European Sustainable Phosphorus Platform

February 2016 n° 119

SCOPE NEWSLETTER

European Union policy

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Deadline to candidate as an expert: 21st March.

EU consults on sustainable bioenergy

Public consultation open to 10th May.
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Brine shrimp eggs -magnesium hydroxide adsorbent for P-recovery

After adsorbing phosphorus, Artemia egg shells can be used as fertiliser

EU Fertiliser Regulation criteria

ESPP working meeting on biochars criteria:
15th March Brussels info@phosphorusplatoform.eu

Sustainable Phosphorus Platform

E-discussion group on P sustainability: use, impacts, resources and recycling, in agriculture, diet and nutrition, industry, chemistry, soil and water. ***Join now at:***
https://groups.google.com/d/forum/sustainablephosphorusplatform

The partners of the European Sustainable Phosphorus Platform

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European Union policy

Nutrients Recycling: EU call for experts

The European Commission funded EIP-AGRI (European Innovation Partnership on Agricultural Productivity and Sustainability) has officially announced the launch of a new Focus Group to look at “How to improve the agronomic use of recycled nutrients (N and P) from livestock manure and other organic sources?”. This follows a submission by ESPP, supported by nearly 60 different organisations (see SCOPE Newsletter n°114) in June 2015.

EIP-AGRI has published a call for experts to participate in the Focus Group, **closing Monday 21st March**.

ESPP will probably submit a candidate or candidate experts. Please contact us if you are interested.

Candidate for the Focus Group

Candidates can be farmers or supply chain operators with practical experience; experts competent in relevant economics, markets, industry or socio-economic aspects; or bring experience in relevant practical research and innovation.

Application is by completing a **short application form** (c. 5 000 characters total maximum) online at *https://ec.europa.eu/eip/agriculture/en/news/new-call-eip-agri-focus-group-experts-now-open-0*

EIP-AGRI Focus Groups are brought together and secretariat ensured by the EIP-AGRI Service Point. The Focus Groups are tasked with **assessing currently available knowledge and research needs and providing new and useful ideas** to solve practical problems, to provide ideas for EIP Operational Groups or research projects. They can eventually generate input for future Horizon 2020 research priorities. Focus Groups do not imply funding for participants, other than travel costs

ESPP proposal with 60 organisations

ESPP, with support of nearly 60 different organisations, submitted the suggestion for establishing a Focus Group on “**Agronomic use of recycled nutrients**” in reply to the EIP-AGRI call for proposals for ideas for Focus Groups in June 2015, see SCOPE Newsletter n°114.

The theme outline submitted by ESPP has been adapted by EIP-AGRI and aims to summarise and take stock of state of practice and research for the following themes:

➔ **technologies for processing** manure and other organic secondary nutrient sources

➔ **tools to help farmers** measure nutrient content and plant availability in recycled nutrient products, recommendations for application to fields

➔ **economic and technical challenges** and obstacles to use of recycled nutrients in agriculture, and how to address these

➔ how to adapt secondary nutrient products to **market demands, including quality**, and business cases

The Focus Group outcomes will be include identifying research needs and knowledge gaps, and proposing research directions, innovation and knowledge transfer actions or other projects.

Opportunities and bottlenecks

The EIP-AGRI published call includes a “Mini-paper: **Opportunities and bottlenecks in the utilisation of new kinds of organic fertilisers**”. This particularly discusses the interactions between organic material present in organic fertilisers and soils (soil microbes, soil physical properties, nutrient availability, greenhouse gas and air pollution emissions), direct and indirect economic impacts (e.g. externalities), social benefits such as local supply chains or new businesses. This paper points to bottlenecks such as lack of quality standards, regulatory issues, knowledge gaps concerning nutrient availability and sustainability, farmer information, lack of data and monitoring. Several examples of field tests from Poland and Belgium are summarised.

The first meeting of the Nutrient Recycling Focus Group is planned for 31st May – 1st June 2016

“New call for EIP-AGRI Focus Group Experts now open”, FG19 Nutrient Recycling “How to improve the agronomic use of recycled nutrients (N and P) from livestock manure and other organic sources?” https://ec.europa.eu/eip/agriculture/en/news/new-call-eip-agri-focus-group-experts-now-open-0 *Deadline for expert candidate submission: Monday 21st March.*

EU consults on sustainable bioenergy

The EU has opened a public consultation on sustainability of bioenergy policy, open to 23rd May 2016. Nutrients are not mentioned in the consultation documents. It is surprising that nutrients are not cited as a potential issue, given that the recently published standard ISO 13065:2015 "Sustainability Criteria for Bioenergy" cites phosphorus and nutrients as key factors, for both limiting eutrophication and ensuring balanced soil fertility (see SCOPE Newsletter 117).

The EU consultation, with 9 questions, asks respondents what type of bioenergy they consider should be developed, what they see as benefits of bioenergies and what they see as risks. Possible risks cited are changes to carbon stock, land use, greenhouse gas impacts, air- water and soil impacts, biodiversity and market effects. Respondents are asked which of these issues should be addressed by EU bioenergy policies, as well as proposing other possible objectives such as promoting energy security, promoting free trade and competition in the EU and developing advanced biofuels.

Questions are also asked about the perception of different bioenergies, including from crops, forestry products, wastes, sewage sludge, agricultural residues, algae, and different forms, such as heat energy, biofuels and liquids, biogas. Respondents are asked their opinion of the effectiveness of existing EU policies in addressing different bioenergy sustainability issues and proposals for policy objectives for EU bioenergy policies.

If you consider that nutrient stewardship should be integrated into EU bioenergy policies, why not respond to the consultation and indicate the importance of nutrient management in bioenergy policies, both resource efficiency and eutrophication limitation. Respond at *https://ec.europa.eu/energy/en/consultations/preparation-sustainable-bioenergy-policy-period-after-2020*

EU consultation on "Preparation of a sustainable bioenergy policy for the period after 2020" *https://ec.europa.eu/energy/en/consultations/preparation-sustainable-bioenergy-policy-period-after-2020* and questionnaire direct link *https://ec.europa.eu/eusurvey/runner/BioenergySurvey2016*

Sustainable diet: nutrition, health and environment

This paper presents a readable overview of health, economic and environmental implications of dietary choices and policies in Germany, including phosphorus use impacts of different food types. Benefits and constraints of moving towards vegetarian or vegan diet are assessed.

The declared objective is "strong" sustainability, that is **natural capital** is considered to be not substitutable by human capital.

The paper considers:

- **Efficiency**: efficiency in agriculture, food processing and disposal
- **Sufficiency in wastage**: food losses from farm to household
- **Sufficiency in consumption**: possibility to reduce food intake whilst ensuring a healthy diet
- **Substitution**: replacement in diets by foods which are less resource-intensive in production

Healthcare and environmental costs

Healthcare in Germany costs around 12% of GDP in 2011, up from 10% in 2000. In 2010, around **14% of the disease burden was estimated to be caused by unbalanced diets**, and 5% by alcohol consumption (DALYs = disability adjusted life years).

In Germany, nutrition (agriculture and food production) is estimated to contribute 95% of all ammonia emissions, 25% of greenhouse gas emissions, 15% of final energy consumption and 50% of land use.

The UN TEEB initiative (The Economics of Ecosystems and Biodiversity) estimated **global welfare loss caused by agriculture at 2.5 trillion US$, compared to only 2.1 trillion US$ income generated**.

