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***Global Phosphorus Network* www.GlobalPNetwork.net *is a new platform to exchange information, news, opinions between stakeholders, policy-makers and experts.***

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## Nutrient Management

# European Court of Justice

## Spain condemned for inadequate sewage treatment

**The European Court of Justice has condemned Spain for failure to collect and treat sewage in agglomerations of > 15 000 person equivalents by the year 2000 deadline fixed in the 1991 Urban Waste Water Treatment Directive 1991/271.**

The 14th April 2011 judgement concerns failure to collect urban sewage adequately in 5 agglomerations, and failure in 36 agglomerations to treat it with at least secondary treatment (biological treatment, achieving treatment levels as fixed in Table 1 of the Directive Annex I). The decision is the final conclusion of a legal process launched against Spain in 2004 by the European Commission, initially targeting some 189 agglomerations of > 15 000 pe identified as non conform.

The agglomerations are situated in different Spanish regions, and are **often tourist seaside resorts**: Andalusia, Asturias, Canary Islands, Catalonia, autonomous city of Ceuta, Valencia, Galicia, Basque Country.

In some of the agglomerations, investments have already been made or are underway to resolve the situation, but not in all.

This European Court of Justice procedure is one of a number engaged by the European Commission in order **to put pressure on Member States to implement sewage treatment, conform to EU legal obligations, including phosphorus removal in all agglomerations > 10 000 person equivalents** discharging into waters potentially susceptible to eutrophication, and “appropriate” treatment of sewage from all agglomerations of > 2 000 pe.

*European Court of Justice decision of 14th April 2011, available at:* http://curia.europa.eu/jurisp/cgi-bin/form.pl?lang=en *(enter case number = “C-343/10”)*

# Finland

## Closing a nutrient loop in aquaculture

**Aquaculture results in small, but growing and locally significant emissions of nutrients (nitrogen and phosphorus) to the Baltic Sea, contributing to eutrophication.**

Aquaculture is estimated to contribute <5% of total nutrient emissions to the Baltic, but the **local impact can be considerable in areas of intensive aquaculture**.

Technical measures to reduce nutrient emissions from fish farms are difficult, but the authors suggest that **significant local reductions in eutrophication could be achieved by replacing externally-sourced fishmeal used in diets by fishmeal produced by harvesting fish (non commercial catch species) locally** around the aquaculture discharge. This would contribute to closing the nutrient loop.

Eutrophication is recognised as a major environmental problem in the Baltic Sea, with the central areas of the Sea being generally nitrogen limited and coastal areas generally phosphorus limited.

**Approximately half of total nutrient loads to the Baltic come from agriculture**, the remainder from wastewaters, atmospheric deposition and other sources. The HELCOM Baltic Sea Action Plan is committed to reducing total nitrogen inputs bè18% and phosphorus inputs by 42% by 2016 (from 1997 – 2003 levels).

Finland has relatively intense Baltic aquaculture, producing approx. 11 000 tonnes of trout for human consumption in 1997, covering 22% of the country’s fish consumption. The fish are cultivated in net pens, from which excreta and uneaten food, containing nutrients, are washed directly into the sea.

### Substance flow analysis

This study analyses nutrient flows (nitrogen N and phosphorus P) for the **Finland trout production system**, assesses the losses to the Baltic, and what could be done to reduce these. Figures are averages for 2004 – 2007.

Atmospheric deposition in the aquaculture farms is considered insignificant, and the study quantifies nutrients input to aquaculture (in fishmeal / fish diet), nutrients removed to waste streams in local fish processing, nutrients exported in fish produced for human consumption and in fish products converted into fishmeal for fur animal production (accounting for 80% of aquaculture solid wastes), nutrient flows in waste handling and processing, and by calculation nutrient losses into the Baltic Sea waters.

On average over the study years, 12 409 tonnes/year of fishmeal were used as diet to produce 10 769 tonnes/year of trout for human consumption. The fishmeal contained an average 6.68% N and 0.93% P.

The assessment concludes that of 829 tonnes N (nitrogen) /year in fish diet, 635 tonnes ends up in the Baltic Sea (542 directly, 93 via waste treatment circuits), and that **of 115 tonnes P (phosphorus) /year in fish diet 83 tonnes ends up in the Baltic Sea** (80 directly, 3 via waste treatment circuits). 170 tonnes N/year and 21 tonnes P/year are transferred into fish meat for domestic consumption.

Thus, overall, around 70% of primary feed input nutrients end up in the Baltic Sea, and around 20% in the fish produced for human consumption.

### Changing feed nutrient sourcing

Currently used trout feeds contain principally herring and anchovy meal of Atlantic origin. They are highly optimised for fast trout growth.

The authors suggest replacing this with **meal produced from local Baltic fish catches**, from the coastal area around the aquaculture, thus partially closing the nutrient loop and harvesting back out of the Baltic the nutrients input from aquaculture. Non-commercial fish species would be targeted. The change would be significant. The aquaculture feed input is derived from around 20 000 tonnes of fish catch, which would represent +16% of current total Finland commercial fisheries. Baltic local fish would also contain higher levels of PCB and dioxin compounds than Atlantic fish, posing contamination issues: processes to remove these in fish meal processing factories do however exist.

Atlantic fish meal could also be substituted with plant-derived materials, eg. from soybean, peas, vegetable oils. Although this may be more ecologically efficient than using fish meal, it would not contribute to closing the nutrient loop.

The authors quote one estimate that the change to local caught fish could increase fish meal prices by +15% and suggest that this should be paid by the aquaculture farms on the polluter-pays principle.

