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Phosphate resources and uses

3rd Sustainable Phosphorus Summit

Developing a blueprint for global phosphorus security

Around 115 participants from across the world, mainly from research institutes and industry, exchanged ideas about phosphorus stewardship and collated suggestions for policy objectives, actions and research at the 3rd Sustainable Phosphorus Summit, Sydney, end February 2012.

Phosphorus flows

Europe P balance

Phosphorus imports, exports and uses

A substance flow analysis for phosphorus in Europe (EU-15) is developed, showing consumption of 4.7 kgP/year/person of which only 1.2 kg reaches the consumer

Switzerland

Agricultural nutrient balances

N, P and K nutrient balances are calculated for Swiss agriculture, assessing the efficiency of nutrient use in farming, changes from 1975 to 2008, with proposals for improving farm nutrient use.

P-recycling from urine

Nepal

Struvite recovery from urine

Struvite precipitation is a simple technology to recover phosphorus from source-separated urine. The cost of magnesium salts can, however, be a significant obstacle to financially sustainable production. Bittern, calcined magnesite rock, and wood ash were tested as possible low-cost sources of magnesium.

Vietnam (I)

Solar nutrient recovery from urine

Solar evaporation was tested to produce a solid fertiliser from source-separated urine. Prior acidification to improve nitrogen recovery was assessed. Fate of micro-contaminants needs to be further studied.

Vietnam (II)

Struvite and ammonium sulphate from urine

Source separated urine was treated to recover phosphorus as struvite and nitrogen by ammonia stripping then ammonium sulphate recovery.

Biological nutrient removal

Sludge fermentation and P-recovery

Experimental comparison of biological P removal performance with and without struvite precipitation from VFA-producing sludge fermenter.

Struvite precipitation

Struvite precipitation

Innovative 2-section seeded aerated struvite reactor

Laboratory experiments show that seeding significantly improves struvite precipitation from pure solutions. A 3 litre experimental reactor with an aerated column surrounded by a sedimentation zone was developed and tested using pure solutions.

Recovered phosphates as fertilisers

2-year pot trials

Fertiliser value of recovered phosphates

The effectiveness of eight different phosphate products recovered from wastewater and thermal processes was compared to commercial TSP fertiliser in 2-year maize pot trials at acidic and near-neutral soil pH.

Conference

Harbin, China, 23-25 September 2012

3rd IWA Nutrient Removal and Recovery 2012

International Water Association conference on nutrient removal in sewage works, with sessions on phosphorus recovery and low carbon nutrient recovery.
<http://www.iwanrr2012.org>

3rd Sustainable Phosphorus Summit

Developing a blueprint for global phosphorus security

Around 115 participants from across the world, mainly from research institutes and industry, exchanged ideas about phosphorus stewardship and collated suggestions for policy objectives, actions and research at the 3rd Sustainable Phosphorus Summit, Sydney, end February 2012.

The first two ‘Sustainable Phosphorus Summits’ took place in Linköping Sweden in 2010 and in Arizona USA in 2011. The 3rd Summit was an initiative of the GPRI (Global Phosphorus Research Institute), a network of several research institutes aiming to develop research into phosphorus security for the future and awareness of phosphorus scarcity issues and solutions.

The objective of the 3rd Sustainable Summit was to bring together interested parties to exchange ideas and collate suggestions for policy and action, and to develop a “**blueprint for global phosphorus security**”. This document, drafted on the basis of participants’ ideas at the conference, aims to present a some visions for future phosphorus security and identify possible strategies, actions and roles of different actors to move this forward.

Participants at the conference were researchers and NGOs, and from the water industry and farming. Most participants were from developed countries, and the Summit organisers recognised the need to extend coverage to developing countries.

The Summit was based on an Expert Panel debate, short soapbox-style presentations by accepted speakers and more participative methods to collect ideas from participants, discussing and debating these in small groups, and synthesizing the resulting content into the proposed “Blueprint”.

Peak-P or P-stewardship ?

The Summit announced as its basic tenet that “**global phosphorus scarcity is likely to threaten the world’s ability to produce food in the future**”, but this was challenged by a number of participants who considered that **significant new**

phosphate rock reserves are now being found and exploited, in response to the 2008 supply shortages and price peak.

Most participants did however agree that phosphorus is **likely to become more expensive in the future and face geopolitical source concentrations**, leading to price fluctuations and supply and accessibility risks. Phosphorus scarcity should not be considered as only a question of quantities of reserves or supply compared to demand, but should take into account these other important dimensions of sustainable and secure access to phosphorus. .

Phosphorus stewardship offers important synergies with other sustainability issues, including management of other nutrients, local/regional resource security, materials recycling, waste and water treatment improvements.

Complex, locally-specific messages

Messages concerning phosphorus stewardship are therefore much more complex than P-scarcity or “Peak P”, and must **place phosphorus management as one facet of sustainability**.

Also, **issues are very different depending on local or regional situations**. Developed countries need to reduce phosphorus loss or profligacy (in agriculture, food wastes, high protein diets) and develop phosphorus recovery and recycling, whereas many developing countries face a phosphorus shortage, with soils chronically under-fertilised (particularly in Africa) or poor farmers unable to purchase fertiliser, thus preventing adequate food production.



Illustration showing which words came up most in Summit participants’ ideas and contributions. (generated using <http://www.wordle.net/>).

