NUMBER 77

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Phosphorus resources

IFDC Report

Reassessment of world P resources

New report suggests phosphate reserves may be greater than previously estimated, but confirms lack of confidence in estimations and geographical concentration of reserves.

<u>Thesis</u>

Phosphorus futures: systems approach

Dr Dana Cordell's thesis proposes a coherent and systemic assessment of phosphorus resource issues, global phosphorus scarcity and food security

<u>Australia</u>

Continental implications of P scarcity

Australia has a high dependency on imported mined phosphate because of P-poor soils and economic dependency on phosphorus-intensive food exports

Nutrient management

Crop P-cycles

Phosphorus, phytic acid and world food security

A phosphate flow for the production of the world's main crops and implications of losses of P in phytic acid in human and livestock diets.

Nitrogen Cycle

Transformation of the global N cycle

Trends, questions and potential solutions to address the major changes already occurred or anticipated in the global balance of reactive nitrogen.

Phosphate recycling

<u>British Columbia</u>

Innovation award for P-recovery developer

Dr Mavinic, of the University of British Columbia (UBC), has received a prestigious innovation award for his contribution to developing P-recovery and recycling.

Multiform Harvest, USA

Full-scale struvite recovery from sewage and animal manures

The cone struvite crystalliser system designed for struvite recovery from agricultural manures and municipal wastewaters has been developed and further tested in pig and dairy manures. A full-scale plant is now being built to treat municipal wastewater.

Minerals

Naturally occurring struvite

Struvite (magnesium ammonium phosphate), the mineral produced by a number of phosphate recovery and recycling processes, occurs in natural deposits and is produced by bacteria in certain conditions

Conferences and networks

Sustainable Phosphorus Summit

Arizona 2-5 February 2011

Phosphorus, food and our future

The conference will explore the complex dynamics of P as a limited resource, and create a stage for constructive discourse and discussion on P sustainability. http://sols.asu.edu/frontiers/2011/program.php

SNB P-recovery website

Phosphate recovery news and information

The Netherlands sewage sludge processing company SNB (N.V. Slibverwerking Noord-Brabant) has launched a website on phosphate recovery and phosphorus resource management www.phosphaterecovery.com

Global Phosphorus Network

Phosphorus stewardship, resources, recovery and recycling

TheGlobalPhosphorusNetworkwww.GlobalPNetwork.netis a new platform to exchangeinformation, news, opinionsbetween stakeholders,policy-makersandexperts.Joinat:http://globalpnetwork.net/user/register

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Phosphorus resources

IFDC Report

Reassessment of world P resources

A major new report by the International Fertilizer Development Center (IFDC), a non profit international organisation, looks at whether world phosphate rock reserves are adequate to meet global food demands.

The report was solely funded by the US Agency for International Development (USAID).

The report concludes that global phosphate rock reserves, suitable for producing industrial phosphate products and fertilisers, will meet demand for several hundred years, assuming current rates of use.

Non renewable resource

Phosphorus is essential to plant growth, and so **phosphorus supply is essential to world food production**. There is no substitute for phosphorus in agriculture, or indeed for life.

Shortages of supply of phosphate rock would lead to "dire" consequences for phosphorus recycling is not today in place.

World phosphate rock production peaked in 1987-1988 and then in 2008 at over 160 million tonnes/year of concentrate (20 - 60%) of phosphate in mined rock is lost in mine site processing, and does not reach the concentrate).

Reserves and resources

The report distinguishes between:

- **reserves** = materials that can be economically used with existing technology, and
- **resources** = all potential sources

Previous estimates of phosphate rock reserves ranged from 15 to over 1,000 billion tonnes, and estimates of resources from 91 to over 1,000 billion tonnes. **The IFDC report estimates world phosphate rock reserves at 60 billion tonnes and resources at 290 billion tonnes**. A 2005 assessment estimated that the US's main phosphate rock reserves (in Florida) would be 60% depleted by 2030.

Need for better data.

The report reassesses existing data and tries to estimate phosphate rock reserves for different countries and regions of the world. It is the first major report to try to do this for 15-20 years and there is a lack of published literature and data since around 1990.

Published data often also fails to clearly distinguish between known reserves, estimated undiscovered reserves and resources.

Also, little exploratory work was undertaken since the 1980's and until recently to look for new phosphate rock resources or assessing feasibility and volumes of known sites.

Geographical concentration of reserves

The IFDC estimate of reserves is nearly 4x higher than the US Geological Survey 2010 estimate, and the IFDC estimate of resources nearly 20x higher. However **nearly all the "increase" in estimated reserves results from a 9x higher estimate of reserves in Morocco**, based not on official data but on one 1988 secondary source estimate.

85% of the world's phosphate rock reserves, according to the IFDC estimates, thus lie in one country (Morocco) and 91% in two countries (Morocco, China).

The IFDC report thus confirms both the considerable uncertainty in phosphate rock estimates, and the certainty that reserves will be increasingly geographically concentrated in 1-2 countries.

IFDC state "it is not known if all of this phosphate rock is truly producible at today's costs and prices. There is no data to assess mining costs".

Peak P?

The Global Phosphorus Research Initiative (GPRI), an association of sustainability research institutes, has published a "**Statement on Global Phosphorus Scarcity**" in response to the IFDC report.

GPRI point out that even with IFDC's revised estimated of phosphate reserves, **a "peak P", where phosphorus supply becomes critical** and insufficient



SCOPE Newsletter – n° 77 February 2011 - Page 2 <u>www.ceep-phosphates.org</u>



to meet global food production needs, would still occur this century.

GPRI emphasise "the seriousness of the geopolitical dimensions of phosphate rock. Importing countries ranging from sub-Saharan Africa, South Asia to the European Union cannot afford to continue relying so heavily on such a geopolitically concentrated resource, which is critical to food production ..."

