SCOPE NEWSLETTER

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Water quality regulation

Water quality

Europe puts on pressure to implement sewage treatment

The EU Commission has published reports on implementation of European water legislation: sewage treatment, agricultural nitrates and Water Framework Directive, and has brought further legal actions against a number of Member States, as part of a strong policy to push for full implementation of the European 1991 Urban Waste Water Treatment Directive. Three EU Commission actions have resulted in recent European Court judgements against Member States for failures to adequately treat sewage and to install nutrient removal.

Rebecca

Defining "Reference Conditions" for lakes

Definition of the Reference Conditions, that is the "undisturbed state", for implementation of the EU Water Framework Directive – definition of "Quality Status"

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. Final conference information and registration:

www.environment.fi/syke/rebecca

Oslo – 21st – 24th May 2007

Water Framework Directive

Quality assessment

The EU Commission's Joint Research Centre summary of current knowledge on indicators and methods for assessing "ecological status" under the Water Framework Directive.

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Nutrients and eutrophication

Baltic Sea

Cyanobacterial blooms

Fossil records indicate that cyanobacterial blooms have occurred naturally over the last 8,000 years in the Baltic, since it stopped being a freshwater lake.

Baltic Kattegat

Primary production and nutrient loads

Variations in phytoplankton primary production in the entrance area of the Baltic Sea (Kattegat and Belt Sea) are compared to trends in phosphorus and nitrogen loads from land and atmospheric sources.

Danube

Dam not retaining nutrients

A study of the Iron Gates barrages on the Danube river shows that phosphorus and nitrogen outflows exceed inflows: the dams are not at present acting as nutrient sinks. Silica retention in the dam is also considerably lower than has been previously suggested.

Phosphate recycling

North Carolina – Idaho - Washington

Cone-shaped crystalliser for struvite recovery

Mathematical modelling, reactor design and testing of laboratory and pilot scale reactors precipitating struvite from anaerobic lagoon liquor from pig and dairy farms.

North Carolina

Testing struvite precipitation from swine lagoon liquors

Beaker experiments were carried out on anaerobic wastewater lagoons from two different piggeries in order to establish optimal pH and magnesium ratios for struvite precipitation and to determine rate constants

Pot trials

Plant availability

Pot trials tests of recycled phosphates and of different calcium and magnesium phosphates fertiliser value.

Water quality regulation

Water quality

Europe puts on pressure to implement sewage treatment

The European Commission has published progress reports on implementation of three major pieces of water legislation: the Urban Waste Water Treatment Directive 1991/271 (sewage treatment), the Nitrates Directive 1991/676 (agricultural nitrate pollution) and the Water Framework Directive 2000/60 (water quality status objectives and management plants). The Commission is also continuing to engage legal actions in the European Court against Member States for failures to implement these Directives, in particular concerning sewage collection and treatment.

To media, the European Commission indicated that despite progress towards better water quality, implementation is still inadequate for many aspects of these Directives in a number of Member States.

Inadequate municipal waste water treatment

EU Commission report SEC(2007)363 (Annex to COM(2007)128 below) covers implementation of the Urban Waste Water Treatment Directive in the old EU-15 states through until end 2003. The Commission emphasises that 81% of total sewage discharges considered were treated adequately at this date (that is, treated conform to directive requirements). The directive requirements applicable for end 2003 covered for 1998 agglomerations > 10,000 pe in eutrophication “sensitive areas” and for 2000 agglomerations > 15,000 pe elsewhere, that is a total of 470 million person equivalents (pe).

In areas potentially susceptible to eutrophication (“sensitive areas”), 84% of sewage load was treated adequately (agglomerations > 10,000 pe), that is phosphorus is removed before discharge. The inadequately treated discharges into sensitive areas represented in 2003 only 10.3% of the 470 million pe total sewage concerned.

The Commission indicates however that in some Member States **“sensitive areas” have not been adequately designated**, in Spain, UK, Italy, Ireland, France and Portugal. These areas, which need to be designated, or have been designated since 2003, represent some **21.5% of the 470 million pe total sewage**.

In non sensitive areas, 79% of sewage was treated adequately (agglomerations > 15,000 pe). Where figures were not reported by members states, treatment was assumed inadequate.

The number of big cities without adequate sewage treatment was reduced from 27 in 1999 to 17 in 2003.

The final deadline of this directive, requiring collection and **“appropriate” treatment of sewage for agglomerations > 2,000 pe by 2005** was not covered, but the EU Commission’s implementation report estimated that this will concern a further 80 million pe.

Nitrates Directive

EU Commission report COM(2007)120 covers implementation of the Nitrates Directive for the period 2000-2003. Over this period, total inputs to the EU environment (land, surface water) of nitrates have dropped from around 17,4 million tonnes N in 1995, to 18 million tonnes in 1999 and 16,5 million tonnes in 2003.

Over the report period, **17% of EU groundwater monitoring stations showed average nitrate concentrations over 50 mg/l**, that is the European legal limit for drinking water, and a further 22% were higher than 25 mg/l. Belgium (Wallonia), France, Spain, Portugal, Ireland, UK, Netherlands, Luxembourg and Germany reported trends of increasing groundwater nitrate levels for at least 30% of monitoring sites.

47% of surface water monitoring stations reported nitrate levels > 10 mg/l, with a trend to increase at only 14% of sites.

The total percentage of the EU-15 states territory designated as nitrate "vulnerable zones" increased from 35% in 1999 to 45% in 2003. Corresponding action plans had been established in all member states (in Ireland only after 2003), but in a number of cases are not considered adequate (not conform to the directive requirements).

Water Framework Directive

EU Commission report COM(2007)128 assesses progress in implementing the EU Water Framework Directive 2000/60, and in particular summarises the results of the assessment carried out by member states of the risks that water bodies will not achieve the Good Quality Status objective fixed by the directive for 2015. Results are not optimistic, with **less than half of water bodies being on course for this objective** (data available, "not at risk") in all EU-27 states except Luxembourg, Estonia, Cyprus, and Romania, and <20% in Netherlands, Germany, Belgium, Hungary, Czech Republic, Slovenia.

The Commission notes problems with incorrect transposition of the Water Framework Directive into national legislation in nearly all states (serious discrepancies in 19 states), and wide variations and gaps in environmental and economic analysis processes. Infringement procedures are therefore underway against a number of states.

Key recommendations made to members states are to progress on implementation of the Urban Waste Water Treatment Directive, to improve water pricing systems (to give economic incentive to better water management), and to improve ecological assessment systems and water status methodologies.

