
SCOPE NEWSLETTER

NUMBER 84

February 2012

Phosphate resources and uses

EU Resource Efficiency policy

European Commission Green Paper on Phosphorus

As part of its Roadmap to a Resource Efficient Europe, the EU Commission is preparing a Green Paper on Phosphorus for 2012, addressing P-consumption, use patterns, losses and recycling, and to be followed

Phosphate reserves

Geopolitical trends for phosphate rock supply

Analysis of recent (IFDC, USGS) figures for phosphate rock reserves and estimated global P-consumption suggests that Morocco will be supplying 80% of the world's phosphorus needs by 2100, and will need to increase production by 700% to meet demand.

Inorganic polyphosphates

Outlook for applications in industry and biology

Recent knowledge shows that polyphosphates have a range of essential functions in cell metabolism and so important applications in biochemistry, medicine, developing bio-industries, as well as a range of industrial applications.

Phosphorus in the environment

European Union

Waste water treatment progress

The EU Commission has published its 6th assessment of sewage treatment implementation, concluding that significant progress has been made, but that considerable investments remain necessary. In particular, 'Sensitive Areas' have been extended as Member States recognise the need to remove phosphorus from sewage to reduce eutrophication risks.

UK lakes

Reference phosphorus levels

Paleolimnological methods were used to assess the reference algal populations and phosphorus concentrations in over 100 UK lakes.

Phosphate recycling

ICL Fertilizers Europe

Recycling phosphates into fertiliser production

Europe's biggest PK fertiliser manufacturer aims to replace 10-15% of raw materials by secondary (recovered) phosphates such as sewage sludge incineration ash manure and wood ash as well as struvite.

Seafood wastes

Oyster shells for phosphate removal

A number of studies show that pyrolysed oyster shells can provide a material which is effective for removing phosphates from wastewater. The possible agricultural value of the resulting solid does not seem to have been assessed.

P and N adsorption

ETC reacted wheat straw for P-recovery

Epoxypropyl triethylammonium chloride (ETC) reacted agricultural wheat straw was tested for adsorption and recovery of phosphate and nitrate ions.

Polymeric anion exchanger

Iron loaded resin can recover phosphate

Three polymeric anion exchangers impregnated with iron oxide nanoparticles were tested for P-removal from laboratory phosphate solutions, followed by P-release regeneration and phosphate precipitation for recovery.

Conferences

3rd sustainable phosphorus summit

Phosphorus stewardship conference

Sydney, Australia, 29th Feb. – 2nd March 2012

Phosphate resources and uses

Global TraPs 4th Workshop

El-Jadida, Morocco, March 16th – 18th 2012

Phosphates 2012

Phosphate industry conference

El-Jadida, Morocco, 19th – 21st March 2012

EU Resource Efficiency policy

European Commission Green Paper on Phosphorus

The EU published in 2010 a report on “Sustainable use of phosphorus” (See Scope Newsletter n°79), underlining that EU food security relies on imported phosphorus, both in fertilisers and ‘embedded’ in imported foods and animal feeds, and that actions should be engaged to reduce Europe’s phosphorus dependency, including optimising land use and agricultural P use, P-recovery and recycling, reducing food wastes and P-losses. The Commission has now confirmed the objective to publish a “Green Paper” on phosphorus in 2012, as a basis of discussion with stakeholders and institutions, to define a phosphorus resource efficiency strategy.

This announcement follows the publication of the “**Roadmap to a Resource Efficient Europe**” (EU Commission Communication COM(2011)571 final, 20th September 2011), which recognises that sustainable phosphorus supply is an issue for long term global food security and fixes the objective to “further assess the security of supply of phosphorus and potential actions towards its sustainable use” in a Phosphorus Green Paper in 2012.

This Roadmap also fixes the objectives, by 2020, to **reduce by 20% the EU food chain’s resource inputs and to reduce by 50% edible food waste** (with a Commission Communication on Sustainable Food in 2013).

EEA resource efficiency report

Also, the European Environment Agency (EEA) has published a report into “Resource efficiency in Europe” in which **phosphorus is identified as a priority resource**.

This report notes that to date only one European State has regulatory objectives for phosphorus stewardship, that is Sweden’s objective to recover at least 60 % of phosphorus compounds in wastewater by 2015 for use on productive land, with at least half returned to arable land. Denmark has an objective to reduce P release from agriculture by 210 tonnes by 2015.

The EU Commission (DG Enterprise) indicated in a presentation in October 2011 that the huge increase in resource use of the 20th century cannot be maintained, or would result rapidly in depletion and scarcity. A 4 – 10 fold increase in resources efficiency by 2050 is

necessary. The Phosphorus Green Paper is of major interest to this objective.

The Commission notes that phosphorus is a limited resource, with global demand rising, is easily lost in the use and waste chain, but is essential for long term food production. Resources are concentrated in a few regions. Major education processes need to be undertaken, and solutions need to be integrated into infrastructure planning to avoid excessive end-of-pipe costs.

The Commission sees synergy with the resource efficiency agenda, and opportunities for biotech companies in areas such as enzymes in animal feed or fertilisers.

Areas of action cited included: improving phosphorus processing and agricultural techniques, recycling and reuse of P in sewage sludge and biowastes, manure management and processing, limiting food chain P losses. Issues include looking at production/consumption patterns and barriers to recycling.

Stakeholder input will be invited in response to the Phosphorus Green Paper in 2012.

