SCOPE NEWSLETTER

NUMBER 66 December 2006

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Danube

Nutrient impacts on the Black Sea

The final report of the daNUbs project provides a detailed assessment of nutrient sources to the Danube, impacts on the Black Sea, and management scenarios for ensuring improvement of ecological quality.

California Central Valley

Assessing eutrophication

Issues in assessing impacts of nutrient loads, including water quality and beneficial use impairment, nutrient availability, and nutrient criteria development.

Danish coastal waters

Relating nutrients to phytoplankton and transparency

Analysis of ten years' data from 162 sampling stations shows that Danish coastal waters are heavily eutrophied, with algal development strongly related to total nitrogen concentrations.

Detergent phosphates

EU policy assessment

Detergent phosphates bans, industry voluntary agreements and ecotaxes are assessed, looking at environmental impacts in the context of developments in sewage treatment.

Phosphorus recycling

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Germany

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Bittern and struvites

Precipitating struvite for recycling from salt production wastes

Several different groups have published initial studies looking at using bittern, a magnesium-rich waste liquor from salt production, to recover phosphate as struvite from wastewaters, or conversely adding phosphate to bittern to recover magnesium and potassium as K-struvite.

Quebec

Struvite precipitation from swine effluent

Struvite precipitation from piggery wastewater without magnesium addition. Reports of beaker, batch and laboratory pilot studies.

The Scope Newsletter

The SCOPE Newsletter is produced by the Centre Européen d'Etudes des Polyphosphates, the phosphate industry's research association and a sector group of CEFIC (the European Chemical Industry Council).

The SCOPE Newsletter seeks to promote the sustainable use of phosphates through recovery and recycling and a better understanding of the role of phosphates in the environment.

The SCOPE Newsletter is open to input from its readers and we welcome all comments or information. Contributions from readers are invited on all subjects concerning phosphates, detergents, sewage treatment and the environment. You are invited to submit scientific papers for review.

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Phosphorus management policies

Danube

Nutrient impacts on the Black Sea

Major EU-funded research project carried out in close cooperation with the International Commission for Protection of the Danube River (ICPDR), DANUBS combines extensive monitoring data, nutrient source information, and models linking nutrient loads to river concentrations to ecological impacts in ground water, rivers and in the Black Sea (Moneris, DWQM, DDM, Black Sea models). The final DANUBS report is now published, as well as a number of full reports for the project's different workpackages, on http://danubs.tuwien.ac.at

The Danube is 2,900 km long and its 800,000 km^2 catchment represents one third of the Black Sea catchment. The average discharge is 6,500 m^3/s. The basin population of 82 million is 42% of the Black Sea basin population;

The project links the **Moneris model**, which estimates nutrient emissions, to marine ecological impact models. The difficulty is that Moneris uses a five year timescale, whereas intervals by hour are necessary to model marine impacts, to reflect changes in winds, which modify mixing. This was resolved by using daily flow and bi-weekly nutrient concentration monitoring data as input to the dynamic Danube Water Quality Model (DWQM). A specific model, the Danube Delta Model (DDM) assesses the effects of the delta area. In fact, most of the Danube's water crosses the delta directly in the three river branches, with thus a residence time of only 1-2 days. The nutrient retention in the delta is only 2-3% for both nitrogen and phosphorus.

For Moneris, the Danube was broken down into 388 subcatchments. Investigations in a number of subcatchments and for five tributary rivers were used to improve information on interactions between surface runoff, intermediate and ground water, to improve Moneris modelling.

Key factors influencing nitrogen and phosphorus loadings to surface water showed to be slope of land, geological factors, climate and in particular precipitation. Historic water quality data were used to verify and calibrate the models.

The Black Sea impact model developed is based on the POM Princeton Ocean Model, taking into account wind, water movements, and modified to include the Danube river plume dynamics and Black Sea climatology and a biological compartment model based on the Fasham model.

Nutrient retention

The average deviation between Moneris estimated loads and monitoring data measured nutrient levels, for the different subcatchments, was 16% for nitrogen and 50% for phosphorus. This is higher than deviations found previously in basin-wide studies (30% for P).

For phosphorus, it was shown that high flow events significantly influence the phosphorus load, although this effect decreases with larger catchment areas considered (it is more significant for the tributary rivers than for the Danube itself). One high flood event can transport phosphorus loads of the order of magnitude of the annual total phosphorus transported.

The Iron Gates dam (Eisernes Tor, between Romania and Serbia, downstream of Belgrade) in the Danube, opened in 1972, has a considerable effect: it is estimated that **one third to 40% of the phosphorus inflow into the dam reservoir is retained**, although it is not clear whether this will continue to be the case or whether in the coming decades a retention capacity will be attained.

