SCOPE NEWSLETTER

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Estuary

Variability of nutrients and phytoplankton in Arcachon Bay

A one-year study looks at the relations between nutrients (P, N, Si) and phytoplankton in the Arcachon Bay estuary / lagoon, near Bordeaux, France, and estimates primary production for the Bay.

Chinese coastal waters

Modelling river nutrient export

The Global NEWS model is used to assess past and possible future trends for nutrient loads in 16 Chinese rivers, and so export to coastal waters.

Ushuaia Argentina

Need for sewage treatment to protect coastal ecology

Collection and treatment of domestic sewage is needed to prevent discharges from Ushuaia City impacting both Encerrada and Ushuaia Bays, South Argentina.

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Review concludes that statistical methods are scientifically valid for deriving nutrient criteria, but only if applied in combination with other case-specific biological evidence.

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Groundwater phosphorus

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British rivers

Significance of soluble phosphorus

Several studies show the high contribution of sewage works discharges to soluble phosphorus in British rivers, their significance in eutrophication quality issues and the difficulty in achieving EU Water Framework Directive quality objectives.

Phosphate recycling

Phosphorus recycling

Thames Water UK to install P-recovery

Thames Water has announced the first full-scale phosphorus recovery and recycling installation in the UK

Ieper, Belgium

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Stirred reactor calcium phosphate precipitation by lime addition tested to remove phosphate from soy protein plant wastewater

Japan

Oranges and P-recovery

A pectin-containing orange juice production waste shows to be effective for P-removal and recovery.

Phosphorus flows

Phosphate resources

Global phosphorus flows

Looking at phosphorus flows from consumption and production perspectives.

Conferences

Nutrient recovery and management 2011

Florida 9-12 January 2011

Water Environment Federation - International Water Association
http://www.wef.org/Nutrient/

Sustainable Phosphorus Summit

Arizona 2-5 February 2011

Phosphorus, food and our future

The conference will explore the complex dynamics of P as a limited resource, and create a stage for constructive discourse and discussion on P sustainability. ***http://sols.asu.edu/frontiers/2011/program.php***

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Eutrophcation

Estuary

Variability of nutrients and phytoplankton in Arcachon Bay

Arcachon Bay is a macrotidal coastal lagoon of 174 km^2 on the South West coast of France. It is made up of a 156 km^2 inner lagoon, connected to an intertidal area by tidal channels. 4/5 of its fresh water inflow comes from the Leyre river, with a total annual freshwater input of 1.25 million m^3.

The study is based on one complete year (2003) data plus supplementary data from Spring 2002, from twice weekly sampling at two points, one in the inner lagoon (flushing time 13-20 days) and one in a deep channel representative of the oceanic water masses entering the lagoon (flushing time 4-5 days). Soluble phosphate, soluble inorganic nitrogen and soluble silicate were analysed, as well as ammonium. Phytoplankton cells were counted and identified, and primary production assessed using carbon uptake experiments. Data were also collected for salinity, temperature, solar radiation, daily river flow and nutrient concentrations in the Leyre river.

Dissolved nutrient concentrations

Soluble nitrogen was relatively high in the winter periods and higher in the inner lagoon than in the outer bay, with peaks following high flows in the Leyre river (peak 62 µM and 16 µM respectively in the inner and outer Bay). Ammonium represented 34% of dissolved inorganic nitrogen as an annual average, and up to 56% in summer.

Soluble silicate concentrations varied in the same way as soluble nitrogen, again with high concentrations relating to high freshwater inflows.

Soluble phosphate concentrations however did not follow the same pattern, remaining low all year with only a small increase in winter, and no apparent correlation to the Leyre river flow or to salinity.

Nutrient ratios

Comparison of observed soluble nutrient ratios to the Redfield ratio suggested that **the limiting nutrient during Summer was nitrogen**, with secondary phosphorus or silicon limitation, and phosphorus (Spring 2003) orsilicon (Spring 2002) during Spring.

