SCOPE NEWSLETTER

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Detergent phosphates

Eutrophication Risk Assessment

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Impacts of detergent phosphates

The Vollenweider-OECD eutrophication model covering 750 lakes, reservoirs and estuaries suggests that detergent phosphate bans do not result in measurable improvements in water quality in almost all water bodies.

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Effectiveness of grass buffer strips

Review of the effectiveness of grass bands along water courses as a means for limiting phosphorus run off from agricultural land.

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Integrated P + N recovery from dewatering liquors

Integrated recovery of nitrogen and phosphorus is assessed as a route to improving the economics and operation of removing nutrients from wastewater.

P-recovery

Struvite in municipal waste water plants

Several papers present new information regarding struvite precipitation parameters in sewage treatment plants

Kinetics

Effects of major ions on struvite precipitation

The effects of majors ions and anions (calcium, sodium, chloride, sulphate, carbonate) on induction time for struvite precipitation from synthetic wastewaters.

Nitrogen recovery

Struvite precipitation from human urine

Hydrolysis of urea to ammonia, followed by struvite precipitation, is assessed as a route for removing and recovering nitrogen from human urine.

Struvite

Ammonia precipitation from animal waste

Struvite precipitation was tested as a route for removing ammonia from dairy manure digester liquors

REBECCA final conference

The EU - REBECCA project aims to provide scientific input to implement the EU Water Framework Directive, describing relationships between biological and chemical properties of surface waters and water quality status.

The project's final conference will take place

Oslo – 21st – 24th May 2007

Information and registration:
www.environment.fi/syke/rebecca

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Detergent phosphates

Eutrophication Risk Assessment

The EU has published a eutrophication risk assessment of phosphates in detergents, carried out by INIA Spain for CEEP, in the context of the EU Detergent Regulation. The objective of the study was to develop, with expert peer review of the methodology, a (quantitative) risk assessment model for eutrophication, allowing the comparative assessment of different sources of phosphates and particularly the contribution from phosphorus-based detergents.

The methodology is based on the same principles as the standard industrial chemical risk assessment methodology developed by the European Chemicals Bureau (ECB) for assessing the risk of industrial chemicals, but with significant adaptations because of the many different natural and human sources of phosphorus, and the biological complexity of eutrophication.

The model was based on:

- A simplified **generic exposure assessment model**, allowing the identification of the expected total contribution of phosphorus in a river basin, based on the catchment characteristics.
- The development of **criteria for eutrophication risk** based on the document (1), developed in 2006, under the Common Implementation Strategy of the Water Framework Directive (WFD) and its application to a database of published field studies.
- The combination of both for producing **quantitative estimations of the likelihood for eutrophication** in sensitive water bodies within the river basin.

In all cases, the definition for "eutrophication occurring" is that the most sensitive part of a water system should fail to achieve Water Framework Directive "good quality" status because of eutrophication criteria. The model has been developed for large river basins and assumes that the risk for the whole basin should be quantified through the risk for its sensitive areas, such as still fresh waters (lakes, reservoirs, wetlands…).

The **probabilistic distributions** derived can then be used to assess, for generic river basins, the change in the risk of eutrophication occurring for different scenarios of use of phosphates in household detergents (as additional to other phosphates loads from sewage, agriculture …).

Effect assessment

Probabilistic distributions of the risk of eutrophication occurring / not occurring for given water total phosphorus concentrations were derived from **303 European data items** on sensitive zones, each assessed for eutrophication status based on the EU Water Framework Directive criteria.

The reliability of the assessments was verified by comparison with additional criteria including the Morphoedaphic Index for addressing the role of anthropogenic contributions (developed by Vighi et al., 1985). Potential inconsistencies were evaluated and a final decision adopted case-by-case.

The derived probabilistic distributions enable the estimation of the eutrophication risk based on the probabilistic distribution of phosphorus concentrations (total phosphorus annual average) in water bodies with good and less-than-good status. The use of probabilistic distributions effectively takes into account the variations in ecosystem complex reaction to phosphorus outlined above.

The effect assessment treated separately **three eco-region/types:** Mediterranean lakes and reservoirs, Atlantic and Central Europe shallow lakes, Atlantic and Central Europe deep lakes, Mediterranean. The number of data points for Atlantic and Central Europe deep lakes was not enough and therefore this class was not further considered in the assessment.

Exposure assessment and scenarios

Estimated phosphorus concentrations in water bodies (PEC = Predicted Environmental Concentration, as annual mean total phosphorus) were calculated for a generic river basin from characteristics of river flow; agricultural intensity and land-use with per hectare P run-off coefficients, population emissions through sewage (human metabolism), different scenarios of P-removal at sewage works, P emissions from domestic detergents.

Data on consumption of P in domestic detergents were provided by AISE, the International Association for Soaps, Detergents and Maintenance Products, giving a total of 61,500 tonnes P per year (2004 data, EU-25). The EU average (0.36 gP/person/day) and highest national figure (0.84gP/person/day) from AISE data, excluding one outlier, were used as model scenario inputs.

Risk characterization

The eutrophication risk is defined as the likelihood of a sensitive site, susceptible to be affected by eutrophication, to be in less-than-good eutrophication status. This value is obtained using the probability distributions described in the effect assessment part, corrected by the percentage of sites with a potential for suffering eutrophication problems.

Due to the complexity of the eutrophication process, the inherent biological variability and the uncertainty in the assessment, **the risk is not presented as a single value but as a range** (i.e. the eutrophication risk is between this and that value). In addition, the most likely value within the range is calculated.

