
SCOPE NEWSLETTER

NUMBER 88

September 2012

Policy & Perspectives

Policy Position Statement

CIWEM position on phosphorus stewardship

The Chartered Institution of Water and Environmental Management (CIWEM) has published a statement on the wastewater industry's role in phosphate resource stewardship

P-REX EU 7th Framework Project

Demonstrate and validate full-scale P-recovery

The 3-year EU funded P-REX project will demonstrate, assess and disseminate results of full-scale phosphorus recovery and recycling routes operational in Europe, including P-recovery from ash, in sewage works and through bio-solids reuse on land.

Technology perspectives

Expert opinion survey on P-recovery processes

A survey of nearly experts worldwide identified processes for P recovery and recycling from sewage, concluding that P-recovery will be widely established in 20 years, and that the quality of the recovered product is decisive.

Life Cycle Assessment

Comparing routes for P-recycling to agriculture

LCA and cadmium loads of three routes for P-recycling to agriculture in Sweden (agricultural spreading, P-recovery from sludge incineration ash, struvite recovery) were compared to use of mineral phosphate fertiliser.

Food wastes and sludge

Optimising greenhouse gas emissions and P-recovery

Different options for treating food wastes with or separately from sewage sludge are evaluated for greenhouse gas emissions, phosphorus recovery and health risks.

Global phosphorus cycles

Natural and anthropogenic phosphorus

The literature assessing global phosphorus reserves and cycles is limited but a number of recent papers are completing the information developed in the last decades.

Recovered phosphates

Struvite fertiliser

Fertiliser efficiency and impurities in urine-derived struvite

Struvite precipitated from urine by different technologies was evaluated for its fertiliser value in greenhouse using ryegrass and maize, and heavy metal contaminants were evaluated.

Biofuels production

Using wastewaters for microalgae production

Microalgae production may provide a major route to biofuel production, and the use of wastewater nutrients may be the key to sustainability.

Iron phosphate sludge

Extraction of phosphorus and P-recovery

Alkali and acid extraction of phosphate from sewage sludge containing ferric phosphate, to enable calcium phosphate P-recovery, was tested at different temperatures.

Electronics industry

Struvite recovery from semiconductor manufacture wastewater

Electronics factory waste streams have high ammonia and phosphate concentrations. Struvite precipitation can treat this and recover the nutrients. Tests on lettuce demonstrate the fertiliser value of the recovered struvite.

Conferences

Cincinnati, 21-25 October 2012

P Removal and Reuse from Manures

Brussels, 6-7 March 2013

European Sustainable Phosphorus Conference

Vancouver, 28-31 July 2013

International Nutrient Removal and Recovery 2013: trends in resource recovery and use.

Policy Position Statement

CIWEM position on phosphorus stewardship

CIWEM's 'Policy Position Statement' on wastewater's role in stewardship of phosphorus resources, published in August 2012, highlights the urgent need to achieve phosphorus recovery from urban wastewater to improve food security and reduce geopolitical risks.

CIWEM is the leading international body of professionals in the water and environment management sector, providing information, training and advice in 98 countries. Its members are professionals, and also scientists, engineers, ecologists and students.

The CIWEM position presents the context of phosphorus resources and uses worldwide and of **agricultural need for phosphate to ensure food production.**

One third of imports

The paper indicates that **total P in urban wastewater (in Europe) is around one third of total annual phosphate imports**, mainly imports for fertilisers. CIWEM estimate that currently only 20% of this phosphorus in EU urban wastewaters is recycled, whereas nearly 50% is lost because it is not captured in sewage treatment (not captured in nutrient removal, or nutrient removal not installed), and around 30% is lost through biomass landfill or non-recycled sewage sludge incineration ash.

CIWEM consider however that **it would be feasible to recover around 95% of phosphorus in municipal wastewater**, if phosphorus removal with P-recovery was universally installed.

Priority to P-recovery

The CIWEM policy statement gives **8 considerations and 6 conclusions**. CIWEM considers that phosphorus reserve depletion is a global issue requiring action now, and that a *"high priority should be given to recovering phosphorus from urban wastewater"*. To achieve this, phosphorus stewardship should be included in public policies and strategies and should be a priority for governments and company corporate social responsibility.

In particular, CIWEM recommends that *"policy makers should make legal obligations to capture phosphorus"*.

Routes for wastewater P-recycling

CIWEM considers that *"land application of suitably treated biosolids (sewage sludge) is the best way to conserve and recycle the P it contains"*. Attention in wastewater treatment should be moved from only removing phosphorus (to address eutrophication problems in surface waters) to focus on capturing phosphorus in waste streams and recovering it for reuse.

In particular, where sewage sludge is incinerated or gasified, *"there should be a requirement to recover the phosphorus"* or if not, to store the ashes so that in the future they could be 'mined' for their phosphorus content.

CIWEM considers that phosphorus can provide more benefits if it is in the future regarded as a resource, not only as a potential pollutant.

The policy statement concludes that phosphorus stewardship will reduce geopolitical risk, improve food security and reduce the introduction of contaminants into the anthropogenic cycle (in mineral phosphate fertilisers, from phosphate rock). **"Phosphorus", concludes CIWEM, "is too precious to squander"**.

"Phosphorus: wastewater's role in stewardship of a vital Resource", CIWEM Policy Position Statement, August 2012

Chartered Institution of Water and Environmental Management (CIWEM), 15 John Street, London, WC1N 2EB, England. <http://www.ciwem.org/knowledge-networks/panels/wastewater-management/phosphorus-wastewater's-role-in-stewardship-of-a-vital-resource.aspx>

P-REX EU 7th Framework Project

Demonstrate and validate full-scale P-recovery



P-REX is a 3-year European Union funded programme bringing together 9 industry partners and 6 scientific institutes, which will demonstrate full-scale P-recovery, examine the technical and economic conditions of different phosphorus recovery and recycling routes operating in Europe, quantify market potential, and define strategies for developing P-recovery from municipal wastewater in different conditions.

The P-REX project launch meeting took place on 24th September 2012 and the project will run for three years to autumn 2015.

The European Union imports nearly one million tonnes of phosphorus equivalent per year in phosphate fertilisers and processed phosphate rock, at a cost of around 2 billion Euros. The **phosphorus contained in sewage sludges in Europe could substitute nearly a quarter of this phosphate import.**

Previous EU-funded projects

P-REX builds on recent European Union funded projects looking at sewage sludge handling :

- **ROUTES** www.eu-routes.org “Novel processing routes for effective sewage sludge management” (production of sludge suitable for agricultural use, sludge minimisation, optimisation of anaerobic digestion)
- **ANPHOS** “Phosphate production from wastewater and digestate”
http://ec.europa.eu/environment/life/project/Projects/files/laymanReport/LIFE03_ENV_NL_000465_LAYMAN.pdf
- **SUSAN** and **SUSYPHOS** “Sustainable and safe re-use of municipal sewage sludge for nutrient recovery” (see SCOPE Newsletter n° 78)
www.susan.bam.de
- **NEPTUNE** “New sustainable concepts and processes for optimization and upgrading municipal wastewater and sludge treatment” www.eu-neptune.org
- **HORIZONTAL** “horizontal and harmonised European standards in the field of sludge, soil, and treated biowaste” <http://horizontal.ecn.nl>
- **END-O-SLUDGE**, identifying and developing innovative system solutions for municipal sludge treatment and management in the context of EU climate change mitigation and energy policies
<http://www.end-o-sludg.eu/>

The aim of P-REX is to bring together information on different promising technologies for phosphorus recovery and recycling from municipal wastewater, and to **assess the technological, economic and agronomic potential of full-scale processes in three technology routes:**

- P-recovery from sewage sludge incineration ash,
- P-recovery from sludge liquors,
- use of biosolids on arable land.