GPRI supports the IFDC proposal that this report be followed by a Phase II more detailed assessment of world phosphate reserves.

IFDC <u>www.ifdc.org</u> and report "World Phosphate Rock Reserves and Resources":

http://www.ifdc.org/Media Info/Press Releases/September 2010/IFDC_Report_Indicates_Adequate_Phosphorus_Resou rce

Global Phosphorus Research Initiative www.phosphorusfutures.net and statement: http://phosphorusfutures.net/files/GPRI_Statement_response IFDC_final.pdf

Thesis

Phosphorus futures: systems approach

Published under the title "The story of Phosphorus – sustainability implications of global phosphorus (P) scarcity for food security", Dr Dana Cordell's thesis is a transdisciplinary and systemic assessment of this complex issue, looking at P resources, data availability, P management, social and institutional factors. A wide range of information and data is presented, posing key questions for future research, sustainable phosphorus management and global governance.

Phosphorus (P) is a key plant nutrient and is applied to agricultural soils to maintain high crop yields. Unlike fossil energy sources, P cannot be substituted and is non replaceable. Unlike nitrogen fertiliser, manufactured from air using fossil energies, phosphate fertiliser cannot be produced by other routes (except recycling).

However, **current agricultural production is largely dependent on the consumption of phosphate rock**, a finite and non renewable resource (taking 10 - 15million years to form). Dr Cordell suggests that demand for high grade P-rock reserves will exceed production within a few decades due to energy and economic constraints of mining lower grade reserves, leading to a "peak phosphorus" situation, and argues that the ways P is sourced and used in the global system must therefore be reassessed.

Transdisciplinary approach

P management, related to global food production, is widely transdisciplinary, like all sustainability issues, involving ecological, economic, geopolitical and social parameters.

There is however a clear lack of "hard" data both concerning P rock resources and concerning management of P in human and environmental systems. The thesis uses "soft systems" methodologies to approach these complex questions in an integrated manner. In particular, semi-structured stakeholder interviews were carried out to assess the perspectives of different stakeholders on phosphorus scarcity and future food and agricultural system needs.

Phosphorus flows

The author estimates that of 17.5 million tonnes P mined annually in phosphate rock, nearly 15 mt goes to fertiliser production, but only 3 mt finally reaches the food consumed by humans: 80% of the phosphate rock P mined for food production never reaches our plates.

Recycling of P in sewage and animal wastes will be a key element in reducing wastage of P and loss to the environment, but considerable efforts to reduce losses throughout the fertiliser – farm – food chain life cycle will also be necessary.

Specific case studies show strong regional differences in phosphorus flows. Australia, a food exporting nation, imports (net) 265 ktP/year of mineral P but exports (net) 105 ktP/year in food, livestock and fibre exports.

Dimensions of P scarcity and sustainability

The thesis identifies five aspects of P scarcity:

- **Physical** scarcity: decreasing availability of high quality phosphate rock
- **Economic** scarcity: financial difficulties for some to purchase phosphorus (e.g. poor farmers)
- **Management** scarcity: system inefficiencies which prevent available P from meeting needs (e.g. losses in the food chain)



SCOPE Newsletter – n° 77 February 2011 - Page 3 www.ceep-phosphates.org



- **Institutional** scarcity: lack of appropriate institutional structure to ensure that P supply will meet short or long term needs
- **Geopolitical** scarcity: access to P resources is restricted by political or geographical circumstances (e.g. oligopolies controlled by governments or corporations)

The author also identifies **11 sustainability criteria for achieving 'phosphorus security'**, with the objective of enabling a "soft landing" for phosphate resource limits and avoiding "Peak P" crisis:

- Minimum waste
- Healthy environment (avoiding P loss contributing to eutrophication, agricultural contamination by heavy metals from phosphate rock ...)
- Reduced energy consumption
- Short and long term availability of phosphorus for farmers' livelihoods
- Global food security
- Cost effectiveness of P use, recovery and recycling
- Fertile soil without over fertilisation
- Balanced human diet
- Avoidance of geopolitical tensions
- Equitable allocation
- Effective governance

Conclusions and recommendations

Dr Cordell concludes that **P scarcity is a real threat to future global food security**, but that the issue is still largely missing from international discussions and political thinking.

Data on both P resources and P use is very scarce, in particular reliable data on P resources because this is controlled by individual companies and is not publicly available. The result of this situation is a lack of any effective national or international governance of P resources or their husbandry, and a **need for multiscale and multi-context analysis** to support such governance.

Consequently, the author recommends:

- **To develop scenarios** for meeting future P demand for food security
- To improve P data accountability and transparency
- To integrate P scarcity into sustainability research strategies
- To analyse what **institutional strategies** are necessary for P governance
- To establish national and regional **P flow analyses**

Dr Dana Cordell dana.cordell@uts.edu.au

"The Story of Phosphorus: Sustainability implications of global phosphorus scarcity for food security", PhD thesis University of Technology Sydney, Institute for Sustainable Futures and Linköping University, Sweden, Faculty of Arts and Sciences, n° 509, 2010 <u>http://liu.diva-</u> portal.org/smash/record.jsf?pid=diva2:291760

See also "Sustainable futures - Why phosphorus supplies, Precycling, and global food security should now be on the world political agenda." In SCOPE Newsletter n°73





Australia

Continental implications of P scarcity

Australia is highly dependent on imported phosphate both for its own and for exported food production. Most Australian soils are naturally deficient in phosphorus. Traditional Aboriginal food systems relied on "firestick burning" to release P into the environment and make it available to plants. European agricultural practices depleted the limited soil P in Australian soils and rapidly met soil fertility problems. Livestock developed sicknesses related to nutrient deprivation. Introduced grasses reverted back to native species whose deeper roots could better tap soil P reserves.

