SCOPE NEWSLETTER

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Pot trials

Struvite as fertiliser for wheat

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The induction time and precipitation rates are derived from controlled experiments for struvite precipitation in synthetic wastewater containing carbonates, glucose, chlorides, nitrates and sulphates.

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Four laboratory scale reactors were used to assess waste lime as and a reagent for phosphate recovery.

Turkey

Struvite and apatite precipitation

Laboratory experiments looked at precipitation of struvite and hydroxyapatite from synthetic and real municipal wastewaters

Struvite

Several papers on struvite precipitation

Several papers present results of experimental and modelling work on struvite precipitation, using different methods and substrates, confirming an increasing R&D interest in struvite.

Australia

Struvite recovery assessment

Laboratory and pilot scale experiments into the chemistry and kinetics of struvite precipitation, investigation of drying of the struvite, and an economic evaluation of struvite recovery for recycling from municipal wastewaters.

Cincinnati, USA

Struvite precipitation/crystallization and sludge digestion enhancement

Various strategies are tested for precipitating struvite from sewage works sludge digester return streams, with possibilities for using industrial waste magnesium-containing chemical sources, for improving sludge digester performance and for reducing phosphorus in return streams.

Phosphorus in surface waters

UK

Updating estimates of phosphorus sources

The UK has published an update of estimated P sources to UK surface waters and of implications for achieving Water Framework Directive Objectives.

Municipal wastewaters

Europe

Characteristics of municipal wastewaters

A survey of characteristics of wastewaters in Europe and elsewhere shows very similar phosphorus contents.

Closing the loop

P-recovery and sustainable development

Phosphate recycling from sewage and animal wastes is finding increasing support, and appears as a necessity for a sustainable future.

The **SCOPE NEWSLETTER** is produced by **CEEP**, a sector group of **Cefic**, av. E. Van Nieuwenhuyse 4, bte 2, B1160, Bruxelles - Belgium. Tel: (32) 2 6767211.
E-Mail: deh @ cefic.be

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Fertiliser value of struvite

Pot trials

Struvite as fertiliser for wheat

The effects of struvite and DCP as phosphate fertilisers for wheat were compared for different plant growth criteria and plant phosphorus content in pot trials, in sand, irrigated and under glass, to simulate conditions comparably to Southern Libya.

Struvite at equivalent 140 kg/ha phosphate application rate was compared to DCP (Di Calcium Phosphate) and to a control (no phosphorus addition) for hard and soft wheat (respectively Karem and Marshush varieties). All plants also received potassium and nitrogen fertilisation and micronutrients.

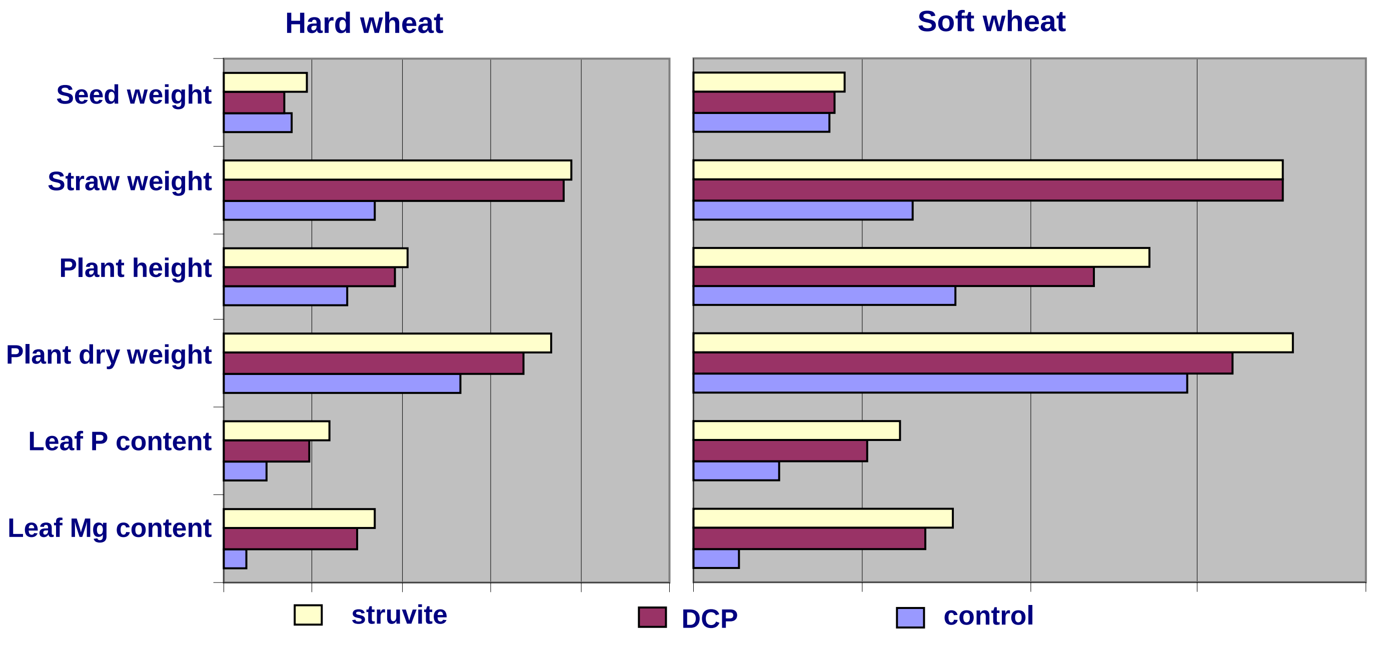
Use of struvite consistently increased yields compared with DCP in terms of seed weight, straw weight, plant height and plant dry weight. This general pattern was observed in all experiments, irrespective of application method (band vs broadcast; ground vs coarse granules). Addition of extra N as ammonium sulphate to DCP treatments to compensate for the presence of N within struvite removed the significant difference to DCP indicating that as sources of P the two materials were similar.

Leaf P content for each variety of wheat was raised by up to 50% by the addition of both DCP and struvite (Table 1). Leaf Mg contents reached 94 mg/kg for struvite applications.

The authors conclude that **this study demonstrates the phosphate fertiliser value of struvite for wheat production**, showing that it is comparable to DCP as a source of phosphate but has the additional advantage of containing available nitrogen.

"Use of Struvite, a Novel P Source Derived from Wastewater Treatment, in Wheat Cultivation", 18th World Congress of Soil Science, 9th-15th July 2006, Philadelphia, Pennsylvania, USA
http://crops.confex.com/crops/wc2006/techprogram/P16683.HTM

D. Manning, School of Civil Engineering and Geosciences, University of Newcastle, Newcastle upon Tyne, United Kingdom. S. Ahmed, R. Shiel, School of Agriculture, Food and Rural Development, University of Newcastle, Newcastle upon Tyne, United Kingdom.
David.Manning@newcastle.ac.uk



Phosphorus recycling

Greece

Struvite precipitation kinetics in complex solutions

Synthetic waste water containing not only the component ions of struvite (magnesium, ammonia, phosphate) but also glucose, carbonate and chloride (NaCl) ions was used to evaluate the induction time and precipitation rate for struvite at constant pH 8.5 or at constant supersaturation, at a controlled temperature of 25°C. This follows previous work by the same authors on struvite precipitation both from pure and complex ionic solutions presented in SCOPE Newsletter n° 55.