The quality and standards of the recovered phosphate products will be studied.

The aim is to then derive proposals for implementation of P-recovery, taking into account different regional conditions (agriculture, contaminants in sewage, logistics ...) and wastewater technologies.

Optimising phosphate recovery routes in sewage works

Phosphate precipitation from liquors in sewage works can be installed **either upstream of sludge treatment** (in biological phosphorus removal return streams, eg. PHOSTRIP) **or downstream of sludge treatment** (eg. in sludge digester filtrate).

Installation upstream of sludge treatment has the advantage of reducing polymer and energy consumption in sludge dewatering, and of avoiding problem struvite precipitation in the sludge treatment line (in digesters, filter presses, piping, etc.). However, the quality of phosphate precipitated is liable to be lower, because of higher levels of organics and other substances. So, depending on purity requirements, subsequent cleaning might be necessary.

In both configurations, however, the phosphorus potentially available for recovery and recycling is only a relatively low proportion of total phosphorus inflow to the sewage works, because **a significant phosphorus content remains in the sewage sludge** (10 – 30% for P precipitation upstream of sludge processing, 30-50% for precipitation from sludge treatment liquors).

P-recovery from sewage sludge incineration ash can recover nearly all of the phosphorus in the sewage works phosphorus inflow, on condition that the sludge is incinerated separately from other wastes (mono-incineration). Furthermore, contaminants are separated and removed to a specific wastestream enabling safe disposal. Although organic nitrogen, carbon and other nutrients are lost in this route, it responds to the ongoing development of sewage sludge incineration in Europe in response to concerns about pathogens, heavy metal and other contaminants in sewage sludge.

The P-REX project estimates that **at present some 10-15% of EU sewage sludge is mono-incinerated, producing c. 0.6 million tonnes of ash with a phosphorus (P) content of 6-10%.** Treatment is necessary both to render this phosphorus bio-available (useable as fertiliser) and to separate out contaminants not eliminated by incineration (heavy metals).

P-REX has identified the following phosphorus recovery and recycling processes with full-scale or demonstration scale installations operational or planned:

P-recovery from liquors in sewage plant side-streams or sludge treatment streams	<p>P-ROC PROPHOS – calcium phosphate crystallisation –Neuburg STP, Germany - http://www.cleaner-production.de/en/projects-publications/projects/sewage-technology/phosphorus-recovery-from-wastewater-by-crystallization.html</p>
	<p>REPHOS (Remondis Aqua GmbH) – struvite precipitation – Attentreptow STP Germany http://www.remondis-aqua.com/en/aqua/serviceproduct-range/industrial-water-management/recovery-of-potential-recyclables/</p>
	<p>PHOSPTRIP and CRYSTALACTOR – calcium phosphate precipitation – DHV – Geestmerambacht STP Netherlands</p>
	<p>Pearl Crystal Green (Ostara) – struvite precipitation www.ostara.com – several plants operating in USA and Canada - see SCOPE Newsletter n°70</p>
	<p>Airprex – struvite precipitation - Wassmansdorf STP Germany (Berliner Wasserbetriebe) - see SCOPE Newsletter n°87 , Neuwerk Möchengladbach STP Germany and Wieden Echten STP Netherlands (P.C.S. Pollution Control Service)</p>
	<p>Stuttgart process – struvite precipitation – Offenburg STP Germany - Weidelener 2010 http://www.iswa.uni-stuttgart.de/Isww/forschung/awt/aktuelle/link_Pilotanlage_MAP.en.html</p>
	<p>PHOSPAQ (Paques) – struvite precipitation – Olburgen STP Netherlands http://en.paques.nl/pageid=199/PHOSPATM.html</p>
	<p>PHOXNAN / LOPROX – wet acid oxidation of sludge (at 160-200°C and pressure - RTWH Aachen – see SCOPE Newsletter n°87</p>
P-recovery from sewage sludge or sludge incineration ash	<p>LEACHPHOS – BSH Umweltservice – Berne MSWI plant (project) – based on FLUWA hydrometallic leaching process, phosphorus extraction and contaminant reduction by leaching with mineral acids, followed by precipitation of calcium phosphate</p>
	<p>MEPHREC – Ingitec – SUN Nurnberg Germany (project) – metal smelter process at c. 2000°C producing a bioavailable P slag low in heavy metals - Scheidig et al. “Profitable recovery of phosphorus from sewage sludge and meat & bone meal by the Mephrec process - a new means of thermal sludge and ash treatment.”, Vancouver Nutrient Recovery conference 2009</p>
	<p>Seaborne – acid and temperature extraction of P from sludge followed by struvite precipitation – PFI – Gifhorn STP Germany - see SCOPE Newsletter n°86 and http://www.seaborne-epm.de</p>
	<p>CAMBI – acid and heat treatment of sludge to release (iron) phosphate – www.cambi.no</p>
	<p>RecoPhos project – high temperature, reducing extraction of P and heavy metals from ash – www.recophos.org</p>
	<p>ECOPHOS (Decophos) – with SNB (N.V. Slibverwerking Noord-Brabant) waste management company, The Netherlands - production of phosphoric acid from ash http://www.phosphaterecovery.com/news/current-news/snb-studies-new-method-of-phosphate-recycling/106</p>
	<p>SUSAN / ASH DEC – Outotec – Berlin Königs Wusterhausen (project) – ash is treated at c. 1000°C with a chlorine donor chemical, to separate heavy metals and generate a bioavailable mineral phosphate - see SCOPE Newsletter n°78</p>
	<p>Thermphos International – Vlissingen Netherlands – use of ash to produce pure phosphoric acid (currently recycling c. 1000 tonnes P/year) http://www.thermphos.com/en/Documentation/Recycling.aspx</p>
	<p>ICL Amfert – use of ash to produce mineral fertilisers – see SCOPE Newsletter n°84</p>

Biosolids disposal to land

P-REX estimates that **some 42% of EU sewage sludge biosolids is spread on agricultural land**. However, this route is under pressure because of concerns about contaminants.

One substance in sewage sludges which has raised questions is **PAA (polyacramide) polymer flocculants** used in sewage works and sludge treatment processes. Alternative polymers, including natural polymers (eg. based on chitin, starch, tannin) are being proposed as alternatives.

P-REX will carry out full scale tests of such polymers, looking both at their performance in sewage works and the effects on P-recovery processes in sewage works or from sludge incineration ash.

Assessing recovered phosphates

P-REX will include both **applied and theoretical analysis of recovered phosphate products**. This will include pot tests to assess the plant nutrient value, toxicity tests, Life Cycle Analysis, Quantitative Risk Assessment and Life Cycle Cost studies.

Pot tests of fertiliser value will be accompanied by **analysis of product solubility** (in water, citric acid and nitrohydrochloric acid) and 'Neubauer' pot trials to assess P-uptake from soil by rye grass.

The recovered fertilisers will also be distributed to Austrian farmers for field testing.

P-REX will also include a **feasibility study for Europe-wide implementation of phosphorus recovery and recycling from sewage works and sewage sludge**, looking at regulatory and societal factors, market (sources and demand, business case studies) and regional conditions, and a **pre-normative study on quality requirements, leading to an Integral Guidance Document on P-recovery**.