A number of generic river basins with different scenarios were modelled, including combinations of domestic detergent phosphates consumption, river flow, population density, agricultural intensity, and level of P-removal at the sewage works.

For each, the following scenarios were assessed:

- risk without detergent phosphates;
- hypothetical risk for zero contribution from agricultural and background P run-off;
- hypothetical risk for zero contribution from sewage

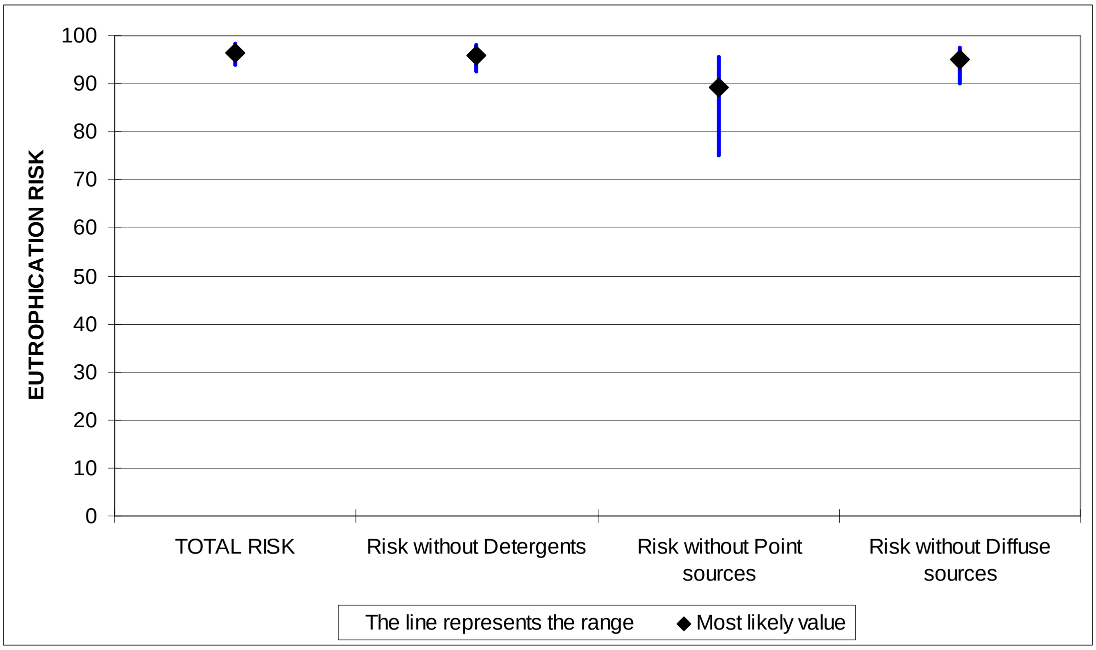
Results and conclusions

The above scenarios generated a total of 20 graphs, reproduced in the full final report. Of these, are reproduced below, graphs corresponding to typical situations for the two eco-region/types, but assuming use of phosphates in detergents across Europe at the current European highest national consumption figure.

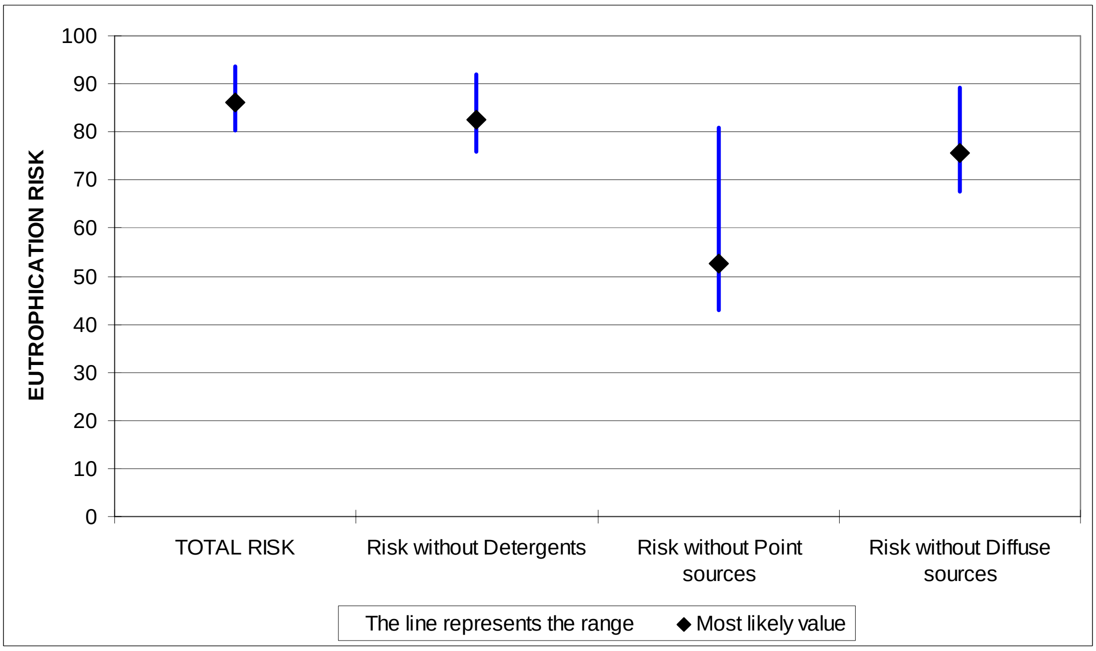
Subject to the limitations of the study concerning in particular data availability and model variability, the study concludes that, at an EU level, the estimated difference between the eutrophication risk (as a % risk of eutrophication occurring at a most sensitive point) with and without detergent phosphates is 2-8% for a Mediterranean ecosystem and 0.4-2% for Atlantic & Central European ecosystems. The eutrophication risks, and also the additional eutrophication risks related to detergent phosphates, are very variable in different regional situations as a result of the characteristics of hydrology, population density and agricultural intensity, among other factors.

