems

Pennsylvania
Comparing nutrients and sediments to biological impairment

Measured concentrations and calculated loads of nitrogen, phosphorus and sediments in 29 Pennsylvania watersheds showed clear differences between

In 2002, approximately 52% of Pennsylvania's 134,000 km of rivers were assessed to be "attaining" their water use designation, 10% to be non-attaining, and 38% were classed as "unassessed". Attainment is defined by assessing biological ecosystem quality, as a function of local river and water use objectives. **Nutrient pollution and/or sediment levels in the water/silting are specified as the primary cause of non attainment for around half of the State's impaired water bodies**.

29 watersheds were analysed in this study, selected because of the availability of data concerning biological status, flows, nutrient and sediment concentrations: availability of biological ecosystem status assessment, availability of data from several years for the different physico-chemical parameters, availability of at least one full year flow data. The data was extracted from the USEPA "Legacy" data base available at *http://www.epa.gov/storpubl/legacy/gateway.htm*

17 of these 29 basins were defined as unimpaired (<2% of the basin river length impaired) and 12 as impaired.

Clear differences for all parameters

For each of sediment, phosphorus and nitrogen concentrations (and also for loads, estimated from flow data), the 95% confidence range for data for impaired watersheds was higher than and distinct from that for unimpaired watersheds (no overlap: lower 95% confidence limit for impaired > upper 95% confidence limit for unimpaired). **The authors conclude that a 95% confidence threshold for impairment can be derived for each parameter:**

- 2 mg N/l for total nitrogen
- 0.07 mg P/l for total phosphorus
- 200 mg/l for sediment (suspended solids)

The authors note that these thresholds are significantly higher than those fixed for the relevant EcoRegions by the US EPA (Environment Protection Agency, see SCOPE Newsletter n°44 at *www.ceep-phosphates.org*), that is: the EcoRegions covering the Pennsylvania watersheds studied. These thresholds are 0.05 mgN/l total nitrogen and 0.023 mgP/l total phosphorus.

Equally, of the 17 basins defined as unimpaired by the local biological ecosystem assessment, only 5 met the EPA's criteria for nitrogen and 4 for phosphorus.

The authors note that this illustrates the **discrepancy between the proposed EPA EcoRegion nutrient criteria and the results obtained using in the field biological stream assessments**, suggesting that this may in part be because of the large geographical areas and range of water body types covered by the EcoRegion criteria, whereas the thresholds derived from the Pennsylvania data may be more indicative of local ecosystem health.

"Estimating nutrient and sediment threshold criteria for biological impairment in Pennsylvania watersheds", Journal of the American Water Resources Association (JAWRA), August 2004, pages 881-888. AWRA Paper Number 03049 www.awra.org

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Lake Apopka

Incipient recovery following phosphorus load reduction

Once the second largest lake in Florida, Lake Apopka, had in the early twentieth century, a surface area of 21.000 ha (including 9.000 ha of floodplain wetland), clear water, abundant submerged vegetation. By the mid twentieth century, more than 7.300 ha of the lake's wetlands had been converted to farmland behind levees with drainage maintained by pumping from the fields into the lake. By 1950, submerged plants had virtually disappeared, the water was turbid, and there was a continuous algal bloom (mean chlorophyll approaching 100 µg chl_{-a}/l).

A **restoration programme** was initiated in the 1990's including reducing external phosphorus loadings by regulating farm discharges and ultimately by purchasing floodplain farms and re-creating wetlands, removing suspended solids (to reduce turbidity) and particulate phosphorus by wetland filtration of the lake water, removal of fish (gizzard shad *Dorosoma cepedianum*) to reduce the recycling and mass of phosphorus, and replanting of submerged, floating and emergent vegetation.

Bachmann *et al.* (1999) claimed that the turbid condition of the lake was the consequence of wind mixing (1947 hurricane) which also destroyed submerged vegetation, and that phosphorus load reduction and wetland filtration would not reduce turbidity for hundreds of years because of continuing wind mixing during storms and internal phosphorus loadings.

Recovery

Partial implementation of the restoration program (some load reduction, shad harvest), however, resulted in a modest reduction in total phosphorus levels in the lake (around 30%) and improvements in transparency followed (mean Secchi Disk depth increased about 48 %) along with improvements in all other indicators of trophic state. Submerged vegetation also reappeared.

The authors suggest that the increased phosphorus loadings to the lake from farmland in the early twentieth century led to an alternative "stable state" (turbid water, no submerged vegetation), with the change in state perhaps being accelerated but not caused by wind mixing (hurricanes). Recent improvements in water quality suggest that the restoration programme underway will enable the Lake to return to a better quality, clear-water, stable state, despite continuing wind mixing.

"The restoration of Lake Apopka in relation to alternative stable states: an alternative view to that of Bachmann et al. (1999)", Hydrobiologia 448, pages 11-18, 2001. www.kluweronline.com/issn/0018-8158

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Lake Apopka restoration programme http://sjr.state.fl.us/ *or alternatively use the direct, non-frames path* http://www.sjrwmd.com/programs/acq_restoration/s_water/lapopka/overview.html

Patuxent River

Quantifying nutrient sources

The Patuxent River (basin area 2,300 km^2) is the 7th largest river flowing into the Chesapeake Bay from Baltimore and Washington DC states, USA. The river basin population has risen dramatically, multiplying from 25,000 in 1940 to over 500,000 by 2000 whilst at the same time land surface used for cropland has decreased, and urbanised land and forest increased.