Phosphorus consumption

A total phosphorus use of **552 000 tonnes P/year is associated with German food consumption, of which 440 000 tP is used in Germany and 111 000 tP abroad** (production of imported food, imported animal feeds). This is the amount of P applied in one year (2006) to agriculture to produce the food consumed in Germany, as mineral fertilizer and as sludges or manure, including P applied inland and abroad. Therefore partly recycled P is included in P from sludge/manure. The data used was from the national farms accounting data network (FADN), which is used to derive the average nutrient balances (for N, P, etc.). Thus, this does not take into account phosphorus lost upstream, e.g. in mining or fertiliser production.

Comparing the 24 different product groups considered in the study, phosphorus use, per kilogramme food, is identified as being

- **very high for beef and veal**;
- **high for other meat** (other than poultry and pork) and butter;
- **significant for poultry, pork and high fat dairy products**;
- lower for low fat dairy products, egg products, vegetable oils and margarine, sugar and spirits;
- very low for other food products (including nuts, grains, vegetables).

This pattern for phosphorus is similar for other impacts considered for the different food products (greenhouse gas emissions, ammonia emissions, land use, primary energy) except for **"blue" water which shows a very different pattern, with use for nuts and seeds much higher than for any other type of foodstuff**. Blue water is water which has been captured or in rivers or aquifers (that is, excluding rain falling directly on fields).

Trends and scenarios

The paper notes that **land use associated to German food consumption has dropped c. 12% over the two decades 1985 – 2006, mainly due to reduced consumption of beef and veal**. Blue water requirements on the other hand have increased.

Germany still shows a net land deficit of around 43 000 km^2, that is around 12% of Germany's total land area.

The paper notes that if current national dietary recommendations were respected (D-A-CH recommendation), that is excess calorie and nutrient unbalance corrected, and food waste reduced, then **Germany's land use "overshoot" could be avoided**.

A general national change to a vegetarian diet (ovo-lacto vegetarian, that is with consumption of eggs and milk products) would result in a significant freeing up of land use. Combined with food waste avoidance, the ovo-lacto vegetarian diet would reduce land use from nearly 2 400 m^2/person/year to just over 1 500 m^2 and a vegan diet to below 1 200 m^2.

The paper suggests that **dietary recommendations for vegetarian and vegan diets** be added to official dietary recommendations (German Nutrition Society DGE). Specific recommendations should be included for populations with particular needs (vitamin B_{12}, proteins, calcium), such as children, pregnant or nursing mothers, sick people).

The paper also recommends that **future Nutrition Surveys should additionally collect information relevant to the environmental impacts of nutrition**, including shopping habits, waste, kitchen equipment, self-sufficiency.

"Sustainable nutrition between the poles of health and environment. Potentials of altered diets and avoidable food losses", T. Meier, Universität Halle-Wittenberg, Institut der Agrar- und Ernährungswissenschaften toni.meier@landw.uni-halle.de

Ernahrungs Umschau 62(2): 22–33, 2015, DOI: 10.4455/eu.2015.005 http://www.nutrition-impacts.org/media/2015_Meier_englisch.pdf

See also: "Environmental Impacts of Dietary Recommendations and Dietary Styles: Germany As an Example", T. Meier, O. Christen

Environ. Sci. Technol 47 (2): 877–888, 2013, DOI: 10.1021/es302152v http://pubs.acs.org/doi/abs/10.1021/es302152v

Critical Raw Materials MSA

The European Commission has put onto its website a report by Deloitte (funded by DG GROW) on Critical Raw Material Material System Analysis (MSA), titled "Study on Data for a Raw Material System Analysis: Roadmap and Test of the Fully Operational MSA for Raw Materials".

The report covers 28 materials, including "phosphate rock" and the other materials currently on the EU Critical Raw Materials list (see SCOPE Newsletter n° 104). **The European Commission website does not state that the Commission validates the report**.

The report was commissioned by the European Commission from Deloitte (tender publication 9/6/2015 *https://etendering.ted.europa.eu/cft/cft-display.html?cftId=842* budget 400 000 €). Deloitte subcontracted the work on phosphorus to Charles University Prague, an institute with no significant published references on phosphorus. The 179 page

Deloitte report states as objectives **to develop a complete overview of data sources, a detailed methodology, *"a complete MSA for the 28 studied materials, with detailed data sources, assumptions"* and recommendations for maintenance and update**.

For phosphate rock the report includes two pages and a summary Sankey diagram (material flows).

The **data and sources justifying the figures in these two pages and in the diagram are not published** (to date). ESPP has emphasised, in our invited comments to the draft report, the importance of full transparency to enable stakeholder review.

Methodology and results rejected by experts

The report claims to be the "*first-ever EU-wide MSA*". For phosphorus, however, a more complete assessment using a different methodology was published in 2015 (Van Dijk et al., see SCOPE Newsletter 117). **This study was scientifically peer-reviewed**. It is not cited in the table of data used by Deloitte.

The Deloitte report states that, for phosphorus, "*the global results of this material [i.e. for P] have not been validated by experts*". The minutes of the stakeholder workshop 30th October 2014 confirm: "***Many experts warn about the scope of the study and the impossibility to establish a MSA for 22 materials with the methodology and planning described**. …Thus, there is a risk of sparing human and financial resources in a project which is likely to provide low quality results.*"

Since then, ESPP and others have provided comments underlining both errors in data and understanding, and fundamental incompatibility between the model applied and the real-world system of phosphorus flows and stocks. See on the ESPP website (under Downloads) our letter of 22/9/2016.

Model versus reality

The problems in the report are probably partly because Deloitte is **attempting to apply to (mainly biological) phosphorus flows a model designed for anthropogenic, industrial materials**, such as rare earth metals used in electronics. This model does not appear to fit for a biological nutrient element such as phosphorus.

As an example, Deloitte indicate that "*data on step manufacturing … reliability is lower for feed and food additives and detergents and other products where some coefficients found in literature must have been used … This required a lot of assumptions to be made on lifespan, dissipation rate and the rate of particular products kept by users after end of life*". Previous exchanges with Deloitte and Charles University failed to clarify why **"in use dissipation" coefficients of 74.19% (sic) were applied to detergents, animal feed phosphates and food additive phosphates**. It remains unclear what these "dissipation factors" are supposed to model, but it does seem unlikely that the dissipation will be the same for these three completely different applications and use routes. The text appears to confirm that these coefficients result from a model designed for industrial products such as electronics: e.g. **what is meant, for example, by detergents or food additives kept by users after end-of-life?**

The problems with the report and with the model applied may derive partly from the fact that **"Phosphate rock" is the specified EU Critical Raw Material, rather than the element phosphorus (P) in whatever form**, that is as phosphates, phosphorus, organic forms, etc. (see discussion in SCOPE Newsletter n° 104).

A fundamental problem in the Deloitte report is the treatment of biological flows of phosphorus. For example, in the first paragraph of the pages on phosphorus it is stated: "*Phosphate rock – besides organic sources as bone meal and guano – is the only source of phosphorus that is inevitable for modern agriculture*". **In reality however, the biggest volumes of P going into agriculture are in manure** (around 1 800 ktP/year, compared to only 1 500 ktP/year together for all of the sources cited by Deloitte).

Incorrect and un-useable results

Consequently, the figures given by Deloitte appear, as written, to be largely misleading or incorrect. For example (p101, Sankey diagram), Deloitte indicate total imports into the EU of c. 1 800 ktP/year whereas Van Dijk et al. (peer reviewed data) indicates c. 2 300 ktP/y, **a 30% difference**. On the other hand, the Deloitte figure for EU exported P (c. 261 ktP/y) is close to the Van Dijk figure (251 ktP/y).