“*Optimizing Natural Resources*”, Michael Hamell, DG Environment, EU Commission, 19th October 2011 (Fertilizers, food and natural resources conference – Fertilizers Europe):

<http://www.slideshare.net/FertilizersEurope/5-hamell>

European Commission Communication Brussels, COM(2011) 571 final, 20th September 2011 “Roadmap to a Resource Efficient Europe”:

http://ec.europa.eu/environment/resource_efficiency/pdf/com2011_571.pdf

European Environment Agency (EEA) “Resource efficiency in Europe — Policies and approaches in 31 EEA member and cooperating countries”, EEA Report n° 5/2011, October 2011:

<http://www.eea.europa.eu/highlights/publications/resource-efficiency-in-europe/>

“Sustainable use of Phosphorus”, EU Tender ENV.B.1/ETU/2009/0025. J. Schröder, D. Cordell, A. Smit, A. Rosemarin, Wageningen University Plant Research International, Stockholm Environment Institute (SEI), October 2010, published February 2011 at:

<http://ec.europa.eu/environment/natres/phosphorus.htm>

Conclusions of the Expert Seminar on the sustainability of phosphorus resources, EU Commission DG Environment, Brussels, 17th February 2011:

http://ec.europa.eu/environment/natres/pdf/conclusions_17_02_2011.pdf

Phosphate reserves

Geopolitical trends for phosphate rock supply

Recent assessments of world phosphate rock deposits (IFDC 2010, USGS 2011) have suggested considerably increased global reserves, with estimates around 4x higher than previous publications. However, these new estimates are based on publications from the 1980's and 90's, which had not been taken into account before. The publications included phosphate rock volumes in Morocco and Western Sahara, from which useable reserves were then estimated. After underlining the proviso that these and other estimates of phosphate rock reserves must be considered susceptible to revision, this paper looks at the implications of these new figures for phosphate production and geopolitical distribution of phosphorus supply throughout the 21st Century.

The 2011 USGS figures estimate world phosphate rock reserves at 65 000 Mt (million tonnes of phosphate rock) of which 50 000 Mt in Morocco. The estimate for Morocco is thus 9 times higher than previous estimates. The authors use as an approximation that rock contains 30% phosphate $P_2O_5 = 13\% P$ whilst recognising that this ratio will change (and probably deteriorate) as the best quality reserves are used up.

The 2011 USGS figures also estimate world phosphate rock production in 2010 at 176 Mt, suggesting a lifetime of around 370 years at constant extraction rates. Global production is currently more balanced than reserves (China 37%, US 15%, Morocco 15%, other countries 33%), although just 7 countries have lifetimes greater than 100 years.

The world's largest phosphate producers, China and the USA, will both have depleted their reserves in 50-60 years at current extraction rates, and over 70% of current production comes from reserves expected to be depleted before the end of the century.

Phosphorus demand and production

Around 90% of phosphorus consumption is in agriculture, and demand is expected to increase significantly with population increase and related food production, as well as fertiliser use for non-food crops such as biofuels. The authors take a conservative estimate of P-consumption increase at +1% per year through to 2050, which then remains stable, suggesting that world phosphate rock production will reach 260 Mt/year from 2050 onwards.

On this basis, and assuming production in different countries will increase in proportion to the size of the reserves, the paper looks at the affect that increased global demand and depleted reserves will have on the future phosphate rock production landscape.

Future phosphate rock perspectives

To meet global demand, Morocco will have to increase its production rate by 7 – 8 times, involving investments of hundreds of millions to billions of US\$. **Morocco is estimated to be supplying 20% of global demand by 2020, 40% by 2050 and 80% by 2100.** Because of the size of Morocco's estimated reserves, the country would nonetheless still have larger reserves than any other country, and a higher share of world reserves by the end of the century (Morocco would hold 88% of remaining world reserves by 2100).

The authors note that the data suggests that **the world will become almost totally reliant on a single country for phosphorus reserves** – and so for food security - by then end of the century, with delicate geopolitical implications, unless significant moves are made towards a food production system which is considerably more phosphorus efficient and to widespread recovery and recycling of phosphorus.

"The future distribution and production of global phosphate rock reserves", J. Cooper, R. Lombardi, D. Boardman, C. Carliell-Marquet, School of Civil Engineering, College of Engineering and Physical Sciences, University of Birmingham, B15 2TT, UK JXC637@bham.ac.uk

Resources, Conservation and Recycling, n°57, pages 78–86, 2011

<http://www.sciencedirect.com/science/article/pii/S0921344911001807>

Inorganic polyphosphates

Outlook for applications in industry and biology

Inorganic polyphosphates are linear polymers built up of phosphate chains ($P_nO_{(3n+1)}$) of varying lengths from $n=2$ (pyrophosphates), $n=3$ (tripolyphosphates) to $n > 1000$. The phosphate ions are linked by energy-rich phosphanhydride bonds which can readily be broken (hydrolysed), releasing energy, or reformed by biological enzymes (polyphosphate kinases and polyphosphatases).

Polyphosphates play a wide range of roles in living organisms, including energy storage, osmotic balance, storage of cations (magnesium, calcium ...), membrane channels, controlling gene activity,

regulating enzymes, blood coagulation, bone tissue formation. The importance of polyphosphate kinases in many pathogens and bacteria opens paths for new antibiotics.

Polyphosphates were first discovered by Graham in 1833, by fusing NaH_2PO_4 under heat then rapid cooling. At the time, he did not imagine that linear polyphosphates would find numerous applications in industry, and that they occur naturally in all organisms (unlike the cyclic polyphosphate sodium metaphosphate $(\text{NaPO}_3)_6$ which does not occur naturally).

Industrial applications

Because they are non toxic and naturally degradable, and because of their different properties, polyphosphates are widely used in a number of industrial applications. Their negative charge means they are effective in binding to (complexing or sequestering) different metal ions and their hydrogen bonding means that they can hold considerable amounts of water.

Ammonia polyphosphate is used as a fertiliser in both agriculture and aquaculture; as a non-halogen, non-toxic, high efficiency flame retardant. Because of their sequestering of iron, manganese, calcium and magnesium, polyphosphates are used in water treatment, to prevent scaling and dissolve mineral scale in cooling circuits and other water systems. Polyphosphates are also used in detergents, where they combine water softening, pH buffering with other cleaning functions.

Polyphosphates produced by microorganisms play an essential role in Enhanced Biological Phosphorus Removal (EBPR) in sewage works (biological nutrient removal), avoiding the addition of precipitant chemicals which increase sludge volumes and reduce their agricultural value. EBPR functions because aerobic and anaerobic cycles are used to develop populations of sludge microorganisms which remove soluble phosphate from water and stock it inside their cells as polyphosphates.

Food applications

Phosphates are naturally present in all living organisms and so in all foods. Sodium, potassium, sodium-calcium, calcium and ammonium polyphosphates are all used as human food additives and in dietary supplements and pharmaceuticals. They offer water retention properties, avoiding dehydration of foods which are stored or frozen then thawed. They act as a buffering agent maintaining pH and so improving food quality after storage periods. They also ensure antibacterial functions, improving food shelf

life and food safety whilst avoiding the use of more problematic bactericides (the possible mechanisms of this antibacterial action are discussed below). They also provide certain technical properties, for example improving lubrication by forming a natural gel, so improving cutting meats and other foods during processing.