Guano

In the early 20th century, Australia's agricultural productivity was revolutionised by the introduction of phosphate fertiliser as guano from the South Pacific island of Nauru and elsewhere. Guano consists of deposits of bat and bird excreta laid down over thousands of years. Demand was encouraged by national fertiliser subsidies.

Nauru's high quality guano reserves were depleted by the year 2000, leaving considerable environmental and social damage to the island.





SCOPE Newsletter – n° 77 February 2011 - Page 5 <u>www.ceep-phosphates.org</u>



Phosphate rock

Reserves of phosphate rock were first discovered in Australia in the early 20th century, but mining only started in the 1960's. Today, domestic rock provides around a half of Australia's P needs, and Australia is a net importer of phosphate fertilisers with an annual total fertiliser cost to farmers of AUD 10 billion.

At the same time, **Australia is a net exporter of food and fibre**, with a net 85 ktP/year moving out in such exports.

P-flow balance

The authors collected data on phosphorus flows in fertilisers and phosphate rock (production, consumption, import, export), P uptake in crops, food production and P content of foods, biosolids generation and use. A balance of annual flows of P in Australia was thus established.

Australia is shown to import (net) 265 ktP/year in P rock and fertilisers. Added to domestic phosphate rock production (220 ktP/year), a total of 455 ktP/year is consumed in fertiliser. The Australian food system is far from 'closed loop' or sustainable from a phosphorus perspective. Only 2-3% (13ktP/year) of the P in applied fertilisers reach the food eaten by Australians, Most of the P applied in fertiliser is accumulating in agricultural soils, or lost to nonagricultural soil, water or landfills (125 ktP/yr) or exported in food, livestock and fibres (105 ktP/year).

In Australian soils, **P** is often tightly bound to clay and organic particles and so lost from plant availability. Agricultural P runoff to surface waters poses eutrophication problems, including to the barrier reef.

Soft landing

Australia's dependency on imported phosphorus, both for domestic food production and economically for export crops and livestock, combined with questions over long term P scarcity, geopolitical accessibility of P resources and global P demand / resource issues ("Peak P") pose significant questions.

The authors suggest that Australia should look at pathways towards a "soft landing" for **sustainable phosphorus use**, including improving farm nutrient management (only 20-30% of P fertiliser is generally taken up by plants in the same year), reducing dietary

meat consumption, developing P-recovery and reuse from human excreta or municipal sewage.

The authors emphasise that for this to happen institutional changes must be initiated to bring P management into focus within research and agricultural institutions.

Cordell, D. (1,2) & White, S. (2) (2010), Securing a Sustainable Phosphorus Future for Australia, Farm Policy Journal, Vol. 7 No.3, August, 2010, p.1-17. http://www.farminstitute.org.au/ product 61693/FPJ0703 Article -

<u>Securing a sustainable_phosphorus_future_for_Australia</u> %2c_Dana_Cordell%2c_Stuart_White

White, S., Cordell, D.J. & Moore, D. 2010, Securing a sustainable phosphorus future for Australia: implications of global phosphorus scarcity and possible solutions, [prepared for CSIRO Sustainable Agriculture Flagship], Institute for Sustainable Futures, University of Technology, Sydney.

http://www.isf.uts.edu.au/publications/whitecordellmoore20 10phosphorusfuture.pdf

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UK Soil Association A rock and a hard place

The UK organic food and farming organisation, Soil Association, has published a report entitled "A rock and a hard place: peak phosphorus and the threat to our food security". The organisation notes that mineral phosphate shortages may occur from 2030, because of global resource limits or concentration of reserves in just a few countries and warns of the consequences for world food supplies. Non-organic crops have been developed to be dependent on regular inputs of phosphate fertiliser, and without these eg. wheat yields would fall from 9 to 4 tonnes/hectare.

The association emphasises the need both to radically change both farming methods and human diets, and to recover and recycle back to agriculture phosphorus in human sewage and animal manures.

Peak phosphorus

The Soil Association report quotes both the recent IFDC study and Dana Cordell *et al.* who suggest that **a**



SCOPE Newsletter – n° 77 February 2011 - Page 6 www.ceep-phosphates.org



peak in mined phosphate rock production could occur from 2030 onwards or a few decades later, as demand exceeds technically useable resources. World resources are concentrated in just a few countries, in particular the Western Sahara – Morocco and China, leading to geopolitical risks. The USA stopped exporting phosphate rock in 2004 and increasingly imports for its own needs.

The geopolitical concentration of phosphate reserves leads to global market price volatility, and further price pressure could result from demand for fertilisers for biofuel production.

Sewage sludge reuse

The Soil Association emphasises **the need to re**establish phosphorus husbandry, where soil phosphorus is maintained by returning animal waste, human waste and crop removed phosphorus back to farmland.

"When water-borne sewage was introduced into our cities, the capital of the soil – its fertility – which is removed from it year by year in the form of crops and livestock, no longer found its way back to the land in the form of the waste products of the community, but was poured into the sea or otherwise destroyed." The Living Soil, Lady Eve Balfour, 1943.

The Soil Association reminds that composting of food and of organic household wastes enables some Precycling, but that the **key points are recovery and recycling of phosphates from human sewage and animal wastes**.

Three million tonnes of human P

Three million tonnes of phosphorus are excreted annually by the world human population, of which only around 10% are returned to farmland. In the UK, the majority of sludge biosolids are returned land, but because of transport costs **biosolids go to only around 80,000 of the 6.2 million hectares of farm cropland**. The fertiliser value of UK biosolids returned to land is estimated at UK£ 20 million/year.

The Soil Association report discusses the problems of contaminants in sewage sludge (pathogens, heavy metals, organic chemicals, pharmaceuticals, natural and synthetic hormones, pollutants washed off road surfaces ...). Courageously, and at risk of criticism for some consumer organisations who have in the past taken the simplistic position that sewage sludge is "polluting", **the association concludes that despite** these issues the use of sanitised (pathogen free) sewage sludge should be authorised on organic crops, subject to strict limits and controls for contaminants.

