SCOPE NEWSLETTER

NUMBER 58 **December 2004**

Danube Basin

daNUbs
Danube and Black Sea nutrient research

EU research project into nutrients in the Danube Basin and the Black Sea shows ecological recovery of the Western Black Sea but also raises many questions.

Nutrients and ecosystems

Great Britain
The costs of eutrophication

Eutrophication in England and Wales costs some UK£ 75-114 million/year in direct and amenity costs and impacts, compared to UK£55 million/year spending addressing the issue.

Illinois
Spate flows and phosphorus run off

A nutrient loading assessment of the Illinois River shows that ¾ of total phosphorus loads come from surface run-off during high water flow events.

Drainage P-removal
Artificial submerged-vegetation wetlands

Submerged vegetation wetlands prove to be effective in removing phosphates from nutrient-rich agricultural drainage waters: more so than wetlands with emergent macrophytes, possibly because of co-precipitation of phosphates with calcium to sediment as well as plant P assimilation.

Phosphorus recycling

Chesapeake Bay
Nutrient recycling policy

20 years after establishing a sewage treatment nutrient removal strategy to protect the Chesapeake Bay estuary waters, plans are now being developed to implement widespread recycling of nutrients as "NutraGreen" composted sludge.

Japan
Struvite from swine waste liquors

A continuous 4m^3/day reactor used aeration to precipitate and recover struvites from piggery waste liquors. Experiments looked at precipitation on different materials.

Cincinnati
Phosphorus recovery research project

The US Environment Protection Agency has announced a research project into struvite recovery and recycling from biological sewage treatment.

Struvite
Lab-scale stirred reactor

A 1.4 litre continuously stirred tank reactor was used to study struvite precipitation with pure reagent solutions at varying stirring speeds, pH, reactor fluid recycle rate and ammonium concentration

Struvite chemistry
Magnesium carbonate interactions

CO_2 stripping from sewage digester effluents can cause struvite precipitation by two mechanisms: pH increase and increased availability of magnesium ions.

Danube Basin

daNUbs
Danube and Black Sea nutrient research

The daNUbs research project (EU 5th Framework) brings together 17 scientific institutes to study nutrients in the Danube Basin, and thus flowing into the Black Sea: sources, transport and retention mechanisms, ecological effects, management scenarios.

The work and preliminary conclusions of the 5 year project were presented by the participant scientists at a **conference at the Vienna Technical University** on 16th December 2004 and the final project report is expected to by approved and published by summer 2005 at the project website *http://danubs.tuwien.ac.at* The project follows from previous research (PHARE see *Scope Newsletter n°48* and *n°46*) which raised questions by showing that actual monitored nutrient loads carried by the Danube at its mouth into the Black Sea appeared as 90% lower than estimated emissions (estimates of nutrients being released by diffuse land or point sources into the river system).

Nutrient loads in the Danube are of key significance for the Black Sea, because the Danube contributes 205 km^3/year of the Sea's total 350 km^3 freshwater inflow.

Nutrient models

The whole Danube Basin was modelled for estimated nutrient emissions, for retention in the different parts of the river system, and thus through to discharges into the Western Black Sea. Modelling covered phosphorus (P), nitrogen (N), with silica (Si) only being estimated. The Moneris model (see *Scope Newsletter n°37* p.14) was used to estimate nutrient emissions into the river system and their retention and/or transport, working with a division into 338 sub-basins, based on point sources, land use coverage, fertiliser use statistics, soil type maps. Specific models were used for retention of nutrients in the Danube and large tributaries channels (DWQM = Danube Water Quality Model) and for the Danube Delta (Danube Delta Model). Finally, the Danube river plume and nutrien transport and fate in the Western Black Sea were modelled using Shelf Models.

The model generated data were compared with real river nutrient load from the TNMN (Trans National Monitoring Network) of the Danube Basin, with satellite photo data of the Danube river plume in the Black Sea and of algal development in the Black Sea, with data from the JDS (Joint Danube Survey – data collection along the Danube River) and with data from two sampling cruises in the Western Black Sea in 2002-2004 (covering water chemistry, algae, sediments, and assessment of ecological condition).

Diffuse **emissions of nutrients to the Danube Basin are estimated by the daNUbs project (Behrendt *et al.*) to be 624 Kt/year N (of which 14% only from urban areas diffuse sources) and 45 Kt/y P (30% urban, 52% from soil erosion/carried in run-off).** ***Total*** **emissions are estimated to be 759 KtN (29% from settlements, including point sources) and 68 KtP (54% settlements). This means 15KtP from diffuse urban sources and 22 ktP from urban point sources.**

For Van Gils *et al.*, dissolved inorganic and organic are the key forms of nitrogen (N). Dissolved organic nitrogen is significant, at 30-50% of dissolved nitrogen, but is inadequately monitored (very little data). For phosphorus (P), there is considerable exchange and interaction between dissolved and particulate inorganic forms, and so total inorganic phosphorus is the key biological parameter. For silica, <10% of total Danube loads are estimated to be of human origin, most coming from natural dissolution of rock (total Basin emissions estimated at 515 Kt/year).

Uncertainty

The scientific presentations at the daNUbs conference emphasised a number of uncertainties in all the project's conclusions, related in particular to the following mechanisms:

- in the Danube itself, 30% of the total annual phosphorus load can occur (be transported) in just one **flood event**, and in small tributaries this can reach 100%, because of P carried in soil erosion (Zessner *et al.*). The P carried in such flood flows is generally not measured through monitoring systems.