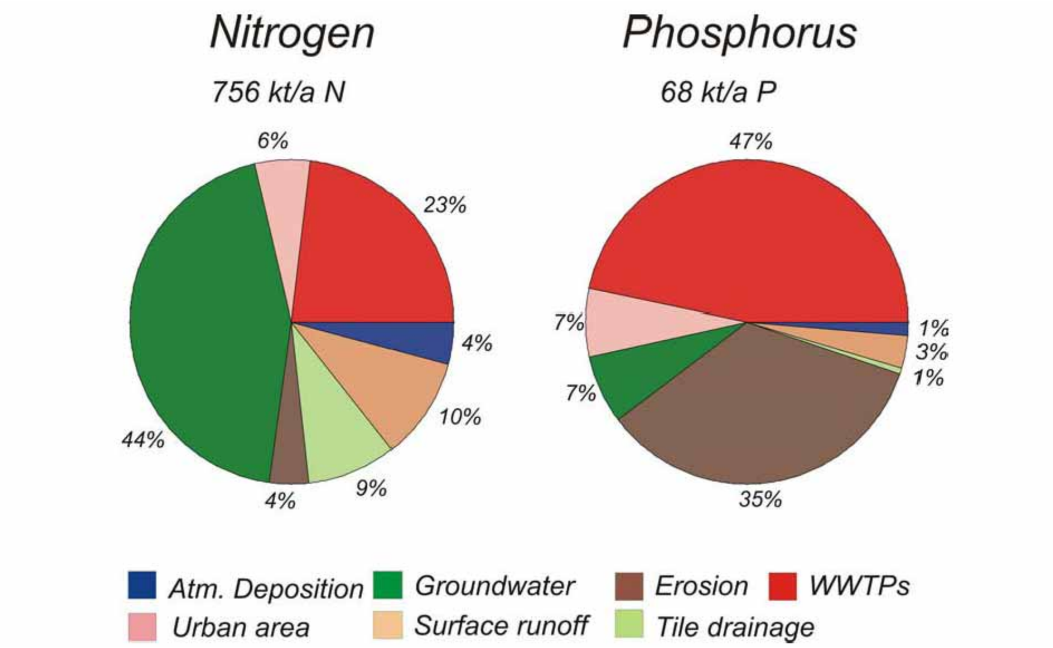
Silica

Dissolved silica is the third nutrient significant for algal development. Human sources are estimated to contribute <10% of dissolved silica. The natural sources are leaching from soil and rocks. Data available suggests that **emissions of natural dissolved silica have declined by around 50% over the last 50 years**.

The mechanisms are unclear, but this may be related to the **damming of headwaters**. Dissolved silica is important for the balance of algal communities, because it is essential for diatoms.

Total emissions

For the whole Danube basin, nitrogen loads are dominated by groundwater (44%) and sewage works emissions (23%) and phosphorus loads by sewage works (47%) and soil erosion (35%). The relative importance of different sources varies widely between the 388 subcatchments but sewage works are the most significant source of phosphorus in all subcatchments except in Germany and Austria, indicating the importance of improving sewage phosphorus removal for reducing phosphorus emissions to the Danube.



Recommendations

The report concludes that the situation in the North Western Black Sea shallow waters has improved considerably over the last decade, with reduced eutrophication symptoms: improved water transparency, deep water oxygen concentrations, phytoplankton diversity (diatoms), regeneration of phytobenthos and macrozoobenthos. This is considered to be the consequence of improved sewage treatment nutrient removal, reduced phosphate in detergents, and reduced economic activity in central and eastern Europe (closure of large animal farms, decreased fertiliser application, closure of fertiliser factories).

Nutrient discharges from the Danube River "should be further reduced but at least kept at its present level".

Five different nutrient management scenarios are examined and compared to the year 2000 situation, each scenario involving a number of different variables including sewage treatment, detergent phosphates, agriculture and land use. These are clearly laid out in the table in the paper by van Gils et al. referenced.

Actions

The daNUbs report recommends the following actions:

- **designation of the whole Danube catchment as a eutrophication "sensitive area"**, requiring nutrient removal in all sewage works serving agglomerations of >10.000 person equivalents, and implementation of comparable policies in non-EU states, with implementation starting immediately
- **nitrogen removal should also be included in sewage treatment**
- development of connection to sewerage and waste water treatment plants should **not be a priority** where nutrient removal is not installed in the plant
- strong control of **industrial point** nutrient sources
- **erosion abatement** based on minimum tillage and much techniques to reduce particulate phosphorus emissions from agricultural land
- **reduction of phosphorus surpluses in agricultural soils** by reducing phosphorus applications where appropriate
- **reduction of nitrogen emissions from agriculture** by best practice in farming (ammonia emissions, manure application, fertiliser use), integrated production and limitation of agricultural intensity (animal density per hectare, nitrogen application surplus).
- **reduction of animal protein production per inhabitant and of human diet protein content**
- **reinforced monitoring** of the Danube basin and of the Black Sea

"Nutrient management in the Danube basin and its impact on the Black Sea", DaNUbs final report, March 2005. Coordinator H. Kroiss, Vienna University of Technology hkroiss@iwag.tuwien.ac.at

DaNUbs project website: download this report and also full reports on the different project workpackages: http://danubs.tuwien.ac.at