The Soil Association states "returning human excreta to agricultural land does reflect three of the principles of the organic movement – the law of return, a holistic or systems approach, and the use of biological and ecological processes. The critical nature of peak phosphorus justifies amendments being made to EU regulation No. 889/2008 to permit the use of sewage sludge on organic certified land where that sewage sludge meets certain quality criteria"

P-recovery from sewage

For the long term, the Soil Association recommends the development of **Ecological Sanitation (ES) systems**, for example with urine separation or composting toilets. Urine can be used after pretreatment directly as a liquid fertiliser. Two municipalities in Sweden have already mandated that all new toilets must be urine diverting.

More immediately, **phosphorus can be reclaimed from sewage through the production of struvite** (magnesium ammonium phosphate). This avoids heavy metal or organic contamination and can be recycled as a fertiliser.

What we eat

The Soil Association also emphasises the importance of a **change in our diet to respond to the phosphate resource issue**. Eating less meat can reduce the demand for phosphate fertiliser, in addition to being generally healthier and reducing climate change impacts of agriculture. Meat from livestock raised by grazing on grassland without fertiliser addition also reduces phosphate consumption, compared to livestock fed on intensively produced grain.

The Association underlines that **organic farming methods use little or no mined phosphates**, relying instead on better practice to improve phosphate availability in the soil and recycle phosphorus within the farm system.

A rock and a hard place: Peak phosphorus and the threat to our food security: The Soil Association, UK: http://www.soilassociation.org/peakphosphate.aspx





Nutrient management

Crop P-cycles

Phosphorus, phytic acid and world food security

An assessment is made of phosphorus flows in agricultural production of the world's main cereal crops (wheat, rice, barley, maize) and main legume crop (soybeans). The balance between P fertiliser consumption and P in crops is considered for different continents. In particular, the important implications of the % of P contained in crop products in the form of phytic acid (inositol hexaphosphate, IP6) are assessed: 50-80% of P in these crops is in this form, but phytic acid cannot be digested and is not absorbed by man, poultry or other non-ruminant livestock, and so is lost to manure or sewage along with the phosphorus it contains. Also, phytic acid can chelate other minerals leading to potential dietary deficiencies.



The authors collected data for the above cited 5 crops plus total cereals and total legumes, by continent and worldwide, for crop production, area farmed, crop yields, P-fertiliser consumption, world population, for nine years (1994-2003).

Data were also collated for typical % of P in the grain of each crop in the form of phytic acid (remaining P was assumed to be present as digestible phosphates). Also, data on existing crop strains with "low phytic acid" were used to estimate the potential impact of a widespread move to such crop strains. Estimates were made for differences in statistics, for example between total crop production on the farm and statistics for crops placed on the market (crops used for biofuel production, farm and transport losses, small self-sufficiency production ...).

Maize, rice and wheat were the major world crops over the nine year period, with mean production of

595, 582 and 580 million metric tonnes/year. Some 850 million hectares of land was devoted to cereal and legume production; that is over 50% of cultivated land surface.

As a world average, maize and rice gave the highest crop yields (4.3 and 3.8 tonnes/ha/year) compared to wheat, barley and soybeans (2.7, 2.4, 2.2 t/ha/year).

Food supply

Although the global cereal yields increased around 10% over the 9 years analysed, growth has slowed greatly since 1997 and was near zero from 1999 to 2003. Consequently, and because of world population growth, per capita global cereal production did not increase over the nine year period and may have fallen slightly (significant year on year variability makes identification of trends difficult).

P in crops

Worldwide, the authors estimate that a total of around 7.9 million tonnes/year of phosphorus (P) was removed from farmland in all cereal and legume crops, with most P being removed in wheat (2.1), maize (1.7) and rice (1.5 mtP/year). The order is different from that of the crop tonnages because of differing P contents in the crops.

This compares to total **world consumption of phosphorus in fertiliser**, estimated at 14 mtP/year, of which 54% was consumed in Asia and just 3% in Africa.

Continental P balance

In the North/Central America and in Europe, the tonnage of phosphorus in applied fertilisers was slightly more than that removed in total cereal and legume crops. In Oceania, around 5x more P was applied in fertilisers than was removed in crops, and around 2x in South America and Asia. In Africa, however P removed in crops was actually marginally higher than that in fertiliser applied.

Because of Asia's high proportion of world fertiliser consumption, and this difference between P applied in fertiliser and P removed in crops (7.5 compared to 3.3 million tP/year), the authors conclude that **more efficient P fertiliser use in Asia will be important for future world security**, whereas higher P fertiliser use in Africa is necessary to increase yields.

Low phytic acid crops



SCOPE Newsletter – n° 77 February 2011 - Page 8 <u>www.ceep-phosphates.org</u>



Strains of major crop plants have been developed by selective breeding or by genetic modification (GMO) which **reduce the levels of phytic acid in crops** (e.g. wheat -38%, rice -45%, maize -58%, soybean -80%) thus reducing the proportion of crop P present as phytic acid from 50-80% to around 30%.

Reducing the proportion of crop P present as phytic acid or other inositol phosphates greatly **increases the availability of crop P to both humans and monogastric (non ruminant) livestock** such as pigs, poultry, fish. This results in lower P contents of human sewage and animal manure (so reducing eutrophication risks of surface waters where wastewaters are inadequately collected and treated, see Turner 2007) and in lower needs for P supplements in livestock diets.

Lower phytic acid content in crops would also **reduce chelation of minerals in human and livestock diets** (K, Mg, Ca, Fe, Zn, Mn, see Lott 2000), which results in these minerals passing through the body and not being absorbed, with possible consequences of dietary mineral deficiencies or the need to include mineral supplements in livestock diets.