- 50-90% of **nitrogen input to agriculture** is, according to the models, retained in soil, but in fact is likely to be reaching underground waters. Most of the nitrogen input reaching surface waters thus comes from a small proportion of land area, close to rivers or streams (Zessner *et al.*).

- **wide variations** in flows from day to day, and variations in water quality and flow rate in different transects of the river at a given site may mean that calculations of nutrient loads made from monitoring data (concentration x flow) will be inaccurate (Literathy *et al.*). Also the monitoring data from the TNMN is often incomplete.

- Danube flows have been significantly lower over recent years (since mid 1990's), and the effect of this reduced flow is to lo**wer nutrient loads to the Black Sea** (nutrient loads are strongly related to total annual flow for the Danube). This reduction in nutrient loads is very significant, as large as the changes in anthropogenic nutrient inputs. (Van Gils *et al.*).

- **nutrient limitation of algal development in the Black Sea** varies with climate, time, algal community composition, geographical situation … In particular, for the Danube inflow, high levels of nutrient in late Spring/Summer are more likely to result in algal development in the Black Sea than high total annual nutrient loads (Velikova *et al.*)

- algal development in certain areas of the Black Sea (eg. around the Danube Mouth) seems to be phosphorus limited, whereas in other areas it is nitrogen limited (eg. Bulgarian coast)

- the "**plume**" of the Danube in the Black Sea can travel Northwards or Southwards along the coast, Eastwards (offshore) or can stay limited to the onshore area around the river mouth, depending on winds and on other climatic factors (Kourafalou *et al.*)

- West winds in the Black Sea can result in **upwellings** along the Romania – Bulgaria coast, bringing nutrient-rich deep sea waters to the surface, and resulting in elevated nutrient supply (Horstmann *et al.*)

Nutrient retention

Nutrient retention in the Danube Basin river system is very significant, but also locally very variable, thus making it necessary to adapt policy measures to the specific local situation and retention capacity.

The three models (Moneris, DRQM, DDM) show that the highest retention of nutrients occurs in small rivers and streams in the lowlands (Danube tributaries). There is little retention in the larger tributaries and the Danube itself, because of low residence times, with the major exception however of **retention of phosphorus behind the Iron Gates Reservoir Dam on the Danube**: approximately 40% of phosphorus flowing into this dam reservoir in the Danube is retained as a result of sedimentation.

The Danube Delta lake and reedbed system retains around one third of both N and P flowing through it, but in fact 90% of the Danube flow effectively "bypasses" the Delta in the three deep navigation channels leading to the sea, so that the positive benefits of the Delta are limited.

Behrendt *et al.* compared retention factors calculated for the Danube Basin to results for other European river systems. For the Danube system, nitrogen retention on land is around 83% (but as indicated above, this does not take into account nitrogen reaching ground waters) and in the river 34%, comparable to other river basins studied. For phosphorus, retention in the Danube system is around 68%, significantly higher than in other studied basins (usual figure around 55%) – this is because of phosphorus retention in the Iron Gates Reservoir.

Good ecological status

Estimated nutrient emissions to the Danube Basin system increased by factor of 2.6 for N and 2.2 for P from around 1955 to 1990, but have since receded, back to 1.8x for N (mainly because of reduced farming activity – fertiliser use, and industrial activity in the ex-communist countries) and back to 1.5x for P (mainly because of improved municipal waste water treatment).

Observed loads of phosphorus in the Danube are however now only 1.1x (10% higher) than in the 1950's, partly because of retention in the Iron Gates Reservoir (see above).

Most of the Danube Basin today shows good water quality as regards nutrient levels (80% of monitoring results in Class I or Class II for both ortho-P and total-P), with mean annual ortho-P concentrations of 0.04-0.07 mgP/l and total-P 0.04-0.26 mgP/l.

Since the mid 1990's, also, the Black Sea appears to have recovered rapidly following this reduction in nutrient inputs, with satellite images showing considerable reductions in algal blooms (Velinkova *et al.*).

The survey cruise of the Western Black Sea in September 2004 (Horstmann *et al.*) confirms the ecological recovery. Mussels (*Mytilus galloprovincialis*) and red seaweeds (*Phyllophora* and *Polysiphoria*) were found to be widespread on the seabed, showing that anoxic conditions (related to algal blooms) are no longer a problem and that the Sea's ecological problems of the 1990's are no longer occurring. Incomplete recovery of fish stocks is probably the result of over-fishing.

Dr Horstmann concludes that the current nutrient load to the Western Black Sea is now compatible with food ecological status (below critical levels) under current climatic conditions.

Management options

Only around one third of the Danube Basin population is today connected to sewerage (collection of sewage) and to sewage works. Increased connection of households to urban waste water treatment (sewage works) would thus result in considerable and undesirable increases in nutrient loads (N and P) in the Danube, unless nutrient removal is installed in sewage works at the same time. Speakers emphasised that connection to sewerage must go hand in hand with installation of nutrient removal in waste water treatments works (wwtps), as is required by the EU Waste Water Treatment Directive (1991/271) in all areas potentially susceptible to eutrophication. However, to limit costs, a **selective installation of nutrient removal in targeted wwtps** would suffice to enable nutrient discharges to be held at present levels.