The authors estimated that **P will generally be the limiting nutrient for phytoplankton in the Bay in Spring**, except in particular cases (following a dry winter / low freshwater inflow) and N in summer, possibly because of high nitrogen uptake by other primary producers (eg. seagrass Zostera noltii).

Primary production

As could be expected, most primary production occurred outside the winter: 84 – 92% from February to October. The type of dominant phytoplankton in primary production varied over the year, including diatoms, dinoflagellates, small phytoplankton species (picoeukaryotes, nanophytoplankton) and cyanobacteria.

The annual primary production rate was nearly twice as high in the inner lagoon than the outer lagoon. The authors consider that this is probably largely **the result of higher soluble nitrogen and silicate, resulting from river inflow**.

The annual rate of phytoplankton primary production in the inner lagoon is estimated at 103 gC/m^2/year, at the lower end of levels reported for European coastal zones (Gazeau, 2004 and other cited studies). This moderate net primary production could be the result of the moderate nutrient concentrations of the Bay and other factors such as residence times or in-site consumption by zooplankton, cultivated oysters and other benthic consumers.

"Variability of nutrients and phytoplankton primary production in a shallow macrotidal coastal ecosystem (Arcachon Bay, France)", Estuarine Coastal and Shelf Science 76 (2008), pages 642-656. http://www.elsevier.com/locate/inca/622823 .

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Chinese coastal waters

Modelling river nutrient export

Rapid population growth, industrial development and increased agricultural production, combined with inadequate sewage treatment and inefficient fertiliser use, has resulted in increasing nutrient export in China's rivers, and eutrophication of coastal waters, with symptoms such as algal blooms. This study models past and future trends in this nutrient loading, using the *NEWS2* model system, applied to 16 large river basins covering around 90% of the catchment area of China's coastal waters (East China Sea, Bohai Gulf, North South China Sea, West Yellow Sea).

The model estimates dissolved inorganic and organic and particulate nutrients (N, P). It is based on land use (land cover, crops) and explicit calculation of anthropogenic inputs, in particular fertilisers, manure and sewage. Sewage nutrients are estimated for human body origins and detergents, based on socio-economic and sanitation data.

Scenarios

The Global NEWS2 model considers four future scenarios, based on the Millennium Ecosystem Assessment:

- GO = Global Orchestration: a globalised world, focused on economic growth, with a reactive approach to environmental management
- OS = Order from Strength: a regionalised world, focused on security, again with a reactive environment approach
- TG = Technological Garden: a globalised world focused on environmentally sound technology and a highly managed environment
- AM = Adapting Mosaic: proactive socio-ecological management, through simple solutions, at the regional and local scale

Nutrient drivers

Population and economic development appear as the key drivers of nutrient discharges. Population increased 50% from 1970 to 2000 in the 16 study basins. The proportion of the population connected to sewage treatment increased from 5% to 20% from 1970 to 2000. The combined consequence of these changes has been a 3x increase in phosphate river loads from detergents and a 6x increase in loads from human sewage.

Over these thirty years, agricultural area also increased by 50%.

Dissolved inorganic nutrients (DIN, DIP) are the main form of nutrient loading in all scenarios. The dominant sources of DIN (dissolved inorganic nitrogen) are fertiliser and manure, and the dominant source of DIP (dissolved organic phosphorus) is sewage.

The model predicts a continuing increase in population through to 2030, at different rates for the different scenarios, and corresponding ongoing increases in nutrient loadings. **Future nutrient loadings related to agriculture are particularly related to consumption of meat and milk**.

Management options

To assess the impacts of different management strategies, effects on nutrient loadings of different variations on the GO scenario were also modelled.

Controls on fertiliser use appears as the most effective measure for reducing DIN and DOP loadings, giving average 10% decreases.

Improved sewage treatment appears as the most effective measure for reducing DIP (dissolved inorganic phosphate) and DON (dissolved organic nitrogen) loadings, by 11% and 5% respectively.