In terms of generating information which could be of use for nutrient stewardship decision, **the Deloitte report does not appear to be a useful tool**. For example, accumulation of phosphorus in agricultural soils (which is largely not a loss but a form of storage, albeit an inefficient and possibly leaky storage) is aggregated with losses to surface waters (which are not only an irreversible loss but also widely environmentally damaging).

Deloitte estimate the flows of phosphorus in recycling at 180 ktP/y, stated to cover "*biogenic flows such as food and vegetal waste, manure and common sludge*". It is not clear by what is meant by "common sludge". This figure is misleading. Van Dijk estimates recycling from sewage sludge, food and vegetable waste and MBM (meat and bone meal) at 150-160 ktP/y but also **around 1 800 ktP/y manure P which is recycled back onto fields**.

The report also gives figures out of context. It is stated for example that c. 2 500 ktP are stored in landfills. However, **such a figure cannot support decision making** without specifying what type of landfills (e.g. municipal solid waste, industrial waste, steel slag), and consequently at what concentration / with what other chemicals, which is the information necessary to define whether recovery is conceivable and under what conditions (see e.g. Lederer et al. in SCOPE Newsletter n° 113 or Matsubae-Yokoyama et al. 2009 "A material flow analysis of phosphorus in Japan" *http://onlinelibrary.wiley.com/doi/10.1111/j.1530-9290.2009.00162.x/full* and SCOPE Newsletter n° 83).

Conclusion: the model must be reconsidered

ESPP considers that the current approach of MSA modelling addressing "phosphate rock" flows should be reconsidered and **phosphorus flows should be assessed taking an overall approach, including biological and organic nutrient flows** (in particular manures, sewage, food wastes). There should be two objectives:

(1) to provide properly useable, stakeholder validated and transparent (source referenced) **data to support updating of the consideration of phosphate rock (or phosphorus) as an EU Critical Raw Material**

(2) to provide nutrient **flow data appropriate for decision makers** (investments in recycling, policy decisions on nutrient stewardship), as proposed by the DONUTSS workshop September 2015, *http://phosphorusplatform.eu/donutss*.

"Study on Data for a Raw Material System Analysis: Roadmap and Test of the Fully Operational MSA for Raw Materials", Final Report, funded by the European Commission DG GROW, contract 30-CE-0612154/00-04, 19 November 2015 *https://ec.europa.eu/growth/tools-databases/msa/content/report-summaries*

Minutes of the DG GROW MSA stakeholder workshop 30th October 2014 https://ec.europa.eu/growth/tools-databases/msa/sites/default/files/reports/meetings/ENTR_MSA_Second_Expert_Workshop_Report.pdf

NL Presidency conference recommendations

Unwrapping the package, towards a circular economy in Europe, conference conclusions are put to Competitiveness Council by Netherlands.

Organised by the Netherlands Presidency of the European Union in cooperation with the European Commission, the stakeholder conference "***Unwrapping the package, towards a circular economy in Europe***" took place in Rotterdam 25th-26th January. The conference recommendations have been **submitted by the Netherlands Presidency to the EU Competitiveness Council of Ministers**, in the Presidency briefing published 15th February. The conference was attended by around 350 companies, stakeholders and policy makers from across Europe.

Stakeholders discussed challenges and opportunities for the circular economy in Europe based on concrete cases from the private sector in various Member States. The discussion addressed the need for national and EU policy to speed up the transition, and the question to what degree the European Commission Circular Economy Action plan offers sufficient support for this. Topics that received extra attention were **stimulating reuse and the market for secondary materials, public procurement, the Ecodesign directive, the role of natural capital, and measures to promote and support innovation**. Participants provided several recommendations on national and EU policies required to support and promote the Circular Economy, including:

- a **long-term focus and strong guidance** and ownership by the EU and Member States to ensure ambitions are translated into practice
- **consistency** in national approaches (**standards** i.e. for reparability, quality of recycling, etc.)
- the need for exchange of **best practices** and lessons learned by Member States and stakeholders for instance in adopting supporting **public procurement policies**
- more **financial incentives and market-based instruments** (tax, VAT, etc.) to stimulate reuse and the market for secondary resources.

Netherlands Presidency briefing to the Competitiveness Council (COMPET) of 29 February 2016 "Mainstreaming competitiveness - the circular economy package" http://data.consilium.europa.eu/doc/document/ST-6008-2016-INIT/en/pdf

Unwrapping the package, towards a circular economy in Europe https://ec.europa.eu/environment/ecoap/events/unwrapping-package-towards-circular-economy-europe_en

Biosolids management

Zurich announces industrial P-recovery pilot

The Canton of Zürich decided in 2007 to implement sewage sludge disposal valorizing both energy and phosphorus. After implementing the first key step, mono-incineration of all sewage sludge at one plant, the next step now announced is an industrial pilot to test a process to recover phosphoric acid from the sludge incineration ash.

In summer 2015, Zürich Canton inaugurated a new mono-incineration plant situated at **Werdhölzli sewage works, Zürich**. This new plant treats the sludge from all the canton's municipal sewage works, that is 100 000 tonnes of sewage sludge per year (wet weight, average water content of 30%). This sewage sludge contains more than 90% of the total phosphorus inflow into the canton's sewage works, that is around **800 t tonnes P/year**.

The Canton has evaluated phosphorus recovery processes available and supported the development of the **Leachphos process** for acid leaching of sewage sludge ash in 2012-2013 (see SCOPE Newsletter n° 108). The process is based on the **FLUWA hydrometallic leaching process**, using chemical leaching with sulphuric acid at ambient temperature to extract phosphorus and separate heavy metals. In previous tests, the phosphorus was then precipitated as calcium phosphate, so requiring alkali dosing. The Canton supported further development at foundation **ZAR (Zentrum für nachhaltige Abfall- und Ressourcennutzung** *www.zar-ch.ch*) to purify the leachate and further optimize the process and product qualities. In the year 2015 ZAR has further developed at laboratory scale together with **Técnicas Reunidas SA** an optimized process using a solvent extraction technology **to now produce a commercial grade phosphoric acid**.

This **3.3 million Swiss Franc industrial pi**lot will be jointly financed by the Canton and Técnicas Reunidas SA to prove the technical feasibility of the process and deliver financial data for a business plan. The capacity of the pilot plant to be built is not published. ZAR and Técnicas Reunidas SA will jointly pilot the purification process in 2016 and, if results are positive, the planning of a full-scale plant to treat sewage sludge ash of at least the canton Zurich will follow.

Canton of Zurich, "Urban Mining: federal decree obliges phosphorus recovery from sewage sludge", 18/2/2016: *https://www.zh.ch/internet/de/aktuell/news/medienmitteilungen/2016/urban-mining-regierungsrat-foerdert-rueckgewinnung-von-phosphor.html*

AWAL, "Production of phosphoric acid from sewage sludge is within reach", Jan. 2016: *http://www.awel.zh.ch/internet/baudirektion/awel/de/abfall_rohstoffe_altlasten/abfall/siedlungsabfaelle/klaerschlamm.html*

AquaEnviro Biosolids & Organic Resources Conference

The 20th European Biosolids and Organic Resources Conference and Exhibition, 10-11th of November 2015, Manchester, UK, organised by AquaEnviro and sponsored by Hach®, brought together over 200 delegates, speakers and exhibitors.

Summary prepared by Katrina Macintosh, Queen's University Belfast, with support from Andrew Gadd, Link2Energy

To mark the 20th anniversary of the Conference, AquaEnviro, organised a special event that recognised the contributions of delegates over the past two decades. The conference reviewed the **changing landscape of biosolids, from a period where they were regarded as merely a waste product requiring disposal, to present, where they are now considered a valuable resource for recovery and recycling**. This shift in paradigm has emanated from lessons learned in the past and how future issues of sustainability, and the need for a circular economy, is now a catalyst for positive change.