Management scenarios presented did not indicate whether a reduction in phosphorus use in detergents would have any significant effect independently of sewage nutrient removal, but if nutrient removal in sewage works is installed as speakers indicated was necessary, then the impact of detergent phosphorus would be minimised.

A recovery of agricultural activities in Eastern Europe is expected to lead to a considerable increase in Danube nitrogen loads, even with "Best Agricultural Practice" (BAP). On the other had, river nutrient load impacts of agricultural recovery, as regards phosphorus, could be controlled by BAP, in particular soil erosion abatement.

The only route to prevent a significant increase in nitrogen loads to the Black Sea would be to both **limit agricultural production to regional needs** (no production for export) and to **reduce meat consumption in diets** (Van Gils *et al.*). Such measures would have other major benefits, including nature preservation, reduced greenhouse emissions (methane, NO_x), healthier human diet and so reduced health costs. Such measures would have very high economic costs, in particular in Austria and Germany, if imposed from above and subsidised, but would offer net economic benefits (cheaper food, reduced health costs …) if developed voluntarily bottom-up by public education (Schönback *et al.*).

Phil Weller, of the International Commission for Protection of the Danube River (ICPDR *www.icpdr.org*), underlined the contribution of the daNUbs project to the Danube Basin Water Framework Directive "ROOF" report (Characterisation and Analysis of the Danube Basin - just published and downloadable at *www.icpdr.org* document IC/084). Considerable information on nutrients in the Danube Basin in provided in this" report pages 66 onwards. He emphasised the need to extract from the science simple messages, understandable to decision makers and to the public.

Conclusions

Helmut Kroiss, Vienna Technical University, presented the project's main conclusions:

- **success of the methodology developed** (combination of different models and linking to management decisions), with potential application worldwide

- **importance of input data quality** (need for harmonisation, to fill gaps, for finer local rather than "country" data on eg. fertiliser use …)

- strong dependence of nutrient discharges to the Black Sea on **Danube flows**

- the main drivers for nutrient loads in the Danube Basin are: **agriculture** (fertiliser use, soil erosion, animal protein production) ; **urban wastewater collection and treatment efficiency** (household connection and nutrient removal) ; **air pollution** (N) ; **land use** ; **morphology of rivers** (nutrient retention is reduced as rivers are made more artificial) ; **climate**

- **phosphorus loads to the Black Sea are now back down nearly to 1950's levels**, but nitrogen loads have only been slightly reduced (-20%) from 1990's levels (the effects of the dramatic reduction in fertiliser use in the ex-communist countries is retarded by soil stocks)

- **small river systems are effective in retaining nutrients**, in particular where natural morphology and connections to wetlands are maintained

- although the **Danube Delta** is largely by-passed, it nonetheless still removes nutrients equivalent to several large cities' releases

- **there is "no doubt" that the Black Sea's ecological situation has dramatically improved over the past 5-10 years and it now apparently "recovered"**

- the proportion of nitrogen loads which can be reduced by medium term management options is 11% through waste water treatment (nutrient removal) and 14% in agriculture (best agricultural practice). For phosphorus, the figures are 23% by wwtp nutrient removal, 20% in agriculture. To limit increases in nitrogen emissions, not only measures for best agricultural practice, but also **limits to agricultural production and productivity** will be necessary

- the same management measures in different countries and in different sub-basins within countries will have **different costs and different effectiveness**

- **recommendation that nutrient emissions to the Black Sea be maintained no higher than current levels, which are considered to be "sustainable"**

- **urban waste water treatment implementation (connection to sewerage) must be accompanied by nutrient removal in sewage works**

daNUbs project website http://danubs.tuwien.ac.at

Nutrients and ecosystems

Great Britain
The costs of eutrophication

This study evaluates the costs of eutrophication of freshwaters in England and Wales and compares these with annual spending addressing the issue. A number of different impacts of eutrophication have considerable economic consequences. The main spending addressing eutrophication is capital spending on nutrient removal installation in sewage works.

The authors categorise the different direct or impact-related costs of eutrophication to society, including direct costs (such as treatment of drinking water to remove nitrate) and indirect costs (such as, income losses in tourism resulting from deterioration of amenity value of surface waters).

Cost categories considered and evaluated include: prevention of access to water bodies for leisure activities, reduction of real estate value of waterfront properties, reduced value of water bodies for functions such as navigation, water abstraction, irrigation, drinking water treatment costs to remove nitrogen, to remove toxic algae and their metabolites, cleanup costs of waterways, release of greenhouse gases (N_2O and CH_4), reduced amenity and recreation attractiveness of water bodies, economic losses in related tourism activities economic losses for commercial fisheries, health costs for humans, livestock and pets (related to nitrate in drinking water, toxic algae), negative impacts on natural ecosystems and species composition.

Total costs to society of eutrophication are estimated at 83-127 m€/y, whereas total policy response costs (costs incurred in responding to or preventing eutrophication are estimated at 61 m€/y. Of these costs, 56 m€/y corresponds to the estimated annual capital investment in sewage works nutrient removal installation to enable compliance with the EU Water Framework Directive and covering the period 2000-2010, plus 0.3 m€/y for nutrient removal operating costs.