"De Madariaga, B.M., Ramos, M.J., and Tarazona, J.V. Model implementation and quantification of the eutrophication risk associated to the use of phosphates in detergents. Final study report. Green Planet Research Report GPR-CEEP-06-2-Final. 2006. Carried out by Green Planet Research and INIA (Spanish National Institute for Agricultural and Food Research and Technology) for CEEP. Published by the EU Commission at http://ec.europa.eu/enterprise/chemicals/legislation/detergents/index_en.htm

(1) European Commission (EC), 2006. Common Implementation Strategy for the Water Framework Directive (2000/60/EC). Towards A Guidance Document on Eutrophication Assessment in the Context of European Water Policies



Generic risk estimations for Atlantic, Northern & Central European shallow lakes using European average conditions



Generic risk estimations for Mediterranean water bodies using European average conditions

Eutrophication

Impacts of detergent phosphates

Lee and Jones-Lee have published an update of an earlier paper assessing the possible environmental consequences of a detergent phosphate ban. This follows work by Maki et al. in the 1980's concluding that detergent phosphate bans in the USA have not led to improvements in water quality. The reason is that this action does not result in a sufficient reduction in phosphate inputs to water to have a measurable effect.

The updated paper is based on application of the Vollenweider-OECD model which links phosphorus loads to eutrophication. This model data base has been expanded to 750 lakes, reservoirs and estuaries. From this model, the authors derive a graph showing situations where a phosphate ban can be expected to have detectable impacts, as a function of the % of P input to the surface water coming from domestic sewage (as opposed to industry, agriculture, land run-off, …), and as a function of the % of P in domestic sewage coming from detergents.

This shows that, where phosphates are used in modern detergents and **the proportion of phosphate in sewage coming from detergent will be below 30%** for example, then a detergent P ban will only have a detectable impact if more than half of P input to the water body is from sewage.

Sewage works phosphorus removal

The authors emphasise that about 90% of the phosphorus in domestic wastewaters can be removed from sewage in treatment works at a cost of <4 cents per person per day for populations over 10,000 and that this is the most effective way to control eutrophication in waters receiving sewage discharges.

Where some sewage is not treated (households not connected, overflows, …) then a detergent phosphate ban will only be effective if such untreated sewage contributes more than 20% of total P input to the surface water. The authors also note that septic tank wastewater systems do not contribute significant amounts of phosphate to surface waters.

The authors conclude that although detergent phosphate bans will not generally result in an overall improvement to water quality, "there may be some situations in which eutrophication-related water quality would be improved by a ban." The results are also applicable to evaluating other questions regarding impacts of changing phosphate loadings to surface waters.

The key information in this updated paper is that **it is possible to predict, with a high degree of reliability, the impact of a detergent phosphate ban on eutrophication-related water quality** as measured by planktonic algal chlorophyll and the diagram explained above which shows the issues to be considered in order to make this evaluation.

This review references previous papers by the authors which present in detail the OECD phosphorus loading – eutrophication response models, based on both data from water bodies comparing phosphorus loading with chlorophyll concentration, and also from a number of cases looking at water quality response to reductions in phosphorus loadings following the introduction of sewage works phosphorus removal. These models show log-log relations between phosphorus loading and chlorophyll concentration, Secchi depth and hypolimnetic oxygen depletion. This information is presented at *http://www.gfredlee.com/pexfert2.htm* .

These papers already suggested that whereas phosphorus removal in sewage works or significant reductions in non-point phosphorus loadings (agriculture) would result in reductions in chlorophyll concentrations perceptible by the public as water quality improvements, **the P load reduction resulting from a detergent ban would not result in a perceptible change in the eutrophication-related water quality.**

The authors emphasised both the simple but effective predictive capability of the OECD phosphorus loading – eutrophication response models, and the need to develop significantly more "before and after" data sets for water bodies where significant phosphorus loading reductions have been implemented.

"Detergent phosphate bans and eutrophication," G. Fred Lee, A. Jones-Lee, 2007. Published at www.gfredlee.com *Based on (updated) "Detergent Phosphate Bans and Eutrophication," Environ. Sci. Technol. 20(4): 330-331 (1986).* http://www.members.aol.com/annejlee/DetergentPBan.pdf

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France

Effectiveness of grass buffer strips

Landscape features, such as hedges, wetlands, wooded areas and permanent vegetation are increasingly recognised as a key element in reducing nutrient and agrochemical transport from fields into surface waters, and in limiting soil erosion. Man made vegetated buffer strips along water courses, in particular grass strips, are now widely recommended as a means of reducing such runoff, and are subsidised or made a condition of EU Common Agricultural Policy (CAP) funding. This paper reviews knowledge of how such grass buffer strips act to reduce phosphorus runoff into surface waters, and current understanding of their short and long term effectiveness.