"Future development of nutrient emissions and river loads in the Danube basin", J. van Gils, J. van Gils, Delft Hydraulics, Delft, The Netherlands, H. Behrendt, Institute for Freshwater Ecology and Inland Fisheries, Berlin, Germany, A. Constantinescu, Danube Delta National Institute for Research and Development, Tulcea, Romania, K. Isermann, R. Isermann, Bureau of Sustainable Agriculture, Hanhofen, Germany, M. Zessner, Institute for Water Quality and Waste Management, TU Vienna, Austria
http://128.130.103.159/D5.12%20final.pdf

Chemistry and Ecology, Vol. 22, No. 5, October 2006, 347–357 "daNUbs: Lessons learned for nutrient management in the Danube Basin and its relation to Black Sea eutrophication", H. Kroiss, M. Zessner, C. Lampert, Institute for Water Quality, Resources and Waste Management, Vienna University of Technology, Karlsplatz 13, 1040 Vienna, Austria. Chemistry and Ecology, vol. 22, No. 5, October 2006, pages 347–357.

California Central Valley
Assessing eutrophication

This paper is based on a detailed review carried out for CVRWQCB (California Central Valley Regional Water Quality Control Board) looking at how to implement the Boards Basin Plan objective that "Water shall not contain … (nutrients) which promote aquatic growths in concentrations that cause nuisance or adversely affect beneficial uses", in particular with the aim of defining discharge requirements for agricultural irrigated lands.

Nutrients themselves are not of concern, they are only of concern if they lead to excessive amounts of aquatic plant or algal development.

The authors point out that plant growth is necessary for a healthy and productive ecosystem, and emphasise that **the key issue is the identification of**

what represents "beneficial use impairment". This will be seen differently by different water users. Fishermen will be happy with increased primary production, with feeds up the food chain to give higher fish productivity. Swimming and other water leisure uses will want a nutrient-poor water, with low algal growth and clear water.

Nuisance plant growth can be in the form of algae (floating or on surfaces and the water bed), but also of macrophytes (floating such as water hyacinth or duckweed, rooted such as cattails, egeria). The coupling between nutrient loading and eutrophication effects will be dependent on the type of vegetation liable to develop.

Availability

An important issue is the bioavailability of the nutrients. Soluble phosphorus is often the limiting factor in plant growth in freshwaters. Particulate forms of phosphorus in agricultural and land run off may not be bioavailable, or may be converted to bioavailable forms under some conditions. The authors estimate that **approximately 20% of phosphorus in particulate loadings to surface waters can be considered as available**.

Another important issue is the transport downstream of nutrients in river systems. Nutrients discharged in one place can contribute to excessive fertilisation and lead to nuisance problems hundreds of kilometres downstream, for example in impoundment reservoirs, in estuaries or sea areas offshore.

TDML criteria

The assessment of impact of nutrients depends on the possible related nuisance or use impairment. This is not a function of the level of nutrients alone, but of **local ecosystem characteristics**, river basin geography, and of expectations of the local population as regards water uses.

Therefore, "**it is not possible to reliably regulate nutrient discharges based on generic, numeric, chemical-specific concentration limits for nitrogen and phosphorus compounds**". The authors conclude that the TDML approach (total maximum daily load, see SCOPE Newsletter n°43) cannot be applied to nutrients. The interpretation of water quality data should be based on existing or potential local problems, and on a stakeholder consultation regarding beneficial use impairment and the definition of desired nutrient-related water quality for the given water system, taking into account downstream effects.

The outline of an approach to establishing appropriate nutrient control programs is given, based on site-specific evaluation of a variety of factors and on stakeholder involvement in defining a statement of the water quality / beneficial use issues.

Summary paper "Assessing the Water Quality Significance of N & P Compound Concentrations in Agricultural Runoff", G. Fred Lee, and A. Jones-Lee gfredlee@aol.com *in "Stormwater Runoff Water Quality Newsletter" Volume 9 no 8, available at:* http://www.gfredlee.com/newsindex.htm

Full 2002 review for CVRWQCB ""Review of Management Practices for Controlling the Water Quality Impacts of Potential Pollutants in Irrigated Agriculture Stormwater Runoff and Tailwater Discharges," California Water Institute Report TP 02-05,128 pp, California State University December 2002. http://www.gfredlee.com/BMP_Rpt.pdf

Danish coastal waters

Relating nutrients to phytoplankton and transparency

Some 1400 data sets collected by Danish counties' monitoring stations were analysed, looking at salinity, nitrogen and phosphorus concentrations, phytoplankton biomass (as chl_{-a}) and turbidity (suspended matter, Secci depth). The data covered ten years (mid 1980's to mid 1990's) from 162 monitoring stations in 27 Danish coastal areas and fjords, thus giving from 510 to 1385 different data points for the different parameters analysed.

Data was reported as monthly averages, but March – October data only were used (because algal development is insignificant in these waters in winter). No attempt was made to compensate for inbalances in number of data sets from different station or types of stations monitored.

Salinity at the various stations varied from zero to near ocean levels (33‰) with 75% of data points below 22‰.