The authors indicate that this paper shows that the global scale model NEWS can usefully be applied for assessing regional management options.

"Past and future trends in nutrients export by rives to the coastal waters of China", H. Qu, Key Laboratory for Urban Habit Environmental Sciences and Technology, Shenzhan Graduate School, Peking University, Shenzhen 518055, China. C. Kroeze, Environmental Systems Analysis Group, PO Box 47, 6700 Wageningen, The Netherlands. Carolien.kroeze@wur.nl

Science of the Total Environment, 408, pages 2075-2086, 2010. www.elsevier.com/locate/scitotenv

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Ushuaia Argentina

Need for sewage treatment to protect coastal ecology

Collection and treatment of domestic sewage is needed to prevent discharges from Ushuaia City impacting both Encerrada and Ushuaia Bays, South Argentina.

This study examines the impact of nutrient fluxes from Ushuaia City on Encerrada Bay into which they flow, and possibly on Ushuaia Bay which is artificially connected to Encerrada Bay.

Ushuaia City (54°49'S, 68°19'W) had a population of around 46 000 in 2001, but with rapid growth in recent years, plus high numbers of summer tourists. The installed sewage network is insufficient, and discharges into Golondrina Bay through an underwater pipeline, but **much of the city's sewage reaches the Encerrada bay untreated in streams and drains**.

Encerrada Bay has a surface area of around 0.3 km^2 and average depth of 0.8m. It is separated from Ushuaia Bay by an artificial pathway, through which two vents allow water exchanges with tide flows.

Nutrient inflows to Encerrada Bay and flows through the vents to Ushuaia Bay, as well as water quality parameters in Encerrada Bay were measured over a one year period, and benthic fluxes were assessed.

Nutrient inputs

Nutrient inputs from Buena Esperanza Stream to Encerrada Bay were estimated at over 100 $gN/m^2/year$. Daily nutrients inputs from effluents were 140 – 670 kgN/day and 10-60 kgP/day, compared to the net export to Ushuaia Bay of around 42 kgN/day and 16 kgP/day. Average Encerrada Bay water ammonium, nitrate and phosphate concentrations were around 100, 10 and 3 µMol respectively. Benthic fluxes showed consumption of dissolved oxygen and nitrate and a release of ammonium and phosphate by the sediment, typical of anoxic conditions.

The authors conclude that the Encerrada Bay is suffering from severe eutrophication impact, with high phaeopigment/chlorlphyll ratio, low dissolved oxygen, and development of macro-algae.

Thus, Encerrada Bay is consuming significant nutrient inputs (in primary consumption), so buffering the impact of wastewater discharges on Ushuaia Bay, but at the expense of its own ecological deterioration.

The authors emphasise **the need for a proper wastewater collection and treatment system in Ushuaia City** to preserve the coastal ecosystem.

"Environmental Characterization of a Eutrophicated Semi-Enclosed System: Nutrient Budget (Encerrada Bay, Tierra del Fuego Island, Patagonia, Argentina)", A. I. Torres, M. N. Gil, O. A. Amín, J. L. Esteves, Water Air Soil Pollut, n° 204, pages 259-270, 2009. Springer
http://www.springerlink.com/content/100344/

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US EPA

Statistics-based nutrient criteria

The United States Environmental Protection Agency (EPA) has been working for ten years now to produce guidelines and TDMLs (Total Maximum Daily Loads, see SCOPE Newsletter n° 43) for nutrient criteria, leading to the publication of a draft guidance document titled "Empirical Approaches for Nutrient Criteria Derivation" (*LINK*).

The Clean Water Act requires numerical nutrient water quality criteria to be derived to protect water bodies from nutrient over-enrichment, and so risk of eutrophication. The EPA recommends three approaches for deriving such criteria: stressor-response analysis, reference condition approaches and mechanistic modelling.