*"Closing a Loop: Substance Flow Analysis of Nitrogen and Phosphorus in the Rainbow Trout Production and Domestic Consumption System in Finland", Ambio, n°39, pages 126-135, 2010*
http://www.springer.com/environment/journal/13280

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## Phosphorus recovery and recycling

## EU SUSAN project

### Thermal treatment of sludge incineration ash

**The EU-funded SUSAN project (see SCOPE Newsletter n°66) looks at treating sewage sludge incineration ash through a thermal process plus chlorine addition in order to remove heavy metals (as chlorides) and to transform the phosphorus content into plant available mineral forms.**

**These papers present the laboratory scale assessment of different treatment temperatures, times and chlorine donor chemicals for seven different municipal sewage sludge incineration ashes.**

**Parallel to this experimental investigation, a 200 kg/h pilot plant was successfully operated in Leoben, Austria (by ASH DEC Umwelt AG, and now by Outotec GmbH) and an industrial scale plant is currently being planned by Outotec GmbH.**

In papers [A] and [B], experiments were carried out in the gas-tight, air flushed, laboratory rotary furnace Carbolite HTR 11/150, using 400g ash samples.

The seven sewage sludge ash samples came from incinerators treating only sewage sludge (mono incineration) in The Netherlands and in Germany, and showed phosphate contents of 14 – 25% (6 - 11 % P), the lower value coming from an incinerator where significant sand was being included in sludge. Iron and aluminium contents of the ashes ranged from 2 – 16% and 5 - 14 % respectively.

Metal concentrations in some or all of the ash samples exceeded levels authorised by German and/or Austrian fertiliser regulations for copper, zinc, arsenic, cadmium, nickel and lead.

## Heavy metals removal

**Heavy metals were removed from the ash by thermal treatment in the presence of a chlorine ion donor chemical**, resulting in vaporisation of heavy metal chlorides which were then collected in the off-gas treatment system. A reaction temperature of 800 – 950°C°C proved necessary to remove metals sufficiently to respect German fertiliser regulation concentrations. Both $MgCl_2$ and $CaCl_2$ proved effective as chlorine donor chemicals, with a residence time of 20 minutes at 1000°C and a chlorine concentration of 50 – 100 g/kg ash.

**Significant variation in the performance of copper removal was noted**, possibly related to different types of mineral phases of copper in the different ashes.

**As, Cr and Ni were not significantly removed using these chlorine donor chemicals**. Preliminary investigations had suggested that they could be removed using chlorine gas, but this is not considered technically feasible because of handling dangers.

40% of potassium in the ash was also removed by the thermal chlorine process, which is not desirable in that this is a valuable fertiliser component (1 – 3 % K in the ash samples).

The thermal chlorine treatment and heavy metal recovery in off gas washing system results in a heavy metal concentrate, representing approx. 1 – 3% of the input ash mass, which will have to be appropriately treated.

## Phosphorus availability

The thermal chlorine treatment using $MgCl_2$ offers a further advantage of improving the plant availability of the phosphorus present in the sewage sludge incineration ash. The raw ashes showed P-solubilities in citric acid of 25 – 40% and this increased to over 95% after treatment at 1000°C with $MgCl_2$ (with smaller but significant increases in solubility after lower temperature treatments).

XRD analysis suggested that this change in solubility corresponds to modifications in the mineral phases of phosphorus, aluminium, calcium and iron compounds present in the ash as a result of the thermal chlorine treatment.

The authors conclude that this thermal chlorine treatment process can produce, from sewage sludge incineration ash, **a product which both respects fertiliser regulations as regards low heavy metal contents and offers a high plant availability of phosphorus content**.

## Crystalline phases and further analysis

Paper [C] presents detailed analysis of the crystalline phases occurring in the ashes during thermal treatment was carried out using X-ray powder diffraction.

Paper [D] presents analysis of the mineral forms of phosphate in fertilisers prepared from the thermally treated sludge incineration ash.

It is shown that only quartz (mineral silicate) and hematite (an iron oxide based mineral) were not modified by treatment. The **phosphorus mineral changes took place** via the formation of an intermediate mineral chlorspodioside $Ca_2PO_4Cl$. The presence of crystalline aluminium phosphate $AlPO_4$ in the sewage sludge incineration ash is demonstrated.

The **principal forms of phosphate found in the ash** after the thermal treatment with chlorine are brushite (dicalcium phosphate dihydrate) and monocalcium phosphate monohydrate when a calcium chlorine donor chemical was used, and newberyite ($MgHPO_4.3H_2O$) and garyansellite ($(Mg,FE)_3(PO_4)_2(OH)_{1.5}.1.5H_2O$) when a magnesium chlorine donor was used.

Paper [E] presents quantitative assessments, based on spectroscopic analysis, of the different mineral compounds in fertilisers based on the thermally treated sludge ash.

Paper [F] presents detailed analysis of the heavy metal removal in this thermal chlorine treatment, using thermogravimetry/ differential thermal analysis (TG/DTA) to provide information about the secession and evaporation of water, HCl and heavy metal chlorides.