The conference showed **examples of best practice in biosolids management within Europe**. The development and application of innovative technologies always brings with it problems, which demand novel solutions. The conference offered contributions from experienced practitioners who have encountered problems and have now developed state-of-art solutions.

Technical sessions were held on the following areas:

- Thermal Hydrolysis Process
- Bioeconomy and Nutrient Recovery
- Anaerobic Digestion
- Dewatering and Drying
- Digestate and Biosolids
- Odour Control
- Sidestream Processes

The session on **'Bioeconomy and Nutrient Recovery'** opened with a presentation from **Amanda Ingram, Zero Waste Scotland,** on 'Scotland and the Bio-Economy'. Zero Waste Scotland was established to reduce wastage and add value to products, and is funded by the Scottish government to help advance their circular economy. A biological resources mapping exercise was conducted to establish the scale of biorefining in Scotland and innovative case studies were presented on biofuel development from whisky distillery residue and the use of potato waste to produce vodka. Scotland is due to publish its circular economy strategy later this year.

Phosphorus recycling

Francisco Simões, Cranfield Water Science Institute, investigated bio-mineralisation and struvite production in sludge dewatering liquors. A key finding from this laboratory-based research is the **use of the bacterium *Brevibacterium antiquum* in sludge liquors to produce struvite** for P recovery.

Ndam Edmond, Newcastle University, presented **nutrient recovery in anaerobic digesters to control downstream struvite formation** from a local sludge treatment centre in NE England, where an optimised combination of pH control and magnesium dosing appeared promising in struvite control and nutrient recovery optimisation. Furthermore, there also appeared to be **potential benefit to biogas yield** due to reduced toxicity to methanogens.

Derek Lycke, Ostara, discussed '**Wasstrip®** Optimisation at Slough Sewage Treatment Works' and the use of Ostara's Pearl® process to produce struvite. Wasstrip®, which stands for Waste Activated Sludge Stripping to Remove Internal Phosphorous, is a pre-digestion phosphorus process that releases phosphorus into the thickening liquor which then goes to the Pearl® unit. The process alleviates nuisance struvite production within the plant, **improves biogas production and sludge dewaterability**, and concentrates phosphorus in the Pearl® sidestream. The application of Wasstrip® with Pearl® can here double phosphorus recovery and the production of Crystal Green® struvite fertiliser product.

Rosanna Kleemann, University of Surrey and Thames Water, compared **phosphorus recovery from pyrolysis and incineration residues**. The research, between University of Surrey and Thames Water at laboratory scale, show benefits for replacement of incineration with pyrolysis in terms of increased energy and phosphorus recovery.

Bert Geraats, Eliquo Water and Energy, detailed recent upgrades at the Amersfoort wastewater treatment plant (WWTP) in the Netherlands, which has become a regional sludge processing hub for a number of WWTPs in the area. Upgrades include a combination of innovative energy and nutrient recovery technologies: **Wasstrip® reactor; LysoTherm® system; Ostara Pearl® 2000 reactor**; replacement of old combined heat and power units by three efficient 500 kW units and upgraded sludge processing equipment. Energy is recovered by the application of LysoTherm® thermal pressure hydrolysis technology which enables the plant to become energy positive. Phosphorus is also recovered, creating a valuable fertiliser product which will generate non-regulated revenue. Plant start up took place in 2015 and **expected payback is less than 10 years**. Visitors to the plant were warmly welcomed by the presenter.

Other topics covered in the session included:

- Phosphorus plant availability in sewage sludge and solubility analysis (**Bengt Hansen, Kemira**);
- Advances in the cultivation of micro-algae in urban wastewaters for sustainable biofuel production, wastewater treatment and the recovery of phosphorous (**Nirmala Khandan, New Mexico State University**);
- A comparison of biogas usage options - combined heat and power, turbine or gas to grid (**Martin Jolly, Black and Veatch**);
- From sludge to biosolids to organic fertilizers – Norway's experiences over the past 20 years resulting in the development of MINORGA® organic fertilisers with a consistency, particle size and balanced nutrient composition similar to those of mineral fertilisers (**Alan Whipps, Pell Frischmann**);
- Phosphorous recovery in a circular economy (**Andrew Godley, Ricardo Energy and Environment**).

UK Nutrient Platform project

The UK Nutrient Platform also hosted a session on Tuesday 10th November. The UK Nutrient Platform project is being funded by **BioRefine** (INTERREG IVB) with the aim to establish a cross-sector platform for all stakeholders with interests in sustainable nutrient use and recycling, nutrient management, security and environmental impact. **Andrew Ross and Miller Alonso Camargo-Valero, University of Leeds**, presented the BioREFINE project and a mass flow analysis for nitrogen and phosphorus in the UK.

Andrew Gadd, Link2Energy, then detailed **a 'road mapping exercise' used to shape the UK Nutrient Platform**. Andrew described how the workshops in Leeds, London and Edinburgh were held to engage with stakeholders and develop the framework and requirements for a nutrient platform within a UK context. Finally, **Malcolm Bailey, Link2Energy**, proposed to develop a **'Green Paper' to inform Government and other agencies** of the importance of a nutrient circular economy and how the UK Nutrient Platform can harness the interest and innovation shown by a wide spectrum of companies and other organisations in this area.

20th European Biosolids and Organic Resources Conference and Exhibition, 10-11th of November 2015, Manchester, UK
www.european-biosolids.com *and* www.aquaenviro.co.uk

Information about the UK Nutrient Platform project:
http://link2energy.co.uk/uk-nutrient-platform-september-2015

Health and environment

High diet phosphorus does not change blood parameters

A human trial carried out on 62 healthy adult volunteers in Germany shows that high diet P levels (with or without corresponding increases in diet calcium) do not result in increases in blood levels of phosphorus nor of relevant hormones, and do not modify blood levels of calcium, iron or magnesium. This suggests that higher phosphorus levels in diets do not pose a health risk.

The number of participants was defined to be sufficient given variation in parameters shown in similar literature studies and to enable reliable results after possible drop-out of volunteers during the trials.

The **risks related to increasing blood phosphorus levels are well known in sufferers of chronic kidney disease (CKD).** A number of epidemiological studies over recent years have reported a **statistical link between blood phosphorus concentrations (serum P) and higher risks of cardiovascular disease (CVD)** or general mortality in the general population, suggesting that there may also be a risk in healthy populations. This is supported by evidence in vitro, in particular showing that increased serum calcium and phosphorus concentrations can lead to calcium phosphate precipitation on smooth muscle cells, and so to **arterial calcification** (stiffening and obstruction).

The question is however raised as to whether increased levels of phosphorus in diets could pose health risks or increase risk of cardiovascular disease, or whether there is no cause-effect link (both the blood phosphorus and health risks may be caused by other factors, such as lifestyle or genetic susceptibility). Diet phosphorus could have either direct effects in the body, or indirect effects related to increases in hormones released by the body in reaction to phosphorus intake.

This study suggests that even a high increase in diet P intake (1 gP additional intake per day, compared to normal daily intake of 1 – 1.8 gP/day), for eight weeks, **does not in fact modify the blood phosphate concentration** (as measured in the morning before breakfast = "fasting"), because the kidneys remove the excess phosphorus.

The study also shows that **relevant hormone levels are also not modified**.