Through the 1960's to the 1980's, this led to significant deteriorations in water quality, followed by widespread introduction of sewage treatment including nitrogen and phosphorus removal in the 1990's.

Nutrient sources

Over two years (1997-1999), the authors used continuous sampling to measure nutrient discharges to 23 different sub-basins of the river system, including from croplands and urbanised land. Different forms of nitrogen (total nitrogen = TN, total organic nitrogen = TON, total ammonium TNH_4^+, nitrate NO_3^-) and of phosphorus (dissolved organic phosphorus DOP, dissolved inorganic phosphorus TPO_4^{3-}, total organic phosphorus TOP, total phosphorus TP), organic carbon, silicate and suspended solids were measured.

This allowed apportionment of nutrients to point sources (in particular sewage works discharges), diffuse (non point) sources and atmospheric deposition; to the coastal versus the piedmont regions of the watershed; to different land use categories (agriculture: cropland, pasture, urbanised land, forest).

Wet and dry years

Concentrations of different forms of phosphorus, of organic carbon and suspended solids were higher in the wet than the dry year. Taken with river flows, thus discharges of all forms of nitrogen, phosphorus and organic carbon were significantly higher in the wet than the dry year.

Cropland

Although only around 10% of the watershed is cropland, this was the most important source of most forms of nutrients. Also, **nutrient runoff was correlated to the proportion of cropland land cover, but not grassland**.

Importance of diffuse sources

Non point sources accounted for a large majority of phosphorus inputs to the watershed, particularly in the wet year:

Total phosphorus	Wet year	Dry year
Non point sources	92%	58%
Point sources	7%	34%

Non point sources also accounted for a majority of different forms of nitrogen inputs in the wet year, with approximately comparable inputs of nitrogen from point and non point sources in the dry year.

Total nitrogen	Wet year	Dry year
Non point sources	75%	22%
Point sources	44%	46%

Nitrates	Wet year	Dry year
Non point sources	66%	29%
Point sources	32%	58%

Atmospheric deposition was a significant source of NH_4^+ nitrogen (28% in the wet year, 53% in the dry year). Although this is only a small part of total nitrogen, it may be significant because of its high biological availability.

The authors conclude that, as well as providing current measurements of inputs of nutrients and sediments to the Patuxent River estuary, the study also suggests which factors influence these inputs: in particular, **cropland tends to release more nitrogen and phosphorus than other land uses**.

"Sources of nutrient inputs to the Patuxent River estuary", Estuaries, vol. 26, n° 2A, April 2003, pages 226-243 www.erf.org

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Alberta

Nitrogen and phosphorus limitation

Water chemistry, epilithic biomass and nutrient limitation of periphyton were analysed at 33 sites in the Wapiti – Smoky – Athabasca river system (52 – 58°N, Alberta, Canada). Sites were chosen either just upstream or <1 – 150 km downstream of discharges from significant municipal waste water treatment works or paper mills.

Water chemistry parameters, including nutrients (nitrate + nitrite, NH_4^+, soluble reactive phosphorus), were measured in the Autumn of 1994, when experimental apparatus for in-situ biometric testing of nutrient limitation of periphyton was deployed. At the same time, epilithic biomass was assessed by scraping samples from stones randomly collected from riffle areas at each site (9.6 cm^2 from 10 stones for each site), followed by chlorophyll$_a$ analysis. Seston chlorophyll (floating algae) was also analysed for 500 ml samples of water from each site.

Nutrient limitation

Nutrient limitation was investigated, for each site, by installing porous clay pots containing nutrient diffusing agar substrates. The method is similar to that used by Dryburgh as reported in *SCOPE Newsletter* n°42 and in Maberly *et al.* in *SCOPE Newsletter* n°59. Theses pots were removed 14-31 days later, and epilithic biomass on the pots was measured as above. 10 replicates of each nutrient diffusion treatment (nitrogen, phosphorus + potassium, nitrogen + phosphorus + potassium) were placed at each site, and the majority of samples were retrieved.

Epilithic biomass on the natural river stones was generally significantly higher (2 - 50 x) downstream than upstream of sewage works and of paper mill discharges. It was significantly related to either river dissolved inorganic nitrogen concentrations (DIN) or soluble reactive phosphorus (SRP).

The nutrient diffusion experiments showed that most upstream sites were nitrogen, phosphorus or nitrogen+phosphorus limited, whereas sites downstream of discharges were on the contrary nitrogen-phosphorus replete (not limited by these nutrients). Discharges modified nutrient limitation for up to 120 km downstream (average 80 km).

Of the sites studies, 18 showed nutrient limitation of epilithon (5 phosphorus limited, 6 nitrogen limited, 7 nitrogen+phosphorus limited) whereas 14 sites were nitrogen-phosphorus replete.

Nutrient limitation predicted from measured DIN and SRP concentrations predicted only very poorly the actual nitrogen and/or phosphorus limitation shown by the in-situ experiments (<40% prediction accuracy). The combined concentration of DIN and SRP was, however, a significant discriminator between nutrient limited and nutrient replete sites.

The authors conclude that the point source nutrient discharges into this river system lead to significant changes in nutrient limitation, but that the river system reverts back to background conditions some distance downstream of each discharge point.

"Cumulative effects of pulp mill and municipal effluents on epilithic biomass and nutrient limitation in a large northern river ecosystem", Canadian Journal of Fisheries and Aquatic Science, n°57, 2000, pages 1342-1354.
http://pubs.nrc-cnrc.gc.ca/cgi-bin/rp/rp2_vols_e?cjfas

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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.

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