The soil and vegetation system of buffer strips receive input phosphorus in both dissolved and particulate form in surface and sub-surface flows. Phosphorus retention can result from a number of mechanisms:

- **slow down and infiltrate into soil**: surface water arriving in the buffer strip meets a rougher and more porous soil surface and vegetation obstacles, causing movement to slow and the water to infiltrate into the soil. Particulate phosphorus attached to soil particles is thus deposited in the buffer strip, often in the first few centimetres, or even in heaps of sediment in front of the buffer strip.
- **finer particles are deposited by "turbulence filtration",** often further into the buffer strip. This mechanism is related not to pore size but rather to the density of roots and organic matter in the soil
- **dissolved phosphorus** can also be held in the buffer strip if it retains water and slows flow
- **particulate phosphorus**, because it accumulates, will be partially transformed to dissolved forms in the buffer strip. This will be to some extent taken up by vegetation (growth of grass), and may then either be removed (grass harvested) or may finally return to the system (decomposition).

The effectiveness of phosphorus retention is thus dependent on the time of contact between the runoff waters and the buffer zone soil. This will depend on external factors (run off flow rate, flow patterns and channels) and internal factors (width and slope of buffer strip, state of vegetation and soil).

Experiments

A number of laboratory and field scale experiments have assessed the effectiveness of buffer strips in retaining phosphorus and reducing agricultural land run off to surface waters, looking at various buffer strip vegetation types and farming practices. This review identifies clear patterns from the conclusions of these different experiments:

- **buffer strips can reduce by >50% the transfer to water courses of sediment and of total phosphorus carried in surface run off waters**
- the retention of dissolved phosphorus is much more variable, ranging from -83% (that is more dissolved P flowing out of the buffer strip than into it) to +95%
- buffer strips reduce the volume of surface water run off by a widely varying 3 – 100%
- **a buffer strip width of 5 – 15 m is generally sufficient**, with little or no improvement in effectiveness for widths increased above this range. Indeed in some cases significantly narrower strips (1-2m) which are **useful for bank stabilisation**, appear to have a lower but still significant effect on both sediment and particulate phosphorus. The width of buffer appropriate to ensure effective phosphorus retention appears to be very variable, making it difficult to give

guidance to farmers, but the ratio between cultivated field area and buffer area appears to be important.

- **the vegetation of the buffer strip is important**. A higher degree of plant cover increases roughness, enhancing particle retention. Also vegetation prevents erosion of the buffer strip's own soil. The height of vegetation does not appear to be significant, whereas plants offering good ground cover outside the summer are preferable. Perennial grass appears as more effective than mixtures of herbs, trees and shrubs.
- **soils** with higher permeability (sandy soils) appear to provide a better phosphorus buffer effect. Obviously soil type cannot be modified in a given site, but the recommendations regarding buffer strip width can be modulated to take soil permeability into account.
- buffer strip effectiveness will **vary with season** and with levels of flow (soil water saturation), and this needs to be taken into account in examining experimental results
- **compacting of the upper soil** in the buffer strip (by machinery or passage of animals) will reduce permeability, and so effectiveness

The authors provide detailed conclusions regarding the effectiveness of buffers, and in particular runoff events, restoration between floods, seasonal dynamics, reduction of other pollutants.

They conclude that in theory, phosphorus saturation of buffer zones might occur in the long or medium term, but that there is no evidence based upon monitoring of this to date, and that the increase in the stock of phosphorus stored in buffer strip soils does not seem to have a significant effect on phosphorus sorption or precipitation.

Practical application

The authors conclude that although long term benefit remains questionable, **grass buffer strips have a role in controlling diffuse phosphorus pollution**. Their application needs to be adapted to specific circumstances and spatial position. Well managed Buffer strips can reduce by at least half the flows of particulate phosphorus and of sediments to surface waters, but overall phosphorus reductions may be lower because of release of dissolved forms, particularly in winter. Some buffer strips also serve the complementary function of preventing bank erosion.

Width and implantation of buffer strips should be adapted to local flow regimes and to the source area. Vegetation should be well rooted, provide dense ground cover, and be maintained by regular cutting. Specific guidelines need to be developed adapted to regional situations.

"The effect of grass buffer strips on phosphorus dynamics – a critical review and synthesis as a basis for application in agricultural landscapes in France", Agriculture, Ecosystems and Environment 117, 2006, pages 4-21.

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Mediterranean
Nile nutrient flows and fish production

Following the construction of the Aswan dams on the Nile river, fish catches in the Nile delta area of the Mediterranean Sea fell drastically, from around 37,000 to 6,500 tons/year of sardines for example. This did not surprise scientists, as it was the expected consequence of retention of nutrients behind the dams, reducing primary production. However, the fisheries recovered by 1979. The author suggests that the explanation may be manmade releases of nutrients from agricultural fertilisers and sewage.

The Nile is the world's longest river, over 5500 kilometres. Without the Nile, Egypt would be little more than desert. Even with the river, only 4% of the country can be used for farming. The Nile's annual floods brought nutrient rich silt onto farmlands, as well as providing water.

The Nile also fertilised the Eastern Mediterranean, which is naturally very poor in nutrients, because the Sea's circulation prevents nutrients from flowing East.

Aswan dams

All this changed, however, with the building of the Upper Aswan dam, some 1000 km upstream from the Nile delta. A lower dam, 54 metres high and 1900 metres wide had been completed in 1902, but had limited effect because flood waters could run over it. This dam was then raised higher, then a larger dam started upstream. The upper dam (Aswan High Dam) stared impounding water in 1964, and was completed in 1970. It is 3600 metres wide and 111 metres high. It created Lake Nasser, 480 km long and 16 km across at it widest point.