Eutrophication

Both nutrient concentrations and indicators of eutrophication symptoms (turbidity, chl_{-a}) were generally high, in many cases comparable to the situation of eutrophied inland lakes, with 75% of the data points exceeding the following values:

Lower quartiles:

343	µgN/l	total N
15	µgN/l	inorganic N
31	µgP/l	total P
5	µgP/l	inorganic P
3	µg.chl_{-a}/l	chlorophyll
< 1.8m		Secchi depth

Total N and P were used for statistical analysis, because dissolved N and P both tended to fall below detection levels in the summer due to rapid cycling by phytoplankton.

Nitrogen correlation

During the summer, around 60% of variation in phytoplankton biomass could be attributed to variations in total nitrogen (N). Nitrogen levels thus clearly appeared as the key limiting factor controlling algal development in the main growth season.

A correlation between phytoplankton and phosphorus (P) appeared essentially in the spring. The authors suggest that this may be because nitrogen runoff occurs from agricultural land with winter rains, thus creating a situation in spring were high levels of nitrogen lead to phosphorus being limiting.

The authors conclude that Danish coastal waters are strongly influenced by terrestrial runoff (low salinities at many stations), and consequently show high nutrient concentrations and symptoms of eutrophication (phytoplankton development and turbidity, with Secchi depth closely related to chl_{-a} concentrations). Strong negative correlations between salinity and both nitrogen and phosphorus pointed to the terrestrial origin of the nutrient concentrations.

Nitrogen concentrations showed the closest correlation to phytoplankton development, comparative to P or N+P, except in very early spring, suggesting that nitrogen limits phytoplankton and so water transparency and summer algal blooms in these waters, with important management implications.

"Phytoplankton, nutrients and transparency in Danish coastal waters", Estuaries, vol. 25, n°5, pages 930-937, 2002. Abstract. *Estuarine Research Federation (ERF)* http://www.erf.org/

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Detergent phosphates

EU policy assessment

This research paper by Jonathan Köhler, of the University of Cambridge Economics Faculty, looks at policies towards detergent phosphates and their environmental impacts. Detergent phosphate bans, industry voluntary agreements and ecotaxes are examined. The author looks at the effectiveness of these policies in addressing the environmental issue targeted – eutrophication – in the context of phosphate sources from human wastes and agriculture, and of EU legislation on sewage treatment and the EU Water Framework Directive.

The use of phosphates (STPP) in laundry detergents is examined, showing that their effectiveness results from their performing several functions : counteracting water hardness (allowing surfactants to function), synergy with washing compounds, breaking up of particles of dirt and oil, and prevention of re-deposition on clothes, pH buffering. The environmental risk related to detergent phosphate use, that of eutrophication, is presented.

Eutrophication problems continue to be a significant issue both in many European countries and in the Americas and Asia. The author points out that detergent phosphates, where used, are a minority source of phosphates in sewage, with agriculture often being an even greater source of phosphates to surface waters (30 – 90% of phosphate loads to river basins is from non-point sources). He concludes that detergent phosphates may lead to eutrophication, but under inherently limited and site specific conditions.

Treatment of sewage to remove phosphates has a greater potential to address eutrophication, because it works on all the phosphate content of waste water and not only the detergent fraction. The author cites the case of Italy, where algal blooms in coastal and inland waters remain a problem despite an effective ban on detergent phosphates.

Detergent ecotax

The example of the French ecotax which targets laundry detergents amongst other products since January 2000, is examined. As part of the "General Tax on Polluting Activities", the ecotax objective is to reduce polluting activities through the polluter-pays principle, and to raise revenue to fund the 35 hour week and so job creation. The ecotax on detergents varies in level by a factor of around one fifth depending on detergent phosphate content, and represents 2 – 10% of detergent public sales prices.

Assessing this tax, the author notes positively its ease of collection (collected with VAT), but negatively that the level of ecotax is too low to affect sales, and "will probably not achieve its environmental aims of reducing cyanobacterial blooms and algae in surface waters".

Markets and perspectives

Looking at developments over the last 25 years, the author notes the considerable reduction in phosphate use in detergents in Europe, resulting in consolidation of the detergent phosphate industry. He suggests this may now stabilise, both because **phosphates are particularly effective as a component of modern, high-performance detergents** (compact powders, tablets), and because the most effective policy for addressing eutrophication is now the removal of phosphates from urban waste waters through advanced sewage treatment.

"Research paper: detergent phosphates: an EU policy assessment", Journal of Business Chemistry, vol. 3, issue 2, May 2006, pages 15-30, available free online at www.businesschemistry.org

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Phosphorus management policies

Susan

P-recovery via sewage sludge incineration

The EU-funded project SUSAN is looking at recovery of phosphorus for recycling from sewage sludge incineration ash, including upstream optimisation through sewage works nutrient removal strategies.

The SUSAN project (**Sustainable and Safe Re-Use of Municipal Sewage Sludge for Nutrient Recovery**), funded under the EU 6th Framework R&D Programme, is looking at pathways to recover phosphorus from sewage sludge via thermal treatment.