Biological and cellular functions

Polyphosphates show a number of specific properties in cells and organisms:

- Polyphosphates are osmotically neutral, thus allowing storage of phosphorus in large quantities without upsetting cellular ionic concentration balances
- The phosphate units in polyphosphates are linked by phosphoanhydride bonds with a potential energy similar to that of the terminal phosphoester bond in Adenosine Triphosphates (ATP), the molecule used for cellular energy cycling
- The polyphosphate anion can complex with both inorganic cations and with other cell compounds (proteins, nucleic acids ...), so modifying their properties and biological functions

Polyphosphates thus contribute to a wide range of functions:

- Phosphorus storage
- Energy storage
- Detoxification of heavy metal ions
- Induction of synthesis of RpoS, an enzyme involved in gene expression
- Bacterial cell motility, biofilm formation and virulence
- Bacterial response to certain messenger molecules, regulation of certain enzymes in bacteria and yeasts
- Transport channels across membranes
- Biomineralisation and bone development
- Blood coagulation

Antibiotics and biosynthesis

Because polyphosphates affect certain enzymes which are present in bacteria but not in mammals, they offer potential as **new routes for antimicrobial products or antibiotics.**

Because bacteria and yeasts produce enzymes which break down polyphosphates, this can provide a cheap and feasible way of detecting contamination or presence of microorganisms.

Because polyphosphates can provide a cheap and practical energy source for cellular processes, it is potentially important as a route for “feeding” artificial biosynthesis processes where microorganisms are used to produce chemicals or drug molecules.

The heavy metal accumulation capacities of polyphosphates in microorganisms enables the development of biological processes for pollution remediation or for concentration of metals.

The discovery that polyphosphates form complexes with poly-β-hydroxybutyrate and calcium which are involved in the formation of channels across cell membranes opens possible routes for delivering target compounds or ions directly into cells to improve effectiveness, in particular for introducing genetic material.

Polyphosphates show a range of antibacterial and antiviral actions, including blocking bacterial spore germination, preventing bacterial growth, and inhibiting the infection in vitro of human cells by AIDS virus HIV-1. The mechanisms of these effects are not fully understood, and may be related to the chelation of calcium and magnesium ions or to the direct binding of the polyphosphate molecule onto cell walls or viruses.

Human body functions

Polyphosphates can impact bone development. They are naturally present in significant quantities in osteoblasts, the cells which regulate bone metabolism and their artificial injection can be used to stimulate and accelerate bone growth or regeneration.

Polyphosphates are also involved in blood coagulation. They are naturally present in human blood platelets involved in thrombosis, hemostasis and inflammation. Different length polyphosphates have been shown to affect different mechanisms of blood clotting. Polyphosphates have already been successfully used to treat certain blood diseases, and a better understanding of their functions may enable other applications in regulating blood clotting.

“Inorganic polyphosphate in industry, agriculture and medicine: modern state and outlook”, Process Biochemistry, in press, Elsevier

<http://www.sciencedirect.com/science/article/pii/S1359511311003850>

T. Kulakovskaya, V. Vagabov, I. Kulaev, Skryabin Institute of Biochemistry and Physiology of Microorganisms, Russian Academy of Sciences, Pushchino, Moscow region, 142290 Russia, alla@ibpm.pushchino.ru

European Union

Waste water treatment progress

From 2007 to 2013, the EU will spend some 14 billion Euros of community funds on improving sewage collection and treatment under the Urban Waste Water Treatment (UWWT) Directive 1991/271. The European Commission implementation summary report concludes that significant progress has been made, but that considerable problems remain, including four cities in the EU-15 which still do not have adequate sewage treatment.

Member States have increased from 68% to 73% surfaces designated as ‘Sensitive Areas’, that is considered as potentially subject to eutrophication and requiring phosphorus removal in sewage treatment for agglomerations > 10,000 pe (person equivalents). This increase is probably **the result of Member States recognising eutrophication risk areas and instituting better protection**, not to an increase in eutrophication. Phosphorus removal from sewage is required in these areas.

Barreiro/Moita and Matosinhos - Portugal, Frejus – France and Trieste – Italy are identified as cities in the EU-15 States which still do not have adequate sewage treatment in place.

The report shows significant differences between the historic EU-15 States and the 12 more recent EU Members (EU-12), but that the situation is improving in the EU-12.

New Member States

Sewage collection showed a very high level of compliance in the EU-15 (except in Italy and Greece) but a lower level in EU-12 (80% of sewage load or higher in all EU-12 States except Cyprus and Romania around 50%).

Secondary treatment is also inadequate to date in the EU-12 new Member States, with only 39% of load achieving adequate treatment (conform to UWWT Directive requirements). However, even in some EU-15 States, compliance for secondary treatment is still not good, for example 65% Belgium, 64% France, 58% Italy, 56% Luxembourg.

Phosphorus removal

73% of the European Union’s land area is now identified as a ‘Sensitive Area’, so that phosphorus removal is required for all agglomerations > 10,000 pe.

15 Member States have designated either their whole territory or all water bodies of their territory as 'Sensitive Areas' (Austria, Belgium, Czech Republic, Germany, Denmark, Estonia, Finland, Latvia, Lithuania, Netherlands, Poland, Romania, Slovak Republic, Sweden). **Thus, 79% of sewage in the EU-15 is now subject to Directive-compliant tertiary treatment (this generally means phosphorus removal), and 89% will be once treatment performance is improved to Directive requirement levels.** In the EU-12 new Member States, the figures are lower at 24% (27%).

Again some EU-15 States are still not achieving good compliance with tertiary treatment requirements, for example Italy 66%, France 56%, Belgium 48%, Luxembourg 34%, Spain 32%, Portugal 15%.