Treatment of drinking water

Considerably the largest estimated cost to society of eutrophication is drinking water treatment costs: 22.3 m€/y for nitrogen removal and 21.1 m€/y for algal toxins. Together these make up one third to one half of all costs to society.

Other significant costs are: reduced recreational value of waters 11-37 m€/y, reduced real estate value of waterfront property 11 m€/y, impacts on ecosystems and species 8-11 m€/y.

Policy response costs are dominated by capital costs of installing nutrient removal in sewage works over the next ten years: 91% of total costs incurred by society in responding to or preventing eutrophication. Spending on adapting farm practices to emit fewer nutrients amounts to less than 3.8 m€/y, and all other policy cost categories (monitoring, dealing with algal blooms …) are < 1.3 m€/y in total.

"Environmental costs of freshwater eutrophication in England and Wales", Environmental Science and Technology http://pubs.acs.org/journals/esthag/index.html *vol. 37, n°2, pages 201-208, 2003* http://dx.doi.org/10.1021/es020793k .

Figures in € derived from figures given in US$ in paper using conversion rate as at October 2004.

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Illinois

Spate flows and phosphorus run off

Non-point sources of nutrients, in particular run-off from agricultural areas, continues to be a major source of water quality deterioration, affecting for example 45% of stream miles in the USA. This paper shows that such run-off is very strongly related, for phosphorus loads, to high flows, so that river monitoring during base flow periods is liable to considerably underestimate transport of phosphorus.

The Illinois River, situated in the states of Arkansas and Oklahoma, is designated as an Oklahoma Scenic River and is used annually be nearly 200,000 canoeists and 350,000 people for other outdoor or aquatic leisure pursuits. The basin has 25% of its surface only under agricultural use, but a major poultry production industry giving rise to waste equivalent to 8 million people. The Illinois flows into Lake Tenkiller which is eutrophied and suffers from algal blooms. This situation leads to intense stakeholder debate on water quality and its management.

This paper examines ten years' data for nutrient concentrations and discharge rates at two sites in the Illinois basin. **The analysis shows that whereas nitrogen concentrations decrease during high river flow periods (because of dilution), phosphorus concentrations increase**. This corresponds to run-off of phosphorus from the land surface, in particular from agricultural areas.

Annual mean measured phosphorus concentrations at the two sites were 0.15 and 0.07 mgP/litre.

Low P contribution from base flow

Data was separated into base flow (flow level occurring more than 70% of the time) and higher flows. Base flows at the two measuring sites were thus estimated to be 21 and 28 m^2/s.

Estimation of the relationship between river flow rate and concentrations of phosphorus and nitrogen at the two sites suggested that 76% and 88% of total phosphorus loads carried by the river were in high flow (24% and 12% only in the base flow).

The paper also indicates that sampling of phosphorus concentrations usually at low flow conditions can result in a significant underestimation of real total river phosphorus loads.

Permanent sources of phosphorus in the river base flow are relatively insignificant within total loading, for example point sources. **The key management practices to reduce total phosphorus input to Lake Tenkiller should target reducing availability of phosphorus on land for direct surface run-off**. Phosphorus run-off is probably related to spreading of poultry manures, given the large poultry industry in the region. In the case of the Illinois River, run-off is particularly occurring in Arkansas, as the majority of the phosphorus carried by the river is coming from surface run-off during high flows from within this State, and is already in the river when it flows into Oklahoma.

"Nutrient loading assessment in the Illinois river using a synthetic approach", Journal of the American Water Resources Association (JAWRA http://awra.org/jawra/ *), Vol. 39, N°4, Paper n° 02001, pages 757-769, August 2003.* http://awra.org/jawra/papers/J02001.html

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Drainage P-removal

Artificial submerged-vegetation wetlands

Nine mesocosms (4.7 m long x 0.8m wide x 1m deep tanks) were used to test the phosphorus removal capacity of submerged vegetation communities under different conditions (hydraulic residence time and thus phosphorus loading rate) and to study the development of the aquatic vegetation communities. After 21 months of operation, the tanks showed results comparable to a full-scale 147 hectare submerged aquatic vegetation (SAV) wetland, suggesting that the mesocosms provided an appropriate scale for developing and optimising the design and operation of such wetlands.

The study was carried out at the **Everglades Nutrient Removal Project Site (ENRP), Florida, USA**. The mesocosms were constructed of wood and fibreglass and included baffles approx. 30 cm downstream from the waste water inflow end of the tank in order to ensure mixing. The tanks were filled with 15cm of highly organic soil from a farm field and maintained at 76cm water depth. Nutrient-rich agricultural drainage water was pumped into a single, shared holding tank, then fed by gravity to the nine mesocosms. These were operated as triplicates of three hydraulic residence times (1.5, 3.5 and 7 days) corresponding to horizontal water speeds along the mesocosms of 51, 22 or 11 cm/day respectively, and phosphorus loading rates of 19.7, 8.3 or 4.5 g Total Phosphorus/m^2/day.

The inflow drainage water had a Total Phosphorus concentration in the range 34 - 42 µgP/l, with the phosphorus being mainly in the form of bioavailable dissolved inorganic phosphorus (SRP), and Total Organic Nitrogen concentrations of 2.3 – 2.8 mgN/l, of which ammonium 0.28 – 0.33 mgNO_4^+-N/l and 0.5 – 1 mgNO_X-N/l.