Stirred batch reactor (beaker scale) experiments were carried out using 1:1:1 molar ratio solutions of the ionic components of struvite (magnesium ammonium phosphate), based on $MgSO_4$ and $NH_4H_2PO_4$ solutions, at concentrations of 2.2 – 4.2 mM (ca. 70 - 130 mgP-PO_4/l). The synthetic wastewater used also contained 52 mM glucose (100 mg/l COD), 18 mM carbonates ($NaHCO_3$), 10 mM chlorides (NaCl) and 0.6 mM nitrates ($NaNO_3$). In the constant supersaturation experiments, 12 mM sulphates (Na_2SO_4) was also included in order to maintain background ionic concentrations using reagent addition.

A flow of water-saturated nitrogen gas maintained over the supersaturated solutions ensured that intrusion of atmospheric CO_2 was avoided. pH to 8.5 or supersaturation were constantly adjusted, in response to 0.005 pH unit decreases, by simultaneous titration of sodium hydroxide and of magnesium and phosphate ions (at a 1:1 ratio) calculated to correct ions precipitated as struvite as a function of pH change (resulting from proton release in struvite precipitation).

Surface energy

The objective was to **establish the formation curve of struvite** in such complex solutions. The driving force for struvite precipitation is the difference between the chemical potentials in the supersaturated solution from the corresponding value at equilibrium. The theoretical basis of supersaturation calculations and chemical potentials are presented, along with thermodynamic constants K for the different chemical complex equilibria possible in the solutions tested. The experiments established induction time and struvite growth rate R for different supersaturations.

The point of transition from homogeneous to heterogeneous nucleation was established (crystal growth to nucleation of fines, important for controlling phosphate recovery processes to produce a recoverable precipitate), and was shown to be situated at a higher supersaturation in the constant supersaturation experiments – when additional sulphates were present – than in the constant pH experiments – without additional sulphates.

A **surface energy** of 15 mJ/m^2 was calculated for the precipitated struvite. The relatively low value showed the significance of the heterogeneous character of the spontaneous precipitation.

The **dependency of precipitation rates** on supersaturation showed a power function >1 (as in the previous work cited), indicating a surface controlled mechanism.

Preliminary light scattering experiments had indicated that secondary nucleation (nucleation onto existing crystal surfaces) was not a significant mechanism. The experimental results, showing precipitation rates proportional to crystal surface area, confirmed this, indicating that agglomeration of crystals was not significant.

The experiments with constant pH and with constant supersaturation gave the same results for kinetics measurements.

Struvite precipitate

The precipitate was shown to be struvite by X-ray diffraction. The crystals had a needle like morphology, with small crystals initially formed growing in 90 minutes reaction time to 30 µm. The BET surface area of the precipitated struvite was relatively high (150 m^2/g), coherent with the observed morphology and with a porous surface structure shown in micrographs.

This paper thus provides detailed chemical and kinetic information for struvite precipitation from complex ionic solutions comparable to real waste water supernatants, of relevance for the design and operation of P-recovery processes.

"Spontaneous precipitation of struvite from synthetic wastewater solutions", Crystal Growth and Design, vol. 5, n°2, pages 489-496, 2005
http://pubs.acs.org/journals/cgdefu

A. Kofina, P. Koutsoukos, Dept. Chemical Engineering and, Institute of Chemical Engineering and High Temperature Chemical Processes, University of Patras, PO Box 1414, 26500, Greece. pgk@iceht.forth.gr

Korea

Waste lime for P-recovery

Industrial waste lime is generated by the chemical, cement and fertiliser industries. In Korea, 95% of waste lime production comes from soda ash plants, which produce180,000 tonnes/year containing (dry weight basis) 60% cations (mainly calcium, some magnesium, small amounts of iron, aluminium). The objective was to assess the feasibility of using waste lime for phosphate recovery from anaerobic sewage sludge digester supernatant, coming from high performance fermenters (55°C, pH 9 operation).

Four 0.52m high, 1.5l volume upflow crystalliser reactors were tested (for 0.5 – 3 hour batch runs), firstly with synthetic waste water, then with effluent from a laboratory fermenter. Recycling of the reactor liquor from the top to the bottom at 1 litre/minute ensured mixing. The fermenter is described in a previous study (Ahn & Speece, Wat Res 40, 2006). The synthetic waste water was composed to resemble the fermenter effluent: pH 9, phosphate 20-30 mg/l P-PO_4, ammonia 62-105 mg/l N-NH_4. The high pH of the waste lime has the advantage of driving phosphate precipitation when it is added to the reactor, and could also be used to increase the pH in the sludge fermenters.

Four reactors

In the first experiment, the four reactors were operated with and without magnesium chloride (provide cations for phosphate precipitation), and with and without air stripping (based on US EPA Waste Water Technology Fact Sheet – Ammonia Stripping – 832-F-00-019, 2000). Little phosphorus or ammonia removal was noted in the control reactor compared to some 60% removal of both in the reactors receiving magnesium dosing. The air stripping removed ammonia in both cases, but did not significantly improve phosphate precipitation.

In the second experiment, therefore, aeration was not used. Magnesium chloride and lime waste were both tested, dosed at levels corresponding to approximately 1:1 to 4:1 stoichiometric ratio of cations:phosphorus.

0.86gMg/gP, that is approximately **1:1 Mg:P stoichiometric dosage proved optimal**, giving 50% P removal in the batch runs (3 hours) and 30% ammonia removal. A dosage of 4.75g waste lime/gP was also optimal, giving 40% P-removal and 80% ammonia removal. When lime was used, the pH increased slightly during the reaction (decrease with magnesium chloride) which may account for the ammonia loss.

Precipitated struvite

Microscope examination showed that the precipitated product was very different: prism shaped crystals which could be grown by long term reactor operation with magnesium chloride, amorphous crystals with waste lime.

Application to the mass balance of the Daegu City (160,000 m^3/day) sewage works is modelled, concluding that such a fermenter + phosphate crystalliser system would significantly reduce return in the recycle sidestream of phosphorus and nitrogen to the sewage works inflow, reducing main treatment stream inflow concentrations by 0.13 mgN/l and 0.19 mgP/l.

The authors conclude that the use of waste lime for phosphorus recovery for recycling in biological nutrient removal sewage works is feasible, economic, and offers a sustainable use for this industrial waste stream.

"Waste lime as a potential cation source in the phosphate crystallization process", Environmental Technology vol. 27, pages 1225-1231, 2006 www.environtechnol.co.uk

Y-H. Ahn, School of Civil and Environmental Engineering, Yeungnam University, 214-1 Daedong Gyungsan, 712-749 Korea. R. Speece, Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, TN, 37215, USA yhahn@yu.ac.kr dick.speece@vanderbilt.edu

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Turkey

Struvite and apatite precipitation

Two series of experiments are presented, both carried out in the laboratory. In the first, struvite precipitation from pure chemical solutions was tested at different pH, temperature and phosphate concentrations. In the second, apatite was precipitated from real municipal wastewater, after treatment in a lab-scale biological nutrient removal reactor producing a high-phosphate supernatant. In this case, experiments were carried out at different pH and temperature, with and without the addition of bentonite clay for seeding.