The European Commission reports that total EU funding for waste water collection and treatment in the Member States for the period 2007-2013 is **around 14 billion Euros (EU money only, not considering the funding by Member States' national budgets and by local authorities)**. Assistance is provided to the EU-12 new Member States through the EU Cohesion Funds, as well as 5.5 billion Euros of European Investment Bank funding. The Commission press release emphasises that if Member States' implementation does not progress adequately, then further legal action will be taken.

The Commission indicates that an aspect of the UWWT Directive which needs implementation is the **requirement for sewage collection in agglomerations >2 000 pe.**, suggesting that this does not necessarily mean a centralised sewage works and that on-site sanitation systems could be acceptable where appropriate.

Enforcement of P-removal

The EU Commission has also taken Luxembourg to the European Court of Justice, a second time, for **failure to ensure phosphorus removal from sewage in four agglomerations of > 10,000 person equivalents** discharging into a 'Sensitive Area'. Work is underway to ensure compliance in two of these agglomerations by end 2011, but is seriously delayed for two sewage works (Bleesbrück sewage plant in Diekirch and Bonnevoie plant, Luxembourg city). The EU Commission has asked the Court to impose a fine of 1248€/per day until phosphate removal is installed.

European Commission press release IP/11/1531: "Meeting the waste water treatment challenge", 13th December 2011
<http://europa.eu/rapid/pressReleasesAction.do?reference=IP/11/1531>

European Commission staff working paper SEC(2011) 1561 final, 7th December 2011: "6th Commission Summary on

the Implementation of the Urban Waste Water Treatment Directive": http://ec.europa.eu/environment/water/water-urbanwaste/implementation/pdf/SEC_2011_1561_F_EN.pdf

EU Commission press release IP/11/1273 "Environment: Commission takes Luxembourg back to court over waste water treatment and asks for a fine", 27th October 2011
<http://europa.eu/rapid/pressReleasesAction.do?reference=IP/11/1273>

UK lakes

Reference phosphorus levels

The EU Water Framework Directive (WFD) requires restoration of all surface waters (except those which are heavily modified) to "Good Status", which is assessed by comparison with their Ecological Reference Conditions (before anthropogenic impacts). It is therefore necessary to estimate the reference levels of phosphorus. This is carried out here for over 100 UK lakes, using palaeolimnological methods (looking at sediment core algal community records, specifically diatoms), concluding that >50% of sites studied currently show significant deviation from reference conditions.

This paper (P1) is based mainly on data from the AMPHORA database (Environmental Change Research Centre, University College London), for 169 UK lakes for which sediment core diatom analysis was available. A number of lowland lakes, potentially susceptible to eutrophication, for which data were also available, were added to the data set, and lakes subject to acidification (where algal community changes were probably due to this factor) were removed, giving a final data set of 106 lakes. These lakes were then assigned to lake types using the EcoRegion 18 methodology (Philips 2003), designed to correspond to the WFD river basin classification requirements, and based on alkalinity (catchment geology) and lake mean depth.

Diatom data from the surface of the lakes' sediments (upper 0.5 – 1 cm) were used to provide information on the current algal communities of the lakes, as this represents the last few years' accumulation of algal cell deposits. These were compared to data from deeper in the sediment core, corresponding to pre-1850 (the reference condition). Change from reference diatom population was assessed using the Squared Chord Distance (SCD) dissimilarity coefficient, which gives indications of change. Based on analysis of a wider data set, the authors estimated that an SCD score of 0.39 (2.5th percentile) could be considered as the threshold for minimal modification, corresponding to the cut-off

between “High” and “Good” WFD water quality status, 0.48 (5th percentile) for the cut-off between “Good” and “Moderate”, and 0.58 (10th percentile) for the cut-off between “Moderate” and “Poor” WFD status.

Diatom inferred total phosphorus

Application of an existing diatom-total phosphorus model to the pre-1850 diatom taxa enabled **estimation of each lake’s “reference” total phosphorus concentration**. The low alkalinity lakes, both deep and shallow, had inferred reference conditions of < 10 µgP/l, and in many cases <5 µgP/l, showing that they are naturally oligotrophic (nutrient poor). Medium alkalinity, deep lakes generally had concentrations of 10 – 20 µgP/l, and medium alkalinity, shallow lakes generally had concentrations of 20 – 30 µgP/l. High alkalinity, shallow lakes were typically 30 – 40 µgP/l but with a wide range of values, some up to 50 µgP/l. These results agree with other studies looking at background nutrient levels.

Water Framework Directive quality status

The comparison of algal taxa in the pre-1850 samples with those in the surface sediments revealed that only 25 of the 106 lakes showed low floristic change from reference conditions (2.5th percentile), that is lakes that can currently be classed as “High” WFD quality status (for total phosphorus / algal community). Significant deterioration from High status was exhibited in lakes from all of the alkalinity and depth types.

A further 12 of lakes were assessed as in “Good” quality status, thereby giving a total of 37 of sites meeting Water Framework Directive objectives), with 12 in “Moderate” and 57 in “Poor” status.

The authors note that a more strict transposition of the WFD criteria might lead to an even lower % of lakes being considered as in “High” or “Good” status (e.g. 1st percentile for “High” instead of 2.5th).

The authors conclude that the palaeolimnological data and the SCD value provide a useful tool for assessing change from reference conditions, but that the SCD does not provide any indication as to the nature of this change (type of species shifts), so that other species data should also be taken into account to try to establish the drivers and significance of the environmental changes.

Synthesis of palaeolimnological methods

In a further paper (P2), the authors summarise the **different issues relating to use of lake sediment records for establishing reference conditions and defining restoration objectives, in particular**

relative to Water Framework Directive status quality objectives. The paper considers the question of attributing changes to human activities or to natural causes over time, and the need to distinguish between pristine and reference conditions.

For example, **reduced precipitation or climate warming** might result in water quality changes which are comparable to those relating to human modifications of water systems and flows or increased nutrient loading. The time scales for different types of changes are not the same: organic carbon changed with deforestation, often dating back thousands of years, whereas acidification occurred principally after the industrial revolution and post 1850.

The authors note that recovery objectives must, therefore, take into account changes in reference conditions over time, and not simply refer to conditions at a certain point in the past. Palaeolimnological data can provide a basis for defining restoration targets which are both desirable and achievable.

European lakes

In a third paper (P3), the authors consider **reference conditions and possible restoration targets for nine nutrient-enriched European lakes**, in Norway, the UK, Austria and Italy, based on detailed palaeolimnological data assessment and explore the potential of analogue matching for determining such targets.