Reference conditions, mechanistic modelling

The reference condition approach derives candidate nutrient criteria from concentrations found in pristine or minimally disturbed comparable water bodies (see Scope Newsletter n° 61).

The mechanistic modelling approach predicts the effects of nutrient concentration changes using site-specific parameters and equations representing ecological processes. The draft Guidance suggests using stressor-response relationships, with statistical analysis, to derive criteria. The stressor in this case is nutrient concentration, and the response can be chlorophyll levels, dissolved oxygen or biological index (ecosystem status).

Empirical stressor-response approach

The Guidance proposes 5 steps: defining variables and exploring empirically their relationships, assessing the strength of the relationships using models and literature, data analysis (statistics, deriving effect thresholds), evaluation of the validity of the proposed relationships, and finally evaluation of the validity of the derived criteria.

The EPA justifies this approach because **nutrient impacts cannot be assessed in laboratory studies** (unlike toxic substances) and so criteria derivation must rely on empirical analysis of field data.

Statistical approach valid if used with other approaches

The Science Advisory Board review of the EPA draft Guidance recognises "*the stressor-response approach as a legitimate, scientifically based method for developing numeric nutrient criteria if it is appropriately applied (i.e, not used in isolation but as part of a tiered weight-of-evidence approach ...) ... However, when properly developed, biologically relevant statistical associations can be useful arguments as part of a weight-of-evidence approach*".

This limitation to the empirical approach should be more clearly specified in the Guidance, in particular emphasising that "*considerable unexplained variation can be encountered when attempting to use the empirical stressor-response approach to develop nutrient criteria. The final Guidance should clearly indicate that such unexplained variation presents significant problems in the use of this approach. Further, the final document should clearly state that statistical associations may not be biologically relevant and do not prove cause and effect. ... Therefore, the final Guidance should provide more information on the supporting analyses needed to improve the basis for conclusions that specific stressor-response associations can predict nutrient responses with an acceptable degree of uncertainty. Such predictive relationships can then be used with mechanistic or other approaches in a tiered weight-of-evidence assessment including cause and effect relationships to develop nutrient criteria.*"

This is coherent with positions taken by (e.g.) **Jones and Lee** that the proposed statistical approach is not founded on a cause-and-effect coupling between nutrient concentration/load and eutrophication related water quality.

Jones & Lee, "Comments on US EPA Empirical Approaches for Nutrient Criteria Derivation", 1st September 2009: www.gfredlee.com/Nutrients/EPA_Empirical_CritDevel.pdf

Empirical Approaches for Nutrient Criteria Derivation, United States Environmental Protection Agency, Office of Water, Office of Science and Technology, Draft, August 17, 2009: http://yosemite.epa.gov/sab/sabproduct.nsf/0/5972E2A88464D45E85257591006649D0/$File/Final+Draft+Empirical+Approaches+08-17-2009+for+EPEC+Sept+9-11+2009+Meeting.pdf

Science Advisory Board review, 27-4-2010: http://yosemite.epa.gov/sab/sabproduct.nsf/0/E09317EC14CB3F2B85257713004BED5F/$File/EPA-SAB-10-006-unsigned.pdf

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United Kingdom

Groundwater phosphorus

Assessment of groundwater phosphorus levels in the UK suggests that in certain conditions this can be a significant source of P to surface waters and a possible eutrophication trigger.

Measured orthophosphate concentrations from some 49 000 groundwater samples (from nearly 3 600 monitoring sites) in the UK and Ireland suggest that **in a significant number of cases groundwater phosphorus concentration can be higher than Good Ecological Status river concentration thresholds**. Groundwater can thus potentially be a significant source of phosphorus to surface water, particularly as periods when groundwater is a significant contributor to flow are those when rivers are particularly sensitive to eutrophication.