Struvite precipitation from pure solutions tested pHs in the range 7.6 – 10.5, temperatures of 20°C and 25°C, and phosphate concentrations 120 – 200 mgP-$P0_4$/l. Magnesium, ammonium and phosphate were dosed at a 1:1:1 molar ratio (KH_2PO_4, NH_4Cl, $MgCl_2$) corresponding to struvite (magnesium ammonium phosphate, in 150 ml beakers, stirred at 100 rpm for 2 hours. Results suggest that the optimal pH, at both temperatures, is 9.4, probably because of ammonia loss at higher pH.

Laboratory BNR reactor

For the real wastewater experiments, supernatant from a **30 litre laboratory biological nutrient removal reactor** was used. The reactor was started with active municipal waste water treatment plant sludge and batch fed with real municipal raw sewage. Aerobic / anaerobic cycles generated biological phosphorus removal and release, thus resulting after settling in a high-phosphate supernatant, 500 ml samples of which were then used for beaker precipitation experiments.

Increase of pH only was used to cause phosphate precipitation from the supernatants. Experiments covered pH's in the range 7-11, temperatures 20°C and 25°C, reaction time (stirring at 70 rpm) of 1-7 hours and **seeding / no seeding with a porous bentonite clay** at 5 – 25 mg seed addition per litre.

The clay was of mainly colloidal from, and contained 62% silicon (as SiO_2), 7% iron (Fe_2O_3), 15% aluminium (Al_2O_3), 2% magnesium (MgO) and 0.5% calcium (CaO).

After one hour settling, the supernatant used contained 12 -16 mg P-PO_4/l and approximately 60 mg/l calcium and 40 mg/l ammonia.

80% P-removal

Results show that 5-6 hours reaction time was the minimum necessary to achieve effective phosphate precipitation (longer reaction times did not increase P-removal) and that the **optimal pH was around 9.5**. Under these conditions, 75-80% of phosphate present was precipitated (removed after 0.45 µm filtration or centrifugation). The crystals formed were visible to the naked eye.

The bentonite seeding proved optimal at 20 mg/l, in that higher seed dosages resulted in amorphous rather than crystal precipitates. The seeding enabled reaction time to achieve similar 80% P-removal in just one hour.

In both seeded and unseeded experiments, **the precipitate was calcium phosphate**, with approximately 56% phosphate PO_4 content (18% P) and 41% calcium.

The authors conclude that at pH>8, apatite precipitation (no magnesium addition) was very effective for phosphate precipitation from real wastewater treatment supernatant, but that the small resulting crystal size and corresponding long settling time would make struvite precipitation more easily applicable as a phosphate recovery process.

"Phosphate recovery potential from wastewater by chemical precipitation at batch conditions", Environmental Technology, vol. 28, pages 83-93, 2007
www.environtechnol.co.uk

N. Yigit, S. Mazlum, Süleyman Demirel University, Engineering and Architecture Faculty, Environmental Engineering Department, 32260, Cünür, Isparta, Turkey.
n.yigit@mmf.sdu.edu.tr ; s.mazlum@mmf.sdu.edu.tr

Struvite

Several papers on struvite precipitation

This article summarises a number of published papers concerning struvite precipitation and recovery from waste waters, using different methods.

Struvite and newberyite

Babic-Ivancic et al carried out laboratory studies of precipitation and transformation of **struvite** (magnesium ammonium phosphate $MgNH_4PO_4.6H_2O$) and **newberyite** (magnesium hydrogen phosphate $MgHPO_4.3H_2O$). Pure chemical reagents were used.

10 cm^3 precipitation system diagrams were constructed by initially mixing of magnesium chloride and ammonium dihydrogen phosphate solutions adjusted to pH 6.5, stood for one hour without stirring.

120 cm^3 transformation experiments were carried out using the same mixture, with pH adjusted to values in the range 5-9. Samples were then taken at 20-60 minute intervals, 45µm filtered, and the solids examined by infrared spectroscopy and crystal morphology assessed.

Based on equilibrium constants for the 16 different ion systems present and on the experimental results, the **kinetics of the struvite to newberyite transformation** were calculated.

Struvite was shown to from in nearly all precipitation conditions, whereas newberyite only formed in the presence of excess magnesium concentration. The conditions in which struvite is stable are also much wider than those for stability of newberyite or for struvite and newberyite coexistence. In particular, struvite is more abundant in systems where ammonium phosphate concentrations are higher than those of magnesium (which is the case in animal wastes and municipal waste waters).

Previous papers by the same authors (2002) have suggested that the dissolution of rod-like struvite crystals is controlled by desorption whereas dissolution of dendritic (rhomboid) struvite crystals is diffusion controlled. In these experiments, the transformation of struvite to newberyite appears to be solution mediated. The time for conversion from struvite to newberyite appears to be related to the initial supersaturation ratio (supersaturation for newberyite : supersaturation for struvite).

The authors also report the development of a relatively rapid, simple and accurate **method to estimate the struvite – newberyite ratio in precipitates** based on infrared spectroscopy and the potassium bromide pellet techniques.

In a previous paper (2002), the authors derived **thermodynamic solubility products of struvite** from dissolution experiments, in which the dissolution of struvite was followed using pH monitoring. Pure chemical solutions were used to produce struvite crystals, which were then suspended in 130 cm^3 magnetically stirred, hermetically sealed vessels, in various ion concentrations (magnesium, phosphate, ammonium and co-ions). Dissolution rate constants and activation energies were calculated, with different results for rod-like and for dentritic struvite crystals and the mechanism of the kinetic dissolution rate determining factors are discussed (diffusion of constituent ions away from the crystal surface, desorption of ions from the crystal adsorption layer).

In another previous paper (2004), the authors studied the **formation and transformation of struvite and newberyite in pure ionic solutions** at concentrations comparable to urine at 37°C, discussing the influence of initial pH and temperature on the transformation process.

IXISS ion exchange

Mijangos et al. showed that ion exchange can enable the production of supersaturated struvite solutions using **"ion exchange isothermal supersaturation" (IXISS)**. Magnesium was stripped from Lewatite CNP80 cation exchange resin using ammonium hydrophosphate and dihydrophosphate at pH8. A supersaturated solution of struvite resulted, in which the struvite remained in solution in contact with the ion exchange resin, but then precipitated out after removing from the resin column. MINEQL+ software was used to model struvite solubility.

The **weak acid carboxylic resin** used offers the advantage of a high selectivity towards alkaline earth metal ions such as magnesium versus alkali metal ions such as sodium. Additionally, such resins have a high affinity towards protons, and can so contribute to maintaining high pH appropriate for struvite elution. Experiments showed that magnesium was effectively eluted from the ion exchange resin only for relatively high pH, around 8. In this case, although struvite concentration significantly exceeded saturation, no crystal formation occurred in side the resin bed and no column clogging was observed (IXISS effect). Once the solution was removed from the resin bed, struvite crystallisation began with 2 hours and was completed within 4 hours, with around 75% of the recovered magnesium being crystallised. X-ray diffraction showed the presence of struvite in the crystals formed.

Enzyme and bacterial enhancement

The U.S. Army Corps of Engineers Research and Development Center has ongoing interest in plant nutrient chemistry and use of phosphate and nitrate in training land revegetation. The work has resulted in two patents (U.S. Pat. No. 6,206,945 and 6,776,816) that describe the **use of struvite to control phosphate removal from waste and the formation of a slow-release fertilizer component in the waste**.