They suggest that analogue matching, based on a wider data set (including a broad range of lake types and conditions) and on a combination of biological groups (not only diatom taxa), should be explored as a tool for identifying reference sites impacted by eutrophication.

(P1) “The use of diatom records to establish reference conditions for UK lakes subject to eutrophication”, *Journal of Paleolimnology*, vol. 45, n° 4, pages 469–488, 2011, Springer: <http://www.springerlink.com/content/100294/>. H. Bennion, G. Simpson, Department of Geography, Environmental Change Research Centre, University College London, Gower Street, London WC1E 6BT, UK, hbennion@geog.ucl.ac.uk

(P2) : “Defining reference conditions and restoration targets for lake ecosystems using palaeolimnology: a synthesis”, *Journal of Paleolimnology* (as above), 2011, vol. 5, n° 4, Pages 533-544. H. Bennion, R. Battarbee, C. Sayer, G. Simpson, T. Davidson.

(P3): “Defining ecological and chemical reference conditions and restoration targets for nine European lakes”, *Journal of Paleolimnology* (as above), 2011, vol. 5, n° 4, Pages 415-431. H. Bennion, G. Simpson, N. Anderson, G. Clarke, X. Dong, A. Hobæk, P. Guilizzoni, A. Marchetto, C. Sayer, H. Thies, M. Tolotti.

ICL Fertilizers Europe

Recycling phosphates into fertiliser production

ICL Fertilizers Europe, the biggest producer of PK (phosphate and potassium) fertilisers in the EU, is planning to start using recycled phosphate sources to cover initially 10-15% of its raw material (rock phosphate) needs, that is an objective of around 1,500 to 2,000 tonnes of recycled phosphorus (P) per year. This corresponds to the objectives of national and European waste and recycling policies for closing the loop for raw materials.

For comparison, in the Netherlands, an estimated 3500 – 5000 tP/year ends up in ash from sewage sludge or chicken manure incineration. The intention is that when the production process has been optimised to use secondary raw materials, **ICL should also be able to use a wider range of residues and recovered materials in its production process and increase the quantities used.**

ICL underlines that the use of secondary phosphate materials contributes to **closing the nutrient cycle**, to sustainable food production in Europe, saving primary reserves of phosphate rock, reducing dependence on imported phosphate rock and **reducing CO₂ emissions**.

The company has carried out extensive laboratory research into the processing of chicken manure ash and sewage treatment sludge incineration ash. This research has shown that it is possible to produce a mineral fertiliser based on these secondary nutrient-containing residues without any loss of quality. The agronomic availability of nutrients from this fertiliser was proven and ensured.



In 2011, at ICL's Amfert factory in Northern Holland, the **processing of small quantities of these secondary raw materials in commercial fertiliser production was tested**. This showed that these can be used in the ICL process without any problems.

Process compatibility

Secondary phosphate materials are added to the ICL production process, alongside phosphate rock, upstream of acidulation and granulation. The acidulation process uses sulphuric or phosphoric acid to ensure the required concentration and availability (solubility) of phosphorus in the fertiliser product. In the granulation process, the specific nutrient balance is determined by adding primary, secondary and micro-nutrients and the physical characteristics of the final product are adjusted (particle size and form, dryness, low dust,), before coatings or other specific treatments.

Small quantities of secondary phosphate materials are already used by ICL. To enable the use of larger quantities, **modifications of the plant are planned**, including specific product storage and transport systems, dedicated supply lines with weighing devices and enclosure of the relevant systems. ICL Amfert is requesting an administrative licence from provincial authorities to authorise the collection and use of secondary raw materials. Once this is finalised, the necessary modifications will be made to the storage and process systems. ICL will then initially process sludge incineration ash from a small number of sewage plants and poultry production units, in order to gain practical experience with full-scale processing of these secondary raw materials.

Lower contaminant concentrations

ICL has assessed the implications of contaminants such as heavy metals or trace elements (e.g. copper, zinc ...) present in sewage sludge incineration ash. **These do not pose issues for the ICL production process.** Iron in sewage sludge incineration ash, where used for phosphorus removal in sewage works, is also compatible with the ICL fertiliser production process. Calculations show that the use of phosphate fertiliser made even 100% from such recovered materials would result in **contaminant doses to land lower than those authorised through existing EU regulations** for composts and soil improvers. In fact, ICL will still have to add trace elements such as boron, copper, manganese, molybdenum or zinc, which have a positive effect on the growth, reproduction and resistance of plants, to compound fertilisers manufactured using 10-15% recovered phosphates.

Further information:

<http://www.iclfertilizers.com/Fertilizers/Amfert/Pages/Environment.aspx>

Seafood wastes

Oyster shells for phosphate removal

Waste shells are produced in large quantities wherever shellfish, such as oysters, are farmed, both when the shellfish are processed (sold as products containing only the flesh and not the shell) but also when they are sorted before shipping, as some are inevitably removed as not saleable because of damage or other problems. The shell waste is principally calcium carbonate. One use for this waste which has been investigated by a number of authors is in wastewater treatment, to remove phosphates. For shell waste to effectively remove phosphorus, it must first be heat processed, for example by pyrolysis or high-pressure steam treatment.

High pressure steam treatment

Namasivayam et al. 2005, using pure sodium phosphate solutions, showed that untreated powdered oyster shells did not remove phosphorus, but the **high-pressure steam treated shells achieved P-removal comparable to CaCO_3** . The shells were powdered then subjected to steam at 234°C and 3 MPa pressure for several minutes. Pressure was then released exploding the shell material, which was then washed in water and dried at 105°C.

Phosphate removal was tested in 10 and 50 mg/l phosphate solutions in agitated flasks for up to 10 days, at different doses of shell material and of CaCO_3 , and at different pH. Freundlich and Lagergren rate constants were calculated. **25% - 40% phosphate removal was achieved**, with no significant effect of pH between 5 and 10.5. With initial phosphate concentration of 17 mgP- PO_4 /l, a dose of 24 mg shell material per litre reduced the phosphate concentration to 2 mgP- PO_4 /l in 7.7 days.