The **regional implementation studies** will look at Switzerland, Berlin area Germany, Rügen Island Germany (Baltic Sea), Aragon region Spain and the Czech Republic. This covers a range of situations from Switzerland (agricultural use of sewage sludges abolished in 2006) to the Czech Republic (popular opposition to sludge incineration plants) and Aragon Spain (70-80% of sludge spread on land, low soil organic content but significant distances from population centres producing sewage sludges to farmland)

P-REX brings together 15 project partners with a total budget of 4.4 million Euros (total for 3 years), of which 2.9 million Euros EU budgeted funding (7th R&D Framework Programme, Collaborative Project).

Project lead work areas

WA1 P-recovery from ASH: led by BAM (German federal institute for materials research and testing)

WA2 P-recovery from sludge processes: led by FHNW (Fachhochschule Nordwestschweiz – University of Applied Sciences and Arts Northwestern Switzerland)

WA3 P-recycling through biosolids use on land: led by IASP:

- **green flocculation polymers:** KWB (KompetenzZentrum Wasser – public private research centre on urban water management, Berlin, Germany)
- **biological tests for sludge monitoring:** IASP (interdisciplinary research institute on agriculture, food and the environmental at Humboldt University, Berlin, Germany) and LimCo International

WA4 Environmental and economic assessment of technical options: led by KWB (Berlin Centre of Competence for Water Berlin)

- **plant P-availability and fertiliser value:** IASP
- **LCA of recovered phosphates** including risk assessment: KWB
- **Life Cycle Cost analysis:** FHNW

WA5 Europe-wide implementation: led by FHNW

- **Analysis and proactive development of market potential for P-recycling products:** offer / demand analysis and web-based e-market
- **Identification of regulatory and societal barriers:** recommendations to European and national regulators
- **Business model case study** and recommendations: pre-normative study sale price vs. product quality
- **Case-studies for Europe-wide implementation:** Regional Masterplans towards 80% P-recovery
- **Integral guidance document** for phosphorus recovery: to foster Europe-wide implementation of P-recovery from wastewater stream
- **Policy brief** addressing legal requirements and how they can/should be adapted to foster implementation of P-recovery at EU level.

WA6 Dissemination and Management: led by KWB

P-REX partners

The project's **expert advisory board** includes representatives from the Global Phosphate Forum (world detergent phosphate industry), Thermphos International, the Dutch value chain agreement, the German agrochemicals and fertiliser industry association (IVA) and Stockholm Environmental Institute.

The other project partners are: Veolia Eau (water division of Veolia) France, Outotec Finland, Agro Plus Handelsunternehmen (innovative agricultural nutrient trading company) Austria, BSH Umweltservice Switzerland (engineering and plant), Ingitec Germany (consulting engineering, Mephrec process), LimCo International GmbH (aquatic ecotoxicology research and education company) Germany, Proman Management Austria (business and technology consultants), ASIO Czech Republic (water and air treatment engineering and supplies), Solintel Spain (technology engineering and consulting), PCS Pollution Control Services Germany (water and sludge treatment solutions, AirPrex), PFI Planungsgemeinschaft Germany (environmental technology consulting).

Companies and organisations interested in working with P-REX, for example to exchange information or to contribute to the assessment of P-recovery routes, should contact the project coordinator: Christian Kabbe, KompetenzZentrum Wasser Berlin christian.kabbe@kompetenz-wasser.de

The P-REX project website will be launched by the end of 2012: www.p-rex.eu

Technology perspectives

Expert opinion survey on P-recovery processes

The authors questioned experts in nutrient management and recycling, identified via conferences and specialist emailing lists, by survey and by personal interviews, as well as using literature and online information. First, different routes and technologies for recovering phosphorus for recycling from municipal sewage works were identified. Secondly, expert opinion was collated on these different routes and on the future perspectives for P-recovery development.

22 different P-recovery technologies were identified. These were grouped according to whether the phosphorus is recovered from liquid streams, from sewage sludge, or from sewage sludge incineration ash. Rather than giving a complete overview of all

known P-recovery processes the aim of this task was to **identify the preconditions and basic characteristics** of all relevant types of processes.

P-recovery processes

The technologies listed include some already implemented at the industrial scale, and some which are still only experimental at the laboratory scale:

- **Precipitation of calcium phosphate or struvite from liquid streams:** Phostrip, PRISA, DHV Crystalactor, Ostara, Berlin Wasserbetriebe, AIRPREX
- **Adsorption/desorption from liquid streams:** Prophos (CSH), Recyphos (iron phosphate), Phosiedi (ion exchange), Fixphos (CSH)
- **Extraction of phosphate products from sludge by acid / heat / leaching:** Seaborne (acid), Loprox/Phoxan (low pressure acid oxidation, membrane phosphate separation), Aqua Reci (pressure + temperature), CAMBI (pressure + temperature), KREPRO (acid, temperature, pressure, producing iron phosphate), SEPHOS (acid and alkali leaching, sequential precipitation), PASCH (acid and solvent extraction), BIOCON (acid plus ion exchange), bioleaching (extraction of P from ash or sludge by bacteria followed by bacterial phosphate accumulation, anaerobic dissolution and struvite precipitation)
- **Recovery of phosphate products from sewage sludge incineration ash:** MEPHREC (furnace reduction of sludge), ASHDEC (acid + heat treatment of ash, plus chlorine donor for heavy metal removal), fertiliser industry (use of ash in fertiliser production to substitute phosphate rock), Thermphos (established industrial process, using ash to substitute phosphate rock in pure phosphoric acid production).

Expert opinion

Subsequently, experts were asked to assess certain **preconditions for the wide-spread adoption of P-recovery** in general and the factors influencing the choice between the existing basic P-recovery routes. 417 experts were contacted, and 197 responded (43%). Responding experts covered 28 countries, but nearly half were from Germany.

The consulted experts were presented 23 hypotheses regarding the conditions and context of phosphate recovery development: 6 concerning the need and urgency of P-recovery, 6 assessing the potential of different P-recovery routes from sludge and wastewater streams, 6 assessing routes from sludge incineration ash and 5 addressing transformations of

the wastewater management system to facilitate P-recovery.

Most of the experts considered P-recovery to be an urgent issue (44% stated before 2015) and considered that P-recovery would become economically viable by 2030.

Only a quarter of the responding experts considered **agricultural spreading of sewage biosolids** to be a solution for the future for P-recycling.

Over half of the experts considered that phosphate precipitation from wastewater liquor streams is the most important route for P-recovery, whereas only a minority (1/3) of experts consider that the expense and complexity of dissolving sludge or ash justify the advantages in terms of higher P-recovery or heavy metal removal. However, most of the experts consider that if sludge is incinerated anyway, then it is justified to recover phosphorus from the ash.

Perspectives

Most of the experts consider that wastewater will tend to be managed, and nutrients recovered and recycled, principally in **(semi)decentralised systems** in developing countries. They are however sceptical about the development of material separative flows (eg. urine separation), except in regions with scarce water supply.

Overall, the experts consider that **contaminants in wastewaters** will be an increasingly important issue, leading to decreasing use of sewage biosolids in agriculture (and so an increasing potential for P-recovery technologies). Similarly, the quality of the fertiliser product produced by P-recovery is considered to be a decisive aspect in defining which P-recovery routes will develop.