Legal actions for failure to treat sewage

The Commission initiated in June 2006 European Court action against Greece for **failure to correctly collect sewage from 24 cities** of more than 15,000 pe by the year 2000 deadline fixed by the Urban Waste Water Treatment Directive 1991/271. For four cities, works are still not planned today. For the other cities, works are underway but not completed desite the deadline date being passed by more than 6 years: Artemida, Rafina, N. Makri, Koropi, Markopoulo, Megara, N. Kydonia, Malia, Chrysoupoli, Porou-Galata, Tripoli, Katerini, Preveza, Litohoro, Zante, Alexandreia, Lefkimi, Nafpaktos, Igoumenitsa, Thessalonica tourist zone, Héraklion, Edessa, Kalymnos, Paroikia (Paros).

In December 2006, the Commission initiated European Court action against Portugal for failing to treat adequately sewage from the Estoril agglomeration (700,000 population), following a specific exception decided by EU Commission Decision for this agglomeration in 2001.

Protecting the Baltic Sea

In December 2006, the Commission also initiated **European Court actions against Finland and Sweden, because of failure to remove nitrogen in sewage works of inland towns discharging into rivers in the Baltic catchment**. The Commission argues that because the Baltic Sea is a recognised eutrophication "sensitive area", then also all discharges into rivers flowing into the Sea are also "sensitive areas", and so nutrient removal must be installed. The Baltic Sea is know to be eutrophication sensitive to nitrogen discharges but only around 76% of sewage discharge in Baltic catchment rivers undergoes nitrogen removal in Finland, and 60% in Sweden.

European Court Judgements

The European Court has condemned the UK (January 2007), following an action brought by the EU Commission, for **failure to provide sewage treatment for 13 agglomerations** of > 15,000 pe by the year 2000 deadline fixed by the EU Urban Waste Water Treatment Directive (Bangor, Brighton, Broadstairs, Carrickfergus, Coleraine, Donaghadee, Larne, Lerwick, Londonderry, Margate, Newtownabbey, Omagh and Portrush). The EU Commission announced in April 2006 that it would continue to pursue legal action against the UK for inadequate sewage treatment of four further agglomerations including London (also Torbay, Whitburn and Kilbarchan), where the capacity of the existing sewage works is insufficient, resulting in direct discharge of sewage into surface waters through overflow systems.

Condemned for failure to install nutrient removal

The European Court has also condemned Luxembourg (November 2006) for **failure to have installed nitrogen removal from sewage** up to the level required by the same Directive, that is 75% nitrogen removal for the whole of Luxembourg, because the state has taken the option to declare its whole territory a eutrophication "sensitive area".

Italy has been condemned (November 2006) for **failure to install tertiary treatment (nutrient removal) by the 1998 deadline for several communes situated in the province of Varese** (Lombardia), on the Olona river. This followed failure by Italy to designated the river basin as a eutrophication "sensitive area", despite its being upstream of the Pô river basin, which is a designated "sensitive area" (a separate infraction procedure is underway concerning specifically this failure to designate the upstream basin of the Pô river). The judgement concerns several communes around Gomate Olona, whose total population exceeds 15,000 pe.

European Commission press releases:
- against Greece: IP/06/878, Date: 29/06/2006 :
http://europa.eu/rapid/pressReleasesAction.do?reference=IP/06/878
- actions against Finland, Sweden, Portugal: IP/06/1769
http://europa.eu/rapid/pressReleasesAction.do?reference=IP/06/1769&format=HTML
- actions against the UK: IP/06/444
http://europa.eu/rapid/pressReleasesAction.do?reference=IP/06/444&format=HTML

European Court judgements:
use the "Search form" at
http://curia.europa.eu/en/content/juris/index.htm
- against the UK, reference 405/05 dated 25th January 2007
- against Luxembourg, reference 452/05 dated 23rd November 2006
- against Italy, reference 293/05 dated 30th November 2006

European Commission progress reports on implementation of EU water directives :

EU Commission press release – IP/07/388
http://europa.eu/rapid/pressReleasesAction.do?reference=IP/07/388&format=HTML

COM reports available at: http://europa.eu.int/eur-lex/ *(search by Natural Number)*

COM(2007)120 *dated 19th March 2007, SEC(2007)339 "Report from the Commission to the Council and the European Parliament on implementation of Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources for the period"*

COM(2007)128 *dated 22nd March 2007, SEC(2007)362 "Report from the Commission to the Council and the European Parliament Towards sustainable water management in the European Union - First stage in the implementation of the Water Framework Directive 2000/60/EC" and its Annex "4th Commission Report (Executive Summary) on Implementation of the Urban Waste Water Treatment Directive" SEC(2007)363*

Rebecca

Defining "Reference Conditions" for lakes

The EU Water Framework Directive (WFD) 2000/60 requires Member States to instigate (by 2009) catchment management plans which will ensure that generally surface waters achieve "Good Ecological Status" by 2015, with exceptions only for "Heavily modified" water bodies (which will have to achieve "Good Potential", defined as being close to "Good Status") and for cases where these objectives are not technically or economically feasible. A considerable body of research and inter-calibration work is underway to provide guidelines for the interpretation of the Directive's definitions of "Good Quality" status, in that the Directive (annex V) defines this as a situation such that different biological characteristics (such as species populations, balances and communities) are not significantly different from "Reference Conditions".

The EU-funded *REBECCA* project (see SCOPE Newsletter n° 59), aims to examine the links between chemical conditions in surface waters and their ecological quality status, to provide a basis for water management decisions. The report "Reference conditions of European lakes", draft published on the REBECCA website, proposes indicators and methods for assessing the reference conditions of lakes, that is the **ecological conditions which would be expected in an undisturbed or natural state** ("biological integrity"). The ecological quality status of a given lake, for EU Water Framework Directive implementation, can then be established using an Ecological Quality Ratio which compares the observed biological monitoring results, for different families or compartments of the ecosystem, to the reference conditions derived for the specific lake.

The reference conditions will vary considerably depending on the physical, hydraulic, climatic and other characteristics of a lake. The objective of the WFD intercalibration research is to group lakes into comparable types, for each of which a set of reference conditions can be defined. The report nonetheless indicates that for some lakes with specific characteristics (eg certain large alpine lakes, unique because of their size) "type set" reference conditions may not be meaningful. In a number of cases, where such large lakes have been intensively studied, specific reference conditions for the given lake can however be derived from site-specific studies and/or historical data.