Phosphorus in diet

Higher phosphorus levels in Western diets can result from **higher intakes of meat and dairy products**, or from phosphate food additives (used as food preservatives, in processed foods, as substitutes to salt, in baking powders, or soft drinks …

This result in levels of P in the European diet estimated at an average 1 – 1.8 gP/day, compared to the **recommended minimum daily intake of 0.7 gP/day** (reference EFSA 2015).

Human trial

62 healthy volunteers (30 men and 32 women) were fed a placebo (no additional phosphorus or calcium) for two weeks, and were then randomly assigned to three groups fed **1 gP per day (as monosodium phosphate) combined with zero, 0.5 or 1 gCa (calcium) per day** (as calcium carbonate), in blind tests (products indistinguishable in sherbet), taken in 2 doses during the day, in addition to normal diet.

A range of chemical parameters (minerals, hormones, bone markers) were measured in blood serum/plasma (at fasting = morning before breakfast), urine and faeces, at start, after four and after eight weeks. Information about food consumption was also collected.

Fasting blood concentrations of phosphorus, calcium, magnesium and iron, but also of the two key hormones involved phosphorus homeostasis (controlling kidney phosphorus excretion) - FGF23 and PTH (parathyroid hormone) - were not modified after eight weeks.

The calcium intakes did, as expected, modify levels of bone metabolism markers in blood (osteocalcin, BAP bone specific alkaline phosphatase, CTX serum cross-linked C-terminal telopeptide), indicative of bone formation and resorption, whereas **the phosphorus supplementation alone did not significantly modify these marker levels**.

The results show significant increases in urine and faecal phosphorus, showing that **the increase in diet P is compensated by the body both by renal excretion and also by reduced uptake in the intestine**, possibly the latter being simply a result of phosphate mineral precipitation in the intestine.

Hormone levels unchanged after eight weeks

Parathyroid hormone (PTH) levels were unchanged after four and eight weeks of phosphorus dosage, at all levels of calcium intake. A small increase, well below pathological level, in the hormone FGF23 was apparent after four weeks but **this returned to normal after eight weeks**. The authors conclude that this hormone returns to normal after adaptation to the change in diet. Serum vitamin D - 1,25$(OH)_2$D – increased only in the 1 gP/0 gCa group, that is with a high P diet not balanced by an increase in calcium.

The fact that **the high P diet does not significantly or permanently modify levels of the hormones FGF23, PTH and vitamin D is important** because, as well as controlling P homeostasis, these hormones have other independent metabolic impacts.

Renal calcium and magnesium excretion were decreased in the 1 gP/0 gCa group, suggesting that an unbalanced phosphorus:calcium ratio in diet can impact metabolism of these minerals.

The authors conclude that the study results "***show clearly that additional intake of 1 gP per day did not influence fasting plasma phosphate concentrations of healthy adults after eight weeks of intervention***".

They suggest that it is likely that risks of mortality and cardiovascular disease correlated to serum phosphorus levels are the result of interactions with other factors, such as genetics or non-detected health issues (e.g. kidney problems).

This confirms the **opinion of EFSA** (European Food Safety Agency), 2015 see SCOPE Newsletter n°112 and 2013 see SCOPE Newsletter n°99, that no upper safety limit for phosphorus in diet is necessary and that there is no evidence of a link between diet phosphorus levels and CVD (cardiovascular disease).

The trial was registered with medical authorisation authorities and was funded by PAPA, the European Phosphoric Acid and Phosphate Producers Association.

"Consequences of a high phosphorus intake on mineral metabolism and bone remodeling in dependence of calcium intake in healthy subjects – a randomized placebo-controlled human intervention study", Nutrition Journal 15:7, 2016
http://dx.doi.org/10.1186/s12937-016-0125-5

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P release from mains water treatment

Phosphorus leakage out of mains (drinking) water pipes into the environment in the England and Wales was estimated, based on quantities of P used in water treatment and on data for water supply leakage. 1200 tonnes P/year was calculated to leak from mains water piping, of which 70% into surface waters.

Phosphorus is dosed at 700 – 1 900 µg P/l in over 95% of UK mains drinking water supply. It serves to reduce pipe corrosion, limit lead (plumbosolvency) and copper concentrations in tap water, and reduce iron and manganese precipitates which can deteriorate the aesthetic quality of drinking water.

Water company data were used to evaluate **mains water pipe leakage at a total of 3 245 million litres/day**. Road network maps (1 km grid), data on pipe age, pipe materials and information on soil corrosivity and shrink-swell compressibility (liable to deteriorate pipes) were used to estimate the spatial distribution of leakage.

This results in an **estimated total leakage (England and Wales) of 1 200 tonnes of phosphorus per year into the environment**.

Hotspots

Leakage is concentrated in urban areas, in particular around 30% of phosphorus leakages are estimated to be into the Thames river system in the London area. This is the result of the high leakage rate due to aging water mains and corrosive and compressible clay soils.

The **methodology developed is generic** and could be applied in other countries or to specific water basins or regions.

The authors also recently published a paper on the **isotopic fingerprint of phosphate in drinking water**. The oxygen isotope fingerprint for the phosphate molecule in phosphate dosed tap water is quantified. This isotopic fingerprint is a potentially powerful tool to trace sources of phosphate (including mains leakage) in the environment.

"Estimating the leakage contribution of phosphate dosed drinking water to environmental phosphorus pollution at the national-scale", Science of the Total Environment, in press 2016 http://dx.doi.org/10.1016/j.scitotenv.2015.12.121

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"Isotopic Fingerprint for Phosphorus in Drinking Water Supplies", Environ. Sci. Technol., 2015, 49 (15), pp 9020–9028, http://pubs.acs.org/doi/abs/10.1021/acs.est.5b01137 *and summary* http://www.bgs.ac.uk/research/groundwater/dating/phosphorusIsotopes.html

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Agriculture

Environmental impacts of livestock production

Agriculture is a major contributor to European society's environmental impacts. This paper assesses the part of agriculture's impact resulting from livestock production for nitrogen, sulphur, phosphorus, greenhouse gas emissions, land use, water eutrophication and biodiversity.

Livestock production currently occupies 65% of Europe's agricultural land (28% of total land surface). Livestock production contributes to five major environmental impacts:

- Ammonia and nitrogen oxide emissions, which contribute to formation of airborne particles and ozone. In Europe, ammonium emissions are estimated to account for 5 – 15 % of $PM_{2,5}$
- Greenhouse impacts, including emissions of methane, nitrous oxide and carbon dioxide, both related to fossil fuels consumption and to changes in land use
- Terrestrial biodiversity, both directly through land use and also via ammonia emissions (nitrogen deposition) and climate change
- Surface water quality, in particular eutrophication
- Soil acidification, through deposition of emitted sulphur dioxide, ammonia and nitrogen oxides

Agriculture is a major contributor to these different environmental impacts, ranging from c. 12% of total societal impact for climate change to nearly 60% for nitrogen losses to water.

CAPRI LCA

Impacts were estimated using an **extended LCA (Life Cycle Analysis) approach** as implemented in the CAPRI (Common Agricultural Policy Regionalised Impact) model. The LCA extension covers emissions upstream of agriculture and land use changes. The assessment takes into account both emissions inside Europe and outside Europe (production and transport of imported animal feed).

Emissions from feed imports, transports and land use change represent around 40% of the impacts of EU livestock production on global warming and around 10% of its impacts on air, soil and water (N) quality.

Water quality impacts

Total **diffuse nitrogen emissions** from EU agriculture were estimated at 6 TgN/y, of which 10% occur outside the EU. 73% of these emissions were related to livestock, mainly from animal feed production.