*[A] "Thermochemical treatment of sewage sludge ashes for phosphorus recovery", Waste Management 29 (2009), pages 1122–1128:* www.elsevier.com/locate/wasman

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*[B] "Thermal Treatment of Municipal Sewage Sludge Aiming at Marketable P-Fertilisers", Materials Transactions, Vol 48, no. 12 (2007) pages 3056-3061, Japan Institute of Metals,* http://www.jim.or.jp/journal/e/

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*[C] "Reaction sequences in the thermochemical treatment of sewage sludge ashes revealed by X-ray powder diffraction – A contribution to the European project SUSAN", Z. Kristallogr. Suppl. 30 (2009), pages 459-464* http://www.oldenbourg-verlag.de/wissenschaftsverlag/zeitschrift-kristallographie

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*[D] "Chemical reactions during the preparation of P and NPK fertilizers from thermochemically treated sewage sludge ashes", Soil Science and Plant Nutrition (2010) 56, 627–635* http://www.wiley.com/bw/journal.asp?ref=0038-0768

*C. Vogel (1), C. Adam, B. Peplinski, S. Wellendorf (1)*

*[E] "Spectroscopic Investigation in the Mid- and Far-Infrared Regions of Phosphorus Fertilizers Derived from Thermochemically Treated Sewage Sludge Ash", Applied Spectroscopy, vol. 65, no. 3, 2011, pages 265-271* http://www.s-a-s.org/journal/

*C. Vogel, A. Kohl, C. Adam*

*[F] "Heavy metal removal from sewage sludge ash analysed by thermogravimetry", Journal of Thermal Analysis and Calorimetry, vol. 103, no. 1, pages 243–248* http://www.springerlink.com/content/102948/

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## Sweden

## P-recovery from incineration ash

**Sulphuric acid was tested for extraction of phosphorus from incineration ash produced by an experimental boiler burning a mixture of sewage sludge and wood. Phosphorus yield showed to depend considerably on the additives used in the sewage treatment process (aluminium or iron).**

**In a second paper, the mobilisation of metals in the acid extraction is assessed, to determine whether the extraction leachate could be used directly as a fertiliser.**

An experimental 12 $MW_{th}$ fluidised bed boiler at Chalmers University of Technology (Göteborg, Sweden) was used to burn mechanically dewatered sewage sludge (72 – 77 % water) and wood pellets (made from sawdust). Up to 15% sewage sludge (that is, 85% wood pellets) could be fed without losing temperature.

In some experimental combustion runs, lime was added upstream of the effluent gas bag filter to reduce sulphuric and chloric acid in effluent gases and to assess impact on fly ash composition.

Sulphuric acid was used as the extraction medium, as this was expected to release lower levels of metal contaminants into solution than hydrochloric acid.

Bed ash, cyclone ash and bag filter ash were assessed separately, measuring both quantities of ash produced, ash content of different elements and extraction of phosphorus.

### Iron and aluminium

Two different sewage sludges were tested, from water treatment plants dealing with mainly household effluents. One plant used iron salts for phosphorus removal and other aluminium salts.

**Iron dosed sludge resulted in higher quantities of cyclone ash, whereas aluminium dosed sludge produced more bed ash**. In general, most ash was recovered from the cyclone, except for runs using wood only (no sewage sludge) and aluminium dosed sludge without lime addition.

### Phosphorus recovery

When the ashes were acidified to pH 2.5, only 22 – 30% of phosphorus contained in them was released to solution. At pH 1 this was increased to 74 – 95% for aluminium dosed sludge, but only 49 – 65% for iron dosed sludge. The addition of lime did not significantly modify the phosphorus recovery rates.

Equilibrium calculations were made using the Hydra/Medusa programme package, producing calculations coherent with the experimental results, suggesting that ferric phosphate would form at pH < 4.2, calcium aluminium phosphates in pH range 4.2 – 6 and hydroxyapatite at pH >6, each interfering with the recovery of phosphorus in solution.

The authors conclude that **sewage sludge is more suitable for phosphorus recovery when sewage treatment has not involved iron dosing**. Where iron has not been dosed, most of the phosphorus in sewage sludge (>74%) can be recovered from sludge incineration ash but that this requires acidification to pH1, which means that the low pH leachate needs to be neutralised before it can be used as a fertiliser.

*"Leaching of ashes from co-combustion of sewage sludge and wood—Part I: Recovery of phosphorus", Biomass and Bioenergy, 32 (2008) pages 224 – 235* http://www.elsevier.com/locate/biombioe

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## Japan

## P-recovery from chicken manure incineration ash

**Concentrated agriculture in the Miyazaki and Kyusyu regions of Japan generates significant quantities of chicken manure. Some is used directly as an agricultural fertiliser, but quantities produced exceed local needs and repeated application has resulted in phosphorus excesses in some local soils.**

**Incineration of chicken manure as a disposal solution faces limitations because of difficulties in disposing of ash, whereas also the ash represents a significant potential secondary resource of phosphorus, of which Japan has no natural resources.**

Inorganic acid and alkaline treatment was tested as a route for recovering phosphate from the chicken manure incineration ash. This is considered as potentially of **lower environmental impact than other routes reported elsewhere**: a "dry" process, involving melting the ash, or solvent extraction (acidification, then ammonium addition, then tri-n-butyl phosphate use to recover phosphoric acid, Hino et al. 1998).

Experiments were carried out at the laboratory scale, starting from 10g of ash. The chicken manure incineration ash came from the Nangoku-kousan Company commercial 100,000 tonnes/year manure incineration plant at Miyazaki. It contained approx.. 12% potassium, 8.5% phosphorus, 7.2% calcium, 2.7% sodium, 2.2% magnesium. Contaminants included 0.49% iron and 0.16% copper.

### Acidification and neutralisation

100 mg of 1 molar hydrochloric acid were added to 10g of chicken manure incineration ash, to produce a phosphate-rich solution at pH 2.8. pH correction was made by 1 molar adding sodium hydroxide solution.