Standard sewage sludge incineration processes result in an ash with a relatively high phosphorus content, but where the phosphorus is poorly bioavailable, so not useful for agriculture as a fertiliser. Such sludges may also have levels of heavy metals which are too high to be compatible with agricultural use, or of iron which reduces the availability of phosphorus in the ash and in soils to which it is applied. The SUSAN project will address this through a **second thermo-chemical step to remove the heavy metals** and transform the phosphorus into plant available mineral forms.

The project will concentrate on the objective of P-recovery from ash from mono-sludge incineration, that is incinerators treating only sewage sludge (not mixed with other wastes such as domestic refuse). There are 20-23 such incinerators at present in Germany.

A pre-study of economic feasibility has already been carried out, with calculations based on a single municipal sewage treatment plant (wwtp) producing around 7,000 tonnes of sludge ash per year. Based on ash gate disposal costs of 40-50 Euros/tonne, the study suggested a margin of around 18 Euros/tonne treated ash, and a 5-6 year payback.

Initial thermo-chemical tests have also been carried out on three different sludge types (iron used in P-removal in sewage works / low iron sludge from biological nutrient removal, calcium used/not used in sulphur dioxide removal in sludge incinerator). Three different chlorine donors were used (calcium chloride, magnesium chloride, potassium chloride) at 1000°C for half an hour at 150kg chlorine/tonne ash).

The project will look at how the sewage treatment process affects the chemical composition of the resulting sludge incineration ash, in particular iron dosing for phosphate removal, as compared to the use of aluminium salts for phosphate precipitation or the use of biological nutrient removal processes.

The project is led by BAM, the German Federal Institute for Materials Research and Testing (Division Waste Treatment and Remedial Engineering, Christian Adam *Christian.adam@bam.de*), with the following partners: ASHDEC Umwelt AG (thermo-chemical processing of ashes), SNB N.V. Slibverwerking Noord-Brabant (sludge incineration facility), BAMAG GmbH (engineering), Kemira GrowHow Oyj (fertilisers for agriculture), FAL-PB (Institute of Plant Nutrition and Soil Science, Federal Agricultural Research Center), TU Wien (Vienna Technical University, IWA Institute for Water Quality, Resources and Waste Management).

Summary of project and project newsletters:
www.susan.bam.de

Germany

Phosphorus in sewage sludge incineration ash

A study carried out on three different sewage sludges looked at the differences in sludge incineration ash mineral contents depending on the amount of iron used for phosphate precipitation in the sewage works, on different nitrogen levels in the incinerator chamber and with different incinerator technologies.

Previous work in Japan (Matsuo, see SCOPE Newsletters n° 36 and 41) indicates that incineration ash from sewage works not using iron showed water solubility of phosphorus.

In this study, **three different sewage works sludges were used**: high iron, from a works using iron salts for phosphorus removal; medium iron, mixed sludge from around 20 works ; low iron, from a works not using chemical phosphate removal (biological nutrient removal).

The phosphorus in the low iron sludge ash (from biological nutrient removal) did not prove more water soluble than that in the high iron sludge ash and the authors conclude that the mode of nutrient removal in the sewage works (sludge iron content) has little influence on the form of minerals in the incineration ash. The mineral content also appeared to be independent from the incineration conditions and technology.

The sludges showed respective water contents of 20%, 7% and 23%. They were incinerated in an experimental incinerator, enabling air control and gas analysis, at 850°C. After incineration, they resulted in ashes with nutrient contents as below.

The authors conclude therefore that **phosphorus recovery from incineration ash will be facilitated less by attempting to separate sludges from sewage works using different nutrient removal processes,** but rather by grouping sludges into large centralised sludge incineration centres.

"Systematische Untersuchungen zur Rückgewinnung von Phosphor aus Klärschlammaschen unter besonderer Berücksichtigung von Feuerungsparametern" (systematic research into recovery of phosphorus from sewage sludge ashes under different incinerator parameters), R. Kull, J. Maier, G. Scheffknecht, Universität Stuttgart Institut für Verfahrenstechnik und Dampfkesselwesen IVD,, Pfaffenwaldring 23 , 70569 Stuttgart, Germany IVD@IVD.Uni-Stuttgart.de *. Förderkennziechen BWT 24004, presented at the BWPLUS seminar, Karlsruhe, 21-22 February 2006 (in German).* http://bwplus.fzk.de/berichte/ZBer/2006/ZBerBWT24004.pdf

Nutrient contents of sludge incineration ashes

Type of sludge: level of iron	*high*	*medium*	*low*
* phosphate (P_2O_5 by weight)	13.3%	12.6%	19.2%
* calcium (CaO by weight)	14.3%	14.0%	17.5%
* iron (Fe_2O_3 by weight)	15.2%	12.5%	5.9%
* magnesium (MgO by weight)	1.9%	2.1%	3.5%
* potassium (K_2O by weight)	1.4%	1.4%	2%

Bittern and struvites

Precipitating struvite for recycling from salt production wastes

Several different groups have published initial studies looking at using bittern, a magnesium-rich waste liquor from salt production, to recover phosphate as struvite from wastewaters, or conversely adding phosphate to bittern to recover magnesium and potassium as K-struvite.