Total **diffuse phosphorus emissions** from EU agriculture were estimated at 0.025 TgP/y, plus an additional 0.003 TgP from weathering of agricultural soils. This covers dissolved inorganic phosphorus (DIP) only, whereas most losses from agricultural soils are probably as particulate phosphorus, so that these figures are a conservative estimate. Also, phosphorus losses from manure storage and feedlots are not taken into account.

As with nitrogen, **livestock is estimated to contribute 73% of EU agricultural phosphorus (DIP) losses.**

For the other environmental impacts considered (biodiversity, air quality, soil acidification and climate change), the contribution of livestock is estimated to be even higher, at around 80% of EU agriculture impacts

Overall, **livestock production is estimated to contribute 23 – 47% of total nitrogen loads to Europe's surface waters and 17 – 26% of total phosphorus loads to rivers**.

The authors conclude that although technical measures can reduce environmental impacts and emissions from livestock production, **significant reductions will require changes in dietary choices**.

"Impacts of European livestock production: nitrogen, sulphur, phosphorus and greenhouse gas emissions, land-use, water eutrophication and biodiversity", Environmental Research Letters, 10(2015) 115004 http://dx.doi.org/10.1088/1748-9326/10/11/115004

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Crop P efficiency: P-solubilising rhizobacteria

Five rhizobacterial strains were screened for P-solubilising and release of plant growth promoting (PGP) substances, then tested in 90-day maize greenhouse pot trials, using P-deficient soil with no P amendment, soluble phosphorus (mono potassium phosphate) and poorly soluble phosphate (TCP tricalcium phosphate). Bacteria surface dosing to pot soil enhanced plant tissue growth by up to +100% (2x) and increased P accumulation by maize. The growth increase appears to be related to PGP substances and not only P-solubilisation ability.

The bacterial strains were initially selected by testing *in vitro*, PGP substances production and ACC deaminase activity, cell wall degrading enzyme activity, solubilisation of P in solid medium and in liquid culture. The three best P-solubilising strains (of *Rhodococcus*, *Pseudomonas* and *Arthrobacter nicotinovorans*) were then used in the maize greenhouse tests.

The **greenhouse tests** used 3 seeds, reduced to 2 seedlings, in pots of 500 mg soil. The soil was phosphorus deficient (28 mg available P / kg). After 90 days, plants were harvested and analysed.

The bacteria were inoculated onto the maize pot soil surface, 2 days after seedling emergence, using 5 ml of suspension of c. 10^8 CFU/ml, obtained by overnight culture, centrifuging and resuspension in saline. Five bacterial treatments were tested (no bacteria, 3 different bacteria, mixture of the 3) for each of P treatments: no P amendment, soluble phosphorus, poorly soluble phosphate.

Phosphorus uptake

Without bacteria, the maize grown without P amendments or poorly soluble phosphate showed lower biomass production than with soluble P fertiliser. **Bacteria dosing significantly increased maize biomass production and increased P accumulation in maize shoots and roots for all phosphorus treatments** (no P, poorly soluble P, soluble P).

The different bacterial strains however had different relative impacts depending on phosphorus treatment, and between maize shoots and roots.

The **bacteria inoculated were in all cases detected in the maize rhizosphere (near the roots in the pots)** after 45 days, but were not detected (by the DGGE method used) after 90 days.

The authors conclude that **bacteria (biofertilisers or bioinoculants) can significantly improve crop growth, both by increased phosphorus uptake** (of both readily available and non-plant available phosphorus) but also by the **release of other substances which stimulate plant growth (PGPs)** and that the bacteria can remain present and active in soils for significant periods of time (here 45 days).

"Phosphate-solubilizing rhizobacteria enhance Zea mays growth in agricultural P-deficient soils", Ecological Engineering 73 (2014) 526–535 http://dx.doi.org/10.1016/j.ecoleng.2014.09.060

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Phosphorus recycling

P-recovery: update on technologies and implementation

A paper by Christian Kabbe et al. at IFS (International Fertiliser Society) Conference, June 2015, updates information on current development status of P-recovery from wastewater, technologies and potential for widespread implementation, building on the knowledge developed in the P-REX project (see SCOPE Newsletter n° 115).

The paper outlines the context and motivations for **phosphorus recycling from municipal wastewaters**, and **lists nearly 50 P-recovery installations operational or under construction in Europe**. Key processes and technologies are presented and key challenges to widespread implementation are identified.

Processes presented are:

P-recovery from liquors in sewage works (aqueous phase)

- **Phosphate precipitation**: processes operational full-scale in a number of sewage works today precipitate struvite (magnesium ammonium phosphate) either upstream or downstream of sludge dewatering, e.g. using AirPrex, NuReSys (SCOPE Newsletter 115) or Ostara (SCOPE Newsletter 99) technologies. In biological nutrient removal plants (EPBR), this can result in significant operating cost savings in improved sludge dewatering and avoidance of problematic deposits, scaling or abrasion in centrifuges
- **Enhanced disintegration of (biological nutrient removal) sewage sludge before or combined with anaerobic digestion**. This releases P to a soluble form so that higher recovery rates can be achieved by phosphate precipitation, and also improves methane production. Processes include thermal hydrolysis (e.g. CAMBI, ELIQUO STULZ, EXELYS) or thermo-chemical hydrolysis (e.g. PONDUS)

Leaching of sewage sludge after dewatering (including from plants operating chemical P-removal, that is, with a significant proportion of the phosphorus bound to iron or aluminium):

- **Gifhorn** (Seaborne) and **Stuttgart** processes, both operating or tested in full-scale pilots: using sulphuric acid and sodium hydroxide to achieve pH 3-5 then pH 8.5 – 10. The more extreme pHs result in high operating costs but ensure relatively high levels of phosphorus recovery
- **Budenheim process** (see SCOPE Newsletter 103), currently at the pilot scale, using compressed CO_2 at ambient temperature to extract orthophosphate, which can be recovered as different possible phosphate products (e.g. DCP Di Calcium Phosphate). Pilot plants are currently planned in Mainz and Itzehoe, Germany

P-recovery from sewage sludge incineration ash (SSIA). This is **only considered feasible with current know-how if sewage sludge is "mono-incinerated",** that is not mixed with low-P wastes (industrial sludges, municipal solid refuse)

- **Use in the fertiliser industry**: use as a fertiliser manufacture raw material, input into the acidification/acid phase of production, so mobilising the phosphorus in the ash (e.g. ICL Fertilisers, see SCOPE Newsletter 115)
- **Use in EcoPhos** process to produce high-grade DCP or phosphoric acid (see SCOPE Newsletter 111)
- **Remondis Aqua TetraPhos** process (pilot operational Hamburg)
- **Mephrec** metallurgical process (Ingetec): operating in a furnace at temperatures above 1450°C, this produces a silicate-phosphate "slag" (similar to Thomas Phosphate"). SCOPE Editor's Note: the use of this P-slag remains to be demonstrated, as tests did not indicate plant availability of the phosphorus (SCOPE Newsletter 115)
- **Ashdec (Outotec)** thermos-chemical process: operating at 900 – 1 000°C using Na_2SO_4 or $MgCL_2$ to remove heavy metals. The chloride path offers better heavy metal removal, whereas the reducing path (Na_2SO_4) results in good plant availability of the recovered phosphates. This process is under optimisation, possibly with integration with modern sewage sludge incinerators to enable high energy efficiency.
- **LeachPhos (BSH):** sulphuric acid extraction then alkali pH increase to precipitate phosphates, resulting in a mixed precipitate of iron, aluminium and calcium phosphates.