Estimates of sediment being carried by the Nile are varied. The author quotes figures suggesting that of some 130 – 140 million tons of sediment per year carried by the Nile upstream of Aswan, before construction of the High Dam, probably around 60 million tons actually reached the delta (the remainder being deposited en route) and 25 million tons passed the delta and flowed into the Mediterranean Sea.

Phosphorus

On this basis, he estimates phosphorus flows from the Nile into the Mediterranean, before construction of the High Dam, as around 3200 tonsP/year dissolved phosphate, plus 4000 – 8000 tonsP/year phosphate released from sediment. Comparable estimates for nitrogen are 6700 tonsN/year dissolved and an unknown amount of nitrogen in sediments. **After closure of the High Dam, dissolved phosphate carried by the Nile to the Sea is estimated to have been reduced by 99%, and sediment phosphorus to nearly zero**.

The author estimates that if just 4-5% of the phosphate fertiliser used in Egypt today reached the Mediterranean, this would replace the dissolved phosphate carried by the Nile before the High Dam closure. Similarly, for just 1% of the nitrogen fertiliser used.

At the same time, Egypt's population has grown significantly (Cairo and Alexandria together from 2.5 to 23 million people from 1930 to 2000), and the population's diet has improved, both total food consumption (calories) and part of animal protein. This corresponds to an increase in phosphate release to sewage from 4400 to 12600 tonsP/year from 1965 to 1995, and from 21000 to 87000 tonsN/year. Furthermore, extension of the sewerage system has ensured that a higher proportion of these nutrients are delivered to the Mediterranean Sea.

The increase in sewage nutrients reaching the sea could thus replace, and considerably exceed, the reduction in nutrient loads resulting from the Aswan High Dam closure. By feeding primary production, this could explain the recovery of fisheries.

However, all is not positive, in that the coastal areas are now showing some signs of eutrophication, such as algal blooms and loss of higher vegetation, and the balance between fish species is not the same as before closure of the High Dam.

Other authors indicate that eutrophication symptoms in the Eastern Mediterranean are limited to coastal areas near discharges[1], and point out that there remain questions as to why the fish catches have recovered when primary production does not appear to have done so – but primary production is complex, occurring in localised algal developments when nutrients are available[2]. The ratio between surface and deep water fish also appears to have recovered in the 1980's to pre-dam levels[3].

"Replacing the Nile: Are anthropogenic nutrients providing the fertility once brought to the Mediterranean by a great river?" S. Nixon, in Ambio 32 -1, pages 30–39. http://ambio.allenpress.com

"The Artificial Nile", American Scientist, vol. 92, 2004. S. Nixon, Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882-1197. Internet: swn@gso.uri.edu

http://www.ci.uri.edu/CIIP/FallClass/Docs_2006/UrbanWaterfronts/American_Scientist_Nile.pdf

See also:

1) "Eutrophication Thresholds in the Eastern Mediterranean", M. Karydis http://www.iasonnet.gr/abstracts/karydis.html

2) "The southeastern Mediterranean ecosystem revisited: Thirty years after the construction of the Aswan High Dam", S. El-Sayed, G. van Dijken http://www-ocean.tamu.edu/Quarterdeck/QD3.1/Elsayed/elsayed.html

3) "The impact of the Nile and the Suez Canal on the living marine resources of the Egyptian Mediterranean waters (1958–1986)" Y. Halim, S. Morcos, S. Rizkalla, M. El-Sayed http://www.fao.org/DOCREP/003/V4890E/V4890E02.htm

Phosphorus recycling

Nutrient recovery

Integrated P + N recovery from dewatering liquors

Sludge dewatering liquors can contribute 20% of total sewage plant inflow loads of both phosphorus and nitrogen, significantly affecting the economics, energy consumption and environmental performance of biological nutrient removal. This paper assesses an integrated approach to N and P-recovery, as saleable fertiliser compounds, as an alternative to the traditional treatment by biological oxidation then denitrification of the nitrogen and transfer to sludge of the phosphorus.

The objectives considered are to recover nutrients as nitrogen and phosphate fertiliser products, thus also recovering some costs, to reduce energy consumption necessary for biological nitrogen removal, and to reduce the P-content of the final sewage sludges because this can be a limiting factor for biosolids application to land.

The integrated approach proposed aims to recover phosphorus and nitrogen from the sludge dewatering stream in the sewage works, which offers the advantage of a relatively concentrated liquor, and enables the removal of these nutrients from the stream returned to the sewage works inflow. The approach can be combined with anaerobic digestion of the sewage sludge, optimised to maximise methane production (energy recovery) and reduction of sludge biosolids.

Ammonia stripping

The example of the Veas wastewater treatment plant, Oslo, is presented. Here, the sewage sludges are anaerobically digested for 20 days after acid hydrolysis, reducing organic matter by a claimed 60%. They are then treated with lime and cationic polyelectrolyte before dewatering in a heated vacuum press.

In this case, the soluble phosphate content of the sludge filtrate is low, as most phosphate is precipitated into the sludge cake as calcium phosphate. The filtrate has a pH > 10 and an ammonia content of 1200 – 1500 mgN/l.

Ammonia is stripped by spraying the filtrate down a plastic media packed stripping tower, against an upwards air current. The air carries the ammonia into a second tower, where it is blown upwards against a downwards rain of acid. Sulphuric acid, and more recently nitric acid, have been used, to **produce respectively ammonium sulphate and ammonium nitrate. Both can be sold as fertiliser**, with ammonium sulphate regaining interest with farmers in the UK because sulphur has recently become a limiting factor for crops (as industrial air emissions of sulphur have been reduced by clean air legislation).