Traditionally, groundwater inflows to surface water have been considered as a negligible source of phosphorus, or as diluting phosphorus loads. Groundwater phosphorus monitoring has targeted comparison to the EU drinking water standard (2 200 µgP/l), for which concerns are virtually never identified. This paper looks at the data available in the UK and Ireland, patterns of groundwater phosphorus concentrations, and on the basis of the existing data whether groundwater phosphorus could potentially be ecologically significant for surface waters.

Limit of Detection

Much of the existing data simply indicates that phosphorus concentrations in groundwater were "**below the limit of detection**" (LOD): 53% below LOD in England and Wales, 94% in Northern Ireland, 28% in Scotland, 33% in Ireland. However LOD is variable and inconsistent, ranging from 1 to 100 µgP/l.

This compares with thresholds for eutrophication which can be as low as 10 to 30 µgP/l for some rivers.

Samples below LOD were treated as being half the LOD in the analyses, with the exception of the Northern Ireland data which was omitted due to the high LOD.

Land cover

Land cover was estimated using the predominant CORINE2000 land cover type within an arbitrary 1km radius around sampling points. This is recognised as imprecise, as this circle may or may not correspond to part or all of the "upstream" water basin, but it was considered a reasonable approximation, given the available data.

Land cover estimated in this way accounted for only 15% of the observed variability in groundwater P concentration across the four countries, with groundwater P being significantly higher in the (grouped) England and Wales data than in the Republic of Ireland or Scotland for the same land cover class, and groundwater P being significantly lower where land cover is predominantly semi-natural vegetation (compared to agriculture, grassland or urban land cover).

Implications

The authors conclude that the land cover data suggests anthropogenic influence on groundwater P concentrations, and suggest various possible agricultural and urban sources of phosphorus inputs to groundwater. They conclude however that the available data does not make it possible to identify the significance of different possible sources.

The sensitivity of receptor freshwaters to groundwater P loads is discussed. This sensitivity will depend on factors such as climate, residence time, scale of upstream basin, and synchonicity between delivery of phosphorus from groundwater (base flow) and biological demand (potential algal development).

Recommendations

Because significant numbers of groundwater bodies have phosphorus concentrations which are above ecologically significant thresholds for receiving surface freshwaters, **the issue of groundwater P load should be assessed as a possible contributor to eutrophication risks**. The currently available data are inadequate to do this in most cases, as is generally the understanding of groundwater inputs to and links with the freshwater system.

The authors make the following recommendations to address this and develop appropriate data and understanding:

- standardise sampling to enable data consistency
- standardise LOD (Limit of Detection) and bring this down to a concentration below ecologically significant phosphorus thresholds
- improve sampling strategies
- establish data for the many groundwater bodies in which no sampling has previously been carried out
- improve knowledge of potential point sources of P to groundwater: e.g. agricultural manure slurry lagoons, septic tanks, leaking mains water and sewer pipes
- develop monitoring and research to better characterise the extent of anthropogenic sources of P to groundwater

"An assessment of the risk to surface water ecosystems of groundwater P in the UK and Ireland", Science of the Total Environment 408 (2010), pages1847–1857, Elsevier www.elsevier.com/locate/scitotenv

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British rivers

Significance of soluble phosphorus

A number of recent studies present updated information addressing the significance of municipal wastewater as a source of phosphorus to UK rivers, the reductions achieved by P-removal in sewage works, and the considerable challenges to bringing soluble phosphorus levels down low enough to prevent eutrophication risks and meet EU Water Framework Directive objectives.

Soluble phosphorus, both “soluble reactive phosphorus” (SRP) and other forms of soluble phosphorus (DHP) are considered to be the **significant factor for eutrophication control**, because this tends to be the predominant form of phosphorus during low-flow periods when rivers are particularly susceptible to algal development. **Particulate phosphorus on the other hand tends to largely occur during spate flows**, when rivers algae are less likely to develop.