In many of the processes above, **the fate of input phosphorus bound to aluminium or iron (in particular as a result of coagulant use in sewage works) is unclear**: potential for useful recovery, plant availability in recovered material ?

The paper summarises the **Life Cycle Assessment of different P-recovery processes** carried out in the P-REX project (SCOPE Newsletter 111) *http://p-rex.eu/* noting that the objective of achieving high phosphorus recovery rates often conflicts with energy or chemical use efficiency. Energy efficiency can be improved by integrating thermal processes into existing ash treatment facilities.

The following issues are identified as challenges or **barriers to widespread implementation** of phosphorus recovery from wastewaters:

- **Low market prices of phosphate rock**
- **Complexity of technologies** developed in R&D projects, not readily compatible with potential users and value chains
- Recovered products which are **difficult to integrate into existing logistics and infrastructures**. Processes which are versatile as to input material and can produce products adapted to industry use (e.g. phosphoric acid or white phosphorus P_4) have advantages.
- **Regulatory framework** which is not adapted to recycled products, and which only evolves slowly to enable their production and sale
- **Need for full-scale demonstration plants** addressing the already-accessible recycling opportunities, for example in Germany six existing large mono-incineration plants

The authors suggest that, in addition to removing regulatory obstacles and ensuring a level playing field between rock phosphate based and recycled fertilisers, **P-recovery targets must be developed to support implementation and to move towards a circular economy for phosphorus.**

There is also a **need for reliable data** on phosphorus flows in different wastewater streams taking into account regional contexts.

"Review of promising methods for phosphorus recovery and recycling from wastewater", International Fertiliser Society, Proceedings 763, presented at the IFS Conference, London, 23rd June 2015 http://fertiliser-society.org/Proceedings/US/Prc763.HTM

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Pig manure: Quick wash P-recovery

The QuickWash P-recovery process was presented in SCOPE Newsletter n°78 and uses acid to partially solubilise P in pig manure, followed by calcium phosphate precipitation improved by dosing flocculants. This paper presents further work testing use of organic acid and an anionic organic polymer flocculant (polyacramide PAM).

The tests presented in SCOPE Newsletter n° 78 used pilot scale reactors (**370 and 60 litres**), whereas this new work is laboratory scale (1-2 litres) and was aimed at **testing different acids and extraction pHs**

Only as minority (generally around 1/3) of phosphorus in raw pig manure is soluble, and so available for precipitation processes for P-recovery. On the other hand the P:N ratio (about 1:2) in pig manure is around twice as high as plant needs, so that **excess phosphorus limits efficient land application and crop utilization**.

The **QuickWash process** consists of three steps

- **Solubilisation** of phosphorus using acid at pH 3-5. Here citric acid and hydrochloric acid were tested. Solid is then separated from the acid liquid by settling.
- **Precipitation** of calcium phosphate from the acid solution by increasing pH to 8-10 by lime dosing, recovery by settling
- **Dosing of anionic polymer** (at c. 7 mg/l) to enhance settling and recovery of the precipitated calcium phosphate.

Process generated products

This gives three products:

- **Separated manure solids**, containing organic carbon, nitrogen and some residual phosphorus, with a P:N ratio better adapted to crop production (below 1:2 and as low as 1:1.1)
- **Recovered calcium phosphate**, which can be simply dried by leaving to stand and drain, giving a stable, transportable fertiliser product (see summary of pot trials in SCOPE 78)
- A **stabilized liquid fraction** containing nitrogen but only very low levels of phosphorus, which can be used on-farm as a liquid fertiliser

The process was tested at lab scale on samples from two pig farms: one sample was collected from a farrow to finish farm in South Carolina (US) that used an open gutter and flushing system to handle the manure. The second sample was collected from a barn with a flush system under a slated floor in North Carolina (US). Both samples had relatively high solids contents of respectively 21,3% and 30% dry matter. The first sample contained 37,8 g TN/kg dry matter and 18,2 g TP/kg sample (4,2% as P2O5). The second sample contained 33,1 g TN/kg dry matter and 23,7 g TP/kg sample (5,2% as P2O5).

The results show that **the use of an organic acid is a more rate effective and less corrosive option**. The quick wash process showed to be effective in selectively extracting P, leaving a significant fraction of N in the washed solid residue. **The P precipitation in step three was significantly enhanced by addition of anionic PAM**, precipitating 96-99% of the total P from the acid liquid extracts at pH 8 to 9 (compared to only 26-32% P-recovery without anionic PAM).

The optimum conditions were 10 mmol/L citric acid for P extraction, lime addition to reach pH 8,0, and anionic PAM addition for enhanced recovery of P.

The amount of P recovered from one metric ton of pig manure (26-31% dry matter. containing 9.9 kg N and 16.3 kg P2O5) using the quick wash process would be around 13.0 kg P2O5 with **fertilizer value of US$22.4** (US$1.7 per kg of P2O5). With a total chemical cost of US$11.9 per ton of treated pig manure (citric acid, lime and anionic polymer), the net benefit would be US$10.5 per ton.

As an additional benefit, a total of around 6.9 kg N (US$1.4 per kg of N) and 3.3 kg P2O5 at an equivalent value of US$15.5 per ton of processed manure solids remain on-farm as crop fertilizer. Cost for capital, energy and labor are however not included in this calculation.

"Phosphorus recovery from pig manure solids prior to land application." Journal of environmental management 157 (2015): 1-7 http://dx.doi.org/10.1016/j.jenvman.2015.04.010

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Canada: Greenhouse waste water

Lime was used to precipitate calcium phosphate from greenhouse wastewater and the precipitate was flocculated with biodegradable flocculants to improve solid separation by settling. The use of biodegradable flocculants improves the perspective for the use of the recovered solids as a fertiliser.

The seasonal **concentration of phosphorous (P) in greenhouse wastewater range typically 30-60 mg P-PO_4/l but can be as high as 370 mg.** Other nutrients (nitrogen, potassium, etc.) and micronutrients can also be highly concentrated. Ontario state legislation limits the total P discharges in surface water to 1 mg P_{total} /l. Unlike nitrogen, wetlands, which are currently used for greenhouse wastewater treatment systems in North America, cannot effectively reduce P. The use of lime to precipitate P is efficient and well known, but the complexation of fine calcium phosphate particles with organics generally limits the separation process. The use of biodegradable flocculants is a promising route to enable use of the recovered phosphate solids as fertiliser.

Experimental set-up

The authors tested powder hydrate lime with three different **biodegradable flocculants** (chitosan 13 USD kg^{-1}, guar gum 3.5 USD kg^{-1} and cationic starch 0.6 USD kg^{-1}) in low (78 mg/l $CaCO_3$) and high (tap water 200 mg/l $CaCO_3$) alkalinity simulated greenhouse wastewater (100 mg/l PO_4-P), and in real vegetable (Pepper and Eggplant), Begonia and Campanula greenhouse wastewater (51 and 13 mg/l PO_4-P, respectively). While the alkalinity for vegetable wastewater was 42 mg/l $CaCO_3$, for Campanula wastewater it was nil. All the greenhouse wastewaters contained very low visible organic matter (low turbidity), which is typical of greenhouse wastewaters. The lab scale experiment was performed in triplicate by adding lime in 0.5 l of wastewater sample, obtaining a final pH of 9.5 for simulated wastewater and 9 for real greenhouse wastewater. Respectively, the lime:P molar ratio obtained was 0.7 and 1.3 for the low and high alkalinity simulated wastewater, and 1.3 and 1.4 for vegetable and campanula real greenhouse wastewater. The P removal rate was determined by measuring the higher supernatant composition for each test after 2, 10, 30 and 60 min.