Bittern is a by-product of commercial production of table salt and/or of halogen compounds from seawater. Typical composition (for 1.2 g/ml density bittern) includes 30 g/l magnesium, that is approx 30x concentrations in sea water, 10 g/l potassium, and significant concentrations of sodium, sulphate and chlorine ions and traces of bromine and boron.

Two groups of authors (Korea – Florida and China) have published papers looking at **using bittern as a magnesium source to enable precipitation of phosphate and/or ammonium from waste waters – as struvite**, whereas another group (Venezuela) have looked at **using phosphate addition to recover magnesium, potassium and trace boron from bittern – as potassium struvite**.

P recovery from animal waste waters

The 2003 paper [1] presents 1-litre beaker stirred precipitation studies u**sing bittern as a magnesium source for phosphate and ammonium precipitation as struvite** from pure chemical solutions and from biologically treated swine farm waste water (activated sludge process effluent). Precipitation using bittern as a magnesium source was compared to the use of magnesium chloride solution and seawater.

The initial experiments used pure solutions of 4.3 mM ammonia and 3.9 mM phosphate (concentrations adjusted to be the same as those in the waste water used later), with bittern addition of 0.4%. At an initial pH of 11, different mixing times were tested, showing that 10 minutes stirring followed by 10 minutes settling was adequate. Experiments were then carried out using pure solutions at different pH (from 7 to 12) to compare the effects of bittern, seawater and magnesium chloride (MgCl) as magnesium sources.

Finally, two experiments were carried out to test the effectiveness of bittern as a magnesium source using swine wastewater treatment effluent, at pH 11 with the addition of different amounts of bittern up to 1%. The wastewater after 0.4% bittern addition contained approximately the concentrations of ammonia and phosphate indicated above, 5.3 mM magnesium, 4.6 mM potassium and 0.8 mM calcium.

Results showed optimal ammonia removal (and to a lesser extent, optimal phosphate removal) at pH 9-10 (optimum 9.6). This was conform to MINTEQ modelling which suggested increasing precipitation of struvite (magnesium ammonium phosphate MAP) up to around pH 9, a shift to magnesium phosphate ($Mg_3(PO_4)_2$) up to pH 11 and from pH 10.5 upwards a shift to magnesium hydroxide ($Mg(OH)_2$) precipitation. Bittern gave comparable effectiveness of phosphate removal from the waste water (>75%), but slightly lower ammonia removal (40% compared to 53-54% for seawater and magnesium chloride).

The authors conclude that bittern provided an efficient magnesium source for phosphate removal from this waste water effluent. To achieve a high % of ammonia removal, phosphate addition would be necessary because of the ammonia:phosphate ratio > 1 in the waste water.

This follows a previous paper [2] **magnesium chloride, seawater and bittern were tested as magnesium sources for the precipitation of struvite** from pure chemical solutions and from toxic industrial wastewater from a coke manufacturing process (high pH, nitrogen and phenolic compounds). The seawater and bittern had magnesium concentrations of 1,100 and 31,000 mg/l respectively. Initial experiments used pure chemical solutions with ammonia-N and phosphate-P at 100 mg/l, testing pH 7.5 – 10.5, reaction time 1 – 60 minutes and different molar ratios to magnesium addition. Precipitates were removed by centrifugation at 3,000 rpm.

Conditions of pH 9.5 – 10.5, 10 minutes reaction time or more, and 1.5x magnesium molar ratio showed to be optimal for struvite precipitation, **achieving up to 70% and 98% ammonia and phosphate removal** from pure chemical solutions. In the industrial wastewater, sea water and bittern proved efficient magnesium sources, with 72% and 99% ammonia and phosphate removal for bittern. Struvite (MAP) was precipitated as white plate-like crystals of size 1.5- 7 µm, with good settlability.

K-struvite recovery from bittern

Two papers (1999, 2002) [3, 4] present laboratory scale experiments precipitating K-struvite (magnesium potassium phosphate $MgKPO_4.3H_2O$) from seawater bittern, a residual by-product from seawater solar halide production, as a route to recover the valuable nutrients magnesium and potassium. **The K-struvite is considered to be an efficient fertiliser**.

The bittern used had a density of 1.25 g/ml and contained 11 g/l potassium, 36 g/l magnesium, 0.1 g/l boron, as well as 70 g/l sodium, 52 g/l sulphate and 185 g/l chloride.

Precipitation was achieved by adding phosphate (as NaH_2PO_4) and sodium hydroxide to increase pH. Temperature controlled, stirred 1 litre beakers, were used for batch precipitation experiments. Different bittern dilutions, stirring speeds, temperatures, reaction time and pH were tested.