Defining reference conditions

The report concludes that "Reference conditions" do not necessarily refer to totally undisturbed or pristine state, but can include very minor disturbances or human pressure if these have only minor ecological effects. Reference conditions are thus equivalent to "High Ecological Status" under WFD. If few such undisturbed lakes are available, then relatively unaffected parts of slightly impacted lakes might be taken into consideration.

Reference conditions can be derived from available data by a number of methods:

- - monitoring data from existing lakes in undisturbed condition, taken as "reference lakes". In this case, at least 10 and preferably 20 undisturbed lakes of the relevant type should be considered.
- - lake data distribution approach, taking the "best" 25th percentile of a larger population of lakes, may be a pragmatic approach if comparable reference condition lakes are not available
- - historical data. However, where records are available, sampling methods and quality may render data difficult to use
- - paleolimnological reconstruction of past conditions, again with difficulties as to the accuracy of information which can be derived
- - model based predictions, based on either hindcasting by backward extrapolation of tendency curves, or modelling extrapolation of known variable-response relationships
- - expert judgement

Reference data set

The report also includes a summary of reference data from **reference lakes of different types in Europe**, a total of 300 – 530 lakes for different types of data (approx. 530 lakes in the data set for total phosphorus and for chlorophyll, fewer data sets for characteristics such as phytoplankton, macrophytes, invertebrates, fish).

Indications are given regarding the use of models, expert judgement, and proposals for reference species. The implications for reference conditions of different depths, lake areas, hydraulic regimes are discussed.

Ranges for mean annual total phosphorus are shown for reference lakes in different ecoregions: approx. 5-10 µgP/l in Atlantic lakes, 5-15 µgP/l in Northern Lakes, 10-30 µgP/l in Central European and Baltic lakes, and 30 µgP/l in Mediterranean lakes. The authors note that the "Mortpho Edaphic

Index" model only accounts for around 45% of variation in reference lake total phosphorus, and that apparent differences between reference conditions in the four ecoregions should be treated with caution because of the low number of lakes in ecoregions other than Northern.

Levels of chlorophyll in the data set reference lakes are also very variable, showing ranges of 2-3 µg/l to 5-18 µg/l for different ecoregions and lake depths.

"Reference Conditions of European Lakes, Indicators and methods for the Water Framework Directive Assessment of Reference conditions", Edited by Anne Lyche Solheim. anne.lyche@niva.no *Draft Version 5, 30th December 2005, EU 6th Framework R&D project "Rebecca" deliverable D7. Available at* http://www.rbm-toolbox.net

Rebecca project website:
http://www.environment.fi/syke/rebecca

Final conference of the Rebecca project – EU 6th Framework Programme

"Relationships between ecological and chemical status in surface waters"

21st -24th May 2007, Oslo, Norway (arrival 21st May evening, main conference 22nd and 23rd May, field visit 24th May)

Presentation of Rebecca results for rivers, lakes, coastal waters. End-user perspective, rivers basin manager's toolbox, policy implications and research needs.

Registration and details:
www.environment.fi/syke/rebecca

Water Framework Directive
Quality assessment

The book "Indicators and methods for the ecological status assessment under the Water Framework Directive" also starts from the definition of ecological quality status under this Directive, that is the "an expression of the quality of the structure and functioning of aquatic ecosystems associated with surface waters". Research is underway to define biological indicators of this status, and on the relationship between chemical and biological indicators.

L. Carvalho et al. assess "Nutrients and eutrophication in lakes", starting from the definition of eutrophication in European legislation as "the enrichment of water by nutrients … causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned". In the Water Framework Directive, assessment of this process is based on comparison to "reference" (unaffected) ecosystems.

Regarding algal development, the ecological status can be assessed by changes in relative abundance of different families of algae, by loss of transparency due to algal development (measured by chlorophyll concentration or Secchi disk depth), or by the frequency of algal blooms. In each case, sensitivity to levels of phosphate can be very variable. Examples of indicator species ratios for algal community changes are given For algal blooms, there is no clear definition of what constitutes a bloom.

Macrophytes and phytoplankton

Changes in macrophyte community are a good indicator of nutrient effects on ecological status. A number of classification schemes have been developed, but are not directly related to nutrients, because of the complexity of ecosystem reaction. Phytobenthos, invertebrates and fish population classification schemes are also discussed.

The authors conclude that phytoplankton (algae = primary response) offers indicators of eutrophication which are qualitatively well understood, including concerning changes in species balance, but that quantitative data is lacking. Secondary response (fish, in particular) to eutrophication is a known phenomenon, but data is lacking to build indicator metrics.

Kuuppo et al. provide a comparable assessment for **coastal and estuary waters**. The approach is similar, based on different changes in algal communities, macrobenthos and secondary response, but the assessment is more complex because in coastal waters and estuaries phosphorus is often not the limiting nutrient, and the ratios between phosphorus, nitrogen and silicon are important. Also, understanding of the different causes of coastal algal blooms is lacking, with a range of different factors including nutrient concentrations, nutrient ratios, light, water mixing. It is not possible to build a model linking one nutrient to algal development in coastal and estuary waters. Further detail is found in the Rebecca report D9 "Marine phytoplankton – relationships between ecological and chemical status of surface waters", edited by H. Kaas et al. *http://www.rbm-toolbox.net*

A. Deflandre and H. Jarvie assess the situation for **rivers**. In this case, considerable information is available, and nutrients have impacts both on the level of primary production (growth of algae and plants) and on phytoplankton species balance. However, in many cases in rivers, nutrients are not the limiting factor, because of effects of current, light. Because of the river flow, river bed communities may provide the best indicators of nutrient response, and a number of phytobenthos indices are indicated, mainly referring to diatoms. It is noted that eutrophication of naturally nutrient-poor (oligotrophic streams), up to a certain level, usually results not only in increased primary production and biomass but also in increased community richness, but with a loss of certain nutrient-sensitive species.

Other chapters of this book cover organic pollution, acidification, hydromorphological pressures and toxic pressures.

"Indicators and methods for the ecological status assessment under the Water Framework Directive. Linkages between chemical and biological quality of surface waters". Edited by A. Solomini, A-C. Cardoso and A-S. Heiskananen. EU Joint Research Centre, 2006, EUR 22314EN, ISBN 92-79-02646-1. Available at http://www.rbm-toolbox.net

See also: "Relationships between biological quality elements and physico-chemical pressures: validation and practical use of relationships", H. Duel, S. Groot, D. Boorman, Rebecca Synthesis report D18, January 2007, at the same website. This provides further data regarding ecosystem response to nutrients in lakes, rivers and coastal waters.