In-river mechanisms

However, in-river mechanisms may mean that **reality is more complex that the simplistic assumption that soluble phosphorus comes mainly from point sources (sewage works) and particulate forms from agricultural source (run-off with soil erosion):** biological processes in the river can fix soluble phosphorus into particulate forms (algae biological matter particles) or extract phosphorus from insoluble forms bringing it into the biological cycle.

Phosphate removal in sewage works has resulted in very considerable reductions in river phosphorus levels, but these nonetheless remain in many cases higher than the limits for good ecological status, as defined by the EU Water Framework Directive.

Nine major river basins

A study of nine major UK river basins and 26 major tributaries looked at phosphorus concentrations in different forms (total phosphorus TP, particulate phosphorus PP, total dissolved phosphorus TDP, soluble reactive phosphorus SRP and dissolved hydrolysable phosphorus DHP) to catchment uses and to markers of sewage effluent input (boron and sodium).

Phosphorus concentrations in all forms correlated to effluent discharges, as indicated by the markers. SRP was widely dominant, showing the importance of sewage effluent inputs. In rural areas, DHP had relatively high concentrations and SRP + DHP together often exceeded environmental thresholds defined for SRP, showing a need to take bioavailable DHP into account in monitoring and management programmes.

Results show that even in rural catchments with relatively little pollution, sewage effluent remains relevant for eutrophication management.

Strong correlation between effluent markers and particulate phosphorus (PP) show the importance of in-river biological processes cycling phosphorus between particulate and soluble forms, and a need for better understanding of size and nature of the chemical and biological processes and phosphorus stories involved.

Benefits of sewage P-removal

Data from 18 study sites on 15 rivers were used to compare the relative importance of point and diffuse phosphorus sources using the Load Apportionment Model (LAM), and consequently to assess expected impacts of sewage P-removal. Weekly monitoring data over a 1 – 3.5 year period was used. This period (1993 – 1999) was before the widespread introduction of phosphorus removal in sewage works in the UK.

Correlation to the sewage effluent marker boron showed that the LAM model assumption is correct, that **constant non-flow related phosphorus inputs are related to sewage point source inputs**.

The model shows that point and diffuse phosphorus loads vary widely between catchments. As expected, urban catchments were largely dominated by sewage inputs. However, **most of the catchments studied received a majority of their annual total phosphorus load from diffuse sources**. Nonetheless, 80% of sites were dominated by point sources for most of the duration of the year (the diffuse loading are effectively concentrated, with high loads only over short periods, in particular related to spate flows), and in particular in summer during periods of eutrophication risk.

This supports the conclusions of Jarvie et al. 2006, that the most effective management strategy to address risks of excessive algal growth (eutrophication effects) is to reduce sewage phosphorus inputs.

A reduction of phosphorus loads resulting from sewage P-removal was modelled, assuming different effluent discharge consents of 2 or 1 mgP/l, based on data presented in Mainstone *et al.* (2000) and Jarvie *et al.* (2002). These data suggest corresponding reductions of 77 and 88% in sewage works effluent concentrations.

The study concludes that in urban catchments P-removal down to 1 mgP/l will not be adequate to achieve the environmental objective of bringing down river phosphorus concentrations to <100 µg/l. More stringent P-removal requirements than the 1 mgP/l will be required. **Flow-related (diffuse) inputs will also need to be addressed**. In such catchments, these also appear to be significantly derived from sewage, via septic tanks and sewage storm overflows.

The study shows the effectiveness of a combination of the LAM model with land coverage data and use of sewage effluent markers (such as boron) as a tool for predicting phosphorus concentrations over time and estimating the impacts of various mitigation strategies.

Reductions in sewage P in the upper Thames

Phosphorus concentrations in the Thames River, South-East UK, and in two major tributaries (Thame, Kennet) are assessed over the period 1997 – 2007. Of these, the Thame and Kennet are dominantly urban, whereas the Kennet is a largely rural, upstream tributary. Analysis was carried out weekly, assessing different forms of phosphorus and other trace elements. Flow data was taken from existing gauges situated near the monitoring sites.