“Phosphorus recovery from wastewater – state-of-the-art and future potential”, WEF – IWA NRR Conference (Nutrient Recovery and Management), Jan. 9-12, 2011, Miami

http://www.phosphorrecycling.de/attachments/042_Nutrient2011_paper+_Sartorius-et-al.pdf

“Phosphorus Recovery from Wastewater - Expert Survey on Present Use and Future Potential”, Water Environment Research, vol. 84, n° 4, April 2012, pages 313-322
<http://www.ingentaconnect.com/content/wef/wer>

This work was supported by a grant from the German Federal Ministry for Education and Research (FKZ 02WA0807)

*Christian Sartorius, Jana von Horn *, Felix Tettenborn, Fraunhofer Institute for Systems and Innovation Research, Breslauer Strasse 48, 76139 Karlsruhe, Germany. * = Now at: EAWAG Überlandstrasse 133, 8600 Dübendorf, Switzerland. Christian.sartorius@isi.fraunhofer.de*

See also: the “Impact of supply and demand on the price development of phosphate”, proceedings of the 2009 Vancouver nutrient recovery conference
http://www.phosphorrecycling.de/attachments/040_vonHorn-Sartorius-2009_P-price-development.pdf

Life Cycle Assessment

Comparing routes for P-recycling to agriculture

Three routes for P-recycling to Swedish farmland were compared to the use of mineral P fertiliser, assessing cadmium loadings, overall energy greenhouse gas emissions and eutrophication impacts.

The three routes considered were:

- **Chemical P-removal in the sewage treatment plant**, followed by agricultural spreading of the sewage sludge. The calculation was based on average parameters for Swedish sewage sludge: 22.5% dry matter (77.5% water) with 2.8%P and 4.3% Total-N (% dry matter).
- **Struvite precipitation**, based on the Ostara process. In this case, only 20% of sewage works inflow P was estimated to be recovered as struvite.
- **P-recovery from sewage sludge incineration ash**. The Ash Dec process was considered (as developed by the EU SUSAN project, patent now owned by Outotec). In this process, the sludge is heated to 45°C to reduce water content, then incinerated. The ash is then mixed with a chlorine compound, press pelletised, then reacted at 1000°C.

These routes are compared with using mineral phosphate fertiliser to supply the average 11 kg P/ha/year necessary to replace P in harvested crops on Swedish arable farmland, including permanent grassland.

In the LCA calculations presented, 40% of the total nitrogen and 100% of the phosphorus present in the sewage sludge were assumed to be **available to crops**. The phosphorus may not be fully plant available if iron-dosing is used for chemical P-removal in the sewage works and the plant availability of the phosphorus is briefly discussed in the article. The authors indicate that a calculation assuming only 50% plant availability of this phosphorus was also made, but that this did not modify the overall LCA conclusions.

Energy and greenhouse emissions (GHG)

For both energy consumption and GHG emissions, the **best option for phosphate supply to farmland was agricultural sludge spreading**, considerably better than the other two P-recovery routes and better than using mineral phosphate fertilisers. Agricultural sludge spreading showed 'negative' overall energy use and greenhouse gas emissions, because the recycling of the sludge nitrogen content avoids the production of mineral nitrogen fertilisers.

If the phosphorus content is only valued as 50% available to plants, then twice as much sewage sludge will be needed to supply the plant needs for phosphorus, and therefore twice as much nitrogen will be supplied to land in the sewage sludge, so the calculated 'saving' of mineral nitrogen fertiliser is doubled, giving higher 'negative' values (better LCA results) in terms of energy demand and emissions of CO₂-equiv.

Struvite P-recovery shows higher overall energy use than mineral P fertiliser use, but slightly lower greenhouse emissions (again because some sludge nitrogen is recycled in the struvite = magnesium ammonium phosphate). Sludge incineration with Ash Dec phosphorus recovery shows much the highest energy use and greenhouse gas emissions.

The authors note that a key question in the LCA of **mineral phosphate fertiliser production** is whether or not to include an energy credit for the exothermic production of sulphuric acid from sulphur.

Transport distances for sewage sludge for agricultural spreading are also important. A distance of 40 km is used in the LCA calculation, but the authors estimate that spreading would continue to show zero/negative overall energy balance for distances up to 100 km.

Cadmium

The authors consider cadmium loading to agricultural land to be a key issue in considering P-recycling options, but conclude that there is a considerable lack of data. The authors found little data on cadmium in recovered struvite.

Considerable data exists on cadmium in sewage sludges in Sweden, but **data is lacking on cadmium in foods** (in particular, nearly no data on cadmium in imported foodstuffs) which may be a significant source of cadmium to sewage sludge. Atmospheric deposition is currently the biggest source of cadmium to agricultural land in Sweden, so that non-separated rainwater may also be a significant input to sewage works, and so to sewage sludge.

The LCA uses the following **figures for cadmium loadings** (resulting from supplying the 11 kgP/ha/year required to replace crop phosphorus):

- Sewage sludge: 314 mgCd/ha/year (0.8 mgCd/kg dry matter in sludge)
- Animal manure (for comparison, not used in this LCA): 187 mgCd/ha/year
- Sewage recovered struvite: 60 mgCd/ha/year
- Ash Dec recovered phosphate: 4 mgCd/ha/year
- Mineral phosphate fertiliser as used in Sweden (mainly from igneous phosphate rock, with relatively low cadmium content): 60 mg Cd/ha/year

Eutrophication is not considered a significant issue, and shows no differences between the different routes, because in all cases Sweden's strict legislation for sewage works nutrient discharge will be respected. The LCA takes account of the processes necessary to respect this.

Contrasting conclusions

The authors conclude that the optimal route for P-recycling is clearly agricultural spreading of sludge, but that with the available data this poses significant questions regarding cadmium loadings to farmland.

Further investigation is necessary to understand and reduce the origins of cadmium in sewage sludge, in particular analysis of cadmium in human foods and in rainwater inputs to sewage works.

The study also does not take into account **other potential contaminants in sewage sludge** which may pose questions in agricultural spreading (other pollutants, pharmaceuticals ...).

"Life cycle assessment of phosphorus alternatives for Swedish agriculture", *Resources, Conservation and Recycling*, n° 66, pages 27– 39, 2012
www.elsevier.com/locate/resconrec

K. Linderholm, J. Mattsson, Dept. Agrosystems, Swedish University of Agricultural Sciences, Alnarp, Sweden. A.-M. Tillman, Environmental Systems Analysis, Chalmers University of Technology, Gothenburg, Sweden.
kersti.linderholm@silvberg.se

Food wastes and sludge

Optimising greenhouse gas emissions and P-recovery

70% of sewage sludge in Japan is recycled, mainly as ash in cement (41%), as ash in paving (34%) and in compost (20%). Phosphorus is thus mostly not recycled, and even in the compost is not in a plant available form (Ohtake 2010). 66% of food processing waste and 22% of food distribution waste are recycled to food or fertiliser (so phosphorus is recycled), whereas nearly 100% of kitchen garbage is incinerated (phosphorus thus mainly not recycled).

Recently, **mixing crushed food waste in sewage sludge anaerobic digestion has been developed as a route to increase methane production** and avoid energy consumption in food waste incineration. This paper assesses the implications for overall greenhouse gas emissions, phosphorus recycling and for health risks (from heavy metals) for different options.

Incineration and co-digestion options

The following options are assessed for the food waste processing and for the co-digested sewage sludge and food waste:

- Incineration of food waste at 'low' temperature (800°C)
- Incineration at 'high' temperature (850°C), to reduce N₂O emissions
- Low temperature carbonisation
- Pyrolysis gasification
- Dry granulation
- Composting
- Cement feedstock

P-recovery as calcium phosphate (HAP hydroxyapatite) from food waste processing return waters or as struvite (MAP magnesium ammonium phosphate) from co-digestion filtrate was compared to the low temperature incineration (no co-digestion, no P-recovery) scenario.

Heavy metals

Although chemically recovered phosphates (HAP, MAP) were expected to contain higher lead and arsenic levels than mineral fertilisers, **the overall health risk (DALY Index) was lower** because of lower cadmium levels than in mineral fertilisers derived from phosphate rock.