Nutrients and eutrophication

Baltic Sea
Cyanobacterial blooms

Sediment cores from the Baltic, from the last 8,000 years, were analysed for cyanobacterial pigments, diatoms (microfossils), total carbon, nitrogen and phosphorus, radiocarbon dating, and stable isotopes of nitrogen. To permit comparison, pigments were analysed from filamentous cyanobacteria separated from a Baltic Sea water sample in 1999, and from two cultured Baltic strains of filamentous cyanobacteria.

The Baltic was a freshwater lake, the "Ancylus Lake" until around 8,000 years ago, when eustatic sea level rise created the Danish Straits, linking this lake to the North Sea. The inflow of sea water led to **a salinity level approximately twice today's up to around 4,000 years ago**. Work by other authors has shown a high organic carbon content in sediments from this period, suggesting high primary production, and lamination indicating anoxic conditions on the sea bed.

Of several cyanobacterial pigments analysed in the sediments, only zeaxanthin was found. This is thought to be because many other pigments are not sufficiently stable. Pigment analysis of the Baltic cyanobacteria, confirmed the pertinence of zeaxanthin as a biomarker of such algal blooms. Beta-carotene was also analysed, as a bulk-indicator of not just cyanobacteria, but all other algae that may have been present at the time.

Cyanobacterial blooms

Peaks of zeaxanthin occurred from the entry of North Sea water into the Baltic onwards, indicating blooms of cyanobacteria occurring often over the last 8,000 years. This is confirmed by the zeaxanthin/beta-carotene ratio, by values from stable isotopes of nitrogen and by the trend to higher carbon contents in the sediments (higher primary productivity) and higher N:P ratios (corresponding to the nitrogen-fixing cyanobacteria).

The authors conclude that **blooms of nitrogen-fixing algae have been a natural feature of the Baltic Sea over the last several thousand years**. This may have been initiated by the inflow of relatively phosphorus-rich water from the North Sea into the Baltic, resulting in increased phosphorus availability and lower water N:P ratios, which both facilitate cyanobacteria blooms. This may have been accentuated because phosphorus sequestered as iron phosphates in the well-oxygenated freshwater lake bottom, was released after the sea bed became anoxic following North Sea inflow (because of salinity caused stratification) and high sulphate levels in the inflowing sea water, both of which would cause phosphorus release from sediments.

The authors suggest that cyanobacteria blooms are thus a natural feature of the Baltic Sea, and that nutrient management policies should seek not to eliminate them but to reduce their intensity.

"Cyanobacterial blooms in the Baltic Sea: natural or human-induced", Limnol. Oceanogr. 45(3), 2000, pages 716-726. *http://aslo.org/lo/*

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Baltic Kattegat
Primary production and nutrient loads

Variations in phytoplankton primary production in the entrance area of the Baltic Sea (Kattegat and Belt Sea) are compared to trends in phosphorus and nitrogen loads from land and atmospheric sources.

Danish monitoring data from 6-8 sites in the Baltic Sea entrance zone are analysed, taking into account changes in monitoring methods and sites. Long term and inter-annual variations and trends are compared to data on temporal changes in nutrient loads from land sources (agriculture, sewage treatment) and atmospheric nitrogen loads.

The sea area in question is the narrow entrance to the Baltic, between Sweden, Denmark and Germany, shallow and subject to considerable variations in salinity and to vertical stratification.

Measurements of primary production began in the 1950's, and those of land nutrient sources in the 1970's, although the measuring techniques and the frequency and coverage were progressively modified and increased. In particular, data from the Denmark EPA (now NERI) were used for this paper.

Land nitrogen sources

Previous authors have concluded that **land-based nitrogen sources are the primary limiting factor for primary production in this area of the Baltic**, with estimates of land nitrogen input at around 100 000 tonnes N (4 000 tonnes P) per year from land around year 2000, 45 000 tonnes N atmospheric load (negligible for P). However, deep water input is also significant and has been estimated at 6 000 tonnes N (1 000 tonnes P) per MONTH in summer.

Long term changes show an approximate doubling of primary production over the period 1950's –to 1980's, reaching 400-800 mgC/m^2/day. Primary production is geographically variable, and up to 3-5x higher in inshore waters than in the open waters of this part of the Baltic. Primary production is as expected very variable between seasons, with maxima in the Spring and late Summer. Since 1980's, primary production has begun to fall again, but more slowly than the previous increase. Assessment is made more difficult by a change in monitoring methods in 1997: the authors propose corrections for this change.

Weak recovery

The decrease in primary production appears to show a much weaker response to reductions in nutrient loads since the 1980's than the increase corresponding to nutrient load increases over the 30 years before that.

Nitrogen variation

Since the 1980's, for which detailed monitoring data is available, both phosphorus and nitrogen show a clear inter-annual correlation to primary production data Inflows of nutrient rich waters from the North Sea, through the Skagerrak, are seen in nutrient data from the Kattegat, but do not seem to result in significant responses of primary production.

The authors conclude that the very large reduction in land phosphorus inputs (more than 50% reduction since the 1980's) has resulted in considerably reduced water phosphorus concentrations, but that it is **not clear to what extent lower primary production is related to phosphorus or to nitrogen**. Further research is needed and this should take into account vertical mixing and internal loadings of nutrients from sediments.

"Fifty years of primary production measurements in the Baltic entrance region, trends and variability in relation to land-based input of nutrients". Journal of Sea Research, no 56, pages 1-16, 2006.
www.elsevier.com/locate/seares

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Danube

Dam not retaining nutrients

The Iron Gates dams on the mid-Danube river are the two largest impoundments of the basin, holding nearly 3 billion cubic metres of water with a reservoir surface of over 150 km^2.

It has been suggested that retention in the dams accounts for differences between modelled nutrient loads to the Danube River and measured loads carried by the river into the Black Sea: 40% of phosphorus flowing into the retained waters behind the barrage is estimated to be retained in one recent report (see SCOPE Newsletter n° 66). The 2005 study (Teodoru et al.) examined nutrient flows in the Danube arriving upstream of the dam reservoirs, sediment retention, nutrients in dam reservoir sediments, and nutrient flows out of the Iron Gates I dam, concluding that in 2001, on the contrary, **nutrient flows out of the barrage were higher than flows in**, and that the reservoir sediments do not represent a significant sink for nutrients in the river.