Visions

The Summit suggested the following ideas as some of the “**key visions for a sustainable phosphorus future**”:

- Consider P as a systemic part of sustainability, alongside other nutrients
- Global equity of access to P, global planning and governance to achieve this
- Local opportunities for P stewardship
- Improving efficiency of P use, developing P recycling
- Better information, knowledge-transfer, communication of the multi-faceted, complex nature of the phosphate resource issue and phosphorus stewardship

Actions

The Summit’s creative thinking process generated a wide range of proposed actions to improve phosphorus stewardship, ranging from general policies to specific proposals for certain sectors.

Many participants agreed that there is a need for a **global governance of phosphorus**, whilst recognising that there is no precedent for world government of any resource. Such global governance could be integrated into existing structures, both as a realistic way forward, and to address phosphorus within overall sustainability and development approaches.

Other key areas of action identified by the Summit included:

- **Improving the efficiency of phosphorus use in agriculture and the food cycle**, including addressing over-concentration of livestock production, food waste, diet
- **Developing P-recycling**, such as reuse of biosolids, P-recovery technologies in centralised sewage systems, from livestock manures and from decentralised human waste treatment or urine
- **Promoting exchanges between different stakeholders** and concerned industries: phosphate industries, agriculture, food industries, consumers ...
- **Coordinating research**
- **Informing farmers, decision makers, the public**

- **Developing local food production** and nutrient recycling where appropriate

Blueprint

The “**Blueprint for global phosphorus security**”, drafted by the Summit organisers on the basis of the participants’ collated ideas, will be circulated to all participants for comments and finalisation. Individuals and organisations will then be invited to sign this statement prior to its’ launch via the Summit website, the Global Phosphorus Network and media channels.

4th Sustainable Phosphorus Summit 2014

The next (4th) Sustainable Phosphorus Summit was announced for **Montpellier, France, in the period 25th August – 3rd September 2014** (exact dates to be defined). Hosted by INRA (France’s Agricultural Research Institute), this 4th Summit will be held just after the 5th International Symposium on Phosphorus in the Plant-Soil Continuum and will aim to involve developing countries (for whom some travel grants should be available).

1st Sustainable Phosphorus Summit, Linköping Sweden,
<http://www.ep.liu.se/ecp/053/ecp10053.pdf>

2nd Sustainable Phosphorus Summit, Arizona
<http://sols.asu.edu/frontiers/2011/index.php>

This 2nd Summit led to the preparation of a book “Phosphorus, Food, and Our Future” (Oxford University Press), to be published shortly.

3rd Sustainable Phosphorus Summit, Sydney, Australia 29th Feb. – 2nd March 2012 <http://sustainablephosphorussummit.net/>

Phosphorus flows

Europe P balance

Phosphorus imports, exports and uses

This study aims to complement existing regional or country-level phosphorus balance studies and global phosphorus resource studies with a substance flow analysis carried out at the level of the 15 member states of the “old” European Union (EU-15), taking into account modelling of data uncertainty. The system model uses 10 compartments, with waste management and agriculture compartments having specific sub-models, and 35 different flow routes.

Data was collected from a range of official sources (OECD, International Fertiliser Association, EU,

USGS, FAO ...), using an average of three years' data, and levels of uncertainty were allocated depending on estimated reliability, on whether the data was specifically available for the EU-15 region or was estimated from data for other geographical areas, etc.

Imported phosphorus

Phosphorus is imported into the EU principally as fertilisers (triple super phosphate, di ammonium phosphate, mono ammonium phosphate), phosphate rock and industrial phosphoric acid = 1480 million tonnes (Mt) P/year (net of exports), with smaller imports in food and animal feed products and other imports (255 MtP/y net of exports). **Total net import is thus around 4.4 kgP/person/year.** Imports have however fallen by nearly 50% over the decade to 2008.

Phosphorus use and waste management

Agricultural phosphorus substance flow is estimated from official statistics, combined with literature data on manure nutrient flows, agronomic processes, phosphorus content of crops, etc.

Household phosphorus use is estimated from figures for phosphorus in detergents, human food and diet P-content. Household P discharge and fate of discharge is estimated from figures on municipal wastewater treatment connection and performance, estimates of sewage loss to groundwater, data on septic tanks.

P flows in various industry wastes (food processing industry, animal wastes, food service activities ...) are estimated, and P flow routes in different waste processing and disposal routes are considered, in particular the agricultural reuse of sewage and other sludges after digestion, composting, etc.

The largest annual flows of P in agriculture are **livestock manure to soil** (c. 4 kgP/person/y), **fodder imported or produced on farms and fed to livestock** (c. 2.6 and c. 2.3 respectively) **fertiliser application to soil** (c. 2.7).

P leaving the agricultural system in products is estimated as 3.1 kgP/person/year in plant products, meat, milk and eggs. Of this production plus imported foods, **only c. 1.2 kgP/person/year actually reaches the final consumer.**

P loss, accumulation and recycling

The principal destination of non-consumed phosphorus in the EU-15 is soil accumulation (c. 2.9 kg/person/year), followed by landfilling of sewage sludge incineration ash and industry and domestic refuse (1.4 kgP), with a lower level of loss to waters

(0.55 kg). Only 0.77 kgP/person/year are recycled (this does not include animal manure returning to farmland).

The authors conclude that Europe is currently highly dependent on imported phosphorus, and that optimisation of phosphorus fertilisation in agriculture and recycling of phosphorus from P-rich waste streams, including improving connection and more widespread phosphorus removal in municipal sewage works, could significantly reduce this import dependency.