A first pH correction was carried out to pH 3 for one hour. Solids were then filtered out. This enabled **removal of > 97% of the iron but only 7% of phosphorus** (compared to initial acid solution), resulting in a brown filtered solid, and effectively avoiding coloration problems of recovered phosphates at later stages.

A second pH correction was carried out to pH 4 for 5 hours, stirred. This enabled **precipitation of 77% of the phosphorus** (% of P in initial acid solution) as a white solid which settled one stirring was stopped, and was then separated by filtration.

Finally, pH was adjusted to pH 8 for 1 hour, stirred, again followed by settling and filtration. This resulted in a **final total P removal to precipitate of > 99%,** and also a total calcium removal of around 86%.

### Calcium phosphates

XRD analysis of the second stage filtrate suggests that it is **relatively pure $CaHPO_4.2H_2O$**, which also corresponds well to the molecular ratio. The molar ratio Fe:P was 1:115, showing that iron was a minor component in this precipitate, and that the first pH adjustment to pH 3 was adequate to remove iron.

The final stage precipitate at pH 8 was shown to be **mainly hydroxyapatite**, into which most of the copper, zinc and heavy metals were incorporated. If a higher P-recovery rate (up to 92%) were targeted, pH should therefore be adjusted to pH8, whereas adjustment to pH 4 enabled recovery of 77% of phosphorus with low levels of contaminants.

*"Phosphate recovery from phosphorus-rich solution obtained from chicken manure incineration ash, Waste Management 29 (2009) 1084–1088.* www.elsevier.com/locate/wasman

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## Manure recycling

## P-recovery routes from poultry manure production units.

**The USA alone produces some 11 million tonnes/year of poultry litter, a waste mixture of bird manure, feathers, spilled water and feed waste, containing some 250 000 tonnes/year of potentially recyclable phosphorus (approx. 1.5% P).**

**This is significant, representing around 15% of total US inorganic fertiliser consumption.**

**Although poultry litter itself is a good fertiliser, in many cases it requires processing, because its N:P ratio is higher than crop (P) needs (leading to potential phosphorus overloading of soils), and because its phosphorus content, bulk and density makes transport uneconomic.**

In [2009], the authors assess a number of **different technologies for recovery and reuse of phosphorus in poultry litter**, including densification, biological, thermochemical and chemical processes.

### Bulk and density

The simplest option is **compacting and baling**, which can achieve a reduction in bulk (and so cheaper transport), with limited energy consumption. Pelletising has also been tested in large scale industrial facilities, for example with addition of 3% vegetable oil, but involves significant energy use with no increase in nutrient mass concentration.

**Composting** of poultry litter on its own is not an environmentally viable option, because of high nitrogen losses as ammonia. This can be resolved by adding chemical amendments, or by co-composting with other organic matter, but this does not significantly increase phosphorus concentration.

### Thermochemical conversion (TCC)

Thermochemical conversion processes use **high temperatures** to convert poultry litter into synthetic gas, hydrocarbon fuels and a charcoal residue, thus **producing heat and electricity**.

The solid residues from poultry litter treatment contain a relatively **high level of phosphorus (5 – 10 % P) and can be used as a fertiliser**. Such processes however need high capital investment, and can pose issues of emissions of particulates, nitrogen oxides, carbon monoxide and sulphur dioxide, requiring flue gas cleaning. Pyrolysis systems currently being developed may enable more economic, small-scale TCC processes and are similar to traditional methods of charcoal production in rural areas.

### "Quick Wash" chemical treatment

The Quick Wash process is presented (in [2008a,b]), involving **phosphorus selective extraction with acid, calcium phosphate precipitation by lime addition and finally enhancement by polyelectrolyte addition**.

Use of acid at pH 4.5 enabled extraction of 60-80% of total phosphorus from the poultry litter, leaving a solid washed litter residue with P:N ratio reduced from c. 1:2 to c. 1:6, so better adapted for use as a soil amendment and fertiliser. The resulting recovered phosphorus product represented only around 15% of the initial litter volume, and so provides a relatively transportable phosphorus fertiliser. The USDA granted an exclusive license (patent pending) to a U.S. company for the use of the Quick Wash process.

The field trials presented in [2008a] used two 374 litre reactors, plus a 57 litre mixing tank, operated for 60 minute experimental runs.

### Economics of P-recovery

The economics of **three scenarios** were assessed: Quick Wash, Quick Wash followed by anaerobic digestion, Quick Wash plus pyrolysis. These scenarios offer potential economic benefits of c. US 20 / tonne of litter, corresponding to the difference in sale value of the phosphate fertiliser product compared to raw litter, less the costs of chemicals used. Farmers may also benefit from water quality credits related to phosphorus removal, which would amount to nearly 80 US$/tonne of litter (Mid-Atlantic Water Quality Program, 2007). The second and third scenarios offer the additional advantage of energy production: 200 - 350 litres equivalent LPG per tonne of litter (value c. US$ 60 - 100)

### Fertiliser tests

In [2010], the authors present **pot trials of the Quick Wash poultry litter recovered phosphate product**, compared to raw broiler litter and Triple Super Phosphate (TSP) fertiliser, on ryegrass. The results showed that biomass production was similar for the three products, whereas the TSP resulted in higher soil extractable phosphorus contents, suggesting that the recovered phosphate products would provide effective slow release fertilisers.