Although there are some operating issues with the ammonia stripping plant, particularly related to carbonate deposition (requiring monthly acid washing), it has proven reliable (99.2% availability). 3000 tonnes/year of ammonium nitrate (dry weight) are produced in an installation with an estimation capital cost of around 750,000€ (650,000 pe).

Phosphate recovery

Struvite precipitation is a known nuisance problem in sludge dewatering streams. Controlled precipitation of phosphate from this stream can be achieved by adding magnesium and increasing pH, the latter being possible depending on circumstances without chemical addition by air stripping of CO_2. Examples of struvite recovery at Slough UK (Thames Water), Shimane Prefecture (Japan) and Edmonton (Canada) are cited.

Struvite has shown to be a saleable fertiliser, sold by ICI as "N-Mag" and in the USA as MagAmp or MagAmp®K. Its plant availability was confirmed in recent field trials by Johnston and Richards, 2003.

Integrated nutrient recovery

The author proposes an integrated nutrient recycling concept, **with a struvite precipitator operating on the sludge dewatering liquor**. After this phosphate removal, the liquor would be sent to an ammonia stripper and ammonium recovery installation, as outlined above. Alkali used to increase the pH for struvite recovery, will also contribute to raising the pH to >10 for ammonia air stripping. Any unreacted magnesium will eventually return to the digesters, and contribute to improve phosphorus removal. The use of CO_2 stripped air in the struvite reactor and in the ammonia stripper should reduce carbonate deposition and increase efficiency.

On the basis of current prices for struvite and ammonium sulphate as fertilisers, discounted 50%, the **product sale revenues are estimated to cover 75% of operating costs** (input chemicals, maintenance, manning). This ratio is expected to improve with increasing fertiliser prices, which are linked to energy costs. The capital costs for a 500,000 pe sewage treatment plant sludge dewatering line are estimated at < 1,500,000€. The system offers considerable advantages compared to the return of the nutrients in sludge dewatering liquors to the inflow of biological nutrient removal sewage plants.

The main issues for implementation are considered to be water company willingness to install a relatively complex (but automated) reactor plant, and confidence in supplying recovered nutrient products as fertilisers to users or intermediaries (which will modify the product sale margin).

"Treating dewatering liquors – is physico-chemical better than biological? Can a problem be turned into an asset?" 11th European Biosolids and Organic Resources Conference 2006 www.european-biosolids.com

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P-recovery

Struvite in municipal waste water plants

Struvite (magnesium ammonium phosphate) is well known as a nuisance deposit in sewage treatment plants, but is also increasingly seen as an important route for recovery of phosphates from sewage for recycling. A number of papers provide information concerning the physical and chemical conditions for struvite precipitation in sewage works.

Barat et al. (2005) examine the **relations between magnesium, potassium and calcium ions and enhanced biological phosphorus removal (EBPR) processes**. They used a laboratory scale sequencing batch reactor to compare the take up and release of these ions with phosphate, in anaerobic and aerobic phases comparable to biological phosphorus removal operation. Acetate was included in the synthetic wastewater fed to the batch reactor, to feed biological phosphorus removal cycles during seven 6-hour experiments.

The **relationship between ionic conductivity and ions concentration variations** in these experiments was further studied in depth (Aguado et al., 2006). The authors obtained the molar ratios of potassium: phosphorus (0.28 mol K / mol P) and magnesium:phosphorus (0.36 mol Mg / mol P) accomplishing the charge balance. Conductivity was shown to be strongly correlated to phosphorus concentrations, related to uptake and release, in both the aerobic and anaerobic stages of the EBPR cycle. The conductivity profile in each cycle can thus provide useful information on the EBPR performance and stability.

Magnesium and potassium

The 2005 study showed, as expected, that soluble phosphate increased during the anaerobic and decreased during the aerobic phases, corresponding to biological nutrient removal cycles. **Magnesium and potassium both showed very similar patterns to that of soluble phosphates, whereas calcium remained constant**. This is in accordance with previous results from Pattarkine et al, 1999.

Runs with different potassium to magnesium ratios indicated that they cannot be substituted by each other, and that both are independently taken up / released from biological P-removal cells in parallel with phosphates. Results also indicated that too low levels of potassium or magnesium will inhibit phosphorus uptake during the aerobic phase, particularly after a number of cycles. The authors observed by simulation that magnesium appears to be more critical than potassium and that further research is necessary to experimentally study biological P-removal performance at low magnesium and potassium concentrations.

Calcium

Later studies by the authors were focused on **the role of calcium in enhanced biological phosphorus removal (EBPR)** and the possible implications of calcium on the metabolic pathway, based on eight months experimental operation of the laboratory scale reactor (Barat et al., 2006). The variations of influent calcium concentration showed a clear influence on the EBPR process, detecting significant changes in the ratio between phosphate release and acetate uptake (Y_{PO4}). This ratio was found to be highly dependent on the calcium concentration, increasing as calcium concentration decreases. Nevertheless, microbiological observations showed no appreciable changes in polyphosphate accumulating organisms (PAO) and glycogen accumulating organisms (GAO) populations. This behaviour could suggest a change in the bacterial metabolic pathway, prevailing polyphosphate accumulating metabolism (PAM) at low influent Ca concentration and glycogen accumulating metabolism (GAM) at high concentration.