The authors estimate that widespread rollout of low phytic acid (low PA) crops would reduce by 10 million tonnes/year the phytic acid (PA) content of world cereal and legume crops. They do not estimate the contribution this could make to **closing the world P-cycle gap**, but if it made an additional 30% of total crop P bioavailable this could mean 2 million tonnes P/year.

Lott, J.N.A., Bojarski, M., Kolasa, J. et al. (2009). A review of the phosphorus content of dry cereal and legume crops of the world. International Journal of Agricultural Resources, Governance and Ecology. 8 (5/6):351-370 http://inderscience.metapress.com/link.asp?id=d81r8186721 44671_Contact: lott@mcmaster.ca

EU DG Environment summary: <u>http://ec.europa.eu/environment/integration/research/newsal</u> <u>ert/pdf/205na4.pdf</u>

See also :

Lott, J.N.A., Ockenden, I., Raboy, V. and Batten, G.D. (2000) 'Phytic acid and phosphorus in crop seeds and fruits: a global estimate', Seed Science Research, Vol. 10, No. 1, pp.11–33 and 3 and erratum 11, 181 (2001) http://journals.cambridge.org/action/displayAbstract?aid=69 3720

Turner, B.L., Richardson, A.E. and Mullaney, E. (2007) Inositol Phosphates – Linking Agriculture and Environment, pp.1–336, CABI, Cambridge MA.

Nitrogen Cycle

Transformation of the global N cycle

The authors provide an overview of the radical transformation of the global nitrogen cycle and pools of reactive nitrogen over the last 150 years. They look at issues for agriculture, industry, climate change, biodiversity and water quality and propose potential key points for action and possible solution.

Anthropogenic production of reactive nitrogen (Nr) has increased massively over the past 150 years, following the invention of the industrial Haber-Bosch process for fixing nitrogen, from around 15 million tonnes Nr/year (mtN/y) in 1860 to 187 mtN/y in 2005 (of which 125 mtN/y was produced industrially in 2005. Reactive nitrogen is also produced through cultivation-induced biological nitrogen fixation (C-BNF) in crops, pasture and fodder legumes. This C-BNF reactive nitrogen production is estimated at 40 mtN-/y in 2005. Reactive nitrogen also results from NO_x production in the burning of fossil fuels, biomass and other thermal processes: around 25 mtN/y from fossil fuel burning in 2005.

Environmental impacts

Most of this anthropogenic fixed Nr is likely to find its way into the environment, through environmental releases of Nr into the atmosphere, soils or surface waters by agricultural losses, fossil fuel combustion, or other pathways.

Around 23 mtN/y of industrially fixed nitrogen was however used in the chemical industry, for end uses ranging from polymers (nylon, melamine ...) to animal food supplements: some of this may ultimately also reach the environment through diet, incineration or other routes.

Accelerating Reactive Nitrogen (Nr) creation

From 1970 to 2005, the world population increased 78% but **anthropogenic Nr fixation increased by 120%**. From just 1995 to 2005, total Nr fixation increased by 14% and industrial (Haber-Bosch) fixation by 20%. At the same time, world cereal production increased by +20% and meat production by +26%. Despite a 24% increase in world energy consumption over the same period, NO_x nitrogen fixation remained stable because of tighter emissions controls.



SCOPE Newsletter – n° 77 February 2011 - Page 9 <u>www.ceep-phosphates.org</u>



Over nearly the same decade (to 2004), **international trading of Nr commodities increased twice as fast as Nr fixation to around 45 mtN/y**. This can result in local or regional distortion of the Nr cycle and Nr pollution risks. Regions consuming Nr rich products (meat, milk) may be distant from areas producing them, where N pollution through agricultural concentration and losses may occur.

In 1999, for example, the Netherlands used 0.4 mtN/y in fertiliser, producing food sufficient to feed more than five times its 6 million population.

Atmospheric deposition

The dominant Nr transport process, at a world scale, is atmospheric deposition following NO_x and NH_3 emissions from soils and combustion of fossil fuels and biomass, estimated at 105 mtN/y. This results in deposition rates of up to 10 KgN/ha in some areas of the world, an order of magnitude higher than natural rates.

Increasing deposition into the world's oceans could increase ocean biomass production by c. 3% but also increase emissions of N₂O, a greenhouse gas.

Fate and impacts

The authors identify 5 key questions regarding the nitrogen cycle and the impact of anthropogenic nitrogen fixation:

- **Final fate of Nr**: the main sink of Nr is thought to be denitrification in soils and freshwater systems, but will these reach saturation and what will be the consequences of increasing Nr loadings to coastal waters and oceans?
- Net effects on climate change: Nr can lead to N₂O and tropospheric O₃, both potent greenhouse gases, but may also affect CO₂ and methane cycles or reduce the greenhouse effect (e.g. by increasing tropospheric aerosols or by decreasing stratospheric O₃)
- **Human health**: at least 2 billion of the world's population could not be sustained without Haber-Bosch nitrogen fixation, but increasing Nr also has many other health implications, including nitrates in water supplies, tropospheric ozone, possible impacts on infectious diseases

• **Biofuels**: N fertiliser use is high where biofuels are grown as currently, that is in intensive agricultural systems with only low efficiency (e.g. only around 30% of applied Nr ends up in sugar cane plant tissue)

Points for action

Conform to the Nanjing Declaration on Nitrogen Management (Erisman, 2004), the authors identify four key points for intervention in the N cycle and estimate achievable reductions in nitrogen loss to the environment:

- Control NO_x emissions from fossil fuel combustion (-18 mtN/y)
- Improve nitrogen uptake efficiency by crops (-15 mtN/y)
- Animal management (-15 mtN/y)
- Connect one half of the world's city dwellers to appropriate sewage treatment (convert 5 mtN/y to N₂)

In total, these points could reduce Nr production and loss by around 28%. The authors emphasise that this is significant but not sufficient, so that other further actions will be necessary. They also underline regional differences: some regions currently do not have sufficient access to Nr to sustain their population, and here it will be necessary to increase Nr inputs to agriculture whilst minimising environmental impacts.

"Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions", Science 16 May 2008, Vol. 320 no. 5878 pp. 889-892 DOI: 10.1126/science.1136674 http://www.sciencemag.org/content/320/5878/889

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SCOPE Newsletter – n° 77 February 2011 - Page 10 www.ceep-phosphates.org



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7: Centro de Energia Nuclear na Agricultura-Universidade de São Paulo, Avenida Centenario, 303, Piracicaba-SP, Brazil.

8: Rutgers, The State University of New Jersey, Institute of Marine and Coastal Sciences, Rutgers/National Oceanic and Atmospheric Administration Cooperative Marine Education and Research Program, New Brunswick, NJ 08901, USA.

9: Centre for Ecology and Hydrology, Edinburgh Research Station, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK.

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British Columbia

Innovation award for P-recovery developer

Dr Donald S Mavinic, of the University of British Columbia (UBC), has received one of Canada's most prestigious innovation awards, the CAD 25,000 Dave Mitchell Award of Distinction, for his contribution to the development of phosphorus recovery and recycling. Mavinic and his team at **UBC** have helped develop the struvite precipitation P-recovery process and spin it off to the technology company Ostara, which is rolling it out in full scale production of 'Crystal Green' struvite fertiliser in municipal sewage works.

The Ostara Pearl® process enables **recovery of phosphorus and (some) ammonia as struvite** (**magnesium ammonium phosphate) from sewage works** operating biological nutrient removal, through a precipitation reactor installed in the sludge processing / return stream lines. The recovered struvite is marketed under the brand name Crystal Green as a high-quality fertiliser. The process has the advantage of reducing or avoiding phosphate returns to the sewage treatment line, thus improving nutrient removal performance and avoiding pipe-clogging and other operation problems.

The struvite recovery process developed by Mavinic, along with Frederic Koch and the team at UBC, relies both on an improved understanding of struvite chemistry, and a practical approach to reliable, operational reactor design. Struvite is precipitated in a fluidised bed reactor, patented in 2004. The reactor is mixed by pumping the inflowing waste water stream through cones, and small additions of sodium hydroxide are used to ensure optimal precipitation pH. The technology was then spun off to Ostara Nutrient Recovery Technologies Inc, named after the Scandinavian Goddess of Spring, Ostara.

Development was supported initially by NSERC and Stantec Consulting Ltd, Greater Vancouver District Council, and more recently by green technology investment Frog Capital's participation in Ostara.

Mavinic says "I've always believed in putting research into practice. It's been a team effort. The researchers and Ostara are thrilled with the Manning Innovation Award win. They're sky high"

Ostara P-recovery installations are already operational or planned at a number of municipal sewage works in the USA and Canada: Nine Springs (Madison, Wisconsin), Nansemond – Hampton Roads (Suffolk, Virginia), York (Pennsylvania), Durham -Tigard near Portland (Oregan), Gold Bar - Edmonton (Alberta). A first plant for Europe was recently announced by Thames Water UK, see SCOPE Newsletter n° 76.

Manning Innovation Awards announcement: http://www.manningawards.ca/awards/winners/dmavinic.shtml

Multiform Harvest, USA Full-scale struvite recovery from sewage

and animal manures

The cone-shaped struvite precipitation reactor initially designed for use in pig manure treatment by North Carolina State University (see SCOPE Newsletters n°s 68 and 55), has continued to be developed and tested on agricultural and municipal wastewaters, in cooperation with Washington State University. A number of recent papers present results of different trials, and in particular work to release phosphate to soluble forms in dairy wastewaters (to enable struvite recovery), countering calcium interference with struvite precipitation, economic assessment and costing.

The reactor is further being developed by **Multiform Harvest Inc**. with activities in phosphorus recovery in the municipal, agricultural, and food processing wastewater sectors.



SCOPE Newsletter – n° 77 February 2011 - Page 11 <u>www.ceep-phosphates.org</u>



The company is achieving 80% total phosphorus reduction in a full-size reactor treating effluent from a digester fed mixed dairy and food processing wastes. Multiform has recently signed a contract with the City of Boise, Idaho, USA, to provide the struvite crystallizer technology to treat 0.6 million gallons per day of high-phosphorus wastewater.

This article summarises the four published papers. Further information about Multiform Harvest struvite recovery operations from manures and municipal wastewaters are available on the company's website <u>www.multiformharvest.com</u>

Phosphorus availability in dairy manures

Paper (1) (Shen, 2010) assesses the potential of EDTA or oxalic acid dosing, to reduce calcium availability, to improve struvite precipitation from liquid dairy manure. Modelling using Visual Minteq 2.60 was used to estimate operating pH and reagent concentrations, which were then tested in 1 litre jar tests using both synthetic and real manure, centrifuged and non centrifuged. Disodium-EDTA or oxalic acid were added to the manure liquid (stoichiometric to calcium concentrations), stirred for 30 minutes then settled for 60 minutes, before adjusting pH using sodium hydroxide and stirring for 10 minutes to precipitate struvite. Struvite was then removed by 0.22 µm filter paper and its structure analysed using electron microscopy (SEM) and X-ray diffraction (XRD).

Manure characteristics were approximately 2.2% suspended solids (non centrifuged) and 0.4% (centrifuged), ammonium nitrogen 1400 mg/l, calcium 1700 mg/l, magnesium 700 mg/l, total phosphorus 500 mg/l and pH 7.

EDTA was estimated to remove around 90% of soluble calcium but only 10% of soluble magnesium from solution by chelation. Oxalic acid removes calcium by precipitation of calcium oxalate. Acidification of manure to pH 4.5 increased soluble phosphorus (dissolved reactive phosphorus, DRP) from around 20 to 300 mg/l.