The Iron Gates reservoirs are a hydroelectric complex of 2 dams situated at the Romania - Serbia border, 900 km upstream from the Danube delta and its outlet into the Black Sea. The upstream dam (Iron Gates I) is a 60m high, 1.3 km wide hydroelectric dam, with a 135 km long reservoir. Iron Gates II, which serves mainly for smoothing peak flow operation, is 35m high and 400m wide, with a 70 km long reservoir. Iron Gates I was completed in 1971 and Iron Gates II in 1984.

Monitoring and discharge flows

Weekly water samples were taken over 9 months in 2001, at 3 water depths and 6 monitoring stations: Danube river inflow to Iron Gates I reservoir, Cerna river inflow to the reservoir, Iron Gates I outflow, 3 bay sites in the reservoir. Soluble and total phosphorus and nitrogen were analysed, and total suspended solids. Dam discharge flow data was provided by the hydropower company, and inflow data was calculated from upstream gauging station data. Additionally, sediment cores were collected, and two sediment traps were used in the reservoir. Radionuclide analysis enabled sediment dating.

Discharge flows during the study period ranged from 2,500 to 10,000 m3/s. Comparison with historic data suggested that 2001 was on average, not an exceptional year concerning the hydrological regime.

Nutrients

The concentrations of nutrients were similar at different sampling depths (surface, mid water, near the bottom).

For dissolved nitrogen and dissolved phosphorus, the concentrations in the dam outflow water followed closely that in the inflow river waters. However, the **outflow concentrations were almost always slightly higher than the inflow concentrations**: averages of 1020 µg DIN/l inflow and 1110 outflow for nitrogen, averages of 32 µg ortho-P/l inflow and 51 outflow for phosphorus. That is, increases in total phosphorus and nitrogen loads of 13% TP and 18% TN between the reservoir inflow and dam outflow. In both cases the difference between inflow and outflow concentrations is statistically significant.

For total nitrogen and phosphorus, outflow concentrations were also generally higher than inflow concentrations, consistently so for total nitrogen, less markedly so for total phosphorus: averages of 1280 µgN/l outflow and 1140 inflow for total nitrogen, averages of 85 µgP/l outflow and 80 inflow for total phosphorus. In this case the difference was statistically significant for total nitrogen but not for total phosphorus.

Sedimentation

Total suspended solids inflow to the dam reservoir was estimated at nearly 9 million tonnes/year, of which, more than half is retained by sedimentation behind the dam and in the length of the reservoir. Sedimentation rates in different parts of the reservoir were estimated to vary considerably, with an average of 5 – 40 cm sedimentation per year. This represents a **loss of 0.6% of the reservoir water capacity per year**, so that the reservoir storage capacity is already reduced by 20% after 30 years operation today, and its useful life will end after 120 years if action is not taken.

Analysis of the sediments nutrient content, compared to the sedimentation rates, suggests that **sedimentation could only account for a reduction of 5% of inflow total nitrogen load and 12% total inflow phosphorus load**. This represents only 1% of the difference between estimated nutrient loads into the Danube River and measured loads at the Black Sea, the "missing" one million tonnes of N/year and 0.13 million tonnes of P/year. These results are therefore not coherent with the levels of nutrient retention behind the barrage suggested by previous studies.

The actual results showing higher (not lower) outflow nutrient loads may be the result of remobilisation of nutrients stored in sediments over the first decades of dam operation, when nutrient concentrations in the Danube were significantly higher than they are today.

The authors suggest that the observed retention of nutrients in the Danube river system may be more the result of the **many smaller dams along the river**, in particular in the smaller headland tributaries. Over 120 hydropower dams have been built on just two tributaries, the Olt and the Siret, since the completion of Iron Gates I.

Role of impoundments

The authors conclude that the hypothesis is disproved that the largest impoundment on the Danube River, Iron Gates I, plays a significant role in nitrogen and phosphorus elimination, and that nutrient storage in large reservoirs cannot be taken for granted.

Silica retention

The other studies cited address the retention of silica in the Iron Gate Reservoir. Similarly to the above study for phosphorus and nitrogen, and based on analysis of the same water samples from 2001 it is concluded that **the Reservoir cannot be**

responsible for retention of the large annual loads of silica which has been suggested. One key reason, is that conditions in the Reservoir except in the Orsovo Bay area, are unfavourable to primary production. Silica retention in the reservoir is estimated at 16 – 19,000 tonnes Si/year, that is at most **5% of inflowing silica**, compared to figures quoted elsewhere of 600,000 tonnes. The Iron Gate Dam cannot therefore be the principal reason for decreasing silica loads arriving downstream in the coastal Black Sea.

The rate of retention of sediment in the Iron Gate Reservoir shown by these studies is also considerably lower than has been suggested by previous authors: around 5 millions tonnes of suspended solids per year retained behind the dam (55% of inflow), compared to 20 – 30 millions suggested elsewhere. Other causes, in particular retention in the Danube river system upstream of Iron Gate, must therefore be largely responsible for the loss of sediment load to the Black Sea, accused of accentuating coastal erosion.

"Retention of sediments and nutrients in the Iron Gate I Reservoir on the Danube River", Biogeochemistry 76, pages 539-565, 2005 http://www.jstor.org/journals/01682563.html

C. Teodoru, B. Wehrli, Swiss Federal Institute for Environmental Science and Technology (EAWAG) and Swiss Federal Institute of Technology (ETH), Limnological Research Center, Seestrasse 79, CH-6047, Kastanienbaum, Switzerland cristian.teodoru@ing.unitn.it

"Is the Iron Gate I reservoir on the Danube River a sink for dissolved silica?", Biogeochemistry 68, pages 21-32, 2004. G. Friedl, C. Teodoru, B. Wehrli,

"Silica retention in the Iron Gate I Reservoir on the Danube River: the role of side bays as nutrient sinks", River Research and Applications 22, pages 441–456, 2006 http://www3.interscience.wiley.com/cgi-bin/jhome/90010544

D. McGinnis, S. Bocaniov, C. Teodoru, G. Friedl, A. Lorke, A. Wüest, Limnological Research Center, EAWAG, CH-6047 Kastanienbaum, Switzerland

"Biogenic silica accumulation in the sediments of Iron Gate I Reservoir on the Danube River", Aquatic Science, vol. 68, n°4, pages 469-481, http://www.springerlink.com/content/101191

C. Teodoru, A. Dimopoulos and Bernhard Wehrli, Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-6047 Kastanienbaum, Switzerland and Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, CH-8092 Zurich, Switzerland

"Nutrient Retention in the Danube's Iron Gate Reservoir", EOS (Transactions American Geophysical Union), Vol. 87, No. 38, 2006 www.agu.org *C. Teodoru, D. McGinnis, A. Wüest, B. Wehrli.*

Phosphate recycling

North Carolina – Idaho - Washington

Cone-shaped crystalliser for struvite recovery

Following previous publications of experimental results for a cone shaped fluidized bed struvite crystalliser, four further papers present experimental results in swine and dairy wastewaters and potato processing wastewaters, as well as theoretic design considerations, including ionic rate equations and, cross sectional area calculations and design equations.