Shell porosity

Huang, Yu et al. 2010 looked at the **surface structure of oyster shells and at how heat treatment activated calcium in the shells (to lime, CaO)**, depending on the temperature applied. Chemical analysis of the shells is given, showing that the principal component is calcium. As above, this work showed that the shell material without heat treatment did not remove phosphate from pure sodium phosphate solution.

The cleaned oyster shells were treated for one hour in a muffle furnace at temperatures ranging from 100 to 800°C. Microsurface structure was characterised using X-ray diffraction (XRD) and SEM (Scanning electron Microscopy), and phosphate removal from pure sodium phosphate solution was tested, using 20 g shell

material per litre (initial phosphorus concentration was 5mgP/l).

SEM analysis showed that the untreated shells had a nacreous surface layer and an organic mucous membrane, preventing access to micropores in the calcium carbonate structure (which might remove phosphate by adsorption), whereas these obstacles disappeared at higher temperatures. At higher temperatures (from around 800°C and increasingly above this), the calcium carbonate of the shells was decomposed to lime (CaO) and carbon dioxide, in an endothermic reaction.

P-removal became effective after treatment at 100°C and did not increase significantly with treatment at higher temperatures from 150 to 900°C, except with a treatment at 550°C which resulted in a significantly lower P-removal. This is thought to be because at around 550°C the shell pore structure collapses making the surface area available for P-adsorption significantly lower, whereas at higher temperatures calcium is activated to lime which will can remove phosphate by chemical reaction.

In a second paper by Yu (Yu, 2010) looked at the **surface structure of a material produced by heat treatment of a mixture of oyster shells and fumed silica from a ferroalloy factory**. The fumed silica consisted of 92% SiO_2 . Iron was also present at a low level (c. 1% Fe). A mixture of 58% sieved crushed oyster shell particles to 42% fumed silica was calcined for 1 hour at different temperatures from 700 – 900°C, cooled, then hydrothermally cured at 130 – 180°C for 8 or 16 hours.

XRD, SEM, EDS and XRF were used to analyse the surface structure and the composition of the materials produced. This suggested that the CaCO_3 in oyster shells completely decomposes to CaO at 800°C and then reacts with the fumed SiO_2 to form wollastonite (CaSiO_3). Under thermal treatment, hydration occurs giving tobermorite $\text{Ca}(\text{Si}_6\text{O}_{18}\text{H}_2)_4\cdot 4\text{H}_2\text{O}$. This then reacts with phosphate in wastewater to produce hydroxyapatite $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$.

This work concluded that, for this shell- fumed silica mixture, calcination at 800°C for one hour then hydrothermic annealing at 150°C for 12 hours produced an effective phosphorus removal material.

The generated material **achieved 74% or 92% phosphate removal** from sodium phosphate solution (containing 5mgP/l) in two or four hours. The phosphate was relatively easy to recover, because the material did not break down to a sludge, but formed a single interwoven mineral mass, making removal and recovery of the phosphate relatively simple.

Further work is considered appropriate to improve the P-recovery yield and process efficiency.

Pyrolysis

Kwon et al. 2004 **heated oyster shells at temperatures from 650 to 800°C then tested for removal of phosphates** from pure potassium phosphate solutions (30 mgP-PO₄/l using 5g egg shell material /l). Chemical analysis of the shells is provided, showing that the principal component is calcium (Ca = 37% of dry mass).

The shells came from the seafood producers in southern Korea bays. The area produces some 280 000 tonnes of shell waste, of which around half is used as spat and the remainder poses a disposal issue. The shells were washed, sun dried for three days, then manually crushed. Heating was carried out either with air or under nitrogen (pyrolysis). As above, oyster shell without heat treatment did not remove phosphate from solution (or only very poorly: 10% P-removal after 2 hours).

Shell material pyrolysed at 750 or 800°C removed nearly 100% of phosphate after around half an hour. Material pyrolysed at only 650°C or heat treated (with air) at 750°C removed somewhat less phosphate (60 – 70%). An economic estimate is provided for a 7500 tonne/day, concluding that pyrolysed (activated) oyster shell material could be produced for 42 US\$/tonne, that is 3 – 5 x cheaper than prices for lime or alum additives for chemical P-removal from wastewaters.

Lee et al. 2009 tested **P-removal with pyrolysed oyster shells** (pyrolysed under nitrogen at 750°C, atmospheric pressure, for one hour) then ground and sieved to different particle sizes for P-removal from both pure potassium phosphate solutions and from real wastewater effluent (from a university municipal wastewater treatment plant operating a Bionipho nutrient removal process, including filtration, so that suspended solids were < 5 mg/l). This effluent contained approx. 1 mgP-PO₄/l).

Experiments showed that the particle size made little difference to P-removal at doses of 6 mg shell material per litre, but that smaller particle size enabled faster P-removal at doses ten times lower. In all cases, reaction was largely complete after 10 minutes (stirred at 120 rpm). P-removal was limited below pH9, and increased with higher pH from 7 to around 10.5.

The authors conclude from the data that P-removal is by chemical reaction with the activated calcium (lime), not by adsorption, and is can **achieve near 100% P-removal at pH 10 – 11**.

The authors conclude that the pyrolysed oyster shell material offers around 80% of the OH⁻ capacity of lime, but has a granular nature and a slower reaction time which mean that it is much easier to handle and to dose than lime.

New Zealand

Currie et al. 2007 tested **pyrolysed and heat treated shells of oysters and mussels**. XRD and SEM analysis of the different shell materials were carried out, showing that the untreated mussel shells were principally the calcium carbonate mineral aragonite, whereas the oyster shells were principally calcite, and that both were largely modified to lime after heat treatment, with an increasing lime content resulting from higher treatment temperatures (650 – 800 °C).

In this work, the raw shells showed approximately 40% phosphate removal from 30 mg/l phosphate solution, whereas the **heat treated shell material achieved over 90% P-removal** (in < 30 minutes). XRD analysis suggested that after use for P-removal the lime had been lost from the surface of the shell material particles, leaving mainly calcite.

The P-removal effect found with untreated shell particles in this work, whereas not by other authors (above) may be due to the oven drying in this paper, or to smaller particle size (ring mill grinder used in this paper).