"The European phosphorus balance", Resources, Conservation and Recycling 60 (2012), pages 159–172
www.elsevier.com/locate/resconrec

C. Ott, H. Rechberger, Vienna University of Technology, Institute for Water Quality, Resources and Waste Management, Karlsplatz 13/226, 1040 Vienna, Austria
office@iwa.tuwien.ac.at christian.ott@tuwien.ac.at
<http://iwr.tuwien.ac.at/>

Switzerland

Agricultural nutrient balances

The farm-gate balance method, as defined by OSPAR, is used to calculate mass flow balances for nitrogen (N), phosphorus (P) and potassium (K) for the agricultural system of Switzerland. This method assesses total inputs into agriculture (fertilisers, other intrans) and total exports from farming (in agricultural products). This is considered to be more accurate than the soil surface balance approach (used by OECD), based on data on nutrient inputs to soil and on nutrients leaving the soil, because this method does not accurately link grass production to manure produced from grass and fodder consuming animals.

Data on intrans and products was collected from the Swiss Farmers Union and foreign trade statistics, multiplied by standard nutrient contents figures. **Grassland occupies nearly 70% of Swiss farmland**, and so calculations of grass production and biological nitrogen fixation (by clovers in widespread grass-clover swards in Switzerland) were important: these were based on a standard production figure for grassland (13 tonnes dry matter/ha) and estimates of clover percentage in grassland and clover nitrogen fixation.

Statistics for **fodder production** (grass, silage maize) are not available, so these were estimated from the number of fodder consuming animals and standard feeding rates, and then adding in estimates for harvest and feeding losses.

Farm nutrient efficiency

In 2008, c. 150 kgN/ha (nitrogen) entered the Swiss agriculture system, with imported feedstuffs and mineral fertilisers being the main sources. Only c. 40 kgN/ha left the system in agricultural products, the remainder being presumably mainly lost either to the atmosphere from soil, or to waters as nitrate pollution.

Overall agricultural nitrogen efficiency was thus <30%, with animal husbandry showing an even lower nitrogen efficiency of c. 20%.

Phosphorus inputs to the Swiss agriculture system were 13.5 kgP/ha, almost entirely in imported feedstuffs (largest source) and mineral fertilisers. 8.0 kgP/ha left the system, mainly in animal food products.

Overall agricultural phosphorus efficiency was c. 60%, significantly higher than for nitrogen. Amounts of P in plant feedstuffs for animals and in animal excreta were significantly higher than amounts imported into the system, showing that phosphorus is largely cycled within the farm system.

38 kgK/ha (potassium) entered the Swiss agricultural system, and 10 kgK/ha left in agricultural products.

However, in plant production K efficiency was nearly 90% compared to <5% in animal husbandry. Overall potassium efficiency was thus <30%.

Changes over time

Nitrogen fertiliser use nearly doubled from 1975 to 1988, then decreased around one third to 1997 mainly with the introduction of environmental obligations and incentives for farmers, then remained constant. N in imported foodstuffs has fallen as a result of reduced animal numbers and lower N contents in pig diets. As a result, the Swiss farming nitrogen surplus has been fairly stable since the mid 1990's, at a level very slightly lower than in the early 1970's.

Phosphorus in imported foodstuffs has also been reduced since the 1970's, and phosphate fertiliser use also has fallen since a peak in the 1970's. This has resulted in a considerable reduction in the Swiss agricultural P surplus from around 25 kgP/ha in 1975 – 1980 to around 5 kgP/ha since around 2000.

Potassium has followed a similar pattern to phosphorus, with the Swiss farm K surplus falling from around 50 kgK/ha in the late 1970's to around 20 kgK/ha today.

The author notes that Switzerland is thus near average for nutrient surpluses compared to other European countries.

Recommendations

The author suggests that Swiss agricultural nutrient efficiency could be improved by measures to reduce nutrient losses, by better targeting of nutrient application to the timing of crop needs, by promoting feeding plans in animal husbandry, improved animal diets (reducing excess protein in cattle diets, and by better manure management.

“Nitrogen, phosphorus and potassium balances and cycles of Swiss agriculture from 1975 to 2008”, Nutrient Cycling in Agroecosystems, vol. 91, pages 351–365, 2011

<http://www.springerlink.com/content/r8q186t1613n/>

E. Spiess, Agroscope Reckenholz-Tänikon Research Station ART, Reckenholzstrasse 191, 8046 Zurich, Switzerland, ernst.spiess@art.admin.ch

P-recycling from urine

Nepal

Struvite recovery from urine

Precipitation of struvite (magnesium ammonium phosphate) from source-separated urine is a potentially simple means of producing a concentrated, solid fertiliser. Decentralised production reduces problems of transport, handling, odour and contamination which may be associated with the direct use of urine in agriculture. However, struvite production requires the addition of magnesium, and, depending on the location of production, the purchase price of magnesium salts may exceed the sale price of the struvite. In these papers, wood ash, calcined magnesium rock, and bittern (a waste stream from salt production) were tested as locally available, low-cost alternative magnesium sources.

In the first paper (A), experiments were carried out in Siddiphur, a mainly agricultural village near Kathmandu, Nepal. Only 3% of the population is connected to water-borne sewerage but, as a result of a WaterAid project, over 100 UDDTs (urine diverting dry toilets) have been in operation since 2007.