Pig lagoon wastewaters

Paper 1, 2005, presents as summarised in SCOPE Newsletter no 55, **a 40cm high, 1 litre volume cone shaped laboratory reactor was tested for 50 runs of 1.5 to 5 hours each.** Ammonia and magnesium solution were added to pig farm anaerobic lagoon liquor, with the objective of removing phosphate as struvite. The solid bed was maintained in suspension by the upflow of the treated liquor only, with flow rate of 49 volumes/hour. This proved to be effective in maintaining approx 0.1 litres of bed material in suspension with a bed height during operation of around 30 cm (3/4 of reactor height).

The input liquor from the anaerobic lagoon of the Upper Coastal Plain Research Station piggery, North Carolina, with 30-70 ppm soluble phosphate, 430-

670 ppm ammonium nitrogen and 20-60 ppm magnesium. The reactor was seeded with ground solids precipitated in lagoon water piping and analysed and shown to be 90% struvite.

P-recovery

In runs with addition of ammonium hydroxide only (addition of 100 ppm nitrogen), 24% total phosphorus removal was achieved in the reactor. In runs with this nitrogen addition, but also addition of 30 ppm magnesium, **58% P-recovery was achieved**. The operating pH (pH of the liquid in the cone) were pH 8.3 and pH 8.6 respectively.

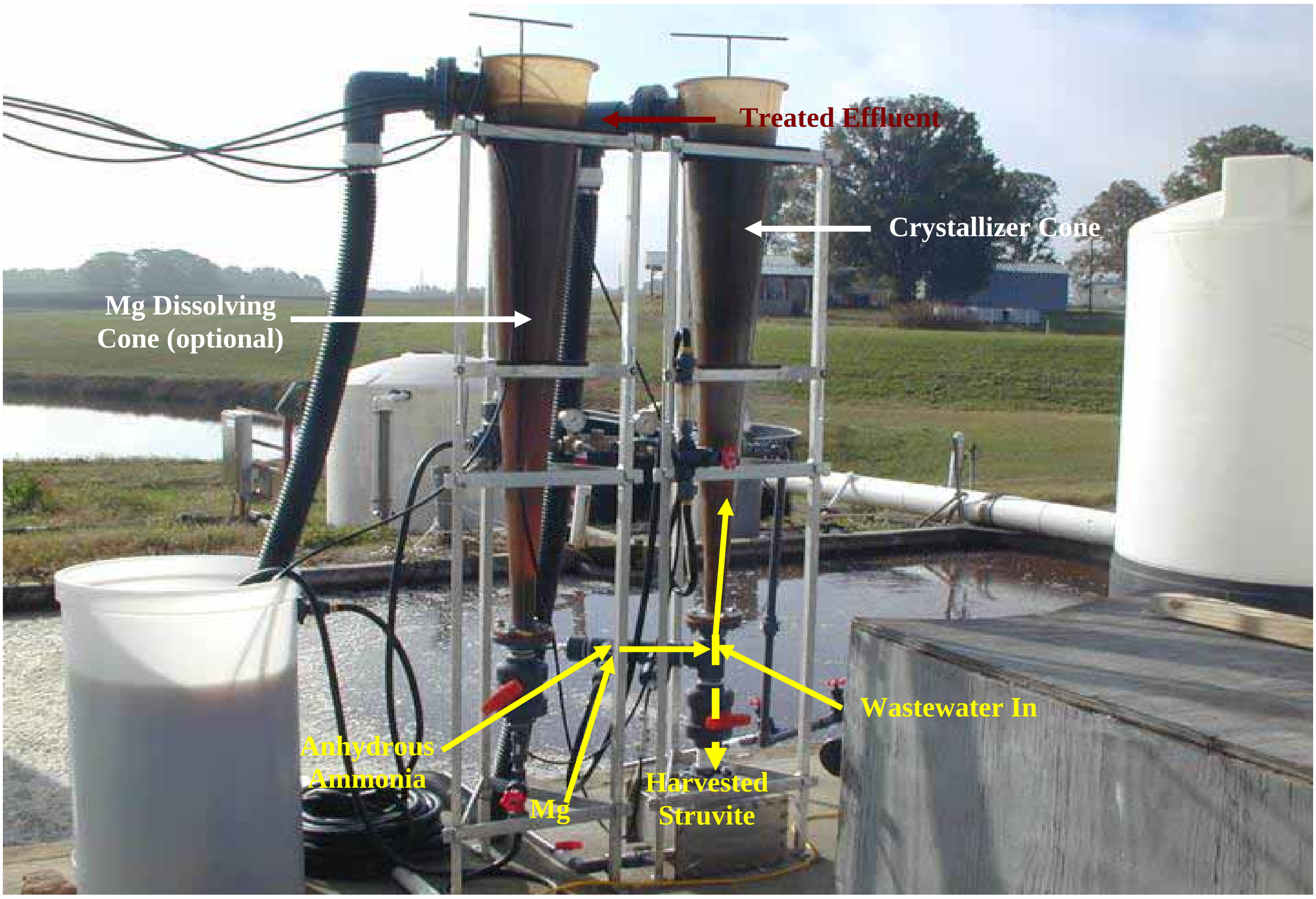
To support reactor design, a rate equation was derived treating separately ion concentrations and bed surface area. Three different models were then used to give design equations, based on different assumptions as to how liquids and solids move in the reactor: MLMB = complete mixing of model and bed, PLMB = plug flow of liquid and complete mixing of bed, PLCB = plug flow of liquid and perfect classification of bed.

Results are compared with model predictions, indicating that the PLMB model best fitted the experimental results, using a rate constant of 10-15 dm/h.

A **pilot scale crystalliser (pictured below)** was designed using the rate information and design equation, and applied in the North Carolina digested swine wastewaters. The system achieved total phosphorus reduction up to 80% of total phosphorus as struvite in the reactor.