In the 2002 paper, a stirring speed of 300 rpm (4-blade stirrer) was found adequate, in that higher stirring speeds did not improve reaction. A 30 minute reaction time gave higher % phosphate precipitation and larger crystals than 15 minutes. Precipitation rate and crystal size were also higher at 15°C compared to 30°C. Higher potassium recovery % and larger crystals were obtained with diluted bittern (1 part bittern to 1 part water).

The most important reaction parameter showed to be pH (tests covered the range pH 7 – 11), with pH 10 giving optimal recovery rates for magnesium, potassium and phosphate (all at 100%) and of boron (90%).

The precipitated product was mainly K-struvite (magnesium potassium phosphate), with some magnesium phosphate $Mg_3(PO_4).4H_2O$ and low levels of magnesium sodium phosphate $MgNaPO_4.H_2O$. The precipitate contained 54% phosphate, 18% magnesium, 5% potassium and 0.05% boron. The precipitate formed uniform rhomboid crystals of size 20-75 µm.

The 1999 paper shows similar results, and includes SEM photos of the precipitated crystals. In this case these contained 67% phosphate, 19% magnesium, 6% potassium and 0.1% boron.

Solubility tests of the precipitated crystals were carried out, showing low solubility in pure water, but 100% solubility in 2% (by weight) citric acid solution, and **are thus considered as showing that the precipitated product offers nutrients available to plants**.

Ammonia precipitation from landfill leachate

A further paper [5] presents experiments into precipitation of struvite from landfill leachates, with an objective of ammonia removal.

The landfill leachate from the North East Territory landfill, Hong Kong, had a pH of 8.5, 910 mg/l BOD, 31 mg/l Mg and 2,750 mg/l ammonia nitrogen ($N-NH_4$). The high levels of ammonia have toxic inhibition effects on micro-organisms and are an obstacle to biological treatment of the leachate.

The combinations of pure chemicals, magnesium chloride $MgCl_2$ plus sodium hydrogen phosphate Na_2HPO_4, magnesium oxide MgO plus phosphoric acid H_3PO_4, and magnesium sulphate $MgSO_4$ plus superphosphate phosphate $Ca(H_2PO_4)_2$ and then **synthetic bitterns were tested as sources of magnesium and phosphate to precipitate struvite from the leachate**. Sodium hydroxide was used to adjust pH. The synthetic bitterns were produced by evaporating seawater at 60°C down to 12% and 4% volume, to give respective concentrations of 9 and 24 mg/l magnesium.

Experiments were carried out in 1 litre beakers, with 15 minutes stirred reaction time, followed by 15 minutes settling. Different pH and different molar ratios of chemical addition were tested with the pure chemicals: PH 6 – 11, molar ratios P:NH_4:Mg of 1:1:1 ; 1.5:1:1 and 1.3:1:1.3.

At the 1:1:1 molar ratio and pH 9, the three different chemical reagent combinations removed respectively 92%, 36% and 70% respectively ammonia precipitation from the leachate.

Using the synthetic bitterns, with phosphoric acid (H_2PO_4) as a phosphate source, the more concentrated one enabled **72% ammonia precipitation from the leachate**, and the more dilute one 80%, with good ammonia removal rates being achieved at pH adjustment 7.5 upwards. Different dosing rates of the bittern and phosphoric acid (above molar ratios of magnesium and/or phosphate) were also tested.

SEM micrographs of the precipitated struvite from the leachate are given, showing a mixture of thick tubular and short prismatic crystals of size 10-50 µm. They contained 5% nitrogen, 10% magnesium and 16.5% phosphorus, with traces of calcium (0.5%).

This work follows a previous 1999 paper [6] testing the same chemicals (but not bittern) for struvite precipitation to remove ammonia from landfill leachate from the WENT landfill site, Hong Kong. In this previous paper, further stirred beaker results are presented at different chemical dosages and pH. The characteristics of the precipitated struvite “sludge” are examined, showing 27% solids content after 10 minutes settling and supernatant removal (settling comparable to fine grit or sand) and stability without further dewatering.

The authors conclude that bittern waste could be a valid alternative to chemicals as a magnesium source (with an additional phosphate source) for removing ammonia nitrogen from landfill leachates.

[1] “Removal of nitrogen and phosphate from wastewater by addition of bittern”, Chemosphere 51, pages 265-271, 2003.
http://www.sciencedirect.com/science/journal/00456535

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[2] “Removal of nutrients in wastewater by using magnesium salts”, Environmental Technology, vol. 19, pages 283-290, 1997
http://www.environtechnol.co.uk/contents.htm

H. Shin, S. Lee, Dept. Civil Engineering, KAIST, 373-1 Kusong-dong, Yusong-gu, Taejon, 305-701, Korea.

[3] “A novel process for the production of multinutrient phosphatic base fertilizers from seawater bittern and phosphoric acid”. Interciencia, vol. 24, n° 5, Sep-Oct 1999, pages 317-320 www.interciencia.org