Co-digestion compost, on the other hand, contained **higher levels of cadmium** than mineral fertilisers. The authors nonetheless consider that these levels would

not pose a health risk and that one application of compost would represent less cadmium than agricultural background concentrations.

Optimal GHG emissions

All co-digestion scenarios were estimated to result in lower overall greenhouse gas emissions (GHG) than the base case (low temperature incineration of food waste without P-recovery). Pyrolysis gasification and composting offered the lowest GHG emissions (pyrolysis reduces emissions of methane and of N₂O) with high P-recovery rates (as struvite MAP).

Composting offered low GHG emissions and high P-recycling rates (by increasing the P content of sludge compost so improving the agronomic value to plants, in addition to P-recovery as struvite MAP from the co-digestion filtrate).

Processing of co-digestion sludge in granulation and use as cement stock both also showed low GHG emissions.

"Comparative assessment of technological systems for recycling sludge and food waste aimed at greenhouse gas emissions reduction and phosphorus recovery", Journal of Cleaner Production, vol. 32, September 2012, Pages 157–172, <http://dx.doi.org/10.1016/j.jclepro.2012.03.026>

T. Nakakubo, A. Tokai, K. Ohno, Division of Sustainable Energy and Environmental Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan, nakakubo@em.see.eng.osaka-u.ac.jp

Global phosphorus cycles

Natural and anthropogenic phosphorus

Despite its overall planetary abundance, phosphorus is effectively a valuable and scarce element. Only a small proportion of world resources are accessible to biological or human use, whilst the element is essential to food production, human health and development.

Phosphorus is vital for all known life forms, because it is an essential element in genetic material and in cellular energy cycling. The nucleic acids DNA and RNA, which store and replicate genetic information, are held together by phosphodiester bonds. Cell processes, in particular the synthesis of complex molecules, are fuelled by cycling of ATP/ADP (adenine tri- and di- phosphate, that is phosphorylated sugars).

Natural P flows and human interference

Smil (2000) provides an overview of phosphorus stores and cycles.

Phosphorus is only present at low levels in terrestrial vegetation, eg 0.025% of tree biomass dry weight, because it is not a constituent of lignin cellulose, nor of most proteins. Vertebrates have a significantly higher P requirement, because calcium and phosphorus are the principal elements of bones and teeth, and the adult human body contains around 9% P dry mass.

Total geological stores of phosphorus are immense, estimated at 4×10^{15} tP, mostly in ocean sediments. The geological processes which slowly render this phosphorus available to biological systems are not however significant within the timescale of human presence on Earth, so that most of this phosphorus store is biologically inaccessible.

Phosphorus in biospheric reserves is estimated at c. 9×10^{10} tP, and is principally in ocean waters (c. 99%). The natural annual biospheric flux of phosphorus is c. 1×10^9 tP/y, of which c. 90% ocean plant uptake and c. 10% terrestrial.

Smil estimated that by 2000, **human activities had multiplied natural phosphorus flows by a factor of around 3x**, through a number of processes: accelerated erosion and runoff (c. + 20 MtP/y), reduced recycling of organic wastes (in particular, animal manures = c. + 14 MtP/y), human sewage (c. 3 MtP/y), application of inorganic fertilisers (13 – 16 MtP/y)

Biochemistry and cycling

Ruttenberg (2001 and 2003) provides updated and more detailed estimates of different geological phosphorus stores, and geological, biological and anthropogenic phosphorus fluxes, with a detailed assessment of reference literature.

The author estimates total sediment stores at around 1×10^{20} moles and land soil reserves (<60cm deep) at c. $3 - 6 \times 10^{15}$ moles. Of this, some 6×10^{11} moles becomes available to biological systems annually as a result of weathering of rocks or release from sediments.

The different mineral pathways involved in geological, sediment and soil phosphorus cycling and storage are presented, looking particularly at calcium phosphates, phosphorites (carbonate fluorapatite CFA), the iron phosphates cycle, inositol phosphates and other organic phosphates.

The author concludes that the oceanic residence time of phosphorus is 10 – 20 000 years, significantly lower than previous estimates. Through the nutrient – CO₂ connection, phosphorus may have a significant impact on climate change on glacial – interglacial time scales.

Updated overview figures for global phosphorus reservoirs and for phosphorus fluxes are given, pre-human and present day in 2005. This concludes that human activities have increased soil phosphorus losses to the ocean and sediments from 16 to 24×10^6 MtP/y.

The author examines **the role of microbes in phosphorus cycling**, and in the cycling between DIP (dissolved inorganic phosphate) and organic forms of phosphorus. The role of phosphorites (carbonate fluorapatite) in sediments, as a global phosphorus sink, is assessed. Phosphorites occur as slowly growing nodules, lumps or conglomerates (growth estimated at 1 – 10 mm per thousand years). These form through inorganic pathways, for example via iron phosphate cycles, but probably also in relation to microbial activities, through mineralisation of microbial polyphosphates. Water column and marine sediment phosphorus cycling are also discussed.

P and N balance scenarios

Bouwman et al. (2009) estimate changes in continental and global phosphorus and nitrogen cycles and soil balances for the period 2000 – 2050, based on the Millenium Ecosystem Assessment development scenarios. In all scenarios, massive increases in N and P flows are expected in developing countries, resulting in increasing N and P balances in these countries' soils.

The 'balance' is here taken to mean the amount by which annual agricultural inputs exceed outputs in harvested crops. This balance is either lost (in leaching, soil erosion, atmospheric ammonia volatilisation, denitrification) or accumulated and stored in soil.

Management aimed at closing nutrient cycles could however considerably impact nutrient balances, through improved efficiency in crop and grassland nutrient use, and potentially through recycling of animal manures and human waste nutrients.

The authors note that uptake of nitrogen from fertilisers by crops in fields is generally around 50%.

Use of fertiliser P by crops ("P-recovery") is often only 10–20% in the short term. Part of the P added to soil in fertiliser and manure is used by the plant in the year of application. A varying but substantial part accumulates in the soil as 'residual P'. This reserve can contribute to P in soil solution and be taken up by crops for many years.

Where the amount of readily available P is below a critical level, however, the rate of P release from residual P may not be sufficiently rapid to sustain optimal crop yields. While building up the soil P status

to the critical value, the crop P recovery may slowly increase to values up to 90%.

Phosphorus availability to plant roots is controlled by both the concentration of phosphate ions in the soil solution and the soil P-buffering capacity (replacement of these ions after plant uptake). Farmers have to maintain a critical level of plant available phosphate in soil to ensure crop yields.

The authors emphasise that P fertiliser application to grasslands is currently globally only around 0.3 million tonnes (Mt) phosphorus (0.3 x 106tP), concentrated in a very few countries. In many regions, grassland soil phosphorus is being depleted as more P is exported in meat or silage production and lost in soil erosion than is being replaced. This is not sustainable.

Global inputs of fertiliser nitrogen to cropland and grassland are estimated at 29 MtN/year in 1970, 83 MtN in 2000 and 68 – 122 MtN in 2050 (for different scenarios).

Global fertilizer inputs of phosphorus to cropland and grassland are estimated at 8 MtP/year in 1970, 14 MtP in 2000 and 10 -33 MtP in 2050 (for different scenarios, the lowest estimate for 2050 is a scenario with 9 MtP from human urine being recycled as fertilizer).

See also “Phosphorus resources: global phosphorus flows” in SCOPE Newsletter n°76.