Precipitation/Flocculation effectiveness

The flocculation experiments showed that the **addition of guar gum and cationic starch improved the precipitation of the produced calcium phosphate** by reducing the settling time and the P concentration in the effluent. For very low alkalinity greenhouse wastewater, such as the studied Campanula case, addition of flocculant was not successful due to the formation of slow settling precipitates. Chitosan did not show an improvement in precipitation for the tested wastewater. This is probably due to the high pH that eliminates the cationic character of the amino groups in chitosan and reduces the solubility.

In all cases with low alkalinity simulated wastewater, the target discharge concentration of 1 mgP/l was achieved. This was also achieved using 12 mg/l guar gum or 24 mg/l cationic starch for the high alkalinity simulated wastewater and for the vegetable greenhouse wastewater, but not for the campanula greenhouse wastewater.

Recovered nutrient product

Elemental analysis on the recovered Ca-P complex from vegetable greenhouse wastewater showed a P content of 5.7% and high levels of K (5.3%) and Mg (5.8%). **The high Mg and K content is probably related to K and Mg-struvite** since the Ca:P molar ratio was only 1.25, which is lower than the theoretical molar ratio for amorphous calcium phosphate (1.5).

More than 90% of the P could be extracted with citric acid, **suggesting applicability of the precipitate for fertiliser applications**.

Cost assessment

The chemical costs of the process for vegetable and campanula greenhouse wastewater treatment **were 0.16 and 0.07 USD/m^3, respectively, when guar gum was used as flocculant**. However, research at full-scale would be necessary for a proper financial and logistical evaluation of the process. Issues that would require more evaluation are for example the **dewatering of the precipitate and possible degradation of the biodegradable flocculent during dosing and storage**.

Also regulatory issues are important since **this process increases the pH of the waste water to values above pH limits for discharge of waste water (pH 9.5 in Ontario).** Reduction of the pH to meet legal limits may add further costs to the process. The authors describe that also the use of the recovered product presents a challenge as the volume is low and the product will have a variable composition. Therefore the main driver for recovery is P removal and any use value of the recovered product is an additional benefit.

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"Combined Precipitation/Flocculation for nutrient recovery from greenhouse wastewater", HortScience, 2015. 50(6): p. 921-926
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http://www.tandfonline.com/doi/abs/10.1080/09593330.2014.924567

Also: S. Dunets, Y. Zheng, M. Dixon, 2015 "Use of phosphorus-sorbing materials to remove phosphate from greenhouse wastewater" Environmental Technology. 36: 1759–1770
http://www.tandfonline.com/doi/abs/10.1080/09593330.2015.1009497

Brine shrimp eggs -magnesium hydroxide adsorbent for P-recovery

The authors studied a novel hybrid material for P-recycling, based on *Artemia* egg shell as supporting material for $Mg(OH)_2$ immobilization.

Adsorption is a widely used basic operation for phosphorus recovery from waters. Many inorganic materials, like $Mg(OH)_2$-based adsorbents, may have high surface area/active sites ratios and high selectivity, but cannot be used in fixed bed or suspension based systems because of the fineness of the material leads to either high bed resistances or difficult solid/liquid separations. A good design of hybrid adsorbents (substances immobilized onto porous matrices) can help to overcome these limitations. However, during regeneration, their stability is not always ensured and large amounts of alkaline solution are needed to remove all the adsorbate. Those drawbacks could be solved if the porous matrix allowed the loaded adsorbent to be applied directly, for example as slow release phosphate fertilizer.

$Mg(OH)_2$-based adsorbents can be used for phosphate removal from waters due to high surface area/active sites ratio and high selectivity.

Artemia larvae

The nauplii (larvae) of the brine shrimp *Artemia* are used as fishing bait or as fish food in aquaculture, **with c. 180 000 tonnes/year cultivated worldwide**, and **the egg shells are discarded as waste material** after collection.

Important characteristics make these egg shells very attractive for hybrid adsorbent synthesis: (1) the shells are **chemically stable**, (2) they exhibit a very special 3D **porous structure** that allows a fast kinetic phosphate adsorption and slow phosphate release behaviour, (3) they are **biocompatible** containing mainly chitosan or chitin, calcium and ferric compounds, (4) they are **biodegradable** and (5) they are **relatively cheap** (discarded).

Preparation of the hybrid adsorbent

5 g of *Artemia* shells were submerged in Mg precursor solution ($MgNO_3$, 1M) for 4 h. Ultrasound is applied in this step. The solution is then agitated for 20 h at 25ºC. **The adsorption process is fast and takes place between NH_2-groups in the egg shells and Mg^{2+} from solution.** After filtration, the resulting *Artemia*/Mg^{2+} is submerged in NaOH solution (1% mass fraction) for 16 h, then dried at 60 °C under anoxic conditions for nano-$Mg(OH)_2$ immobilization.

Phosphate sorption behaviour

Phosphate adsorption equilibrium experiments are carried by the classical bottle-point method with 0.4 g of hybrid adsorbent in 50 mL of different concentrations of KH_2PO_4 solutions, stirred for 2h at 20ºC. pH was adjusted using NaOH or HNO_3. Adsorbent selectivity was tested using different concentration of Cl^-, NO_3^{2-}, HCO_3^- and humic acids. Adsorption kinetics were also tested over time.

Results show that phosphate adsorption is pH-dependent, with a relatively broad optimum range of pH 4 – 10. At pH above 11, adsorption is hindered for anionic substances (like phosphates) by electrostatic repulsion forces due to the presence of MgO^- groups on the adsorbent. Phosphate adsorption also decreases below pH 3. Adsorption efficiencies decreased to 40%-60% in the presence of competing anions like Cl^-, NO_3^{2-}, HCO_3^- and humic acids.

The Redligh-Peterson model adsorption equilibrium models fitted best the experimental data suggesting multilayer heterogeneous sorption of phosphates onto the nano-$Mg(OH)_2$ structure. The maximum adsorption capacity would be 32.7 $mg \cdot g^{-1}$ according to the Langmuir model.

Slow-release phosphate fertiliser

Phosphate availability in soil of the *Artemia* shell–Mg–P complex, tested by the Mehlich3 extraction method, was c. 69 mg P/kg adsorbent. This P content is higher than considered necessary for slow release fertilizers (45-50 mg P/kg). Phosphate release experiments in solution showed that the process is pH-dependent. From experiments in distilled water it emerged that desorption is fast (2 h), while the release equilibrium in slightly acid, neutral or alkaline solutions can take up to 4 days. In release experiments with real soil (soil conditions not specified) phosphorus from the *Artemia* shell-Mg-P complex continued being released after 30 days, whereas P from KH_2PO_4 was rapidly exhausted.

Artemia shell-Mg-P adsorbent also was tested in real **seedling growth experiments**. Mung bean seeds were exposed during 15 days to the loaded adsorbent containing P and to *Artemia* egg shells only. The *Artemia* shell-Mg-P complex resulted in an average seedling length of 12.4 cm as compared to 8.5 cm for *Artemia* shell only, indicating that the adsorbent may be used as a slow release fertiliser Mg and P source.

"Efficient Phosphate Sequestration in Waters by the Unique Hierarchical 3D Artemia Egg Shell Supported Nano-Mg(OH)2 Composite and Sequenced Potential Application in Slow Release Fertilizer", ACS Sustainable Chemistry & Engineering, 2015, 3(10): p. 2496-2503 DOI: 10.1021/acssuschemeng.5b00594

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