The latest patent to **Ringelberg** et al. describes methods for struvite precipitation and recovery from nitrogen-rich bacterial cultural media and nitrogenous waste by magnesium addition, enhanced by various different techniques during incubation for 14-20 days : the addition of an enzyme to accelerate the struvite precipitation and the addition of a bacteria (eg. a specific strain of *Bacillus sphaericus*) which releases such an enzyme, increases pH and "seeds" struvite crystallisation on its cell surface. The enzymes considered include urease, uricase and phosphatase. pH is increased for struvite precipitation if necessary by a combination of chemicals, aeration and the effects of the bacteria. The goal of the struvite work is to produce an inexpensive struvite-rich compost (similar to an artificial guano) that can be safely applied in range of re-vegetation programs.

The precipitation of struvite onto a bacteria cell surface, as a combination of local pH changes induced by the bacteria, local enzyme release and/or the cell surface acting as a "seed" area has previously been explored by Kabdasli et al. see SCOPE Newsletter no 67. Use of urease to improve ammonium release from urine was referred in SCOPE Newsletter n° 41 (Dick et al).

Struvite precipitation on bacteria

Ben Omar et al, 1988, showed that struvite crystallisation occurred on cells of the cultivated soil bacterium *Myxoccocus Xanthus*, in a pH 6.5 medium containing magnesium and phosphate. Struvite was shown to develop on the cell membrane surface only of ageing cells (after 48 hours), where globular surface deformations were appearing, and not on intact (non deformed) cells. The authors suggest that this may be related to cell wall "relaxation" prior to an autolysis (self destruction) phase specific to such bacteria life cycle. Cell wall changes could result in complex, multi-molecular, negatively charged sites appearing, capable of attracting positive ions in solution, such as Mg^{2+}, thus resulting in local supersaturation of struvite.

Rivadeneira et al, 1985, showed that the nitrogen fixing soil bacteria *Azobacter vinelandii* and *A. chroccoccum* were able to produce calcite (calcium phosphate) and struvite crystals, which could be scraped off the bacterial growth, after 48 hours. Mediums with added ammonium sulphate, magnesium acetate and/or calcium acetate, solidified with agar, were used at pH7.

The results showed that calcite was not formed in the presence of certain concentrations of ammonium (0.05 – 0.3%), and that struvite crystals only occurred in the presence of concentrations of ammonium > 0.3% and the authors conclude that although these bacteria can themselves produce ammonium ions, this does not occur sufficiently to inhibit calcite formation or allow struvite formation, which both only occur when ammonium is added, so that ambient ammonium ion concentrations would be important for controlling crystal formation in nature.

"Kinetics of struvite to newberyite transformation in the precipitation system $MgCl_2$*-*$NH_4H_2PO_4$*-*$NaOH$*-*H_2O*". Water Research 40, 2006 pages 3447-3455.*

V. Babic-Ivancic, J. Kontrec, L. Brecevic, D. Kralj, Laboratory for Precipitation Processes, Division of Materials Chemistry, Ruder Boskovic Institute, PO Cox 180, HR-10002 Zagreb, Croatia. kralj@rudjer.irb.hr *or* brecevic@rudjer.irb.hr

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F. Mijangos, M. Kamel Dept. Chemical Engineering, University of the Basque Country, Apdo. 644, 48080 Bilbao, Spain., G.Lesmes, D. Muraviev, Dept. Analytical Chemistry, Autonomous University of Barcelona, 08193, Bellaterra, Barcelona, Spain. iqpmianf@lg.ehu.es

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"Struvite crystallization on Myxococcus cells", Chemosphere vol. 36 n°3, pages 475-481, 1998. http://www.sciencedirect.com/science/journal/00456535

N. Ben Omar, M. Gonzalez-Munoz, J-M. Arias Penalver, Dept. de Microbiologia, Faculdad de Ciencias, Universidad de Granada, 18071 Spain jmarias@ugr.es

"Influence of ammonium ions on calcite and struvite formation by Azobacter in chemically defined media", Folia Microbiol. 30, pages 55-57, 1985. http://www.biomed.cas.cz/mbu/folia/

M. Rivadeneira, J. Gonzalez-Lopez, A. Ramos-Cormenzana, Dept. of Microbiology, Faculty of Pharmacy, Universidad de Granada, Spain. mrivaden@ugr.es

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Australia

Struvite recovery assessment

Several papers present work at James Cook University, Queensland, Australia, into the chemistry, kinetics and operation of seeded struvite precipitation, including drying of the precipitated struvite, from solutions comparable to piggery lagoon waters, along with an economic evaluation of struvite recovery from sewage.

Stirred seeded crystallisation

Ali, Schneider et at. (2005a), Queensland, Australia, carried out laboratory stirred beaker experiments using pure synthetic solutions and borosilicate glass grindings as seeds. A survey of nutrient concentrations at different sites in **four Queensland piggery effluent ponds** was carried out to establish typical concentrations of magnesium, phosphate and ammonium.

Experiments at pH 9 showed that 80% recovery of magnesium and phosphate, as struvite, after filtration at 0.45µm. However, only a fraction of this efficiency was achieved if the pH was not maintained throughout the experiment by alkali addition, as the pH in this case rapidly fell to around 7. A preliminary thermodynamic model of struvite precipitation was developed using gPROMS process software.

This followed an initial paper (Ali et al. 2003) which presented **modelling results, using Visual MINTEQ**, to assess in theory which compounds would precipitate from pure ionic solutions comparable to piggery wastewaters at different pH. The ion concentrations used in the modelling were based on analysis of a Queensland, Australia, wastewater ponds (primary, secondary, final irrigation pond) showing phosphate concentrations of 5 -9 mgP-PO_4/l, ammonium 160 – 250 mgN-NH_4/l and magnesium concentrations of 19-22 mgMg/l.

Light detection of nucleation

In a second paper (Ali &Schneider 2005b), the authors further **stirred beaker experiments** are presented at molar concentrations 0.002 – 0.007 and 1:1:1 phosphate/ammonium/magnesium ratio.

To determine the metastable zone, **red laser light scattering (in a dark room) was used to detect particle formation** (spontaneous nucleation). pH was monitored and adjusted close to supersaturation using progressively diluted sodium hydroxide solution, with one drop added per 15 minutes near the critical pH. Crystals produced were photographed using SEM and X-ray diffraction confirmed that the product was indeed struvite. The laser light scattering method proved able to identify the solubility limit of struvite and the thermodynamic equilibria were validated using PHREEQC software.

To test **different seed materials**, the same experimental system was used but without the light scattering. Quartz sand, borosilicate glass and previously precipitated struvite, each ground and sieved to 45-63 µm, were tested. Crystallisation was detected by changes in pH, because of the release of H^+ resulting from struvite formation. Slower crystallisation reactions were observed for the sand and glass seed materials than for struvite seed, and also less effective crystal growth, with development in this case showing more relation to agglomeration of fine crystals.

Pilot scale semi-batch reactor using controlled supersaturation

In Ali and Schneider 2006, the detailed **design and commissioning of a pilot scale semi-batch struvite reactor** using controlled supersaturation technique are described. This includes investigating the operating supersaturation, selection of seed materials, compositions of feed solutions. The paper demonstrated that controlled supersaturation allows crystals to grow, instead of instantaneous precipitation (creating fines). Experiments were carried out using a 44 litre capacity struvite reactor. Experiment control allowed dosing of titrants by constant monitoring of pH.