Yuangsawad et al. 2011 tested phosphate removal from pure potassium phosphate solutions using **oyster shells untreated, and heat treated** at 773 – 1073°C, under air, nitrogen gas and nitrogen gas plus water. Phosphate removal was tested in both stirred batch experiments and in continuous through flow (a column filled with the shell material)

Results suggested that under nitrogen, optimal P-removal was achieved with shells treated at around 970°C, with lower P-removal resulting from treatments at lower or higher temperatures. **Phosphorus removal was around 2x better with shells treated under nitrogen or nitrogen plus water** (the additional water made no significant difference) compared to air.

XRD analysis suggests that the shell surfaces were 93% calcium carbonate before heat treatment, but over 95% CaO (lime) after treatment under air or nitrogen at 970°C. Heat treatment under air, however, resulted in larger particle size and smoother particles than under nitrogen, which could explain the better phosphorus removal.

“Technical Note. Removal of phosphate by adsorption onto oyster shell powder—kinetic studies”, Journal of Chemical Technology and Biotechnology (Society of Chemical Industry), 80, pages 356–358, 2005

C. Namasivayam*, A. Sakoda, M. Suzuki, Institute of Industrial Science, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan. * now: Dept. Environmental Sciences, Bharathiar University, Coimbatore 641 046, India cnamasivayam@yahoo.com

“Researches on the Treatment of Phosphorous Wastewater with Oyster Shells”, *Chinese J. Struct. Chem.*, vol. 29, n° 12, pages 1886-1892, 2010.

M-L. Huang, Y.Yu, R-P. Wu, State Key Laboratory Breeding Base of Photocatalysis, College of Materials, Science and Engineering, Fuzhou University, Fuzhou 350002, China yuyan@fzu.edu.cn

“Recycling waste oyster shells for eutrophication control”, *Resources, Conservation and Recycling*, n° 41, pages 75–82, 2004 www.elsevier/locate/resconrec

“Phosphate removal by hydrothermally modified fumed silica and pulverized oyster shell”, *Journal of Colloid and Interface Science*, n° 350, pages 538–543, 2010 www.elsevier.com/locate/jcis

H-B. Kwon, B-S. Jun, J-D. Yun, Dept. Materials Science Engineering, Kyungnam University, Masan, South Korea. C-W. Lee, Dept. Civil and Environment Engineering, Kyungnam University, Masan, South Korea. S-Y. Weon, B. Koopman, Dept. Environment Engineering Science, University of Florida, Gainesville, FL, USA. water@kyungnam.ac.kr

“A new recycling material for removing phosphorus from water”, *Journal of Cleaner Production*, n° 17, page 683–687, 2009 www.elsevier.com/locate/jclepro

C-W. Lee, H-B. Kwon, H-P. Jeon, Dept. Environment Engineering, Kyungnam University, 449, Wolyoung-dong, Hapcho-gu, Masan, Kyungnam 631-701, Republic of Korea. B. Koopman, Dept. Environmental Engineering & Sciences, University of Florida, Gainesville, FL, USA water@kyungnam.ac.kr

“Recycling oyster shell as adsorbent for phosphate removal”, paper from the 21st TIChE Conference (Thai Institute of Chemical Engineering and Applied Chemistry), Nov. 10th – 11th 2011, Hatyai, Songkhla <http://www.chem.eng.psu.ac.th/tiche2011/TCHE/data/international/sp.html>

R. Yuangsawad, Chemical Engineering, Faculty of Engineering, Rajamangala University of Technology Krungthep, 2 Nanglinchee Rd., Thungmahamek, Satorn, Bangkok, 10120 and D. Na-Ranong, Dept. Chemical Engineering, Faculty of Engineering, King’s Mongkut Institute of Technology Ladkrabang, 1 Chalokkrung Rd., Ladkrabang, Bangkok, 10520 ratana.porn.y@rmutk.ac.th

P and N adsorption

ETC reacted wheat straw for P-recovery

Epoxypropyl triethylammonium chloride (ETC) reacted agricultural wheat straw was tested for adsorption and recovery of phosphate and nitrate ions.

Crosslinking of biomass materials with epichlorohydrin is a recognised method for preparing anion exchangers from agricultural by products. This paper presents preparation of an exchanger using a new method based on agricultural wheat straw reacted with epoxypropyl triethylammonium chloride (ETC). This exchanger is then tested for removal of phosphate and nitrate ions from laboratory solutions, and for regeneration capacity.

The wheat straw was washed and dried at 105°C for 6 hours, then sieved into 100 – 250 µm particles. ETC is prepared by reacting epichlorohydrin with triethylamine in methanol solution, then introduced into the wheat straw in the presence of a catalyst (pyridine).

The resulting product was tested for adsorption of phosphate and nitrate in 50 – 500 mgP/l phosphate solution, using 2g/l of exchanger material, in 125 ml flasks shaken at room temperature. Breakthrough experiments were then carried out using a throughflow glass column of 200 mm height and 12 mm diameter filled with 1g of exchanger material.

Exchanger material preparation

It is shown that an optimal temperature for the ETC preparation reaction is around 55°C, because the reaction is faster with higher temperatures, but above this a decrease in epoxy values is observed, probably because of opening of epoxide rings in epichlorohydrin by hydrolysis. Analysis shows that the specific surface area of the wheat is increased by the ETC reaction, from 5.3 to 7.6 m²/g, and that the zeta potential is modified with increased positive-charge functional groups.

Adsorption and regeneration capacities

Adsorption capacities of c. 53 mgNO₃/g (5.3%) and 46 mgP-PO₄/g (4.6%P) were achieved with the ETC reacted wheat straw. Both sodium hydroxide and sodium chloride show very good results for desorption of both phosphate and nitrate ions: over 95% for the first cycle, falling slightly to 86 – 90% for the fourth regeneration cycle.

The authors conclude that this material, with amine groups grafted into wheat straw particles, is a potentially effective anion exchange resin for removing phosphate and nitrate from solutions, and possibly for recovery of phosphorus for recycling after regeneration (desorption). The experiments in pure laboratory solutions suggest that the material can be effectively regenerated using sodium chloride (salt)

solution, and reused for a number of adsorption – desorption cycles.