Around 250 litres of urine (slightly diluted by toilet washing) was collected from the UDDTs and used for experiments. **Two different simple reactors (50 litre volume) were built from basic materials:** the first reactor was made from a 50 litre plastic water tank to which a manual stirring mechanism was added (metal

paddles and crank) with a cloth filter tray in the bottom. The second reactor was made from galvanised sheet steel, welded by local craftsmen to make a circular tank with a conical base, again with a manual stirring mechanism, and with a filter bag attached to a tap at the base of the reactor cone. The filter was nylon fabric with a pore size of approximately 160 µm.

Phosphorus removal

The phosphorus concentration of the urine sampled fell significantly during storage (from approximately 390 to 200 mgP/l), presumably by spontaneous precipitation of struvite and calcium phosphates. Analysis showed that the **phosphorus concentration in urine could be reliably estimated from electrical conductivity** using a linear equation, thus facilitating reactor control and reagent dosing.

In both reactors, the **different magnesium sources** were added to urine at a 1.1 to 1 Mg:P ratio, the reactor was stirred for 10 minutes, and then left to settle. In the first reactor, the supernatant was drained through a tap above the filter tray, whereas the second reactor was emptied through the filter bag via the tap at the base of the cone at the bottom of the reactor.

Total phosphorus removal in the first reactor was only around 50%. The addition of different flocculants (lime, alum, synthetic anionic and cationic polyelectrolytes and a natural product prepared from moringa oleifera seeds) did not improve struvite settling in the first reactor.

The second reactor was designed to improve collection of fine precipitated solids (using the filter bag) and achieved over 90% total phosphorus removal. Total batch time, including filtration, was reduced from 6 hours (including settling) in the first reactor, to 1 hour (including filtration) in the second. The costs of the two reactors including labour were about 35 and 60 € respectively.

Magnesium costs and financial sustainability

Costs of different possible magnesium sources were assessed: magnesium oxide, bittern, calcined magnesite rock, and magnesium sulphate. Although bittern is a waste product (brine) from salt production, and free at the source, transport costs from India (Jakhau Salt Company, Gujarat) to Nepal are high, so in fact, locally produced magnesium oxide would be the cheaper option (0.12 €/kg struvite produced). Magnesium oxide is not currently produced locally, but magnesite was previously mined outside of Kathmandu, and if magnesite became available, magnesium oxide could be produced locally by calcination.

Based on local fertiliser prices, **struvite recovery from urine was estimated to be financially profitable if such locally produced magnesium oxide were used** as a magnesium source, but struvite would be produced at a loss if a more expensive magnesium source were used (e.g. imported magnesium sulphate). Based on the estimated magnesium oxide cost, approximately 12 m³ of urine per day (equivalent to the production of 10 000 people) would have to be processed to cover a basic wage of 4 €/day. This illustrates the important role that the magnesium source plays in the overall financial balance of struvite production. For this estimation it was assumed that only the financial value of fertiliser could be used to cover the expenses. No additional revenues, for example, subsidies for waste water treatment or toilet usage fees, were considered.

To improve the financial feasibility, it would be important to collect the **calcium phosphate and struvite that spontaneously precipitated in the urine**, by ensuring short piping between the UDD toilets and the struvite recovery reactor.

The effluent that remains after struvite precipitation still contains high levels of ammonium, sulphur and potassium, meaning that further nutrient recovery opportunities or potential water treatment costs remain. If the nutrients contained in the effluent can be used as a fertiliser this will further improve economics and the overall reuse of the urine nutrients.

Using ash to precipitate struvite

In a second paper (B), **ash from burning wood (in a domestic chimney) was tested as a possible magnesium source for struvite precipitation** from urine in 1 litre experimental stirred reactors.

Fly ash from coal combustion has been shown to be effective for phosphorus removal from wastewaters (Kuziemska 1980, Cheung & Venkitachalam 2000), but wood ash is more widely available in agricultural communities and was therefore tested for its applicability. **The wood ash used contained 3.4% magnesium**, which is compatible with literature values of 1.6 – 6%. However, only around 50% of the magnesium in the ash was available for phosphorus precipitation (i.e. it was soluble in urine). This proportion could be increased if the wood was burnt at high temperatures (> 600°C), but such temperatures are not common in simple wood fires or ovens.

The experiments showed that **the solid precipitated with wood ash from urine was not pure struvite, and had a high calcium carbonate and low phosphorus (<3%) content.** Furthermore, 60% of the potassium in the wood ash dissolved into the urine and was not recovered in the solids. The financial value of

this lost potassium is in a similar range to that of the recovered phosphorus.

Overall, the authors conclude that **wood ash is a suitable reagent for struvite precipitation from urine**. However, several factors can impede the use of the product as fertiliser: the rather low content of recovered phosphorus, the possibly high content of heavy metals and the dissolution of valuable potassium out of the wood ash.