The paper also develops a specific model for "endmember mixing analysis", that is looking at the concentrations of elements indicative of different origins of the water in the river at the monitoring site, using soluble reactive phosphorus as an indicator of water flow originating from sewage effluent. Sodium and boron concentrations are also compared as sewage effluent markers, however boron poses difficulties because of its decreasing use in consumer products, and so decreasing levels in sewage effluents. Detailed data comparing different forms of phosphorus with flow and with sewage effluent markers if presented graphically.

Following the introduction of P-removal in major sewage works, considerable reductions in base-flow soluble reactive phosphorus (SRP) concentrations occurred over this period, from 1584 µG:L to 376 µg/l in the Thames for example.

The analysis shows the complexity of the relationship between SRP river loadings and river concentrations. Mechanisms of phosphorus storage and release from sediments are suggested, including SRP uptake from the water column in chalk or carbonate areas and SRP release from clay sediments in anoxic conditions.

These mechanisms suggest that it may be possible to **achieve environmental phosphorus objectives** (of 50 µgP/l for "high" and 120 µgP/l for "good" biological status) by P-removal in sewage works in the Thames catchment, but not in the Thame, because of the Thames ability to remove SRP under base-flow conditions, whereas the Thame shows sediment release.

The authors conclude that P-removal in sewage works alone is unlikely to be sufficient to achieve environmental phosphorus objectives, in order to prevent eutrophication symptoms, and that **diffuse household and agricultural sources must also be addressed.**

"The strategic significance of wastewater sources to pollutant phosphorus levels in English rivers and to environmental management for rural, agricultural and urban catchments", Science of the Total Environment 408 (2010), pages 1485–1500.
www.elsevier.com/locate/scitotenv

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"Predicting phosphorus concentrations in British rivers resulting from the introduction of improved phosphorus removal from sewage effluent", Science of the Total Environment 408 (2010), pages 4239–4250
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"Declines in phosphorus concentration in the upper River Thames (UK): Links to sewage effluent cleanup and extended end-member mixing analysis", Science of the Total Environment 408 (2010), pages 1315–1330.
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eutrophication than agricultural phosphorus? Sci Total Environ 2006, 360(1–3): pages 246–53.

Mainstone CP, Parr W, Day M. Phosphorus and river ecology. Tackling sewage inputs. English Nature and Environment Agency, 2000.

P-recovery and P-recycling

Phosphorus recycling

Thames Water UK to install P-recovery

Thames Water has announced the first full-scale phosphorus recovery and recycling installation in the UK, to be built at the company's Slough sewage works. The unit will recover phosphorus and ammonia from the wastewater and produce environment-friendly, high quality fertiliser (*Crystal Green* struvite) and should be operational by mid-2011.

Slough sewage works operates biological nutrient removal for a population equivalent of c. 250,000 pe and is expected to generate 150 tonnes a year of struvite fertiliser. The struvite (magnesium ammonium phosphate) fertiliser offers these three nutrient elements to plants, but also has the advantage of dissolving slowly over 6 – 9 months, thus avoiding nutrient leaching to the environment as it becomes progressively available to plant needs. The fertiliser has received UK Environment Agency approval for sale in the UK.

Ostara finance package

The £2m full-scale unit is funded by Ostara, a Canadian company specialised in nutrient recovery and recycling, so that **Thames Water has no capital investment and there is no public funding**. Thames will pay a treatment fee to Ostara, considered to be lower than current operating and chemical costs, and will also receive revenue for the fertiliser produced.

An Ostara pilot plant has been tested at Slough since March 2010, and another at **Severn Trent Water** Company's Derby UK sewage plant in 2009.