The mesocosms were stocked with a mixture of submerged aquatic plant species typical of the region, at densities comparable to those occurring in the field in the Everglades Project Site: *Ceratophylum demersum* and *Najas guadalupensis* at around 1.2 kg wet biomass/m^2; *Chara spp*. and *Potamogeton illinoensis* at around 0.08kg/m^2. After 8 months, *Najas guadalupensis* dominated the plant communities (as biomass) and *Potamogeton illinoensis* largely disappeared.

Effective phosphorus removal

Both the 3.5 and 7 day residence time mesocosms consistently achieved low phosphorus outflow concentrations, in the range 8 – 73 µgP/l (Total

Phosphorus), with averages of 29 and 23 µgP/l respectively. The 1.5 day residence time mesocosm showed occasional higher outflow P concentrations (up to nearly 200 µgP/l) and a higher average (52 µgP/l).

Both the 3.5 and 7 day mesocosms achieved near completed SRP removal (maximum outflow concentrations 16µgSRP-P/l, averages 0.9 and 0.7 µg respectively).

The mesocosms were also very effective at removing soluble nitrogen with Total Inorganic Nitrogen being consistently reduced ten-fold, and ammonium NH_4^+-N and NO_x-N both being reduced below 0.03 mgN/l in the 3.5 and 7 day mesocosms.

The nutrient removal results did not appear to be affected by variations in factors such as the temperature of the water (which ranged from 9°C in winter to 33°C in summer) or incident sunlight. In particular, no nocturnal phosphorus release was observed. Particulate phosphorus levels in the outflow did however increases somewhat during the latter period of the experiment, but this coincided with an increase in particulate phosphorus in the inflow drain water.

Phosphorus balance and removal mechanisms

Phosphorus, calcium and nitrogen concentrations were measured in the initially added soil and plants, in the "new" sediment formed at the surface of the soil in the mesocosms during the experiments, and in the plants at the end of the experiments (after 21 months). This enabled estimates to be made of the phosphorus balance (fate of the phosphorus being removed / trapped in the mesocosms) but with considerable inaccuracies and difficulties as regards the sediment because of the irregularity of "new" sediment deposition in the mesocosms and variation in quantity and phosphorus content along the length of the mesocosm.

The phosphorus storage in the plant community was estimated to be 0.41 – 1.63 gP/m^2 and the storage in the "new" sediment 0.44 – 1.11 gP/m^2. These estimates only accounted for 34 – 39% of the total phosphorus "removed" by the mesocosms, the difference being attributed to the inaccuracies indicated above, or to storage in animal populations (such as snails and fish).

The calcium content of the "new" mesocosm sediment (16.5%) was approximately twice that of the soil initially used (7.6%), suggesting that co-precipitation of calcium / phosphates to sediment could be a significant P-removal process in these submerged aquatic macrophyte systems. This is positive, in that this co-precipitation process is liable to continue over time irrespective of the age of the wetland system, and is unlikely to result in phosphorus re-mobilisation.

Large-scale process

The 3.5 and 7 day mesocosm results were very **comparable to the phosphorus removal being achieved by a large-scale (147 hectare) submerged aquatic macrophyte wetland** at the Everglades Project Site. This system was achieving an average Total Phosphorus in outflow of 21µgP/l with a 4 day residence time, fed with the same drainage water.

The authors conclude that these 37,600 litre mesocosms provide a suitable scale tool for realistic testing and optimising of submerged aquatic macrophyte (SAV) wetland nutrient removal systems, and that the **good, permanent phosphorus removal performance such systems** achieve makes them a potentially valuable tool for drainage water, waste water or stormwater treatment, and to contribute to the Everglades restoration programme.

"Submerged aquatic vegetation-based treatment wetlands for removing phosphorus from agricultural runoff: response to hydraulic and nutrient loading". Water Research, vol.36, issue 6, March 2002, pages 1409-1422 http://www.elsevier.com/locate/watres

Abstract accessible at: http://dx.doi.org/10.1016/S0043-1354(01)00354-2

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Chesapeake Bay
Nutrient recycling policy

The Chesapeake Bay is the largest and most biologically diverse estuary in North America, draining a watershed of more than 165,000 km^2. Studies in the 1970's-1980's suggested that water quality and productivity deteriorations were the consequence of a combination of loss of upriver fish spawning habitats, over harvesting, disease, habitat loss, toxin and nutrient loads. The Chesapeake Bay Program was agreed to address these issues, involving 3 States and Federal and local authorities, in 1983.

Nutrient management policy was based around the **objective of a 40% reduction in nutrient inputs to the Bay**, including fixing a limit of 2 mgP/l in discharge from larger sewage works. By 2000 the 40% reduction objective had been very nearly achieved for phosphorus, but nitrogen reductions were still significantly short of the goal (10-20% of reductions remaining to be obtained).

Population growth

It has become clear that **the largest obstacle to achieving water quality targets is ongoing population growth in the Bay catchment** (population 8.4 million residents in 1950, nearly 15 million by 1990, expected to reach 18 million by 2020). Land use management, in particular preventing urban development of sensitive land areas such as forests, and wetland restoration, are identified as key tools for future water quality management.

Nutrient recovery and recycling

20 years after the initiation of the Chesapeake Bay Program, is looking to enhance the nutrient removal policy, with objectives for sustainability in sewage treatment, and for nutrient recovery and recycling.