Pilot semi-batch reactor

In Ali, IChemE, 2007, results from this seeded 44-litre pilot scale batch struvite reactor are presented, as well as investigations into the drying of the crystallised struvite produced. Mathematical modelling and formulation of struvite precipitation are presented, again referring to simulation using gPROMS and validation using PHREEQC.

A Perspex 44-litre semi-batch suspended bed reactor was tested. A recirculation pump injecting reactor liquor back into the conical base ensured bed suspension. The reactor included a cooling coil, because the liquor recirculation otherwise caused a temperature rise (of 5°C per hour). The reactor was seeded with 30g of previously produced 105-150 µm sieved struvite crystals, and was fed with equimolar magnesium, ammonium and phosphate ions (at 4.5 and at 6 mM), with pH adjusted to 7.2-7.4.

Struvite growth rate is analysed as a function of solution chemistry and variation of different ion complexes in solution as a function of pH. Yield analysis shows that the control of supersaturation enables the recovery of 70% of the precipitated struvite as easy-to-handle grown particles, as opposed to fines.

In a further paper, currently under review prior to publication, Ali and Schneider demonstrate the **estimation of struvite growth kinetics** by incorporating solution chemistry, kinetics and mathematical description of experimental conditions.

Moisture content

The freshly precipitated struvite was analysed for moisture content following wet sieving, 12 hours of fan drying, 1 hour of sun drying, 7 days of air drying. After this treatment, drying in an oven at 40°C or 50°C resulted in little moisture loss, showing that the crystals were already free from surface moisture, whereas higher temperatures resulted in loss of crystal-forming water and ammonium removal. Struvite intended for use for seeding should not therefore be dried at temperatures higher than 40-50°C.

Economic evaluation

Shu, Schneider et al. 2006 provide an economic evaluation of phosphorus recovery as struvite from municipal wastewaters, based on the Great Barrier Reef catchment, Australia. **The authors estimate that 90% of phosphorus in anaerobic digester supernatant can be recovered, that is 50-80% of total sewage works inflow phosphorus.**

The operating costs of struvite recovery are compared to operational savings such as: reduction in sludge handling, disposal costs and landfill. Precipitation of 1 kg struvite = 0.7 litres of sludge results in savings of 3.5 litres of sludge by reduced use of phosphorus precipitation chemicals, reduction in costs of chemical (alum) purchase for phosphorus precipitation, reduction in cleaning of nuisance struvite deposits, and benefits of struvite sales as a fertiliser.

A struvite recovery installation for a 55,000 m^3/day municipal waste water treatment plant (WWTP) estimated at 2 million Australian $ (AUD) that is around 1.2 million €, offers net operating savings of 400,000 AUD/year (244,000 €) and thus gives a payback time of 5 years. A WWTP of this size would produce 201 tonnes/year of struvite (approx 15 tonnes of phosphorus), that is enough to fertilise 1430 hectares of arable land.

Worldwide, assuming 50% connection of the population to sewage works, **struvite recovery from municipal wastewaters could concern around 0.6 million tonnes/year of phosphate** (as P_2O_5), compared to 40 million tonnes/year of phosphate rock currently mined, that is 1.5% of world phosphate consumption.

"An economic evaluation of phosphorus recovery as struvite from digester supernatant", Bioresource Technology 97, pages 2211-2216, 2006 (Elsevier) http://dx.doi.org/10.1016/j.biortech.2005.11.005

L. Shu, P. Schneider, V. Jegatheesan, School of Engineering, James Cook University as above, J. Johnson, Great Barrier Reef Marine Park Authority, Townsville Queensland 4810, Australia. Jega.jegatheesan@jcu.edu.au

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M. I. Ali, P. Schneider, School of Engineering, James Cook University, Townsville QLD 4811, Queensland, Australia. N. Hudson, Intensive Livestock Systems Unit – Technology Innovation, Queensland Department of Primary Industries, PO Box 102, 203 Tor Street, Toowoomba, Queensland, 4350 Australia.

Current address: Imtiaj Ali, Earth Tech Engineering, Level 2, North Tower, 527 Gregory Terrace, Fortitude Valley, QLD 4006, Australia. Imtiaj.Ali@earthtech.com.au

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L. Shu, P. Schneider, V. Jegatheesan, School of Engineering, James Cook University as above, J. Johnson, Great Barrier Reef Marine Park Authority, Townsville Queensland 4810, Australia. Jega.jegatheesan@jcu.edu.au

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Cincinnati, USA

Struvite precipitation/crystallization and sludge digestion enhancement

A series of articles present ongoing studies at the University of Cincinnati and Mill Creek Wastewater Treatment Plant, Cincinnati, Ohio, assessing struvite precipitation for either enabling phosphorus recovery for recycling (precipitation from digester supernatant) or for direct precipitation in the sludge digester, with potential to improve sludge digestion performance in terms of volatile suspended solids (VSS) destruction efficiency and biogas production rate.

The first paper (2001) presents experiments with **32 litre laboratory scale pilot sludge digesters**, run in batch mode for 17-18 days each. Dissolved air flotation (DAF) sludge was fed to the reactors, inoculated with digested sludge (as seed for anaerobic microorganisms, primarily acidogens and methanogens), both from the Mill Creek plant. Struvite precipitation was evaluated in lab scale experiments (plastic bottles and water bath/shaker) and in a pilot precipitation reactor that is 30 cm internal diameter and 3m high. Additional research results on sludge digestion enhancement using magnesium hydroxide are also published in the second paper (2000).

Improved sludge digestion

These experiments showed that magnesium hydroxide addition into the sludge digesters resulted in **improved reduction of suspended solids, COD, phosphate and ammonia in the digester supernatant**, **as well as improved dewaterability**.

TCOD removal, for example, was improved from 40% to 43% by $Mg(OH)_2$ addition in the digester. These improvements may be largely due to the higher pH in the reactor with added magnesium hydroxide and also due to the stimulating effect of the increased magnesium ion concentration.

Although phosphate and ammonia in the supernatant are reduced, the **struvite is deposited in the digester** where it may cause deposit problems, and is not easily separable from the digested sludge and cannot be recovered for recycling.

Further investigation on application of magnesium hydroxide in the anaerobic sludge digester is suggested to ensure that struvite or other magnesium precipitates is incorporated in the digested sludge and not deposited on the digester walls or mechanical mixers.

The authors suggest that the magnesium hydroxide addition results in a pH conducive to methane-producing bacteria, that the magnesium ions stimulate the sludge digestion process, and that polyphosphate hydrolysis is enhanced, as well as reacting with soluble ammonia and phosphate to produce struvite within the reactor (thus reducing phosphate and magnesium concentrations in the supernatant).

Struvite precipitation

The **struvite precipitation experiments at lab scale** used both filtrate and centrate from the digested sludge dewatering facility at the Mill Creek sewage works. Initial pH's for the centrate and filtrate were 7.6 and 7.9 and initial phosphorus concentrations were 108 mg P/L and 33 mgP/L, respectively. The pilot reactor was operated in batch mode, using centrate, with 60 minutes aeration followed by 60 minutes settling time. Magnesium chloride and magnesium hydroxide were tested as magnesium sources. An industrial by-product, magnesium hydroxide, was also tested (Dravo Lime Co.).