J. Fernandez Lozano, A. Colmenares, D. Rosas, Universidad de Oriente, Venezuela.

[4] “Multinutrient phosphate-based fertilizers from seawater bitterns”. Interciencia, vol. 27, n° 9, Sep 2002, pages 496-499 www.interciencia.org

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[5] “MAP precipitation from landfill leachate and seawater bittern waste”, Environmental Technology, vol. 23, pages 989-1000, 2002
http://www.environtechnol.co.uk/contents.htm

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[6] “Ammonium removal from Landfill leachate by chemical precipitation”, Waste Management 19, pages 409-415, 1999.
http://www.sciencedirect.com/science/journal/0956053X
Available at:
http://www.paper.edu.cn/scholar/download.jsp?file=zhaoqingliang-3&title=Ammmonium%20removal%20from%20landfill%20leachate%20by%20chemical%20precipitation

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Struvite precipitation from swine effluent

Iron and polymer coagulant pre-treatment of piggery wastewater, resulting in magnesium release, makes struvite precipitation possible without magnesium addition.

Wastewater from the Viaporc swine farm, Eastern Townships, Quebec, Canada, was used to investigate struvite precipitation. This installation uses a solid-liquid separation process, prior to a trickling filter, to treat and remove odours from liquid manure wastewaters and extracted air. This separation process, including iron addition, causes a release of soluble magnesium, resulting in a high molar soluble magnesium: phosphorus ratio, which makes struvite precipitation possible without addition of magnesium.

The solid-liquid separation process is intended to reduce suspended solids, in order to avoid bed clogging of the trickling filter system. The separation process involves: a preliminary settling tank, addition of ferric chloride and an cationic polymer coagulant under vigorous mixing, followed by a further settling tank with surface skimmer. The solids are transferred to composting. The liquor goes to the trickling filter. However, the plant has been suffering from unexpected struvite deposit formation in the conduits feeding the trickling filter (see SCOPE Newsletter n°57).

Initial beaker experiments were carried out to attempt to achieve struvite precipitation from the raw swine wastewater. The soluble molar magnesium:phosphorus ratio in the raw wastewater was approximately 3:4, and so magnesium was added to achieve ratios 1.1:1 to 1.4:1 as well as sodium hydroxide to increase the pH to 8.5. However, the precipitated struvite was mixed with considerable amounts of colloidal organic material, so that recovery of a useful material was not possible. The use of raw wastewater was thus abandoned.

Pre-treated swine wastewater

In the pre-treated swine wastewater from the piggery (PSWW), that is liquor from the solid-liquid separation, the soluble phosphorus concentration was approximately half that of the raw liquor, that is just under 4 mmol P-PO_4/l, but the soluble magnesium concentration was nearly twice as high at around 11 mmol Mg/l. Thus, the magnesium:phosphorus ratio was approximately 3:1, meaning that magnesium addition was unnecessary to achieve struvite precipitation. The pH of this liquor was 6.3.

Stirred beaker experiments were carried out to show the changes in soluble phosphorus, soluble magnesium and residual (non precipitated) iron as a function of different levels of iron addition ($FeCl_3$). In the actual plant, levels of iron addition are adjusted to levels of suspended solids, to prevent fouling of the trickling filter. The mechanism of the **soluble magnesium release in the pre-treatment** is not known, but could be due to ionic exchange with iron or to compression of the diffusive layer at the solid/liquid interface.

Reaction time and pH

Stirred beaker (batch) experiments, batch experiments using a 15 litre stirred 15cm column reactor (separated vertically into mixed and settling zones), and continuous operation experiments using the same reactor, were carried out to assess struvite precipitation from this PSWW at different pH (achieved by sodium hydroxide dosing) and residence times.

A reaction time of 30 minutes and an optimal pH of 8.5 proved sufficient to achieve high levels of

phosphate precipitation, up to 98% (with a corresponding 17% removal of ammonium).

For pH higher than P, phosphorus removal continues to be achieved but other compounds are found in the precipitated phosphate, in particular calcium phosphates.

With the continuously operated pilot reactor, 86% of the precipitated struvite showed a >75µm diameter.

Experiments were carried out to attempt to avoid sodium hydroxide addition by using aeration (degassing) to increase pH, but these were not successful . The pH of the PSWW increased only from 6.3 to 6.8 after 4 hours of aeration, resulting in no significant struvite precipitation. Presumably the pre-treatment of the swine wastewater does not result in a liquor with significant carbon dioxide content (unlike anaerobic digester liquors), so that aeration does not result in significant CO_2 degassing.

The authors conclude that this solid/liquid separation pre-treatment of piggery liquors is not only efficient at lowering suspended solids (COD and BOD), enabling treatment in trickling filters, but can also be combined with rapid and efficient phosphorus recovery as struvite, without requiring the addition of magnesium.

"Laboratory and pilot-scale phosphate and ammonium removal by controlled struvite precipitation following coagulation and flocculation of swine wastewater", Environmental Technology, vol 26, pages 525-536, 2005
http://www.environtechnol.co.uk/contents.htm

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See also Laridi et al., SCOPE Newsletter n°57*, pages 8-9.*