Further information about Eawag's project on struvite recovery from urine in Nepal (STUN) can be obtained at <http://www.eawag.ch/stun>

(A) "Low-cost struvite production using source-separated urine in Nepal", *Water Research* 45 (2011), pages 852-862 www.elsevier.com/locate/watres

B. Etter, E. Tilley, R. Khadka, K.M. Udert, Eawag (Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland bastian.etter@eawag.ch elizabeth.tilley@eawag.ch raju.khadka@eawag.ch udert@eawag.ch

(B) "Wood ash as a magnesium source for phosphorus recovery from source-separated urine", *Science of the Total Environment*, vol. 419, pages 68-75 (2012). www.elsevier.com/locate/scitotenv

S. R. Sakthivel (a,b), E. Tilley (b,c), K. Udert (b). a: Centre for Rural Development and Technology, Indian Institute of Technology, Hauz Khas, New Delhi — 110 016, India. b: Eawag (Swiss Federal Institute of Aquatic Science and Technology), Überlandstrasse 133, 8600 Dübendorf, Switzerland. c: Nadel (Centre for Development and Cooperation), Swiss Federal Institute of Technology (ETHZ), Voltastrasse 24, 8092 Zürich, Switzerland udert@eawag.ch

Vietnam (I)

Solar nutrient recovery from urine

Urine separating toilets and dry toilets are appropriate technologies for rural areas lacking centralised sewerage. The urine collected is a good fertiliser, but poses considerable problems for use because high pH leads to ammonia emissions and odour problems during storage, transport and spreading. One technical option to address these problems is evaporation of separately collected urine to produce a solid fertiliser. This was tested using a 50 litre urine samples, from which a solid fertiliser was produced and tested. Acidification of the urine prior to evaporation was assessed. Possible issues of pharmaceutical and hormone contaminants are not resolved by evaporation and need to be investigated.

Urine was collected from male students via **waterless urinals and No Mix toilets** in dormitory bathrooms and from students urinating directly into bottles at the University of Can Tho, South Vietnam. The No Mix toilet urine was slightly diluted by flushing of the urinals.

The urine was evaporated in 20 - 50 litre batches in a 2 m² glass covered, black tile "still" constructed locally, exposed to sunlight. Complete evaporation of the urine took 3 - 4 weeks. In two further experiments, the urine was acidified to pH 4 using sulphuric or phosphoric acid before evaporation.

Fertiliser value

The three evaporation products (urine, sulphuric acidified, phosphoric acidified) were analysed for chemical and physical/crystal properties, then tested for fertiliser value in **82 day greenhouse pot experiments using maize and ryegrass** in P-deficient soil, compared to a commercial phosphate fertiliser and a no added nutrient control (5 treatments x 2 different plants tested x 4 replicates of each). The different nutrients were each added at 24 mgP/kg soil, micronutrients and nitrogen fertiliser were added to the pots at the start and after sample harvesting at 27, 40 and 58 days. Phosphorus uptake, nitrogen uptake and dry matter yield were assessed at each harvest date.

Results showed that the **evaporated urine offered similar phosphate fertiliser value to the commercial phosphate fertiliser**, but the acidified urine offered significantly better fertiliser value (2 - 3 x higher).

The evaporated urine was composed largely of sodium chloride (c. 90%) with c. 2% phosphorus and 2% nitrogen content. The phosphorus was highly soluble (85% solubility in water, 95% in citric acid). Around 30% of the urine nitrogen was lost during the evaporation process. **The salt content of the evaporated urine could pose salinisation issues** if used repeatedly in agriculture.

Acidification of the urine considerably increased the nitrogen content of the evaporated solids (2 - 3 x). The principal component of the phosphoric acidified evaporated solid was thus biphosammite NH₄H₂PO₄.

The authors conclude that **solar evaporation is a very appropriate technology for producing a solid fertiliser from urine**, feasible with low cost installations which can be constructed locally and are easy to operate. Acidification improves the fertiliser value of the evaporated solid and reduces nitrogen loss, but is probably inappropriate for rural areas because of the handling risks for the acid. Issues remain with salt content and salinisation. Contaminants in the urine (pharmaceuticals,

hormones) may to some extent be broken down by solar UV radiation but this needs further analysis.

“Solar thermal evaporation of human urine for nitrogen and phosphorus recovery in Vietnam”, *Science of the Total Environment*, Volume 414, January 2012, Pages 592–599
www.elsevier.com/locate/scitotenv

S. Antonini, P. Nguyen, U. Arnold, 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
sam_antonini@uni-bonn.de

Vietnam (II)

Struvite and ammonium sulphate from urine

Phosphorus and nitrogen recovery as fertiliser materials, was tested on undiluted urine and slightly diluted urine (from source separated toilets). The two step reactor consisted of a 50 litre stirred batch struvite precipitation tank, followed by a batch nitrogen recovery step using a 50 litre stripping column followed by a sulphuric acid absorption column (same dimensions) from which liquid ammonium sulphate was recovered.

As in the paper above, urine was collected directly by students urinating into bottles, and slightly diluted from combined outflow of waterless urinals and No Mix toilets at the University of Can Tho, South Vietnam.

Struvite precipitation

In the struvite reactor, magnesium oxide (MgO) was dosed to a Mg:P ratio of 1.5:1, and sodium hydroxide (NaOH) to adjust to pH 9. The batch reactor was stirred for 30 minutes then settled for 1-3 hours. The precipitated struvite was collected using a synthetic fibre filter bag.

Nine 50 litre batch runs were carried out using undiluted urine and six with diluted urine. Various settling times were tested. Beaker tests were used to verify results.

98% removal of soluble phosphate from the urine was achieved from both diluted and undiluted urine, with 1 hour settling time proving to be sufficient. However, recovery of the precipitate from the filter bag proved problematic, with 20% of the precipitate being effectively thus lost for undiluted and 90% being lost for diluted urine.