“Phosphorus in the Environment: Natural Flows and Human Interferences”, *Annu. Rev. Energy Environ. Vol. 25, pages 53–88, 2000*
<http://www.annualreviews.org/doi/abs/10.1146/annurev.energy.25.1.53>

V. Smil, Dept. Geography, University of Manitoba, Winnipeg, Manitoba R3T 2N2, vsmil@cc.umanitoba.ca

“The Global Phosphorus Cycle”, *Treatise on Geochemistry, vol. 8, ch. 8.13, pages 585-643, 2003*
<http://www.sciencedirect.com/science/article/pii/B0080437516081536>

“Phosphorus Cycle”, *Encyclopedia of Ocean Sciences, vol. 4, pages 401-412, 2001*
<http://www.sciencedirect.com/science/article/pii/B9780123744739002770>

K. Ruttenger, University of Hawaii at Manoa, Honolulu, HI, USA kcr@soest.hawaii.edu

“Human alteration of the global nitrogen and phosphorus soil balances for the period 1970–2050”, *Global Biogeochemical Cycles, vol. 23, GB0A04, 16 pages, 2009*,
<http://www.agu.org/pubs/crossref/2009/2009GB003576.shtm>

F. Bouwman (1,2) A. HBeusen (1), G. Billen (3). 1 = Netherlands Environmental Assessment Agency, Bilthoven,

Netherlands. 2 = Earth System Science and Climate Change Group, Wageningen, University Research Centre, Wageningen, Netherlands. 3 = UMR Sisyphé, University Pierre et Marie Curie, CNRS, Paris, France.
lex.bouwman@pbl.nl

Recovered phosphates

Struvite fertiliser

Fertiliser efficiency and impurities in urine-derived struvite

Six different urine-precipitated struvites were tested for fertiliser effectiveness, and assessed for heavy metal contaminant content. The struvites were precipitated from diluted or undiluted urine collected in Germany and in Vietnam, using different precipitation technologies, with differing characteristics resulting from magnesium dosage (ranging from 1.1:1 to 2:1) and drying method (ambient temperature – 200°C).

The struvite precipitation technologies were as follows:

- **collection of sludge sediment spontaneously accumulated in a storage tank** downstream of a waterless urinal (Bonn Germany),
- **precipitation from diluted and undiluted urines** by magnesium oxide (MgO) addition (Can Tho Vietnam, Berching Germany, Bonn Germany),
- **precipitation from undiluted urine** by circulation through a MgO filter bag (Aachen Germany).

The struvites dried at 105°C and 200°C showed respectively 15% and 100% mono-hydrate form of struvite (Dittmarite $\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$), instead of the more usual hexahydrate ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$). The struvite precipitated with a higher magnesium ratio (2:1 Mg:P) showed 26% Nesquehonite ($\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$).

Magnesium content of the struvites correlated to magnesium dosing rates used in their precipitation.

Differences in human diet between Vietnam and Germany did not result in differences in the struvite composition.

The struvites were ground and sieved to 0.49mm to ensure comparable particle size, then analysed by X-ray diffraction (XRD) and for elemental composition including trace elements by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Solubility was tested in distilled water and 2% citric acid.

Plant fertiliser tests

Fertiliser value tests were carried out in pots in greenhouses using Italian ryegrass (*Lolium multiflorum*) and maize (*Zea mays*), with harvesting after 82 days (plus intermediate harvests). A commercial phosphate fertiliser (Cedera, a partially acidulated phosphate rock PAPER fertiliser) were tested for comparison. Phosphate was dosed at 24.4 mgP/kg to the pots at the start of the tests, and nitrogen was made up to 1530/9 = 170 mgN/kg (by adding additional ammonium nitrate).

Biomass harvested was analysed as dry matter yield per pot, and phosphorus uptake was calculated by comparing this with the biomass P content (then calculated as a % of total initial pot P).

Although the solubility of the struvites was lower than that of the commercial fertiliser, **the struvite pot trial results showed dry matter yields and phosphorus uptake for ryegrass significantly better than for the reference fertiliser** (c. 120% - 200%). For maize, the struvites showed results comparable to that with the commercial fertiliser (c. 80-90%) or significantly higher (c. 200%).

The control experiments with no phosphate added showed yields c. 50% lower than any of the pots with struvite or commercial fertiliser.

The results showed that the fertiliser value of struvite was not affected by the presence or not of water molecules in the crystal structure (mono- or hexahydrate form).

Heavy metal levels

The heavy metal contents of the urine-derived struvites were in all cases (for all heavy metals) lower than German fertiliser regulation requirements (DümV 2008). When heavy metal loadings were calculated based on calculated maximum tolerated loadings, heavy metal doses to soils were also below those fixed by the German Federal Soil Protection Act (BBodSchV 1999), and below those calculated for other fertilising agents (commercial inorganic fertilisers, sewage sludge, animal manures) except possibly for mercury for which the ICP-OES detection limit was higher than some threshold values.

The authors conclude that urine-derived struvite is a hygienically safe fertiliser, which contributes less heavy metals to farmland than recycled biosolids or commercial phosphate-rock derived fertilisers. When combined with other compounds, urine-derived fertiliser is an efficient fertiliser, providing magnesium and phosphorus to plants.

“Greenhouse evaluation and environmental impact assessment of different urine-derived struvite fertilizers as phosphorus sources for plants”, Chemosphere 2012 (in press), Elsevier (Science Direct)

<http://dx.doi.org/10.1016/j.chemosphere.2012.07.026>

S. Antonini, M. Alejandra Arias, T. Eichert, J. Clemens, University of Bonn, Institute of Crop Science and Resource Conservation, Department of Plant Nutrition, Karlrobert-Kreiten Straße 13, 53115 Bonn, Germany
samantha.antonini@yahoo.co.uk sam_antonini@uni-bonn.de

Biofuels production

Using wastewaters for microalgae production

Microalgae offer considerable potential as a route to sustainable biofuel production, because they do not compete with food production for agricultural land or water resources (e.g. by cultivation in salt water). Biomass productivity is potentially higher than for land-based crops. Microalgae can be converted to energy by a range of processes, ranging from drying and burning their biomass, through to extraction of lipids for processing to biodiesel.

However, a significant question in the economic and ecological sustainability of microalgae is the sourcing of the nutrients necessary for their growth (and the recycling of these nutrients, see SCOPE Newsletter n° 87).

Use of wastewaters (sewage, animal manures, industrial wastewaters) as a nutrient source for microalgae production can offer the double advantage of supplying at no cost the needed nutrients (P, N, micronutrients) and also contributing to treatment of the wastewater.

Pittman et al. review information currently available concerning production of microalgae in wastewaters and the potential for biofuel production.

Microalgae are already **used to treat wastewaters**, although only at a minor scale compared to ‘traditional’ sewage treatment systems, in many countries and in different types of installation, ranging from algal pond lagoon systems to high-rate systems with mechanical mixing.

Many studies have been carried out on such systems, particularly looking at the **ability of microalgae to remove N, P and toxic metals from sewage and animal manures**. An important aspect is that in sunlight, the algae produce oxygen, which facilitates breakdown of organic pollutants by bacteria.

Raw sewage

A number of studies show that **certain species of microalgae can grow effectively in raw sewage**. Most species are dependent on light, so mixing may be necessary and/or upstream settling of the sewage. *Chlorella minutissima*, however, has been shown to also grow heterotrophically in the dark as well as in light, using various carbon substrates, as well as tolerating salt and consuming both nitrate and ammonia (Bhatnagar et al., 2010).

Other species have been shown to grow effectively in **piggery manure-based wastewater** (with very high nutrient concentrations), dairy manure, and in certain industrial wastewaters (where different species may be adapted to high levels of specific toxins or relatively low nutrient concentrations).