Enhanced Biological Phosphorus Removal is identified as the most sustainable route for nutrient removal, offering phosphorus removal and denitrification with lower energy consumption, lower chemical use, and lower sludge production than chemical P-stripping. These advantages can be further improved if nutrients are recovered for reuse.

This has been implemented by the Hampton Roads Sanitation District, Virginia, at the York River sewage treatment works (biological nutrient removal plant treating at the time 26 million litres/day, with anaerobic sludge digestion). Analysis of dewatered digested sludge showed the **presence of spontaneously precipitated struvite** (magnesium ammonium phosphate), visible as sparkling crystals in light. Mass balances showed that around 70% of the phosphorus removed in the sewage treatment line was being retained in the digester solids, and 30% was being returned to the head of the works in the supernatant. Chemical assessment suggested that all magnesium present and most of the available ammonium in the digested sludge were being precipitated as struvite, and that a higher proportion of soluble phosphorus (present at 300 mgP/l) would be precipitated as struvite if magnesium ions were added.

The sludge was composted to ensure sterilisation and improve handling, then packaged as 18 kg bags, marketed locally as "NutraGreen". Its fertiliser value is enhanced by the struvite and calcium phosphates being precipitated within the digester.

Plans are underway to encourage similar nutrient recovery and recycling programmes throughout the Chesapeake Bay catchment, with regulations to ensure that the nutrient rich product is used appropriately so as to minimise nutrient run-off.

"Nutrient reduction policies and management strategies of the Chesapeake Bay water quality restoration program", Water Science and Technology, vol.44, n°1, pages 25-32, 2001
http://www.iwaponline.com/wst/04401/wst044010025.htm

"Potential societal and economic impacts of wastewater nutrient removal and recycling", Water Science and Technology, vol.48, n°1, pages 11-17, 2003
http://www.iwaponline.com/wst/04801/wst048010011.htm

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Water Science and Technology:
http://www.iwaponline.com/wst/toc.htm

Japan

Struvite from swine waste liquors

The pilot aeration struvite recovery reactor operated by the Japanese National Institute of Livestock and Grassland Science was presented in Scope Newsletter *n°50*. Further recent work was also summarised in Scope Newsletter *n°57* (Cranfield workshop summary). Here we summarise the results obtained with 60 days operation of a $4m^3$/day reactor, presented in 2003.

In Asia, urine and washing water in piggeries are separated into solid and liquid fractions by separation, the solid fraction is composted for use on fields, and the liquid fraction undergoes treatment before discharge into surface waters (whereas in Europe and the USA, all fractions are usually mixed and treated together). Struvite and scale deposit problems are known to occur in the biological liquid fraction treatment plants.

Initial batch and pilot reactor

Previous work (Scope Newsletter *n°50*) reported batch and then a $0.6m^3$/day continuous reactor mixed using aeration to precipitate struvite. **This reactor precipitated around 65% of the inflow phosphates to ¾ struvite and ¼ calcium phosphates**. The struvite settled into a sludge at the reactor base, which could be composted for use on fields.

2 years reactor operating experience

This paper reports operation of a stirred and aerated $4m^3$/day reactor, 3.6m high and 1.5m diameter, again operating on the liquid fraction of piggery wastes. Aeration rate was 360 m^3/day. In particular, experiments looking at precipitation rates onto different materials are reported.

As reported in Scope Newsletter *n°57*, **this reactor has now been operated for 2 years, achieving 70% removal of phosphate from inflow water without magnesium addition, and 90% with magnesium addition**. The recovered solids however were only 2.0- 25% struvite with significant organic content, and had to go to composting before agricultural re-use. However, significant accumulation of nearly pure struvite, free from organic materials, was noted on the reactor air tubes (up to 1.3 g struvite/cm^2 after 35 days).

For this reason, experiments were carried out to test the precipitation of struvite onto flat surfaces of different materials placed in the reactor. This showed very different rates: 40 mg/cm^2/day on stainless steel rods (SUS-304), 7 mg/cm^2 on wooden plates, and 0.9 mg/cm^2 on rubber plates.

Consequently, a specific precipitation "tool" was designed, made simply of 1mm stainless steel mesh (600 cm^2 surface x two sides). After 30 days, over 1 kg of struvite crystals had accumulated on this structure submerged in the reactor. **These could be scraped off, and were relatively pure, needing no dehydration, composting or other treatment before storage and use as a fertiliser**. However, the struvite precipitating onto the mesh represented only around one quarter of the struvite precipitating in the reactor, the remainder going to the sludge high in organics in the reactor base.

"Recovery of phosphate fro swine wastewater through crystallization", Proceedings of IWA Asian Waterqual Conference, Bangkok, Thailand, 19-23. www.iwahq.org.uk *October 2003, 2Q1F06, pages 1-9. (CD-ROM).*

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Cincinnati
Phosphorus recovery research project

The US Environment Protection Agency (EPA) has announced a research project at the University of Cincinnati, into "Phosphorus recovery from sewage".

The EPA's National Center for Environmental Research points out that the future sustainable use of phosphorus must include recovery from municipal sewage, and that global research is addressing this issue but research in the USA is lagging.

The project will look at bioprocess engineering for biological nutrient removal from sewage, phosphorus precipitation as struvite, and assess the bioavailability of struvite phosphorus for use as a fertiliser.