"The role of potassium, magnesium and calcium in the enhanced biological phosphorus removal treatment plants", Environmental Technology, col. 26, pages 983-992 http://www.environtechnol.co.uk/contents.htm

R. Barat, T. Montoya, J. Ferrer, Dept. Ingenerio Hidraulica y Medio Ambiente, Universidad Politecnica de Valencia, Camino de Vera s/n, 46022 Valencia, Valencia, Spain and A.Seco, Dept. Ingeieria Quimica, Universitat de Valencia, C/ Dr Moliner 50, 43100 Burjassot, Valencia, Spain. Email: Aurora.Seco@uv.es

"Relating ions concentration variations to conductivity variations in a sequencing batch reactor operated for enhanced biological phosphorus removal", Environmental Modelling and Software, vol 21, pages 845-851

D. Aguado, T. Montoya, J. Ferrer, Dept. Ingenerio Hidraulica y Medio Ambiente, Universidad Politecnica de Valencia, Camino de Vera s/n, 46022 Valencia, Valencia, Spain and A.Seco, Dept. Ingenieria Quimica, Universitat de Valencia, C/ Dr Moliner 50, 43100 Burjassot, Valencia, Spain. Email: Aurora.Seco@uv.es

"Calcium effect on enhanced biological phosphorus removal", Water Science and Technology, vol 53, n°12, pages 29-37 http://www.iwaponline.com/wst/toc.htm

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Preventing struvite deposits

Neethling and Benisch provide an overview of sewage works design and operating strategies to avoid nuisance struvite deposit problems, suggesting that control of phosphorus release and CO_2 degassing are important, but that **the best solution is to design the plant so that struvite deposits form at points where it is not a problem**, such as in sludge or at points where removal and maintenance is easy. Annual operating costs relating to problem struvite nuisance deposits, when they occur, are estimated to reach 780 – 3,900 € per million litres / day capacity.

Solubility coefficient

Rahaman, Mavinic, Buiyan and Koch studied the solubility product of struvite in different solutions (anaerobic digester supernatant, distilled water solutions) and at different pH, ionic strength and temperature. See SCOPE Newsletters 56 and 65 presenting this team's ongoing development work on phosphorus recovery as struvite. Previous authors have calculated very varied results for the solubility coefficient K_{sp} of struvite, with differences of over 4 orders of magnitude.

The authors carried out three sets of experiments using 1.5 litre stirred beakers for 24 hours, in which tested solutions were placed along with struvite crystals. The first set of experiments used distilled water solutions and digester supernatant from the City of Penticon sewage treatment plant. An initial molar ratio of 1.3:1 magnesium:phosphate was used, as in currently ongoing P-recovery work. A second set of experiments used tap water and synthetic supernatant, at 10°C and 20°C. A third set of experiments used synthetic supernatant and anaerobic digester supernatents from two other sewage works, Annactis Island and Lulu Island. Calcium, magnesium, phosphate and ammonium were measured.

The authors note that the **variation in solubility coefficient results reported by previous authors** may result from non controlled or widely varying conditions of experiments both as regards methodology, and for temperature and ionic strength. In experiments exposed to the atmosphere, and carbon dioxide, the formation of magnesium carbonate may create a sink for magnesium, making struvite more soluble. Higher ionic strength will also increase struvite solubility because the electrostatic interactions of the ions in solution will reduce their interaction activity).

The authors' results show that **the ionic strength of the medium is in effect very important**. The solubility coefficient for a specific pH increases rapidly with ionic strength for each of the different liquors tested, but there are nonetheless considerable differences between the liquors resulting form other factors. The derived solubility coefficient also decreases at higher pH and increases for a given pH at higher temperatures in the range up to 40°C.

The authors conclude that **it remains very difficult to predict the struvite solubility coefficient for any given solution** with results varying significantly from correlation estimates.

"Struvite control through process and facility design as well as operation strategy", Water Science and Technology, vol. 49, n°2, pages 191-199
http://www.iwaponline.com/wst/toc.htm

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"Exploring the determination of solubility product from analytical results", Environmental Technology, col. 27, pages 951-961
http://www.environtechnol.co.uk/contents.htm

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Kinetics

Effects of major ions on struvite precipitation

This paper aims to provide information concerning the process kinetics of struvite precipitation from synthetic solutions with phosphate and ammonia at concentrations comparable to domestic wastewater if magnesium is added to precipitate struvite. In particular, the impact of concentrations of other ions found in wastewaters, such as calcium, sodium, sulphates, carbonate, chloride, was studied.

Experiments were carried out in stirred 1500ml beakers, using distilled water, boiled (to remove dissolved carbon dioxide), and pure chemical solutions, after filtration. 500 rpm rapid stirring for 5 seconds was followed by a slower 300 rpm mixing speed. Light absorbance (at the wavelength of 350 nm), pH and electrical conductivity were measured at 1 minute intervals for 80 minutes in each experiment. The mixed samples were then kept and settled for 10 days before filtration.

The initial concentrations of ammonia, phosphates and magnesium were 2.45 mmol/l, that is approx 75mgP-PO$_4$/l of soluble phosphorus and 34 mg/l of ammonia. Initial pH was increased to 8.5 – 9.3 using sodium hydroxide to facilitate struvite precipitation.

This ammonia concentration was considered typical of that found in domestic wastewaters. The phosphate concentration is significantly higher than that generally found in raw sewage, but comparable to that found often in sludge digester liquors, in which ammonia is often in the range of 300 – 100 mg/l. Magnesium dosed stoichiometrically is comparable to the addition of magnesium in a struvite precipitation reactor.