Aeration alone enabled 60% phosphorus removal, because of the pH increase resulting from CO_2 stripping. However in this case, and at low magnesium dosages (100 mg Mg/l), the 60+60 minutes reaction time was insufficient (phosphorus concentrations continued to fall at the end of the 120 minutes). The industrial by-product magnesium hydroxide gave slightly better results than the pure reagent form for the same dosage (based on Mg^{2+}), possibly because of smaller particle size (resulting in faster dissolution) and the presence of a calcium sulphate impurity (precipitation of calcium phosphates).

Testing different conditions

A third paper (Wu & Bishop, 2004) presents **2-litre glass beaker scale struvite precipitation experiments** using anaerobic centrate as above. Effects on struvite precipitation due to seeding with different materials, and to different magnesium ion supplement chemicals (pure magnesium hydroxide and magnesium chloride) are investigated.

The effects of initial acidification (to pH 6.2) of the centrate were also tested. Illustration of the struvite precipitation process in sludge dewatering unit operations, struvite chemistry, and nucleation and crystal growth are explained in this article.

One litre of centrate was added to a series of 2-litre glass beakers and was then aerated for 3 hours. Phosphate precipitation was assessed by monitoring pH and soluble phosphate concentrations at 20 minute intervals.

Two different sizes of struvite crystals (removed from the centrate steam in the same wastewater treatment plant), approx 0.1 and 0.5 mm, and quartz sand, 0.1 mm, were tested as seed materials.

The results suggest that **both sand and struvite seeding accelerated struvite precipitation**, with struvite seeds being more effective, and effectiveness being increased with smaller crystals within one hour reaction time, but that the endpoint after 2 hours is not significantly modified by the seeding.

Prior acidification of the centrate accelerated struvite precipitation and increased the final soluble phosphorus removal, particularly in the case of aeration only (no magnesium addition) and when magnesium chloride was used, but will not be useful if magnesium hydroxide is used (because acidification will lower the final pH below that where $Mg(OH)_2$ is useful).

Results also show that if magnesium hydroxide is used, it should be mixed earlier in the process or pre-mixed because of its slow dissolution process.

Phosphate fixation in sludge

A fourth paper (Wu, Bishop, Keener 2005) presents further laboratory and field studies, continuing the investigation of struvite precipitation into sludge or in a **P-recovery reactor operating on sludge digester centrate**.

Phosphate fixation into sludge was tested using dewatered anaerobically digested sludge from the Mill Creek plant (above). For well digested sludge, a dosage of 250 mg/L magnesium hydroxide resulted in 53% P removal within 90 minutes, while for a poorly digested sludge (initial pH 6.1), magnesium hydroxide dosed at 250 mg/L resulted in 23% P removal within 1 hour (about the same result within 2 hours). An even higher dosage of 500 mg/L resulted in 36% P removal within one hour. Comparison was made with other chemicals based on the same molar cation addition: iron chloride showed a significantly higher phosphate removal, but aluminium sulphate a lower phosphate removal. All three reagents improved sludge dewaterability (measured as capillary suction time, CST).

Addition of an industrial by-product, magnesium hydroxide (Dravo as above), was tested in the South Dearborn Regional Sewer District Plant at Lawrenceberg, Indiana. The by-product magnesium hydroxide was made in the form of a slurry (30% w/v), and dosed at 400 mg/l as $Mg(OH)_2$. Dosing was tested at two different points: one was at the suction end of the sludge pump transferring digested sludge to a belt press, and the other one was at the polymer dosing point just before the belt press. A 1% higher solids content of the filter press cake and a 24-54 % reduction in filtrate phosphate (as P) concentration were achieved.

The authors emphasize, however, that the effectiveness of magnesium hydroxide addition varies considerably with sludge characteristics: pH, carbonate – bicarbonate system, volatile fatty acids.

2-litre glass beaker-scale laboratory experiments were also carried out **using anaerobic digester centrate from the Mill Creek plant to compare phosphate precipitation** using aeration only, magnesium hydroxide, iron chloride, aluminium sulphate and lime dosages. Results can be summarized as follows:

P-removal	**Control: aeration only**	**Magnesium hydroxide**		**Aluminium sulphate**	**Iron chloride**	**Lime**
		at 1.7mM (as Mg) dosage	*at 3.4 mM dosage (as respective cations)*			
30 minutes	31%	60%	68%	Approx 86%		Not significantly better than control
1 hour	58%	84%	Approx 86%			
2 hours	81%	>90%		Approx 86%		

The authors note that after one hour magnesium hydroxide, iron chloride and aluminium sulphate offer the same effectiveness, but that the iron and aluminium salts act faster. This is probably because of the slow dissolution of magnesium hydroxide, and may be improved by pre-mixing or by dosing as a slurry. Magnesium hydroxide actually achieves better P-removal than the iron or aluminium salts after 2 hours. Lime is not effective. Crystals in the magnesium hydroxide added to the reactors (struvite precipitation) showed larger sizes than for the iron or aluminium salts.

The authors conclude that a reactor, properly designed and placed in between the sludge dewatering unit operation and the centrate/filtrate discharge line, and receiving magnesium supplement chemicals added to the anaerobic sludge digester centrate or filtrate, can reduce risks of nuisance struvite deposits in the sewage treatment plant, reduce nutrient loads returned to the sewage works inflow, and produce a valuable recovered phosphate product, struvite, saleable as a fertilizer. The authors recommend aeration for mixing and CO_2 stripping in this regard.

Potential applications of magnesium hydroxide in biological phosphorus removal

In a fifth paper, the effect of pH and magnesium on biological phosphate uptake and release is examined. The research results indicate that Mg^{2+}, supplied either by $MgCl_2$ or $Mg(OH)_2$, stimulated phosphate uptake during the aeration period, while pH increase caused by the application of $Mg(OH)_2$ enhanced phosphate release during the sedimentation period. The authors also noted in their experiments with $MgCl_2$ that Mg^{2+} slightly inhibited the anaerobic phosphate release.

1] "Sludge digestion enhancement and nutrient removal from anaerobic supernatant by $Mg(OH)_2$ application", Water Science and Technology vol. 44, n°1, pages 161-166, 2001. www.iwaponline.com

Q. Wu, P. Bishop, T. Keener, I. Stallard, L. Stile, Dept. Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH45221-0071, USA
paul.bishop@uc.edu

2] "Improving anaerobic sludge digestion using magnesium hydroxide", Proceedings International Symposium on Biogas Technology (Anaerobic Digestion) and Sustainable Development, Beijing, China, Oct. 24-27, 2000. Q.Wu & P. Bishop, as above.

3] "Enhancing struvite crystallization from anaerobic supernatant", J. Environ Eng. Sci 3, pages 21-29, 2004. http://scitation.aip.org/eeo *Q. Wu & P. Bishop, as above.*

4] "A strategy for controlling deposition of struvite in municipal wastewater treatment plants", Water Environment Research, 77 pages 199-207, March/April 2005. www.weronline.org *Q. Wu, P. Bishop, L. Keener, as above.*

5] " Biological phosphate uptake and release: Effect of pH and magnesium ions", Water Environment Research 78(2): 196-201, Feb 2006. www.weronline.org *Q. Wu, P. Bishop, L. Keener, as above.*

Phosphorus in surface waters

UK

Updating estimates of phosphorus sources

A report published by DEFRA (UK ministry of environment) provides a detailed assessment of methods for estimating phosphorus loads to surface waters and for apportionment of between different sources. The conclusions significantly modify the source estimates from Morse et al. 1993, showing a higher proportion of phosphorus to come from municipal sewage works discharges. This is despite considerable reductions in sewage works phosphorus releases, resulting from installation of nutrient removal. In England, sewage discharges appear as the source for a majority proportion of phosphorus loads, but not in Scotland and Wales.