“Preparation of agricultural by-product based anion exchanger and its utilization for nitrate and phosphate removal”, *Bioresource Technology*, vol.101, issue 22, pages 8558-8564, Nov 2010. www.elsevier.com/locate/biortech

X. Xu, B.-Y. Gao, Q.-Y. Yue, Q.-Q. Zhong, *Key Laboratory of Water Pollution Control and Recycling, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China.* bygao@sdu.edu.cn

Polymeric anion exchanger

Iron loaded resin can recover phosphate

Phosphate removal from wastewaters by adsorption using materials with a regeneration cycle offers the potential to then precipitate the phosphate from a relatively clean, concentrated liquor and so recover it in a form appropriate for industrial recycling or use as a fertiliser.

This paper presents laboratory scale studies using synthetic wastewater (pure chemical solutions) and three different commercially available **polymeric anion exchanger resins impregnated with iron oxide nanoparticles**. Batch and fixed bed column flow P-removal experiments were carried out, as well as regeneration (release of the removed phosphate) and precipitation of the phosphate from the regeneration solution for P-recovery.

Commercially available polymeric anion exchange resins offer durability and mechanical strength, but not specific affinity for phosphates (affinity also for sulphates which are widely present in wastewaters). **However, these materials can be modified to form PLEs (Polymeric Ligand Exchangers) which are phosphate specific, by loading with certain metals.** Loading with copper enables selectivity for orthophosphate (rather than chloride, sulphate, carbonate or nitrate, Zhao & SenGupta, *Water Research* 32(5), 1998). This paper tests polymeric anion exchange resins impregnated with hydrated ferric oxide (FeOOH) nanoparticles.

Iron impregnation of DOWEX M4195 resin (which is based on Bis-picolylamine) was achieved by mixing with FeCl₃ at pH2, then progressively increasing the pH to 8 by sodium hydroxide addition to form FeOOH precipitate, followed by drying. This resulted in an iron loading of 4-5% by weight. The same Dow resin was also used when first loaded with copper ions to approx. 6%, and then loaded as above with iron FeOOH. Also, the commercially available HAIX resin (which is based on quaternary ammonium impregnated with FeOOH nanoparticles) was tested for a third comparison. The resins had particles sizes in the range 300 – 1200 µm.

Phosphate adsorption tests

The three different resin combinations were first subjected to batch equilibrium and kinetic tests: 48 hours, agitated beakers, using 0.5 – 1 g of exchanger per litre of 5 – 75 mgP/litre solutions of sodium phosphate. The exchanger was then filtered out, washed, and stirred with c. 20 bed volumes of a regenerant solution of 2.5% sodium chloride and 2.0% sodium hydroxide. Fixed bed up-flow tests were carried out using a 10 mm diameter, 300 mm tall column with an empty bed contact time (EBCT) of 3 minutes. Regenerant was then passed in downflow, before washing the bed and reusing for another run.

The influence of varying concentrations of sulphate and chloride on the phosphate uptake was assessed.

Sorption isotherms, sorption capacities, kinetic modelling of sorption and sorption mechanisms are evaluated and discussed. **The phosphate sorption capacities of the three materials, at around 23 mgP/g** suggest that each two molecules of FeOOH bind to one molecule of phosphate.

Phosphate recovery

Phosphate was recovered from the regenerant solution, after analysis, by adding either calcium nitrate (to precipitate calcium phosphate) or magnesium sulphate plus ammonium chloride (to precipitate struvite), followed by settling, filtration, rinsing, drying and analysis (Energy Dispersive X-ray EDX and a Scanning Electron Microscope SEM). This enabled precipitation of >90% of the phosphate present in the regenerant. Sodium hydroxide was added to the recovered regenerant, to replace depleted OH⁻ ions, which was then used again for regeneration.

The authors conclude that all three exchangers showed high selectivity towards orthophosphate compared to other ions and can be readily regenerated, with only a very small phosphate sorption capacity reduction (1.5%) after 10 exhaustion – regeneration cycles. No significant loss of iron or copper from the exchangers was noted in the regenerant.

“Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer”, *Water Research*, Vol. 45, Issue 11, May 2011, pages 3318-3330 www.elsevier.com/locate/watres

S. Sengupta, Dept. Civil & Environmental Engineering, University of Massachusetts Dartmouth, 285 Old Westport Road, North Dartmouth, MA 02747, USA ssengupta@umassd.edu and A. Pandit, Dept. Civil & Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.

3rd sustainable phosphorus summit

Phosphorus stewardship conference



The 3rd Summit will bring together key international science, policy and industry stakeholders from different parts of the food production and consumption chain concerned about the role of phosphorus availability and accessibility in global food security, about protecting the environment, and about supporting rural and urban livelihoods.

- Sustainable food systems
- Global phosphate rock production and reserves
- Phosphorus use efficiency in mining, agriculture, food processing
- Phosphorus recovery and reuse
- Phosphorus pollution and waste
- Sustainable phosphorus strategies and global governance

Sydney, Australia, 29th Feb. – 2nd March 2012

<http://sustainablephosphorusummit.net/>

Phosphate resources and uses

Global TraPs 4th Workshop



Global TraPs is an international, transdisciplinary project, bringing together scientists, industry and stakeholders to work on the following guiding question: What new knowledge, technologies and policy options are needed to ensure that future phosphorus use is sustainable, improves food security and environmental quality and provides benefits for the poor?

The 4th Workshop's objective is "Defining case studies and setting priorities" and will complete the conceptualisation phase of Global TraPs.

El-Jadida, Morocco, March 16th – 18th 2012

<http://www.uns.ethz.ch/gt>

Phosphates 2012

Phosphate industry conference



The major 2-yearly conference which brings together the worldwide phosphate industry (rock production, fertiliser, animal feeds, food, detergents, other industrial uses).

- Phosphate rock production and project developments
- Global fertilizer outlook with a focus on key country demand projections and requirements
- Developments in optimizing / streamlining and maximizing the phosphate resource
- Survey of changing industrial phosphate demand, update of regulations and substitutes
- Outlook of future feed phosphate demand and focus on regional growth

The event also offers **site visits to the Jorf Lasfar Chemical Facility and to the Khoulbga Mine Facility.**

El-Jadida, Morocco, 19th – 21st March 2012

<http://www.crugroup.com/events/phosphates/>