Biodiesel

Various studies show that certain microalgae can produce relatively high levels of cellular lipids, up to c. 30% dry weight, appropriate for **extraction for processing for biodiesel production**. However, these species often require specific culture conditions (not open ponds) or have low biomass production. Some first pond-scale studies of cultivation of such algae have now been published, using swine and dairy effluents, and more work is underway to assess the feasibility of biodiesel extraction.

Future development needs

The authors identify several areas where further work is needed to move towards cost-effective biofuel production using wastewaters:

- Improving algae harvesting techniques
- Overall life cycle analysis of microalgae-derived biofuels
- Combining high biomass productivity and lipid productivity, at the pond scale

Michigan dairy manure

A recent study by **Chen et al. 2012** tested different algae species, collected from a natural pond, in **anaerobic digester effluent from dairy manure treatment** in a 200 m³ raceway pond. The algae tolerated high nutrient concentrations, but turbidity of the effluent reduced algal growth (by limiting light) and optimal biomass production was achieved in effluent treated with mineral coagulants. Stable algal biomass productivity of 6.8 g/m²/day was achieved.

Levine et al. 2011 also used **dairy manure digester effluent**, with the objective of cellular lipid concentration, appropriate for biodiesel production feedstock. *Neochloris oleoabundans* was able to

assimilate 90-95% of effluent nitrate and ammonium. The authors estimate that around 1.7 g/m²/day biomass could be produced, with c. 30% lipid content. Around 330 000 litres of biodiesel per year could thus be produced on 25 ha, corresponding to the annual fuel consumption of the 1000 cow farm.

“The potential of sustainable algal biofuel production using wastewater resources”, *Bioresource Technology* 102, pages 17–25, 2011. Elsevier:

<http://www.sciencedirect.com/science/article/pii/S0960852410010163>

J. Pittman (a), A. Dean (a), O. Osundeko (a,b). a = Faculty of Life Sciences, University of Manchester, Michael Smith Building, Oxford Road, Manchester M13 9PT, UK. b = Sustainable Consumption Institute, University of Manchester, 188 Waterloo Place, Oxford Road, Manchester M13 9PL, UK

“Freshwater algal cultivation with animal waste for nutrient removal and biomass production”, *Biomass & Energy* 39, pages 128-138, 2012. Elsevier:

<http://www.sciencedirect.com/science/article/pii/S0961953411006647>

R. Chen (b), R. Li (c), Lau. Deitz (a), Y. Liu (a), R. Stevenson (b), W. Liao (a). a = Department of Biosystems & Agricultural Engineering, Michigan State University, East Lansing, MI 48824, USA. b = Department of Zoology, Michigan State University, East Lansing, MI 48824, USA. c = College of Marine Life Science, Ocean University of China, Qingdao, Shandong 266003, PR China.

“Neochloris oleoabundans grown on anaerobically digested dairy manure for concomitant nutrient removal and biodiesel feedstock production”, *Biomass & Energy* 35, pages 40-49, 2011. Elsevier:

<http://www.sciencedirect.com/science/article/pii/S0961953410002928>

R. Levine (a), M. Costanza-Robinson (b), G. Spatafora (c). a = University of Michigan, Department of Chemical Engineering, 2300 Hayward Drive, 3074 HH Dow, Ann Arbor, MI 48109, USA. b = Middlebury College, Department of Chemistry & Biochemistry and Program for Environmental Studies, VT 05753, USA. c = Middlebury College, Department of Biology, Middlebury, VT 05753, USA.

Iron phosphate sludge

Extraction of phosphorus and P-recovery

Phosphorus extraction was tested using sewage sludge from a works operating P-removal by iron electrolysis, a works without P-removal and using sludge incineration ashes. Extraction of phosphorus was tested using alkali (sodium hydroxide) and acid (nitric acid), at temperatures from 20°C to 80°C. 60 – 90% of phosphorus was extracted. Use of alkali shows little improvement in P-extraction at higher temperatures, low metal extraction levels and better extraction results with raw sludge than with sludge incineration ash. The use of alkali also means that a high pH solution results, appropriate for P-recovery by calcium phosphate (hydroxyapatite HAP) precipitation.

The form of the extracted phosphorus is soluble orthophosphorus, making subsequent HAP precipitation possible.

In total, **three different sewage sludges and two sludge incineration ashes were tested**. Different concentrations of sodium hydroxide (NaOH) 0.5% - 5% were tested, and compared to extraction using nitric acid (HNO₃) at 1.26%. Extraction over time (0 – 30 minutes) and at different temperatures (20°C – 80°C) were also tested. Extraction phosphorus, of different metals (magnesium, aluminium, calcium, iron, copper, zinc, various heavy metals) as well as COD (carbon) were analysed.

Heavy metal retention

The authors note that **extraction of organics was lower with alkali than acid extraction**.

Heavy metal extraction was low (1 – 10% of sludge heavy metal content), and distinctly lower in the sludges rich in iron (sewage works using iron in P-removal process), possibly because iron binds to the heavy metals preventing their extraction. Overall, only 2 – 4 % of sludge iron was extracted whereas most to nearly all aluminium was extracted.

Phosphorus extraction was higher with alkali than acid extraction for the iron containing sewage sludges, but lower with alkali for the sludge from sewage works without P-removal. Alkali P extraction from the sewage sludges was 90 -95%.

Phosphorus extraction did not significantly improve at higher temperatures within the range tested, whereas COD extraction did increase at the higher temperatures.

The authors conclude that, for alkali extraction, raw sewage enables better extraction than sludge

incineration ash, and that for iron-containing sludges it is not useful to apply heat.

The alkali extraction gives relatively low heavy metal extraction (especially in iron-containing sludges), low iron extraction (but significant extraction of aluminium). It provides a phosphate solution at high pH, appropriate for P-recovery by calcium phosphate precipitation.

“Extraction of raw sewage sludge containing iron phosphate for phosphorus recovery”, Chemosphere, in press, 2012 www.elsevier.com/locate/chemosphere

A. Sano (a), M. Kanomata (b), H. Inoue (c), N. Sugiura (b), K-Q. Xu (a,d), Y. Inamori (e). (a) = Environmental Restoration and Conservation Technology Section, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan. (b) = Agrobiological Resource Sciences and Technology, Graduate School of Life and Environmental Sciences, Tsukuba University, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan (c) = Building Center of Japan, Testing Laboratory for Wastewater Treatment Tanks, Oyama, Inashiki-gun, Ibaraki 300-0402, Japan. (d) = School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China. (e) = Facility of Symbiotic System Science, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan. sano.akira@nies.go.jp

Electronics industry

Struvite recovery from semiconductor manufacture wastewater

Semiconductor manufacturing uses very pure phosphoric acid and ammonium hydroxide, as well as other chemicals (e.g. sulphuric acid, hydrogen peroxide, hydrochloric acid) in the circuit etching and cleaning processes. This results in different waste streams, some of which contain high levels of soluble phosphate and ammonia. These papers present laboratory and full-scale factory testing of struvite precipitation from such waste streams, to remove phosphate and ammonium before discharge, and testing of the recovered struvite (magnesium ammonium phosphate) as a fertiliser in lettuce plant pot trials.

Warmadewanthi & Liu tested struvite precipitation from a waste stream from a leading **semiconductor producer’s facility at Hsinchu Science Park, Taiwan**, rich in phosphate (65 mgP-PO₄) and ammonium (200 mgN-NH₄), and also containing in particular around 1300 mg/l fluoride and 1400 mg/l sulphate (pH = 8.3).

Bobierrite

Struvite was precipitated in batch, stirred, 1 litre beaker tests, by adding MgCl₂ and adjusting pH with NaOH. Only 47% of phosphate was precipitated at 1:1 Mg:P ratio (at pH 9), increasing to 92% at a 3:1 Mg:P ratio.