*2007: "Status of Water Quality Credit Trading in Virginia", Mid-Attlantic Water Quality Program*

http://www.mawaterquality.org/publications/pubs/VA_Trading_Sum_MidAtlanticExt%202_Mar_07.pdf

*2008a: "Phosphorus recovery from poultry litter", A. Szogi, M. Vanotti, P. Hunt. Transactions ASABE 51, 1727–1734,* http://www.asabe.org/pubs/trans.html

*2008b: "Mining Manure for Phosphorus", Agricultural Research magazine, February 29, 2008* http://www.ars.usda.gov/is/pr/2008/080229.htm

*2009: "Prospects for phosphorus recovery from poultry litter", A. Szogi, M. Vanotti. Bioresource Technology, n° 100 (2009) pages 5461–5465,* www.elsevier.com/locate/biortech

*2010: "Fertilizer effectiveness of phosphorus recovered from broiler litter", A. Szogi, P. Bauer, M. Vanotti. Agronomy Journal, n° 102 (2010) pages 723-727, https://www.agronomy.org/publications*

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# Phosphorus in biosolids

## Biosolids questions

### Why recycle nutrients in inorganic forms ?

**The authors present the history of sewage collection and treatment on different continents, an analysis of nutrient flows in Sweden and in Zimbabwe, and an assessment of the obstacles to recycling sewage nutrients in organic forms.**

**They conclude that recovery of nutrients from sewage in inorganic forms, useful as fertilisers, is necessary for a sustainable future.**

The **accumulation of nutrients**, with limited redistribution, has been identified as a major problem of human ecology (Günther, 1998). In the two examples studied, Sweden and Zimbabwe, the nutrient cycle is far from closed. In Sweden, this is accentuated because agricultural spreading of sewage sludge has disappeared. In Zimbabwe, only 43% of the population is connected to sewage treatment.

**Most historic civilisations developed some sort of sewage collection system** to remove sewage from cities, including Indian, Roman and Greek civilisations back to 3000 BC. In nearly all cases, these systems used water to flush sewage away. Sewage solids were often nonetheless valued, and collected for recycling to agriculture. Only in Asia (China, Korea, Japan) have dry toilet systems been historically identified, facilitating this collection and recycling.

### Obstacles to sewage sludge reuse

In modern societies, there are a number of considerable **obstacles to sewage biosolids reuse** in agriculture. The authors suggest that even if problems of pollutant contamination (heavy metals, organic contaminants, pharmaceuticals) and public opinion were resolved, considerable obstacles would remain.

The first issue is **geographical**. Cities and intensive livestock production units both lead to localised surpluses of nutrients. Biosolids have relatively low nutrient content compared to high water content. Sludge volumes are 3-5 x higher than volumes of harvested crops, for example, so that the energy needed to dry and/or transport and apply biosolids is much higher than that needed to harvest crops. Transport distances are thus a significant bottleneck to recycling of nutrients in organic forms.

Secondly, the authors consider **obstacles to separative toilets**. Urine (free of faeces) is a relatively hygienic fertiliser, but poses problems with the presence of pharmaceuticals. Precipitations may block pipes. Completely new infrastructure (new toilets, separative piping, storage tanks) would be needed in cities. Storage for up to one year would be necessary to enable application at periods corresponding to crop needs: a 50 000 $m^3$ tank would be required for a 100 000 population town.

More fundamentally, **urine is a very dilute fertiliser** and so would require high energy inputs to redistribute for agricultural use, and does not contain nutrients balanced to crop needs (P is too low compared to N and K). Urine separation will thus be only appropriate in specific circumstances or for only part of the population.

### Inorganic forms

The authors therefore suggest that **processes to recover nutrients from sewage and animal wastes in inorganic forms should be developed** to contribute to closing nutrient cycles.

Nutrient precipitation processes (for example, P and N as struvite = magnesium ammonium phosphate), ion exchange processes and nutrient extraction from sludge incineration ashes are cited as possible routes for achieving this.

These processes can **enable nutrients to be recovered in a concentrated form, allowing storage, transport and application to agricultural land** with nutrient rates appropriate to crop needs.

*Recycling municipal wastes in the future: from organic to inorganic forms?Soil Use and Management, 21, pages152-159, 2005*
http://onlinelibrary.wiley.com/journal/10.1111/(ISSN)1475-2743

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## Biosolids phosphorus

### Sustainable nutrient management for sewage biosolids

**The authors summarise key issues for sustainable phosphorus management in application of sewage biosolids, that is the need to take into account biosolids phosphorus availability, soil phosphorus retention capacity, land runoff characteristic, in order to supply phosphorus according to crop needs without risks of loss to surface water. Each of these characteristics is locally specific, including the plant availability of phosphorus in biosolids which can be very different depending on sewage and sludge treatment processes.**

**Appropriate tools, including phosphorus availability testing and land management techniques, are necessary to ensure both short and long term nutrient management of both phosphorus and nitrogen.**

Firstly, the authors emphasise that **land application of sewage biosolids, conform to regulations, is both safe and desirable**, as an optimal route for recycling both nutrients (phosphorus, nitrogen, other elements) and organic matter. Appropriate treatment of sludge before application can avoid risks from pathogens, and monitoring of contaminants as well as increasing separation of industrial wastewaters can avoid risks of accumulation of heavy metals or other potential pollutants.

The authors note, however, that **sustainable nutrient management is likely to increasingly constrain biosolids reuse**: where biosolids are applied to limited areas of farmland up to spreading limits, nutrient accumulation (in particular phosphorus), can exceed crop or agronomic requirements, posing risks of transport to surface waters. This is accentuated as phosphorus is increasingly transferred to sludge with the implementation of sewage P-removal.