X-ray diffraction showed the precipitate to be 85% struvite (magnesium ammonium phosphate

hexahydrate $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) and 15% to be dittmarite (magnesium ammonium phosphate monohydrate $\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$). As well as the minerals Ca, K, Na, S and Si, the precipitated struvite also showed aluminium, copper and zinc at concentrations $> 50 \mu\text{g/g}$. **Heavy metals were very low**, significantly lower than fertiliser quality standards.

Nitrogen recovery

The second reactor step involved a **stripping column to remove ammonia, followed by an ammonium sulphate absorption column**. Ammonia stripping was achieved by pumping air upflow in the column (with liquor downflow), using NaOH to adjust to pH 10 and heating to 40°C. The ammonia carrying air was then passed through a sulphuric acid column, enabling recovery of liquid ammonium sulphate.

90% of the nitrogen present in the urine leaving the struvite reactor could thus be recovered as liquid ammonium sulphate.

Various upflow and liquor recycle rates were tested in the stripper column. Energy consumption, reagents (MgO, NaOH, H_2SO_4) and total cycle duration were calculated for different operating conditions.

S. Antonini, T. Eichert, J. Clemens, Department of Plant Nutrition, University of Bonn, Bonn, Germany and S. Paris, Huber SE, Industriepark Erasbach A1, Berching, Germany. Email as above.

“Nitrogen and Phosphorus Recovery from Human Urine by Struvite Precipitation and Air Stripping in Vietnam”, *Clean – Soil, Air, Water* 39 (12), pages 1099–1104, 2011 (Wiley)
www.clean-journal.com

Struvite precipitation

Biological nutrient removal

Sludge fermentation and P-recovery

A lab scale biological phosphorus removal sequencing batch reactor and sludge fermenter, operated to produce readily available carbon (volatile fatty acids VFA) to “feed” the bio-P reactor, were tested with and without struvite precipitation from the fermenter return stream. The bio-P reactor had an operating capacity of 5 litres, and was run with three 8-hour cycles per day. 6% of this reactor’s sludge was bled to the 1 litre fermenter each cycle, and the fermenter had a residence time of 5 days.

The bio-P reactor was seeded with sludge from another laboratory reactor, and was fed with synthetic

wastewater COD 300 mg/l, acetic acid 30 mg/l, NH₄-N 30 mg/l and PO₄-P 10 mg/l. Its 8 hour cycle consisted of 15 minutes' feeding with 2 litres of synthetic wastewater, then 1.5 hours anaerobic (at the end of which, 6% of sludge was transferred to the fermenter), followed by aeration for 4 hours (after which wasted sludge was removed to maintain a solids residence time of 12 hours), followed by 60 minutes settling time (after which supernatant was decanted for 15 minutes to allow addition of new wastewater). The fermenter thus received sludge three times per day. It was sealed and fully mixed. The fermenter effluent was returned to the bio-P reactor, by overflowing 0.2 litres of mixed fermenter content to compensate for the sludge addition. This initial set-up was tested for 60 days.

To assess the effects of including a P-recovery step in the process, **the set-up was modified to include an upflow separator on top of the fermenter**, in order to retain solids in the fermenter and give a low-solids supernatant. **Struvite was then precipitated from this supernatant**, by addition of magnesium oxide, before returning it to the bio-P reactor. Two different modes were tested, first by return of the supernatant to the bio-P reactor at the start of its cycle, and secondly (with a slightly higher MgO dosage to increase struvite removal) return to the bio-P reactor 30 minutes after the start of its cycle (in order to add it after consumption of the initial acetate content of the synthetic wastewater). These modes were tested for a total of 2 months.

Poor phosphate removal with no fermentation

A control run (2 months) using the bio-P reactor only, without return of supernatant from the fermenter, showed poor phosphate removal (only 30% total P-removal). Analysis suggested that this was because of **inadequate VFA supply** (the initial acetate was consumed after 15 minutes of the anaerobic cycle of the bio-P reactor). Nitrate remaining in the reactor from the end of the previous cycle was fully removed after c. 30 minutes from the start of the anaerobic cycle, suggesting that denitrifying organisms in the sludge were outcompeting phosphorus accumulating organisms for the limited VFAs, resulting in poor phosphate removal.

When the bio-P reactor was operated in connection to the fermenter, the return liquor from the fermenter was providing approximately 35 mg of VFA-COD, compared to 60 mg VFA-COD in the synthetic wastewater (acetate). In this case **anaerobic phosphate release in the bio-P reactor increased**, showing the higher activity of phosphorus accumulating organisms, and the total phosphorus removal was c. 55%. This is still a poor level of P-

removal, considered to be because of the P loading in the fermenter return stream.

Struvite precipitation

The MgO dosage used for struvite precipitation was marginally higher than the theoretical 1:1 ratio to phosphorus, in order to ensure good P-removal (90 – 95% removal). 70% nitrogen removal also resulted. The MgO addition ensured a pH increase which facilitated struvite precipitation. XRD analysis and the 1:1 molar ratio of phosphorus and nitrogen removal showed that the precipitate was indeed struvite.

In the set-ups with **solid-supernatant separation from the fermenter followed by struvite precipitation**, very little phosphorus was returned to the bio-P reactor in the fermenter liquor. Consequently, phosphorus removal in the bio-P reactor was improved, achieving 80% - 99% P-removal, as well as complete nitrification. The P-removal in the bio-P reactor was significantly better when the fermenter supernatant (VFAs) were added not at the start of the anaerobic cycle, but after 30 minutes, when denitrification was complete.