The report identifies and examines different **methods for estimating phosphorus loads to surface waters**: those based on data from river flow and monitored river phosphorus concentrations, those based on inventories of point P sources and estimates of diffuse loadings. The authors note that river retention of phosphorus can be considerable, with up to 50% of diffuse loads being retained during summertime, and often remobilised during autumn or winter high flows.

Phosphorus from sewage works and septic tanks

Where precise data are not available for point sources, estimates can be made. The report indicates a figure of 0.42 kgP/year/person (1.1 gP/day) discharge from a sample of sewage works (Severn Trent Water), an average of 0.2-0.4 kgP/year for septic tanks. This corresponds to P-removal of around 50% in sewage works and 50-75% in septic tank systems, on the basis of a total of around 2gP/person/day in raw sewage for the UK (1.5 gP/day from human metabolism, 0.43 gP/day UK from detergents AISE 2004 figures, plus other sources).

Export coefficients

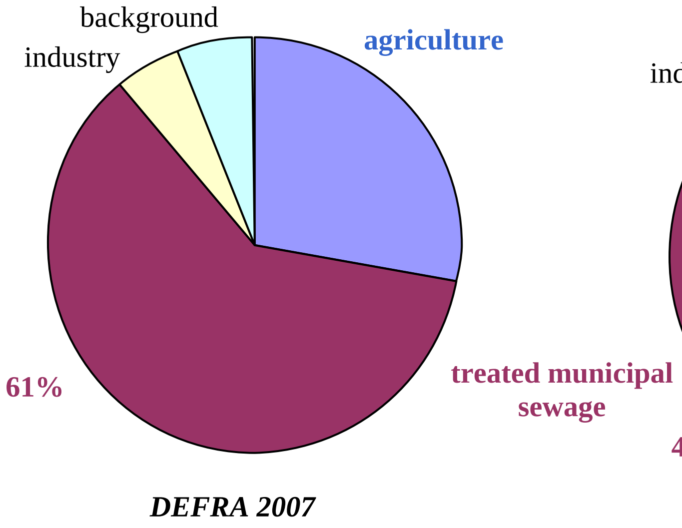
Various export coefficients for estimating phosphorus land runoff from land cover types are examined and presented in tables. The variation in estimated coefficients is emphasised as well as other limitations to this method including spatial resolution of land cover, and design of coefficients to give annual average values without providing information on seasonal variations. The questions of diffuse urban runoff (driveways, gardens, construction sites, leaf fall, car washing …), much of which is soluble phosphorus, and of diffuse loads from animals and atmospheric deposition are addressed. Diffuse sources can also be estimated from mechanistic models, but these are generally adapted to a given catchment and are difficult to generalise

The **overall total phosphorus load estimate in this study** is considerably lower than that of Morse et al., 1993 (total 42 000 tTP/year to UK waters DEFRA 2007, compared to 82 000 tTP Morse 1993). This period has seen considerable improvements in sewage nutrient removal, lower levels of phosphates in detergents, reductions in industrial discharges, reduced phosphorus fertiliser applications and livestock numbers. The per capital contribution from human populations, after sewage treatment, was estimated at 0.62 kgTP/person/year in Morse 1993, and 0.43 in this report.

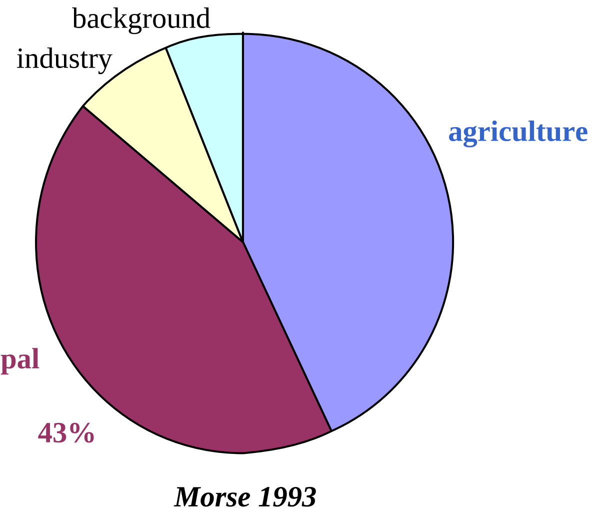
Soluble phosphorus

The report emphasises that soluble phosphorus levels is immediately available for growth of aquatic plants and algae, and may be more significant for surface water sensitivity to eutrophication than total phosphorus. On the other hand, biota and sediments accumulate phosphorus throughout the summer, releasing it in autumn and winter, and strong microbial activity can produce a flush of bioavailable phosphorus in the spring.

Most phosphorus from sewage works discharges will be soluble. From agricultural run off, 15-28% during high flow rates and 44-69% during low flow rates (summer) will also be soluble.



DEFRA 2007



Morse 1993

% contributions Total Phosphorus to UK waters

Water Framework Directive status

Thresholds for Water Framework Directive "Good Ecological Status" of 40-50 µg SRP (soluble reactive phosphorus) for non calcareous rivers, and 120 µg SRP for calcareous rivers have been suggested for the UK. 58% of river lengths in England have average SRP concentrations > 100 µg SRP.

Statistical comparison with assessment of rivers and lakes assessed as being potentially "at risk" under the Water Framework Directive showed no correlation between diffuse phosphorus sources and risk, a correlation between point sources and risk, and a correlation between the estimated TP loads and soluble phosphorus concentrations in the waters. Higher lengths of rivers have been identified as "at risk" because of diffuse phosphorus sources, than lengths identified as "at risk" because of point sources.

"Updating the estimate of the sources of phosphorus in UK waters", DEFRA project WT0701CSF, P. White, J. Hammond, 2007
http://www.defra.gov.uk/science/project_data/DocumentLibrary/WT0701CSF/WT0701CSF_4159_FRP.pdf

Municipal wastewaters

Europe

Characteristics of municipal wastewaters

Data were collected from a survey sent to wastewater treatment plant managers (France, Austria), from national contacts, data bases and literature, covering in all 18 countries. Information on organic load (COD, BOD$_5$), suspended solids, nitrogen and phosphorus were gathered.

Results show variable concentrations of organic load, nitrogen and phosphorus. COD and BOD5 vary by a factor of up to 4, nitrogen by a factor of 4, and phosphorus a factor of more than 5 (from 3 mg/l in Norway to 16 in Cyprus). However, much of this variation is related to dilution by rainwaters entering the sewerage system.

The ratios P/COD and N/COD vary much less between the different countries studied, and are generally situated around 0.013 – 0.019 for P/COD and 0.097 – 0.12 for N/COD. Figures from Morocco and Australia (Perth) also fall into these ranges. Norway however also has low P/COD ratio of 0.01 and N/COD of 0.09.

The P/COD ratio seems to show no relationship with whether phosphates are today widely used in laundry detergents or not. This is confirmed by the time series from 1 city in Belgium and 4 in France over 2-7 years, where P/COD and N/COD show annual variability but no systematic trend, despite reductions in phosphate use in detergents in France.

Average values of 0.1 for N/COD, 0.016 for P/COD and 0.5 for SS/COD are proposed.