They note that long-term land application of biosolids can result in an accumulation of phosphorus in the top 10-15 cm of topsoil which is greater than that necessary for optimal crop yields.

### Soil indexes

In the USA, soil phosphorus indexes aim to minimise the P-loss from agricultural soils. However, these do not currently take into account the **specific characteristics of sewage biosolids**. They are based on the properties of manures, for which P solubility, bioavailability and transport potential are significantly different than for biosolids.

Furthermore, **plant P uptake mechanisms mean that crop availability is significantly different from water solubility**. Plants release organic acids around their roots, improving P availability, and can thus access phosphorus which is not water soluble, and so does not risk transport to surface waters.

Also, **the relationship between total soil P and risks of P transport is not linear**. At higher soil total P contents, P fixing sites on soil particles become saturated, and transport risk increases more rapidly with a “change point” in the response curve, corresponding to a “saturation” threshold. This threshold, beyond which runoff to surface waters becomes significant, is often 3 – 4 x higher than the soil P content necessary for crop needs.

## Landscape management

P transport to surface waters is also highly dependent on **landscape management, in particular to distance and vegetation buffer separation from waterways**, as well as field slope. The width of buffer zones, but also the type of vegetation, management practices (e.g. grazing) are important. Such buffer zones are increasingly being required by regulation in many US States. P transport is also very dependent on the slope of fields.

## Variations in biosolids nutrient availability

Figures in Stehouwer 2000 show that **sewage biosolids phosphorus content has tended to increase over the last 20 years (1978 – 1997), by around +20%, to around 0.22 g/kg, probably due to increasing implementation of sewage phosphorus removal**.

Biosolids have very **widely varying solubility of phosphorus**, as measured by WEP (water extractible phosphorus), and so widely varying susceptibility to P transport. Examples show a variation of 40x in the % of WEP. Another example shows no correlation between biosolids P loading rates and P concentrations in measured runoff. Grass fertiliser experiments showed **sewage biosolids fertiliser value** (% compared to triple super phosphate fertiliser for phosphorus content) varying from nearly 100% down to <5%.

**Phosphorus solubility is particularly low in biosolids from sewage treatment plants using chemical phosphate precipitation, heat treatment and/or alkaline sludge treatment.**

**Untreated biosolids from BNR (Biological Nutrient Removal) sewage plants on the other hand have relatively high phosphorus transport potential**, and can be considered to offer phosphorus availability comparable to fertilisers.

The authors note that a standard agreed testing procedure is needed to assess the water soluble phosphorus in biosolids, and thus the phosphorus runoff risk.

## Work needed

The authors point to the need for further work into the phosphorus runoff potential and plant availability of phosphorus in BNR (biological nutrient removal) sewage sludges, including when the sludges have been modified by chemical addition or heat treatment. This should include long term field tests to look at phosphorus release over time.

More widely, **studies are also needed to assess the long term stability and plant availability of phosphorus in land-applied biosolids**, in particular the iron- or aluminium-bound P in sludges from sewage works using chemical phosphorus precipitation.

*"Phosphorus management for sustainable biosolids recycling in the United States", Soil Biology and Biochemistry 39, pages 1318-1327, 2007, Elsevier* http://www.sciencedirect.com/science/journal/00380717

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*See also "Chemical Monitoring of Sewage Sludge in Pennsylvania: Variability and Application Uncertainty", Journal of Environmental Quality 29(5), pages 1686-1695, 2000. R. C. Stehouwer, A. M. Wolf, W. T. Doty* rcs15@psu.edu

# Nutrients in the environment

## Central China

### Phosphorus flow analysis for an urban area

**Hefei is the capital of Anhui Province, central China, with a metropolitan area population of around 2 million, which has doubled over thirty years, and a land surface of 83852 hectares. Agricultural activities include production of pigs, poultry, dairy, vegetables and fodder, as well as gardening. Phosphates are also used in detergents.**

**Substance Flow Analysis (SFA) was applied to assess phosphorus flows, using existing data, field research, interviews and literature. Figures are for 2008.**

Hefei city discharges its sewage into the Western part of Chaohu Lake (China's fifth largest lake), with significant eutrophication problems occurring

The substance flow analysis carried out looked only at **direct impacts of human activities**, and did not take into account for example P losses from land to water through soil erosion. Atmospheric fluxes of phosphorus were assumed negligible.

### 8 000 tonnes P import

The Hefei city area has no local phosphate rock resources, so the total annual phosphorus use of 7 810 tonnes was imported, including phosphate rock, fertilisers, and phosphorus in industrial products, crops and fodder. **Most phosphorus was imported in the form of crops and in fertilisers**. The total phosphorus exported from the area was around 1/3 of imports, indicative of considerable losses both from agriculture and urban sewage to surface waters.

Nearly 5 800 tonnes of phosphorus (P) in fertilisers were used in agriculture and gardening, in addition to over 300 tonnes P in pesticides. Around 40% of imported phosphorus was used in agricultural crop production, resulting in an estimated 1 100 tP being absorbed to soil and 1 000 tP lost to surface waters. Some 1 200 tP were used in livestock production, of which most was returned to agricultural soils as manures, 271 tP were supplied to households, 190 tP were exported in animal goods. Losses to surface waters were estimated at 220 tP via runoff following manure application to land and 63 tP direct discharge of manure to surface waters.