The fermenter consistently produced c. 157 mg of VFA-COD per g of biomass input. With the solid/supernatant separation on the fermenter, a reduction of c. 20% in sludge production from the bio-P reactor was also achieved.

The authors conclude that this experimental work confirms the **essential role of VFA (readily available carbon as volatile fatty acids) in biological phosphorus removal**, and that effectiveness can be improved by adding to the bio-P process at different points in the anaerobic – aerobic cycle.

They also conclude that fermentation of the WAS (waste activated sludge) from the bio-P reactor can produce such VFAs, and that if this is combined with settling of solids and phosphorus precipitation from the fermenter return stream, biological phosphorus removal efficiency can be significantly improved, in addition to complete nitrification, and **phosphorus can be recovered for recycling as struvite**.

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Q. Yuan, J. Oleszkiewicz, Dept. Civil Engineering, University of Manitoba, Winnipeg, Manitoba, Canada R3T 5V6 umyuan3@cc.umanitoba.ca

Struvite precipitation

Innovative 2-section seeded aerated struvite reactor

Addition of struvite particles as seeds was shown to significantly reduce the reaction time necessary for struvite precipitation to occur in stirred beaker tests using pure phosphate and ammonium solutions with added magnesium. An experimental struvite precipitation reactor is presented based on this assumption, where small struvite particles are carried upwards by aeration from the bottom of main reactor zone to a smaller aerated reaction column within the main reactor into which the influent flows and where magnesium is dosed. Using pure phosphate and nitrogen solutions, this reactor achieved 78% phosphate removal at soluble phosphorus concentrations of 22 mgP/l, with a total hydraulic retention time just over one hour.

Batch 2 litre stirred beaker struvite precipitation experiments were carried out to **test the effect of adding struvite seeds**, using pure sodium phosphate and ammonium chloride solutions, with magnesium chloride addition and initial pH adjustment using sodium hydroxide.

Beaker seeding tests

Tests were carried out at two different phosphate concentrations (21 and 51 mgP/l) with ammonium and magnesium to phosphate molar ratios of 3.5:1 and 1:1. Initial pH was adjusted to 9. Struvite particles were produced by precipitation from pure phosphate, ammonium and magnesium solutions then using the solid filtered at 0.45 μm . 0.422g/l of seed was used when to the seeded beakers. Supersaturation ratios and ion activity calculations are presented.

The results show that in non-seeded experiments, precipitation hardly started for the first 20 minutes, but then took place gradually over the 20 – 40 minute period. In the seeded experiments, precipitation occurred rapidly in the first five minutes, with equilibrium being reached within 15 minutes.

Overall, at the higher phosphate concentrations, **equilibrium** was reached after around 35 minutes without seeding, and after around 9 minutes with seeding. For the lower concentrations, the times were 90 and 15 minutes.

The authors conclude that **struvite crystal addition significantly shortens both induction and equilibration times**, and should be ensured for efficient struvite reactor design.

Innovative two stage MAP reactor

The authors present an experimental struvite precipitation reactor and results of a range of experiments testing the performance of the reactor under different operating parameters, using pure phosphate and ammonium solutions, and pH adjusted to 9.2 – 9.7 using sodium hydroxide.

The “IRSR” (Internal Recycle Seeding Reactor) uses two separated reactor sections to ensure recycle into the initial reaction zone of small struvite particles from the bottom of main reactor zone. The main reactor is about 3 litres volume, with a conical particle accumulation zone at the bottom, and a column sedimentation zone above this and the effluent outflow via a weir at the column top. Within the main reactor, a smaller 0.35l column receives the influent and magnesium dosing, which flows down and into the centre of the main reactor. Aeration of the main reactor ensures CO₂ stripping and mixing, and also carries small struvite particles up into the entry zone reactor, which is also separately aerated (see diagram in 2008 paper).

Experiments were carried out to assess this reactor using :

- (a) different concentrations of influent phosphate (22 – 150 mgP-PO₄/l)
- (b) different seed concentrations in the reaction zone, controlled by adjusting the aeration and the level of struvite accumulated in the bottom of the main reactor
- (c) molar ratio of magnesium dosage to soluble phosphorus (from 1:1 to 2:1)
- (d) the total hydraulic residence time (from 0.6 – 4.6 hours).

Efficient phosphorus recovery

The IRSR reactor achieved **recovery of 78% of influent soluble phosphorus as struvite at the relatively low phosphate concentration of 22 mgP/l**, that is around 20% better than without seed recycling. The advantage of seed recycling in the reactor was reduced at higher phosphate concentrations. Seed recycling requires energy (aeration) and it is concluded that a relatively low recycle rate giving a seeding level of 0.4 – 1g seed/l in the initial reaction zone is optimum for good performance.

With magnesium to phosphorus dosing of 1.3 – 1.5:1, phosphorus recovery improved up to a total hydraulic residence time of 1.14 hours (8 minutes in the initial reaction zone, 60 minutes in the main reactor and settling). This could be reduced to a total hydraulic

residence time of one hour whilst still achieving good P-recovery levels.

The authors conclude that further work is needed to address the problem of NH₄ stripping by the aeration and to assess the risk of fine struvite crystals causing problems, either by loss in effluent outflow or by coagulation onto reactor surfaces.