However at higher magnesium to phosphorus ratios, the predominant precipitant was bobierrite (Mg₃(PO₄)₂·8H₂O) not struvite. Struvite precipitation was improved by ammonium addition and increasing pH up to 10. **Fluoride was shown to remain in solution and is not expected to contaminate the struvite** (analysis not shown).

Ryu et al. (2008) tested struvite precipitation from fluoride-rich waste water from a large **semiconductor manufacturing plant in Cheongju, Korea**.

After laboratory batch experiments, a **full-scale continuous-flow precipitation system was retrofitted into the factory's 500 m³/day wastewater treatment plant**.

The factory wastewater had concentrations of 5 – 390 mgP-PO₄, 80 – 250 mg/l N-NH₄, 75 – 800 mg/l F and 220 – 440 mg/l COD.

Initial laboratory tests using real and synthetic wastewaters showed that the optimal pH for ammonium removal was pH 9.2 and for phosphate removal pH 10. Over 80% removal of both phosphate and ammonium were achieved at pH 9.2.

COD was also reduced by 80% probably by the flocculation effect of adding magnesium. [*Editor's note: this could result in contamination of the recovered struvite by organics, possibly leading to recovery, drying or storage problems.*]

Fluoride inhibition of struvite precipitation

The laboratory studies showed that **fluoride concentrations affected struvite precipitation**. When fluoride was below c. 500 mgF/l, some 70 – 80% ammonium and phosphate removal were achieved. The removal efficiency was reduced at c. 600 mgF/l, and drastically lower at > 700 mgF/l. This may be due to fluoride reacting with magnesium to form magnesium fluoride, thus reducing magnesium available to form struvite.

Full-scale factory operation

The full-scale plant was operated for 176 days in the semiconductor factory, achieving 89% ammonium removal (residual phosphate was in any case removed in the fluoride treatment stage of the existing waste water treatment plant). X-ray diffraction

indicated that the precipitant generated was indeed struvite.

The cost of chemicals for operating the full-scale struvite precipitation plant (NaOH, MgCl₂) were estimated at 996 US\$/day, producing approximately 10.8 tonnes of struvite/day.

Ryu et al. (2011) analysed and **tested the fertiliser value of the struvite produced in the full-scale reactor** above. The struvite was chemically analysed, tested in laboratory pot trials of lettuce plants (*Lactuca sativa*), tested for nitrate leaching and assessed for acute aquatic toxicity to invertebrates (*Daphnia*).

The recovered struvite contained mainly oxygen, nitrogen, phosphorus and magnesium, but also 19% carbon, 5% iron and 1.4% fluorine.

Nitrogen leaching and daphnia toxicity

Laboratory soil column tests showed that more nitrogen is leached from struvite than from a commercial NPK fertiliser (N, P and K in the forms of (NH₄)₂HPO₄ and K₂SO₄) during the first 48 hours, but that struvite then took longer to reach a steady state. This suggests that **struvite has better slow-release fertiliser properties**.

Five different concentrations of dissolved struvite were used for acute aquatic toxicity testing on *Daphnia magna* (OECD EC50 24-hour), showing no effect at the highest concentration tested (0.938g struvite / litre). **Struvite thus has no apparent aquatic toxicity, at least up to this concentration**.

Fertiliser effectiveness

Struvite's fertiliser value was compared to a control (no fertiliser added) and to three commercial fertilisers: commercial NPK, organic fertiliser, compost (each in triplicate). Fertiliser dosage was adjusted to 100 kgN/ha (NAAS recommendation for lettuce). Three lettuce seeds were planted per pot, and grown for 63 days before harvesting. The fertilisers were added to the soil in one dose only before planting the seeds. Leaf length was monitored throughout the trial, and dry mass, nutrient content and heavy metal concentrations in leaves on harvesting.

Struvite fertilised lettuce showed the fastest initial growth, the longest final leaf lengths and the highest harvested fresh and dry weight.

Struvite grown lettuce showed **lower levels of As, Hg, Pb, Cr and Ni than lettuce grown with inorganic, organic or compost fertilisers and levels of Cu and Zn within the ranges for these fertilisers**. Cadmium (Cd) was not detectable in any of the lettuce plants.

The authors conclude that **struvite recovered from semiconductor factory wastewater is a very effective fertiliser, with low heavy metal levels, low aquatic toxicity and good slow release properties.**

“Recovery of phosphate and ammonium as struvite from semiconductor wastewater”, *Separation and Purification Technology*, 64 (2009), pages 368–373,
<http://online.liebertpub.com/doi/abs/10.1089/ees.2011.0207>

Warmadewanthi, J. Liu, Dept. Chemical Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 106, Taiwan,
liu1958@mail.ntust.edu.tw

“Application of struvite precipitation in treating ammonium nitrogen from semiconductor wastewater”, *Journal of Hazardous Materials*, 156 (2008), pages 163–169
www.elsevier.com/local/jhazmat

H-D. Ryu, D. Kim, S. Lee, Dept. Environmental Engineering, Chungbuk National University, Cheongju, South Korea, nanumenv@hanmail.net dkeuny@gmail.com
gatorlee@chungbuk.ac.kr

“Recovery of Struvite Obtained from Semiconductor Wastewater and Reuse as a Slow-Release Fertilizer”, *Environmental Engineering Science*, IN PRESS 2011, Mary Ann Liebert publications.
<http://online.liebertpub.com/doi/abs/10.1089/ees.2011.0207>

H-D. Ryu, Geum River Basin Environmental Office, Ministry of Environment, Daejeon, Chungnam, Republic of Korea. C-S. Lim, Y-K. Kim, K-Y. Kim, S. Lee, Dept. Environmental Engineering, Chungbuk National University, Cheongju, Chungbuk, Republic of Korea
gatorlee@chungbuk.ac.kr

Conferences

Cincinnati, 21-25 October 2012

P Removal and Reuse From Manures

Wed. 24th October, international symposium: “**Opportunities and Limitations of Phosphorus Removal and Reuse From Manures**”, looking at policy perspectives and technologies for phosphorus recycling from manures.

21-24th October ASA, CSSA and SSSA International Annual Meetings “Visions for a Sustainable Planet”

24-25th October SERA-17 (USDA / Phosphorus Index Core Team) 2012 meeting addressing minimising phosphorus losses from agriculture

P-recycling symposium:

<http://scisoc.confex.com/scisoc/2012am/webprogram/Session9632.html>

ASA, CSSA and SSSA Meetings:
<https://www.acsmeetings.org/>

SERA-17: www.sera17.ext.vt.edu

Brussels, 6-7 March 2013

European Sustainable Phosphorus Conference

Looking at European policies, including the legislative framework and business cases).

Please note: this conference was previously announced for 1st November 2012 – this date is replaced by 6th – 7th March 2012

Vancouver, 28-31 July 2013

International Nutrient Removal and Recovery Conference

Combined WEF and IWA-NRR conference:

Nutrient removal and recovery 2013 – trends in resource recovery and use.

Vancouver, British Columbia, Canada, 28th – 31st July 2013.

Call for abstracts (for papers and posters) is open **until 12th December 2012** on categories including:

- nutrient recovery processes
- nutrient recovery from source-separated urine and agricultural effluents
- nutrient management of biosolids

Conference organised by WEF (Water Environment Federation), IWA (International Water Association), WERF (Water Environment Research Foundation) and British Columbia Water & Waste Association.

<http://www.wef.org/nutrients/>



International
Water Association



Water Environment
Federation
the water quality people®