### Households and sewage

Total input to households was around 1 300 tP, from both imported food products and detergents and from flows within the system, of which 170 tP was discharged directly to surface waters. Some 800 tP reached in sewage treatment works, of which only 55 tP reached surface waters after treatment. However, a further 57 tP also reached surface waters from landfill leachate, after treatment, much of this probably coming indirectly from sewage treatment sludges.

The study concludes that **the principal source of phosphorus enrichment of surface waters is agriculture** (1283 tP) compared to municipal and industrial wastewaters (383 tP).

### Reducing agricultural P losses

Consequently **the most effective way to prevent phosphorus discharge into surface waters in the Hefei City area would be to improve fertiliser use** through, for example, best management practices. At the same time, the authors suggest, phosphorus recovery and recycling from sewage and animal manures should be developed to both reduce indirect losses into surface waters and to reduce dependency on imported phosphorus.

*"Anthropogenic phosphorus flow analysis of Hefei City, China", Science of the Total Environment (Elsevier), 2010, n° 408, pages 5715–5722*
www.elsevier.com/locate/scitotenv

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## Reference manual

## Inositol phosphates

**The majority of phosphorus contained in most plants and in crops is present in the form of inositol phosphates or their salts (phytates). Because these phytate molecules cannot be digested by monogastric animals (e.g. pigs, birds, man ...), the phosphorus they contain is not available for nutrition, and passes undigested into manure. This poses significant issues for both feed diets and for environmental management of manure nutrients.**

**This book is the outcome of a first major conference addressing inositol phosphates, sponsored by the Soil Society of America, held in Idaho in 2005. It includes 16 papers presented at this conference plus index (total 288 pages).**

Themes covered include:

- **definitions, nomenclature and chemistry** of inositol phosphates, identification and analysis methods, in particular applied to environmental samples
- inositol phosphates in **animal nutrition**, including phytase addition in diets, low phytate crops
- **inositol phosphates in the environment**, quantities, forms, biological availability, fate, in particular for inositol phosphates originating in manure

### Chemistry

Inositol phosphates are organic molecules consisting of a cyclitol (6-carbon ring with a hydroxyl group associated to each C atom) to which are associated one or more phosphate groups. Inositol phosphates form salts with mineral ions (sodium, calcium, magnesium ...), referred to as "**phytates**", "**phytin**", or InsP or IP.

Definitions, nomenclature and chemistry of inositol phosphates are clarified, in that often in literature inositol phosphates are referred to using inexact or ambiguous terminology. **The chemistry of inositol phosphates is presented in detail**, in particular the different conformers, stereoisomers and positional isomers, and the different degrees of phosphate esterification (number of phosphate groups attached to the inositol ring, from 1 to 6).

State of the art techniques for **analysis and identification of inositol phosphates** by NMR (nuclear magnetic resonance) spectroscopy, HPC (high performance chromatographic) separation and MS (mass spectrometry) are presented. Methods for characterising inositol phosphates in soil, and knowledge of the transformations of inositol phosphates in soils, can contribute to determining the origin and pathways of soil inositol phosphates.

## Making inositol phosphates biologically available

Papers present current knowledge concerning natural phytates, that is **enzymes capable of breaking down inositol phosphates** and rendering their phosphorus available for uptake by plants or absorption and use by animals. Microorganisms capable of degrading phytates have been isolated and cultivated from a range of soil and aquatic environments, including filamentous fungi, yeasts, gram-negative and gram-positive bacteria. Some have been produced commercially as an additive for animal feeds. However, the variety of phytate-degrading organisms and of phytates suggests that other types remain to be identified.

In different detailed papers are presented :

- properties of phytases from 14 different organisms are summarised
- synthesis of phytases in microorganisms and plants (mechanisms, regulation
- classification, catalytic mechanisms and applications of different phytases: histidine acid phosphatase, B-propeller phytase, cysteine phosphatase, purple acid phosphatase

## Inositol phosphates and agricultural efficiency

**Phytic acid (PA) is ubiquitous in the cells of eukaryotes** (advanced plants including crops), that is the free acid form of myo-inositol hexakiphosphate. It plays a role in many key cell processes, as well as in the storage of phosphorus and other minerals: signal and transduction, vesicular trafficking, stress response, RNA transport, DNA metabolism, development regulation. In plant seed development, PA accumulates mainly as phytin salts of minerals, in particular of K and Mg, but also of Ca, Mn, Fe, Zn. It is often deposited in seeds as discrete globuloids, within protein storage vacuoles (PSVs).

**This inositol phosphate is not available to monogastric livestock (in particular, pigs, poultry), nor to man**, so that most phosphorus in plant materials (crops) and in diet is thus inaccessible. Examples given show that inositol phosphate is around 75% of phosphorus in standard maize (total P = 4.5 gP/kg) or 70% in soybean (total P = 8 gP/kg).

This poses considerable **issues for animal nutrition** (see Lott *et al.* In SCOPE Newsletter n°77). Routes to address this include the development of "low PA" crop genotypes, which can contain three times more animal-available phosphorus (for similar total crop P levels). The different metabolic pathways for low-PA crops are presented, as are human and animal studies with such crops and implications for ruminant nutrition.

Another route is the **addition of phytase enzyme (of microbial origin) to animal feeds**. Current knowledge of such techniques is presented, concerning phytase mechanisms in animals, development of thermostable and protease-resistant phytases, phytase production, nutritional effects of phytase, implications for reducing phosphorus content of manures.