“Effect of struvite seed crystal on MAP Crystallization”, *Journal of Chemical Technology and Biotechnology*, vol. 86, issue 11, pages 1394–1398, 2011

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Z.G. Liu (a), Q.L. Zhao (b), L.L. Wei (b), D.L. Wu (a) and L.M. Ma (a) lzg0532@tongji.edu.cn

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Z.G. Liu (a,b), Q.L. Zhao (b), N. Yang (b), D-J. Lee (c) qlzhao@hit.edu.cn

(a) National Engineering Research Center for Urban Pollution Control, Tongji University, Shanghai 200092, China

(b) State Key Lab of Urban Water Resources and Environment (SKLUVRE), School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

(c) Dept. Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617, China

Recovered phosphates as fertilisers

2-year pot trials

Fertiliser value of recovered phosphates

The effectiveness of eight different phosphate products recovered from wastewater and thermal processes was compared to commercial TSP fertiliser in 2-year maize pot trials at acidic and near-neutral soil pH.

Fertiliser value of eight different recovered phosphates was assessed and compared to commercial phosphate fertiliser (TSP triple super phosphate) and phosphate rock, in 2-year pot trials using maize (*Zea mays*) with soil pH 4.7 (loamy) and pH 6.6 (sandy) [pH(CaCl₂)], 2 plants grown to maturity per 6 litre pot.

The phosphate fertiliser was mixed with the soil at the start of the two years (with no further applications made), in each case at **two doses** (suboptimal = 60 and highly fertilised = 200 mgP/kg soil), plus control (no added fertiliser), in each case with 4 replicates. Other

nutrients were dosed to all pots at the start of the trials (K, Mg, N) and N was added during the trials in two further applications.

Recovered phosphates

The recovered products tested were **three struvites** (magnesium ammonium phosphate) and **one calcium phosphate** recovered from different urban waste water treatment plants (UWWTP), and **four thermal process phosphates** (detailed list below). All phosphate products were finely ground and sieved to 500 µm.

Recovered phosphate products tested:

- Calcium phosphate precipitated using Tobermorite
- Struvite from Seaborne at Gifhorn UWWTP, Germany (Günther et al. 2008)
- Struvite from Seaborne process at Owschlag UWWTP, Germany
- Struvite from waste water at Stuttgart University (Weidener 2010)
- Sinter phosphate, produced by calcination at 1000°C of wastes including meat and bone meal
- Cupola slag, recovered by smelting sewage sludge and filter dust (Scheidig et al. 2009)
- Phosphate recovered by thermal treatment of sewage sludge incineration ash (Adam et al. 2009)
- Ash from incineration of meat and bone meal at 1000°C

Soil solution phosphorus

Soil samples from each pot were analysed for **soil soluble phosphorus quantity** (IEP = isotopically exchangeable phosphorus) three weeks after application of the phosphate fertilisers and after two years. **Soil solution phosphorus concentration** (intensity C_{Li}) was also measured by slowly percolating water down an extracted soil column to displace the soil solution, then measuring phosphorus concentration colorimetrically (Murphy & Riley method).

The authors note that for the phosphate products tested, **neither water solubility nor 2% citric acid solubility are good indicators** of these soil phosphorus concentrations.

Maize plants were harvested at the start of flowering (80 and 70 days after sowing for the first and second years respectively), and above ground biomass dry matter weight and P-concentration were measured. Phosphorus uptake was calculated from shoot dry matter and P concentration.

Phosphorus availability in the soil (C_{Li} P concentration in soil solution) varied for the different products at different soil pH. TSP increased C_{Li} at both soil pHs, whereas phosphate rock did not increase C_{Li} at either pH. The recovered calcium phosphate increased C_{Li} in acidic but not near-neutral soil. One of the struvites increased C_{Li} in near-neutral but not in acidic soil, whereas the other two struvites increased C_{Li} in both soils similarly to TSP. The thermally recovered phosphates mostly did not increase C_{Li} in either soil, with some exceptions.

Plant phosphorus uptake

Plant P uptake was significantly higher at 60 mgP/kg TSP than in the control, and higher again at 200 mgP/kg. This showed that the **experiments were situated in the ascending zone of the response curve**, which is a necessary condition for fertiliser test validity.

Plant P uptake results were similar to C_{Li} measurements, with calcium phosphates proving effective only in the acidic soil, struvites proving generally as effective as TSP, and the thermal recovered phosphate products showing variable results. The Sinter phosphate product was effective in both acidic and near neutral soils, Cupola slag as effective in near-neutral soil and the two ash recovered products were effective in neither soil.

Plant P uptake showed to be correlated to IEP (soil solution P quantity) but not to C_{Li} (soil solution P intensity). The authors suggest that this is to be expected in pot trials where there is significant inter-root competition, and that results could be different in field trials where there is not such competition.

The authors conclude that struvite is a good fertiliser in soils of different pH (acidic, near-neutral), as is to some extent the Sinter phosphate product, whereas recovered calcium phosphate is only an effective fertiliser in acidic soils, and other thermally recovered phosphates are only effective in certain pH conditions or not at all. They suggest that further long-term field trials are needed to obtain further data.

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R. Cabeza, Departamento de Ingenieria y Suelos, Facultad de Ciencias, Agronomicas, Universidad de Chile, Casilla 1004, Santiago, Chile rcabeza@u.uchile.cl and B. Steingrobe, W. Römer, N. Claassen, Dept. Crop Sciences, Section of Plant Nutrition and Crop Physiology, Georg-August University, Göttingen, Germany

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