90% recovery of soluble P

In all cases, over 90% removal (precipitation) of soluble phosphorus was achieved, suggesting no significant impact of the suspended solids level on phosphate precipitation. However, struvite crystals were found using synthetic solutions with high Mg/Ca ratios, and in real manure treated with EDTA or oxalic

acid, but not in untreated real manure. Struvite was more present using centrifuged rather than non centrifuged manure.

The authors conclude that acidification of the manure to 4.5 (to make total phosphorus available as DRP) combined with EDTA or oxalic acid dosing (to remove calcium which interferes with struvite precipitation through calcium carbonate precipitation or competition for phosphate ions) enables effective phosphorus recovery as struvite. **Struvite precipitation was adequate for P-removal and P-recovery even without centrifuging the manure and raising the pH to 7 was sufficient for struvite precipitation**.

Making phosphorus available for recovery

Paper (2) (Zhang, 2010) presents similar work **testing** acidification and EDTA treatment of the manure. This work used liquid manure from the anaerobic digester at a dairy farm in Washington State, USA, collected after the solid-liquid separation screen at the digester outflow and before lagooning.

Acidification used concentrated hydrochloric acid , with 60 minute mixing, to achieve pH in the range 3.8 -7.8 (the raw manure pH). This was followed by centrifuging at 10 000 rpm for 10 minutes. EDTA was added at 0 -70 mmmol/l, mixed for one hour, and then centrifuged as above, followed in this case by adjustment of pH to 8.5 At higher doses of EDTA, magnesium (MgCl) was added to compensate chelation of magnesium ions (necessary for struvite formation) anticipated by EDTA.

The work was continued using a pilot scale cone struvite reactor on a dairy farm site. The reactor was as presented in SCOPE Newsletter n° 68: 2.3m high, top diameter 0.46m, and was operated with an effluent through flow of around 2 litres/minute. EDTA was dosed and mixed in agitated 1200 – 5700 tanks upstream of the reactor.

EDTA was shown to be effective in releasing both calcium and phosphate to soluble forms (from manure suspended solids. When doses stoichiometrically to total calcium, EDTA released around 90% of total manure phosphorus to soluble forms.

The pilot reactor studies showed the **importance of pretreatment for possible P-recovery as struvite from dairy manure**. Total P-reduction, without pretreatment, varied from near zero (1%) to only 13% in 9 experimental runs at reactor pH of 7.5 – 8.5. This



SCOPE Newsletter – n° 77 February 2011 - Page 12 <u>www.ceep-phosphates.org</u>



is incomparably lower than the high P-removal performance (>80%) previously achieved using the same pilot reactor with swine manure (see SCOPE Newsletter n° 68), presumably because much of the phosphorus in dairy manure is immobilised in the suspended solid fraction.

In four EDTA pretreated runs, however, P-removal rates of 30%, 60%, 70% and 80% were achieved at pH 6.8-7.5

The authors conclude that this work demonstrates the potential for P-recovery as struvite from dairy manure, if a pretreatment is used to release the phosphorus from solid to soluble forms. They note that the use of EDTA at the concentrations use in this experimental work is not realistic in full scale application, because of both cost and questions regarding the environmental fate of the substance.

The work was not intended to demonstrate the feasibility of using EDTA as such, but rather the principle of struvite precipitation after using appropriate pretreatment to convert phosphorus in dairy manure from solid to soluble form.

Field testing of reactors

Paper (3) (Bowers, 2007) presents further testing of cone-shaped struvite precipitation reactors similar to that previously tested for P-recovery from pig manure wastewaters, see SCOPE Newsletter n° 68. In this paper, the reactors were tested on swine (pig) wastewater and on two types of dairy (cow) wastewater: digester effluent and lagoon water. The reactors were tested at the 1,000 head North Carolina State University swine research farm, Raleigh, NC; a 700-head dairy farm in Snohomish County, Washington; Vander Haak Dairy, Whatcom County, Washington.

The reactor used on the swine wastewater and dairy digester effluent treated an average 443 l/hour (1.52m high, 0.25m top diameter). The dairy lagoon water reactor was 1.5 x larger (linear dimensions) in order to enable a slower up-flow for the more viscous liquor.

These experiments showed that **reactor phosphorus removal performance was considerably lower in the dairy wastewaters than in the swine wastewater**, where total P removal ranged from 63% - 80%, conform to results achieved in previous studies. In the dairy wastewaters, P-removal in the digester was <25% (lagoon) or around 16% (digester effluent). These levels could be improved to around 50% for the dairy lagoon water through pretreatment by acidification to pH5 or 35% in the dairy digester effluent by adding a settling stage after the cone reactor.

The authors noted that **P-removal performance was inversely proportional to visible liquor viscosity and to calcium concentration**, and suggest that P-recovery is lower in dairy wastewater because of particle levels, and because of interference of calcium with struvite precipitation. EDTA pretreatment was tested (see above) and showed to be successful in releasing P into solution, reducing calcium inhibition, and improving struvite precipitation.

Field testing of precipitation parameters

Paper (4) presents **further results on swine wastewater, using the 1.52m high cone reactor** indicated above on effluent from a covered earthen anaerobic digester designed for ambient temperature operation and biogas production at a pig farm.

Twenty four combinations of pH increase and magnesium dosage were tested (30 minute runs) to derive conditions used for longer run tests (pH +0.5, Mg + 40 mg/l). Forty 2-hour tests were then operated under these conditions to compare use of anhydrous ammonia and sodium hydroxide for pH adjustment.

Digester inflow total P concentration was around 72 mgP/l (65 mgP/l soluble). Both pH adjustment reagents achieved very similar phosphate precipitation performance, around 55% removal of total P (65% removal of soluble P) and statistical analysis indicated that this choice of reagent had no significant effect.