## Inositol phosphates and P in manures and soils

Papers included examine:

- The implications of inositol phosphates for **manure P management** and for manure P availability in soils, and in particular of low PA crops or phytase complements used in feeds
- In-situ ligand-based enzymatic hydrolysis method for **analysing inositol phosphates in manure**, enabling the assessment of inositol phosphate and inorganic phosphate stability

- Amounts, forms and origins of inositol phosphate stereoisomers in **soils**
- Abiotic **reactions of inositol phosphates in soils**: adsorption to soil particles, complexation and mineral dissolution, roles of iron, aluminium, calcium, clays and organic matter
- Interactions between inositol phosphates and **soil constituents**, and implications for the breakdown of inositol phosphates (phytase, hydrolysis)
- **Plant uptake and utilisation** of soil inositol phosphates, including release by plants of extracellular phytase
- **Inositol phosphates in aquatic systems**: sources and occurrence of inositol phosphates in surface waters and sediments, physiochemistry, P remobilisation

*"Inositol phosphates: linking agriculture and the environment", 288 pages, ISBN 1-84593-152-1, 2007*

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## Urban and rural streams

### Biomass response to nutrient enrichment

**The effects on periphyton development (algae growing on steam bed surfaces) following different durations of nutrient enrichment and nutrient doses were assessed in a rural and an urban reach of the Onondaga Creek stream, flowing through Syracuse, in upstate New York.**

**The study enables a comparison of response to nutrient inputs in the two different reaches to be made. It also enables assessment of the long term effect of "pulse" (short duration) nutrient enrichment.**

The study compared the stream headwaters, in an essentially rural catchment (mainly forest and agricultural land), with reaches downstream of Syracuse, where the catchment is more urban and the stream receives dilute untreated sewage from some 50 sewerage storm overflows.

The authors indicate that **previous studies of pulse nutrient inputs have only looked at immediate effects, whereas this study monitored effects up to 6 weeks after the nutrient addition**. The previous studies have indicated that short-duration pulse nutrient inputs appear not to lead to significant algal development in fresh water (Fujita 1985 showed however response to pulse nutrient addition in brackish waters). Previous studies have however shown that repeated or long-duration nutrient addition to streams can result in significant periphyton development.

### Urban stream ecosystem

To assess the initial situation in the two different stream reaches, three sites were sampled in both the rural and urban reaches, during the summer (one date). Periphyton and sediment were scraped and collected from 3 $m^2$ of stream bed area at each sampling site, and organic content assessed. Organic biomass was approximately 2x higher in the urban reach.

The water dissolved nutrient concentrations were also measured, and showed to be higher in the urban reach, and **a relationship between nutrient concentrations and organic biomass was apparent**.

### Nutrient enrichment

After studying the patterns of storm flow events in the stream, nutrient dosings to the stream (applied to both the rural and the urban reach) were defined, with two different dose concentrations, and three different dosing periods (2, 4, 8 weeks). Nutrients were dosed by suspending mesh bags of slow release fertiliser (1:1:1 N:P:K) in stream riffles (40g or 80g of fertiliser for low and high dose). Controls (no nutrient addition) used similar suspended bags containing plastic beads. Bags were replaced every 2 weeks for the longer dose times, to ensure consistent dosing. Five experimental units were used for each different treatment.

The bags were attached to the bricks used as a growing surface for assessing periphyton response. After 8 weeks, the bricks were photographed to analyse % algal cover, and the biomass was assessed after scraping. Water samples were taken 1 cm above each brick to verify that the nutrient dosing was indeed changing water nutrient concentration.

### No response to nutrients in urban reach

The nutrient dosing increased dissolved water nutrient concentrations in the rural reaches (+60% and +70% for nitrogen compared to the controls for the high and low fertiliser dosages, +95% and +98% for phosphorus) whereas in the rural reaches nitrogen was increased only at the higher dosage (+62%) and phosphorus was increased (no difference between dosages).

**In the rural reach, the addition of nutrients over longer periods resulted in increasing periphyton development**, and after 8 weeks nutrient dosage periphyton reached coverage levels comparable to the "natural" level in the urban reaches.

**In the urban reach, however, the nutrient additions, for all of the time periods tested, had no effect on periphyton development**.

In the controls in the rural reaches, periphyton development was low (approx 20% cover, 1g biomass on a 140x140x50 mm brick), whereas with nutrient dosage over 8 weeks coverage reached levels comparable to those found in the controls in the urban stream (c. 60%, 3g).

### No response to nutrient pulse

The experiments also showed that there was **no significant response (in the rural reach) to a short duration "pulse" nutrient addition**, that is one bag of fertiliser left for two weeks only, even after 8 weeks from the start of the dosage. This shows that a single pulse nutrient addition has no significant effect on periphyton development, even in the long term.

*"Nutrients and their duration of enrichment influence periphyton cover and biomass in rural and urban streams", T. Elsdon, K. Limburg, Suny College of Environmental Science and Forestry, Syracuse, NY 13210, USA.*
TElsdon@skm.com.au

*Marine and Freshwater Research, 2008, 59, pages 467–476. CSIRO Publishing* www.publish.csiro.au/journals/mfr

## Conferences and networks

### 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**

The Global Phosphorus Network *www.GlobalPNetwork.net* is a new platform to exchange information, news, opinions between stakeholders, policy-makers and experts.

Join at: *http://globalpnetwork.net/user/register*

### Phosphates 2012

**Phosphate industry conference**

The 2-yearly conference for the worldwide phosphate industry (rock production, fertiliser, animal feeds, food, detergents, other industrial uses) will take place in El-Jadida, Morocoo, 19th - 21st March 2012:

*http://crugroup.com/Events/phosphates/Pages/Phosphates2012.aspx*