Dairy wastewaters

Papers 2, 2005 and 3, 2007 present experimental **results testing the same cone-shaped design of struvite crystalliser in dairy wastewaters** and also further experimental results in swine wastewaters. In these studies, the field scale pilot described also in



Scope Newsletter n° 55 was used. This reactor was 152 cm high with an internal top diameter of 25 cms (25 litres volume).

For the dairy wastewater work, small pilot reactors identical to that pictured below were used in similar systems by the University of Idaho and Washington State University. In addition, **a larger pilot cone reactor** (229 cm height by 38 cm top diameter) was tested in Washington State. Experiments using these reactors were carried out at the 4 000 head Si-Ellen dairy unit near Jerome, Idaho and the 600 head Werkhoven dairy unit near Monroe Washington, in both cases operating on liquors from wastewater storage lagoons (non digested, cattle waste flush waters). The crystalliser set up differed slightly for both systems from that presented in the previous work, in that the magnesium input was directly into the reactor cone bottom (not into the inlet pipe.)

For the dairy wastewaters, results show a lower removal rate for total phosphorus but, at the 50% total P removal achieved by the larger pilot cone, performance reached that viewed as adequate in the dairy industry. Lower P reduction than that seen in swine wastewater was attributed to the lower proportion of the wastewater phosphorus which was in a soluble form, available for struvite precipitation.

Results cover 2-7 hour runs on a total of 22 days for the two dairies.

A significant improvement of P recovery potential resulted from the conversion of phosphorus present in the raw dairy wastewater (only 55-60% soluble) to DRP (dissolved reactive phosphate) by digestion (93% DRP after digester).

Operating problems with the dairy wastewaters included calcium content (which both removes phosphorus as calcium phosphates but also inhibits struvite precipitation, possibly by coating the seed crystals in the fluidised bed with calcium carbonate) and viscosity (inhibiting mixing and resulting in carry-over of particles out of the top of the reactor).

The observed phosphorus removal may also be lower because **higher concentrations of magnesium and ammonia nitrogen in the dairy wastewaters** (compared to swine wastewaters) could mean that struvite is already formed in the wastewaters and precipitated in the storage lagoons or as fine suspended solids not available for capture in the reactor.

A summary **economic analysis** of application to digested dairy waste is given.

Potato wastewater

A further paper, 4, 2006, presents application of the reactor to wastewater from a potato processing factory in Twin Falls. The process wastewater is treated in an UASB (upflow anaerobic sludge blanket) reactor, before going to the municipal waste water treatment plant (wwtp). The factory contributes up to 5% (2.6 million gallons per day peak) of the wwtp inflow, and 80% of wwtp phosphorus load, posing problems for the respect of increasingly tight wwtp discharge consents to the Snake River.

The reactor was tested for 6 hour runs at different magnesium addition rates ($MgCl_2$) and pH adjustments. The potato wastewater contained on average 37 mg/l total phosphorus, of which only 16 mgP/l was soluble phosphate, 138 mg/l magnesium and 140 mg/l ammonium nitrogen, with a pH of around 7.

Removal of 32-37% of total phosphorus, and 55-92% of soluble phosphorus, was achieved with a pH increase of +1, with lower removal effectiveness for a pH increase of +0.5. Because of the high magnesium content in the potato wastewater, magnesium addition did not improve P-removal.

The authors suggests that prior acidification of the wastewater could reduce the proportion of insoluble phosphorus, and so improve the % total phosphorus removal, but even without this the 90% removal of the soluble phosphate would already represent a **very significant reduction in phosphorus loads** to the municipal wwtp.

[1]: *"Design of cone-shaped fluidized bed struvite crystallizers for phosphorus removal from wastewaters", Transactions of the AESE – American Society of Agricultural Engineers (now ASABE), Vol. 48 (3), pages 1217-1226, 2005.* www.asabe.org

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[2]: *Paper "Application and evaluation of a cone-shaped fluidized-bed phosphorus crystallizer in dairy wastewater" and available at* http://www.cals.ncsu.edu/waste_mgt/natlcenter/sanantonio/Sheffield.pdf
Slides "Phosphorus removal on dairies in the Pacific Northwest: applying a cone shaped fluidized bed phosphorus crystallizer" available at: http://www.cals.ncsu.edu/waste_mgt/natlcenter/sanantonio/phosphorusremoval.ppt
From: Proceedings: Animal Waste Management Symposium, October 5-7, 2005, Research Triangle Park, North Carolina, The Development of Alternative Technologies for the Processing and Use of Animal Waste http://www.cals.ncsu.edu/waste_mgt/05wastesymposium/proceedings.htm

R. Sheffield rons@uidaho.edu*, Twin Falls Research & Extension Center, University of Idaho, CSI Evergreen Building, 315 Falls Avenue East, Twin Falls ID 83301 , USA. K. Bowers, J. Harrison, Washington State University Puyallup Research Center, Dept. Animal Science, 7612 Pioneer Way East, Puyallup, WA 98371-4889, USA* jhharrison@wsu.edu

[3]: *Conference presentation slides : "Fluidized Bed Crystallizer for Phosphorus Removal and Production of Granular Struvite Fertilizer". K. Bowers, Multiform Harvest Inc, as above. From: Harvesting Clean Energy Conference VII - Biogas Digesters: Innovations and Co-Products, Boise, Idaho, USA, January 30, 2007* http://www.harvestcleanenergy.org/conference/HCE7/PDFs/Bowers.pdf

[4]: *"Evaluation of a phosphorus crystallizer to treat potato processing wastewater", 2006 ASABE International Meeting, Portland, Oregon, 9-12 July 2006, paper n° 064108 ASABE – American Society of Agricultural and Biological Engineers (previously called AESE), Vol. 48 (3), pages 1217-1226, 2005.* www.asabe.org *R. Sheffield, as above.*

North Carolina

Testing struvite precipitation from swine lagoon liquors

Samples of anaerobic lagoon effluent from two different swine farms in North Carolina were used to test struvite solubility at different pH and magnesium:phosphate ratios, in simple 250 ml beaker batch precipitation experiments and in 1100 ml stirred beaker continuously measured batch reactor experiments.

The different effluents contained around 50 mg/l magnesium, 50-60 mg/l soluble phosphorus, 150-500 mg/l ammonium nitrogen, over 300 mg/l potassium and around 150 mg/l calcium. They were settled at 4°C for 24 hours before use.