Further 2 hour tests were carried out to confirm the effects of higher pH increase or magnesium dosing, showing that around 80% soluble P removal was achieved with a pH increase of +1 and slightly higher P removal with magnesium dosage of +60 or +100 mg/l.

Overall, the experimental work lasted some 14 months.

Economics of struvite recovery

Analysis of the recovered struvite showed growth rates of around 120 g/h and relatively pure struvite (approx 1.3 - 2.2% calcium).

Detailed analysis of chemical costs and projected investment and operating costs for a 1,000 head swine farm are provided, suggesting a **seven year recovery**



SCOPE Newsletter – n° 77 February 2011 - Page 13 <u>www.ceep-phosphates.org</u>



of capital costs through sale of the recovered struvite as a fertiliser.

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Minerals

Naturally occurring struvite

Struvite (magnesium ammonium phosphate), the mineral produced by a number of phosphate recovery and recycling processes, precipitates to form natural deposits in certain ecological conditions, and is naturally produced by certain bacteria.

Although struvite does not occur frequently in nature, it is sometimes found, usually related with specific

ecosystem situations or produced directly or indirectly by bacteria.

The first record of bacterial precipitation of struvite was presented by Robinson in 1889. Recent papers have presented the probable mechanisms by which certain bacteria either directly produce struvite or indirectly cause its precipitation by generating local concentrations of minerals and locally modified pH.

Struvite is widely known as a nuisance deposit in piping and equipment in sewage treatment works, sewage sludge installations and in various industries. This recognised tendency to deposit, so that struvite recovery can avoid such nuisance deposits, and struvite's value as a controlled release fertiliser, make **struvite an attractive option for P-recovery for recycling**.

Lake deposits of struvite

Donovan and Grimm found a series of 34 layers of struvite deposits in lake sediment cores from Kettle Lake, North Dakota (near the USA – Canada border) dating from the Holocene period (9000 - 4000 years before the present = BP).

They note that **most reports of naturally occurring struvite are related to concentrations of animal wastes** (eg. Mcfarlane *et al.*, 1995, in caves used by bats), bird colonies (Cullen, 1988, Tatur *et al.*, 1997), as well as in **renal calculi** – **kidney stones**. Nonetheless, several studies have also found struvite in Halocene lake sediment cores from the subarctic Bounty Islands, California, Long Island Sound USA.

The authors suggest that the deposits found in the Kettle Lake may be a consequence both of anoxic sediment conditions (preventing struvite inverting to Newberyite) and of periods of drought when the lake had **specific ecological conditions**. Because Kettle Lake is relatively deep, during dry climate periods water mineral concentrations would increase so that magnesium would reach sufficient levels for struvite precipitation to occur. Furthermore, the lake would be one of only a few remaining (shallow lakes would disappear), and so would concentrate high numbers of wildfowl during migration stopovers, resulting in high ammonium concentrations from their droppings.

This is confirmed by **isotope ratio mass spectrometer analysis**, showing a high ratio of ¹⁵N nitrogen in the sediment struvite, indicative of a nitrogen source outside the Lake.



SCOPE Newsletter – n° 77 February 2011 - Page 14 <u>www.ceep-phosphates.org</u>



Bacterial production of struvite

Robinson (1889) first reported bacterial production of struvite, suggesting that it could be the consequence of metabolic ammonium ions combining with environmental phosphate and magnesium. Other authors have since also shown the **crystallisation of struvite on bacterial cells** (eg. Ben Omar *et al.*, 1998) **or that bacteria cause the precipitation of struvite** crystals in solid or liquid fresh water culture media (for example: Gonzalez-Munoz *et al.*, 1993; Rivadeneyra *et al.* using 96 bacterial strains from soil, 1983, etc).

Recent papers (Sanchez-Roman *et al.*, 2007; Gonzalez-Munoz *et al.*, 2008) show struvite production by a variety of bacteria in seawater salinity media (respectively: *Halomonas, Marinomonas and Marinobacter* strains; *Idiomarina* strains).

Gonzalez-Munoz *et al.*, 2008, found that the struvite appeared **encased in Ca-Mg Kutnahorite** [CaMg(CO₃)₂ coverings, regularly distributed in the bacteria colonies. They suggest that the struvite precipitation is caused by ammonia and CO₂ release by the bacteria, which locally increase pH, and possibly also by heterogeneous nucleation on negatively charged points on the bacteria surface.

Sanchez-Ramon *et al.* suggest that the struvite precipitation is related to the **bacterial metabolic activity which causes local concentrations of magnesium, phosphate and ammonium**, through breakdown of the food sources releasing these ions and because of adsorption of the ions by the bacterial cell walls, combined with local pH increases.

Carbonates

Because carbonate competes with or can co-precipitate with struvite precipitation (calcium carbonate, calcium phosphate precipitation), in addition to affecting local pH, the **bacterial production of struvite is highly dependent on carbonate / CO₂**, either from bacterial metabolic activity or from breakdown of their food,

It is suggested that struvite deposits are not often found in nature because the struvite is significantly more soluble than carbonate and other mineral precipitates, and so will dissolve and disappear unless organic and mineral concentrations remain high so that further precipitation can continue.

Episodic struvite deposits in a Northern Great Plains flyway lake: indicators of mid-Holocene drought?

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The Holocene 17, 8 (2007) pages 1155–1169 – SAGE Publications <u>http://hol.sagepub.com</u>

Biomineralization of carbonate and phosphate by moderately halophilic bacteria

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FEMS Microbiol Ecol 61 (2007), pages 273–284. Wiley <u>http://onlinelibrary.wiley.com/journal/10.1111/(ISSN)1574-6941</u>

Ca–Mg kutnahorite and struvite production by Idiomarina strains at modern seawater salinities

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Chemosphere 72 (2008) 465–472. www.elsevier.com/locate/chemosphere







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