Further details: US EPA National Center for Environmental Research:

http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/7345/report/0

Project title « Phosphorus recovery from sewage », EPA Grant Number SU831817. Project period 2004-2005

Struvite

Lab-scale stirred reactor

The lab-scale experimental installation consisted of a 1.4 litre continuously stirred reactor tank, followed by a 1 litre settling tank (enabling recycling of part of the flow from the bottom of this tank, with effluent outflow from the top) – see diagram. The tanks were made from coated steel. Hydraulic residence times of 63, 83 and 125 minutes were tested.

The stirred reactor tank used a three-blade propeller diameter 48 mm and four vertical tank baffles of 11 mm, designed to optimise mixing whilst avoiding resonance. Initial tests were carried out to assess the stirring speed necessary to obtain perfect mixing, showing that 500 rpm was sufficient and necessary, corresponding to a Reynolds number of 19,100.

Struvite precipitation experiments used solutions of magnesium sulphate, ammonium chloride and di-sodium hydrogen phosphate, with dosing concentrations to the first reactor of 43 mg/l magnesium, 462 mg/l ammonium and 260 mg/l phosphate (excess ammonia at a molar ratio of 1P: 9.4 NH_4^+). pH was adjusted using sodium hydroxide.

Initial experiments at pH 8.5 showed that struvite precipitation (measured by drop in magnesium concentration) was increased by higher stirring speeds (200, 350 or 500 rpm) at a hydraulic residence time (HRT) of 63 (inflow rate 38.4 ml/minute) and 83 minutes, but that this effect was significantly less apparent at time 125 minutes.

pH dependency

Struvite precipitation was shown to be more effective at higher pH dependent, with residual magnesium being reduced to 5 mg/l at pH9 but only to 16 mg/l at pH8.

Previous batch experiments by the authors had shown that a molar excess of ammonium improved struvite precipitation. Ammonium: phosphate ratios of 2.5:1, 5.2:1, 6.7:1 as well as the 9.4:1 above were therefore tested, at pH 8.5, HRT 83 minutes, stirring 500 rpm. This showed that increasing ammonium concentrations reduced residual magnesium concentrations from 15 progressively down to 7 mg/l.

Under the conditions indicated above (ammonium:P at 9.4:1), and with reactor continuous run times of up to 5 days, work was carried out to assess whether the recycle of crystals from the settling tank (at 20% of the flow from the base of the second reactor vessel (settler) would increase crystal size. It was expected that the recycling would improve crystal growth in the reactor, but the opposite was observed with mean crystal size of 0.43 mm after 5 days operation without recycle compared to 0.165 mm with recycle.

X-ray diffraction showed that the precipitate in all experiments was mainly struvite, with traces of magnesium phosphate.

The authors conclude that the optimal hydraulic residence time was 125 minutes, but that reducing this to 83 minutes only marginally reduced struvite precipitation. The optimal pH was 9, but reagent addition to achieve this pH would not be economic in a sewage works, however, it was possible to significantly decrease magnesium concentrations through the precipitation of MAP at a pH achievable within sewage treatment plants, through the use of ammonium to phosphate molar excess of 9.4:1, which was beneficial in the removal of magnesium as struvite.

"Removal of struvite to prevent problems associated with its accumulation in wastewater treatment works. Water Environment Research 76 (5): 437-443 Sept-Oct 2004. Published by the Water Environment Federation http://www.wef.org/

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Struvite chemistry

Magnesium carbonate interactions

Two paper (both freely available online) explain in simple terms the chemistry of struvite precipitation and the consequences of $C0_2$ stripping, as well as looking at the pH related changes in forms of soluble phosphate and ammonium ions.

Digester gas typically contains 30-35% CO_2 (compared to 0.03% in the atmosphere. Resulting dissolved CO_2 in digester effluents can be off-gassed in sewage works as a result of pressure reductions (eg. in pumps, odour removal suction devices, loss of pressure in outflows from tall digester tanks ...), turbulence or aeration. This can cause precipitation of struvite (magnesium ammonium phosphate = MAP), often generating nuisance incrustation problems in pipes, pumps, filters or other equipment. If struvite precipitation is controlled, it can also provide a mechanism for phosphate recovery for recycling.

pH, magnesium

Dissolved CO_2 in the pH range approx. 6-10 will predominately form bicarbonate ions HCO_3^-, thus increasing pH:

$H_2O + C0_2 \rightarrow HCO_3^- + H^+$

(= carbonic acid H^2CO^3)

In this range, increasing pH reduces struvite solubility, so that off-gassing of CO_2 is liable to lead to struvite precipitation.