Precipitation

In the first set of experiments, after effluent analysis, soluble magnesium was added to the effluent in beakers to adjust the magnesium:phosphate ratio, followed by sodium hydroxide to adjust pH in the range 7.5 – 9.5. The beakers were mixed for 10 minutes, then covered with a paraffin film to reduce ammonia loss and stood for 24 hours at 25°C before analysis of magnesium and phosphate concentrations. pH was not controlled during the reaction, and so was also measured at the end. Ammonium was not measured because it was present in excess. The precipitated solids were analysed chemically for magnesium, phosphorus, carbon and nitrogen contents and by X-ray diffraction.

Results showed increased precipitation of struvite at higher magnesium:phosphate ratios and at higher pHs, corresponding to visibly increased precipitate deposits. The precipitated solids were shown by chemical analysis and X-ray diffraction to be struvite, with no other crystals detected but some presence of organic carbon.

Maximum phosphate removal (minimum struvite solubility) occurred at pH 8.9 – 9.25 for the different effluents, with **91-96% soluble phosphate removal** being achieved at these pH levels and for a magnesium:phosphate ratio of 1.6:1 The optimal pH was not dependent on the magnesium ratio, but at all pH levels higher Mg:P ratios resulted in improved phosphate removal.

Continuous stirred experiment

The second set of experiments used a continuously stirred flask filled with 1100 ml of lagoon effluent at room temperature. Again after effluent analysis, magnesium was added and pH adjusted (to 8.4; 8.7 and to 9.0). Samples were taken at 5 minutes intervals for the first hour or reaction, and then at 10 minute intervals, and analysed for soluble phosphate, magnesium and ammonium.

The kinetic rate constant was determined by fitting a first-order kinetic model to the data, using MINTEQA2 v3.11. The equilibrium phosphate concentrations were consistently lower than those predicted by this model, particularly at pH away from 9. Organic compounds in the lagoon liquid may be responsible for this, as they can form soluble complexes with magnesium reducing its availability for reaction to form struvite. Entering citrate into the MINETAQA2 model at concentrations 0.5 or 0.75x the anion charge deficit measured for the effluents minimised the model errors, but some discrepancies between predictions and observed results remained even then at pH>9.

The measured rate constants were 3.7/hour at pH 8.4 and 13.3/hour at pH 9.0. This is slightly lower than results from Ohlinger et al. 2000 (4.2/hour at pH 8.3). The authors suggest the difference may be the consequence of induction time in these stirred batch reactor experiments, not affecting Ohlinger et al. results which used a reactor in a steady state.

The authors conclude that struvite precipitation, by magnesium addition at a Mg:P ratio of 1.2:1 and at pH 9.0 can reduce soluble phosphorus concentration from around 50 mg/l to a stable concentration of around 7.5 mg/l in around 30 minutes reaction time, that is sufficiently rapidly to make the process technically feasible as a method for phosphorus removal from pig farm wastewaters.

"Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant", Bioresource Technology 89, pages 229-236, 2003. *www.elsevier.com/wps/product/cws_home/405854*

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Pot trials

Plant availability

Rye grass was used for 21-day growth chamber pot trials, to test the fertiliser value of 26 different pure calcium and magnesium phosphate compounds, recovered phosphate products and commercial P-fertilizer from former time. The pure phosphate compounds used were laboratory supply chemicals (for the basic phosphate compounds) or were specifically supplied by Chemische Fabrik Budenheim for several of the more complex phosphate compounds.

The rye grass plants were grown in 150g of mixed sand, with initial addition of 50 mg N (nitrogen), 50 mg K (potassium), 5 mg Mg (magnesium) and 20 mg P (phosphate), the P being added by a calculated amount of the tested phosphorus product. Magnesium was not added when contained in the tested phosphorus product being used, whereas nitrogen was not adjusted (so that plants receiving phosphorus products containing nitrogen had a higher total nitrogen input). 4 pots were used for each product tested (100 plants per pot) and 4 control pots without P.

For each phosphorus product, the total % P content and the % phosphorus solubility in water and in 2% citric acid were measured. **The plant phosphorus availability was assessed by comparing total plant P content (shoots and roots) of the fertilized plants**, after 21 days, with the P amount in the control plants (P-0: 7.4 mg P/pot).

Results: plant availability of phosphorus

Calcium phosphates (pure)

$Ca(H_2PO_4)_2$ (net uptake:13,6mgP/pot)	= calcium dihydrogen phosphate	100%
$CaHPO_4$	= dicalcium hydrogen phosphate	93%
$Ca_3(PO_4)_2$	= tricalcium phosphate	60%
$Ca_5(PO_4)_3.OH$	= hydroxylapatite	64%
Apatite mineral (Russia)	10%	

Magnesium phosphates (pure)

$Mg(H_2PO_4)_2$	= magnesium dihydrogen phosphate	97%
$MgHPO_4$	= dimagnesium hydrogen phosphate	117%
$Mg_3(PO_4)_2$	= trimagnesium phosphate	101%

Ammonium phosphate (pure)

$(NH_4)_2HPO_4$	= diammonium hydrogen phosphate	96%

Commercial fertilizers

Superphosphate	107%	Hyperphosphat	16%
Triple superphosphate	98%	Rhenania phosphate	63%
Tang-humu-phos	112%	Alkalisinter phosphate	65%
Novaphos	91%	Magnesiumsinter phosphate	42%

Iron and aluminium phosphate compounds

$FePO_4$	Iron (III) phosphate	<1%
$AlPO_4$	Aluminium phosphate	47%

Phosphate containing industry slags

Thomas phosphate 1	43%
Thomas phosphate 2	47%

Recovered phosphates from sewage works (struvites)

Berlin sewage works (10.2% P)	112%
Heilbronn sewage works (13.7% P)	125%
Least Significant Difference 5%	*24%*

The 26 compounds and products tested and the relative plant availability of the phosphorus - shown as a % of P-availability compared to calcium dihydrogen phosphate $Ca(H_2PO_4)_2$ - were as above. The author concludes that (pure) magnesium phosphates and struvite, and struvite by precipitation in municipal sewage works, are all potentially interesting products as agronomic phosphate sources for plants, but that further experimental work is needed to assess plant availability in different types of soils and in field trials.

"Vergleichende Untersuchungen zur Pflanzenverfügbarkeit von Phosphat aus verschiedenen P-Recyling-Produkten im Keimpflanzenversuch" (Plant availability of P from recycling products and phosphate fertilizers in a growth-chamber trial with rye seedlings). Paper in German with summary in English. J. Plant Nutr. Soil Sci. 2006, 169, pages 826-832
www.interscience.wiley.com/jpages/1436-8730

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