"Wastewater characteristics in Europe – a survey", European Water Management Online (European Water Association EWA), 2004. http://www.ewaonline.de/journal/online.htm

M. Pons, Laboratoire des Sciences du Génie Chimique, CNRS-ENSIC-INPL, BP 451, F-54001, Nancy cedex. Marie-Noelle.Pons@ensic.inpl-nancy.fr *H. Spanjers, Lettinga Associates, Wageningen,The Netherlands. D. Baetens and J. Nouwen, Vito, Flemish Institute for Technological Research, Mol, Belgium. O. Nowak, Institute for Water Quality and Waste Management, TUW, Wien, Austria. S. Gillot, present address: Cemagref, Anthony, France. N. Schuttinga, AEST, Wageningen University, PO Box 8129, NL-6700 EV, The Netherlands.*

Closing the loop

P-recovery and sustainable development

A report published by Green Alliance, UK, presents the need to 'close the loop' of nutrient cycle management, by reducing loss of phosphates and nitrogen, with impacts on greenhouse gas emissions and on water quality. Recycling phosphorus in sewage is a "key prerogative for long-term sustainability. Phosphorus recovery during wastewater treatment is highly efficient … under these circumstances, it may not be necessary to control inputs of phosphorus to the wastewater collection system." This echoes positions already taken in favour of P-recovery for recycling by EUREAU (European water industry association), and by officials in Sweden and Germany (see SCOPE Newsletter 50).

Green Alliance's report "The nutrient cycle: closing the loop" suggests that the imbalance in the management of the phosphorus and nitrogen cycles is comparable to that of the carbon cycle, responsible for climate change. However, the global carbon cycle is modified by man by less than 10%, whereas the global nitrogen cycle is modified by 90%.

The report also demonstrates the implications of nutrient losses in terms of **greenhouse gas emissions**. While mineral fertiliser manufacture requires significant energy input, water companies are using energy to remove nutrients from sewage, energy is used in fertiliser transport, as well as water quality being deteriorated and non renewable natural resources of phosphate rocks depleted.

The report conclusions recommend **making the "safe sludge matrix" statutory**, in order to safeguard agricultural reuse of sewage biosolids, which is the most efficient route for recycling phosphates, nitrogen, other minerals and organic carbon in sewage. The report also recommends promoting P-recovery for recycling from sewage; redistribution of animal wastes from areas of intensive livestock production to areas of agricultural crop production; promotion of organic sources of nutrients to farmland; precision agriculture, adjusting nutrient input more precisely to livestock or crop plant needs.

Costs of nutrient losses

The report is made up of seven short essays by specialists covering: the nutrient cycle, the water industry, biosolids recycling, farm management, composting, impacts on biodiversity and energy and economic aspects.

Rob Lilywhite (University of Warwick HRI) indicates that approximately **40% of UK greenhouse emissions come from agriculture**. The loss of nitrogen from agricultural soils in the UK is equivalent to 340 million € of fertiliser, or 2.65 million tonnes of CO_2. Costs of reducing nitrates in drinking water supplies are estimated at 81 million € per year (annualised investments plus operating costs). An estimate of **10% of phosphate fertilisers applied in UK agriculture are lost**, equivalent to 13 million € or 10,000 tonnes of CO_2 in phosphate fertiliser production from phosphate rock.

However, he emphasises that the farm gate value of UK agricultural production is around 24,000 million €, so that the combined economic **costs of the lost nutrients and of drinking water nitrate removal are <2% of turnover**. The embodied energy in UK annual agricultural production is over ten times higher than that in nutrient losses, so that although there are nutrient leakages, the system cannot be considered inefficient, particularly as some losses will be inevitable in an open system such as farm fields.

Stephen Smith (Imperial College London) estimates that current world reserves of exploitable phosphate rock will last around 250 years at current rates of consumption. However, he considers that cadmium inputs to soil from fertilisers produced from rock may be a more important driver for phosphorus recovery:

> *"Recycling phosphorus in biosolids is therefore a key prerogative for long-term sustainability. Phosphorus recovery during wastewater treatment is highly efficient and the sludge is an effective phosphorus fertiliser source that closes the nutrient loop through the food chain, provided it is carefully managed. Under these circumstances, it may not be necessary to control inputs of phosphorus to the wastewater collection system. In any case, the largest input of phosphorus originates from dietary sources, which emphasises the important link apparent between recycling in sludge and the food chain."*

Dr Smith indicates that phosphates in sewage sludge supplied to UK farmland currently contribute around **15% of the phosphates supplied in mineral fertilisers**, with a fertiliser replacement value of 30 million €/year. As well as nitrogen, sewage biosolids also provide other beneficial minerals, in particular magnesium and sulphur. The Safe Sludge Matrix, adopted in voluntary agreement between the UK water industry and the food retail sector in 1999 defines the acceptable uses of sewage biosolids on different types of crops, including specifications for microbial quality after different sludge treatments for each case. The incorporation of this Matrix into statutory instruments is seen as a priority to safeguard sewage biosolids use in agriculture, which is the most sustainable option for nutrient recycling.

Phosphorus recycling

Sweden and Germany have already taken national positions in favour of phosphate recycling (see SCOPE Newsletter 50). EUREAU, the European union of national water industry associations, published a position in 2005 also supporting P-recycling. **EUREAU** estimates that animal excreta in Western Europe contain around 1,600,000 tonnes of phosphorus per year (tP/y), and recoverable sewage sludges around 300,000 tP/y, compared to EU consumption of 1,340,000 tP/y in mineral fertilisers and 250,000 tP/y in animal feed supplements. For information, 61,000 tP/y of phosphorus is used in detergents in the EU (AISE 2004, in INIA 2007).

EUREAU questions the political or economic feasibility of P-recovery from sewage by then-available techniques, concluding:

> *"Sludge utilization in agriculture is regarded a safe and energy-efficient way to ensure phosphorus reuse … a more efficient recycling of phosphates should be encouraged, concerning phosphorus present in animal excreta, in wastes from abattoirs (chemically treated bone), wastes and phosphorus in sewage sludge."*

Phosphate rock reserves

Other estimates, cited by **EcoSanRes**, April 2005, place at 60 – 130 years the current known reserves of commercially exploitable phosphate rock: 60 – 130 years according to Steen 1998 in « Phosphorus Availability in the 21st Century: Management of a Non Renewable Resource », Phosphorus and Potassium 217; 90 years according to Tiessen 1995 in « Phosphorus in the Global Environment: Transfers, Cycles and Management. Introduction and Synthesis », Scope 54, Wiley.

Green Alliance's report "The nutrient cycle: closing the loop", 2007: http://www.green-alliance.org.uk/uploadedFiles/Publications/reports/TheNutrientCycle.pdf

EUREAU (European Union of National Associations of Water Suppliers and Waste Water Services), position paper EU2-04-SL09, "The reuse of Phosphorus", 21st February 2005: http://www.apda.pt/apda_resources/APDA.Biblioteca/eureau%5Cposition%20papers%5Cthe%20reuse%20of%20phosphorus.pdf

EcoSanRes, Fact Sheet 4, "Closing the Loop on Phosphorus", April 2005: http://www.ecosanres.org/pdf_files/Fact_sheets/ESR4lowres.pdf

AISE 2004 figures for EU consumption of phosphates in detergents (as tonnes of phosphorus P/year): http://ec.europa.eu/enterprise/chemicals/legislation/detergents/studies/ceep_final_study_april_2007.pdf

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