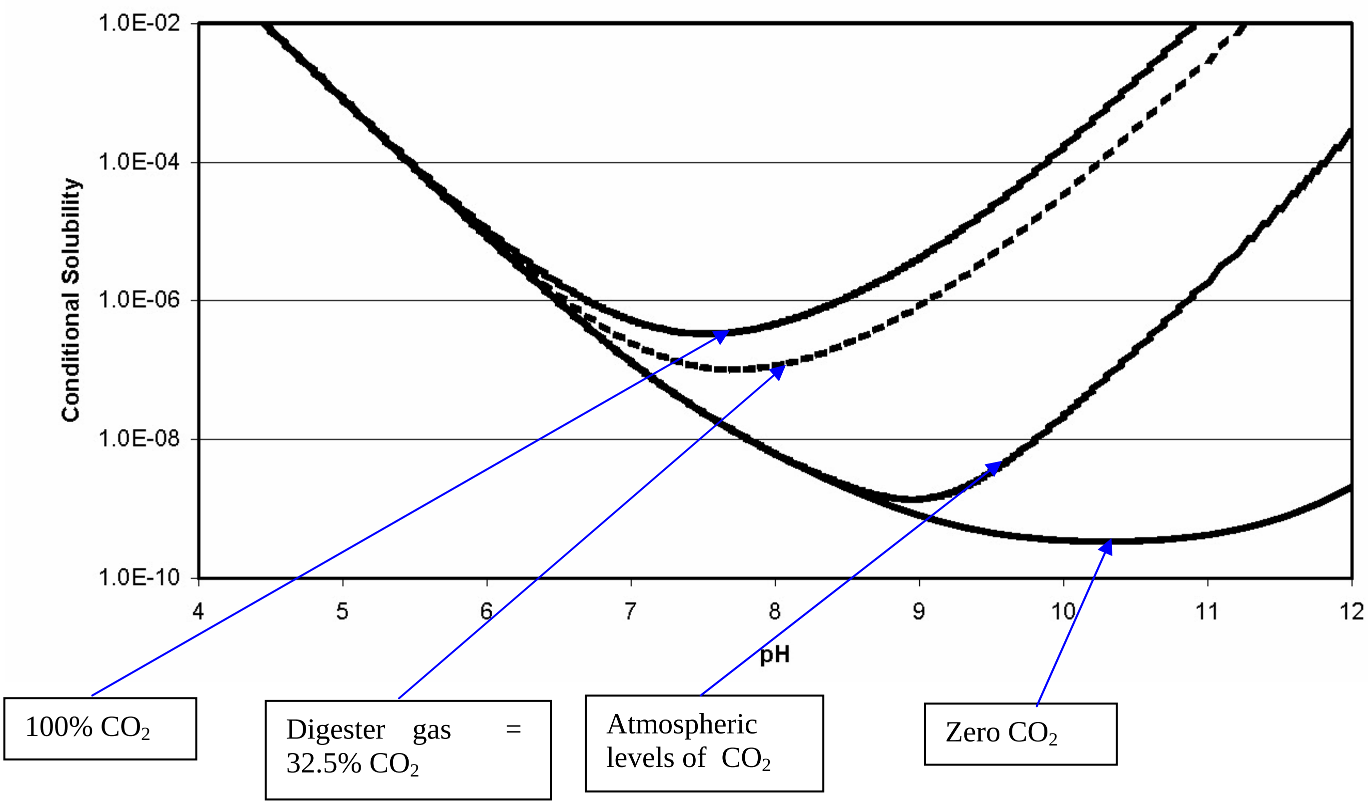
However, struvite precipitation is also accentuated by changes in availability of magnesium ions. The authors explain that carbonates form "ion pairs" with magnesium:

$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3$

$Mg^{2+} + HCO_3^- \rightarrow MgHCO_3^+$

$Mg^{2+} + 2HCO_3^- \rightarrow Mg[HCO_3]^2$

Thus off-gassing of CO_2 will make available magnesium ions. This can be critical for struvite precipitation because magnesium is usually the limiting ion for struvite precipitation (soluble phosphorus and ammonia are generally present in digester liquors at relatively high concentrations).



Phosphate, ammonium

The papers also give theoretical curves for availability of soluble ammonium and phosphate at different pH values. Ammonium ions NH_4^+ tend to be lost as ammonia gas NH_3 as pH increases from approx. pH 8 upwards. Ammonium NH_4^+ is the prevalent form below pH 9.3, whereas most will be lost as NH_3 above approx pH 10.5.

Soluble phosphate (orthophosphate) exists in four forms in water:

H_3PO_4
$H_2PO_4^-$
HPO_4^{2-}
PO_4^{3-}

Of these, $H_2PO_4^-$ is the prevalent form between pH 2 and pH 7. Significant proportions of HPO_4^{2-} appear from approx. pH 6 and this form is prevalent from pH 7 to approx. pH 12.

The papers show (figure below) that the minimum solubility of struvite both shifts from pH 8.9 when atmospheric CO_2 is taken into account to pH 7.7 with digester gas levels of CO_2, but that minimum solubility also increases by a factor of around 10x.

"Carbonate effects on struvite solubility", 16th Annual residuals and Biosolids Management Conference, March 2002.

R. Hill, Morris Associates, 9 Elks Lane, Poughkeepsie, NY 12601, USA. D. Grasso, Smith College, Northampton, MA 01063, USA. dgrasso@email.smith.edu rhill@morrisengineers.com

"Low pressure formation of struvite", WEFTEC 2000.

R. Hill – as above, P. Williamsen, L. Betty, NYC DEP, 498 Seventh Avenue, New York, NY 10018.

Above available at: http://www.wef.org/index.jhtml

WEFTEC 2005 will take place in New York – October 29th – November 2nd 2005 – see above website.

"Silicate Inhibition of Struvite Formation", R. Hill, D. Grasso (as above)

This paper and the above are available (abstracts or full paper on request) under "publications" at: www.hazenandsawyer.com

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.

The SCOPE NEWSLETTER is produced by CEEP - a sector group of CEFIC,
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