Different concentrations of other ions tested were: sodium (Na^+) and chloride (Cl^-) 5 – 155 mmol/l, sulphate SO_4^{2-} 12.5 – 75 mmol/l, carbonate Ca_3^{2-} 2 and 5 mmol/l, calcium Ca^{2+} 0.25 and 0.5 mmol/l.

Induction time

Conductivity measurements alone were not adequate for determining induction time, that is the time difference between achieving supersaturation and the appearance of struvite crystals. This is because struvite precipitation releases hydrogen ions, which affect other complex ions. The link between pH change and precipitation is dependent on the other ion interactions present, and the buffering capacity of the solution, which varies with overall ionic strength. Optical density measured by light absorbance did however prove to be a reliable means of determining induction time.

The results are not always easy to interpret, because changes in ionic strength impact both pH and supersaturation, but it appears that the **significantly higher concentrations of sodium and chloride ions tested (> 50 mmol/l) increased induction times**, to the limit of practicable struvite precipitation for the higher concentrations (comparable to those found in some industrial wastewaters). **Sulphates also increased induction times, whereas carbonates at the concentrations tested appeared to have no significant impact and calcium reduced induction times in some cases**.

Micrographs of the struvite crystals produced show different morphologies at different supersaturations and with the presence of different ions. A theoretical model of crystallisation kinetics taking into account the effects of the different ions is proposed.

"Effect of major ions on induction time of struvite precipitation", Croatica Chemica Acta CCACAA 79 (2), pages 243-251, 2006. Full paper available for download: http://hrcak.srce.hr/index.php?show=clanak_download&id_clanak_jezik=6800

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Nitrogen recovery

Struvite precipitation from human urine

Human urine contains 75% of the nitrogen and 50% of the phosphorus in human emissions (urine plus faeces). Separate collection of urine is considered as a potential route to recovery of significant proportions of the key nutrients in human emissions. To achieve this, as well as specific separation systems in toilets, and a separate collection system, routes need to be developed for nutrient recovery. This paper looks as the hydrolysis of urea in urine to ammonia followed by struvite precipitation as a possible such route.

The experiments were carried out in 500 ml beakers, using a urine sample mixed from 20 persons. Its composition was typical compared to literature indications, 6,000 – 8,500 mg/l total inorganic nitrogen TKN, 5,000 – 8,000 mg/l organic nitrogen

Org-N and 400 – 650 mg/l soluble phosphorus PO_4-P, with around 8,000 mg/l organic carbon COD.

Hydrolysis of urea

The hydrolysis of urea in urine can be achieved either chemically or biologically (enzymes). Hydrolysis by chemical means was very slow: fresh urine with pH adjusted to 2 – 7 only showed around 25% hydrolysis of urea after one month. **Hydrolysis by enzyme was on the other hand very efficient**, with complete hydrolysis in 1.5 hours for doses of 25 – 50 mg/l of enzyme. Lower doses significantly slowed hydrolysis. The enzyme used, jack bean urease, is considered to be comparable to enzymes in bacteria found in urine collection pipes and tanks, so that in a real system where urine is collected and stored, urea can be expected to be hydrolysed by bacteria present.

Struvite precipitation was tested on pure hydrolysed urine, and on hydrolysed urine diluted 1:1 with tap water (to simulate a urine flushing system product). Magnesium and phosphate were added at 1:1:1 ratio to the ammonia present and pH adjusted with sodium hydroxide. After struvite precipitation, the precipitate was separated by 0.45µm filtration.

95% of the inorganic nitrogen from the hydrolysed urine was precipitated by struvite precipitation at pH 8.0 – 9.5, and even at pH 7.5 90% efficiency was recorded. Reaction time was short. 50% of the organic nitrogen was also removed during the struvite precipitation. Foaming during the reaction was noted because of carbon dioxide release and could be an operating problem depending on magnesium source (i.e. $MgCl_2$) and the order of addition of precipitation agents.

"Nitrogen recovery by urea hydrolysis and struvite precipitation from anthropogenic urine", Water Science and Technology vol. 53, n°12, pages 305-312, 2006
http://www.iwaponline.com/wst/toc.htm

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Struvite

Ammonia precipitation from animal waste

Struvite precipitation was tested in stirred 50 ml beaker experiments, as a route for removal of ammonia from digested dairy manure effluents. Two liquors were tested, from different anaerobic digester configurations, both fed with dairy manure from the Washington State University Dairy Centre, Pullman, WA, USA.

The liquors had respective ammonia concentrations of 500 and 250 mg/l and total phosphorus of 150-450 mg/l and 100-250 mg/l. Magnesium addition as magnesium chloride or magnesium hydroxide were tested, with pH adjustment, and with phosphate added to above excess of stoichiometric requirements for struvite (as sodium phosphate).

To bring ammonia below 10 mg/l, that is removal efficiencies of 95%, magnesium at >3:1 stoichiometric ratio had to be added. Higher pH, above the initial pH of the digester liquors (pH range 7.5 – 7.9) on the other hand did not appear to significantly improve ammonia removal in the range pH 7.5-8.5. Because the pH adjustment effect of magnesium hydroxide was not useful, magnesium chloride thus appeared as more effective for ammonia removal than magnesium hydroxide, possible because of its better solubility.

"Ammonia removal from anaerobically digested dairy manure by struvite precipitation", Process Biochemistry 40, pages 3667-3674, 2005.
www.elsevier.com/locate/procbio

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