Lord Peter Melchett, Policy Director at **the Soil Association (the UK association for organic food)** said: "*We must learn to recycle all the phosphate in wastewater to have secure food supplies in future, and this initiative by Thames Water and Ostara is a significant step in the right direction. The new facility will also help Thames Water meet environmental regulations on nutrient levels ...*"

Plants operating in the USA and Canada

Ostara already have several P-recovery plants operational in municipal sewage works in Canada and in the USA and estimate that "*several hundred*" plants in Europe are potential candidates for this technology of nutrient recycling.

Robert F Kennedy Jr, board member at Ostara and leading US environmentalist, said: "*This partnership between Thames Water and Ostara provides a cost-effective solution that benefits the environment at all stages, and truly exhibits the shift that we are seeing towards closed-loop sustainable technologies*."

Ostara P-recovery installations are already operational or planned at Nine Springs (Madison, Wisconsin), Nansemond – Hampton Roads (Suffolk, Virginia), York (Pennsylvania), Durham - Tigard near Portland (Oregan), Gold Bar - Edmonton (Alberta).

Ostara Nutrient Recovery Technologies: www.ostara.com *and Crustal Green fertiliser* www.crystalgreen.com

Ostara: http://www.ostara.com/news/news-releases/2010/thames-waters-slough-sewage-works-build-ostara-facility

Thames water: http://www.thameswater.co.uk/cps/rde/xchg/corp/hs.xsl/10953.htm

BBC News, 28th September 2010: http://www.bbc.co.uk/news/uk-england-london-11428384

Severn Trent Water UK pilot trial: http://www.crystalgreen.com/docs/news/Severn-Trent-NR-20090910.pdf

See also: Potential phosphorus recovery by struvite formation, Y. Jaffer, T.A. Clark, P. Pearce, S.A. Parsons, Water Research n°36 (2002) pages 1834–1842 http://dx.doi.org/10.1016/S0043-1354(01)00391-8

Ieper, Belgium

Calcium phosphate from soy plant water

DuPont have tested their "high aspect ratio draft tube crystallisation reactor" (HARD) for phosphate removal by calcium phosphate precipitation from the wastewater of the SOLAC ® (DuPont and Bunge) plant, Ieper, Belgium, producing soy protein and other speciality food ingredients.

The plant's existing wastewater treatment plant uses an **enhanced biological nutrient removal system** to achieve 99% removal of organic and nitrogen loads, and reduces around 170 mg/l total phosphorus in the raw wastewater 25-30 mg/l soluble phosphate in the effluent. However, authorities are implementing a 2 mg/l phosphorus discharge limit, requiring this to be achieved without increasing effluent salt concentrations.

Initial onsite testing of a **fluidised-bed phosphate crystallisation process**, based on lime addition and sand seed particles, was not successful with inadequate particle growth and retention on the sand. This failure was thought to be due to high carbonate and magnesium concentrations in the effluent.

This paper reports tests of onsite testing, using the real plant effluent, of a steel pilot scale 18.5 litre stirred crystallisation reactor, operated with (upstream) a carbon dioxide stripping column and (downstream) a clarifier (particle settling). Based on the DuPont "high aspect ratio draft tube crystallisation reactor" (HARD), the set up was operated in double draw-off (discharge and recycle) configuration.

The CO_2 stripping proved in fact to not be necessary for adequate phosphate removal, and was bypassed during much of the trial operation.

Hydraulic residence time was 64 minutes in the reactor and 69 minutes in the clarifier. Phosphate removal at different operating pHs was assessed. The system reduced outflow soluble phosphorus to 1.8 mgP/l at pH 9.8 to 1.3 mgP/l at pH 10.2. An anionic-charged flocculent was found to be optimal to "polish" the outflow, at 1-2 ppm addition, further reducing total phosphorus to ensure respect of the discharge limit and also reducing remaining suspended solids.

The resulting solids thickened by settling to 33% solids, 67% water by weight, after 25 minutes.

Solids production at 0.6-0.8 g/l was much lower than conventional lime addition processes. The authors suggest that this is because the crystallisation reactor ensures that there is very little unreacted lime and enables a lower operating pH, thus reducing calcium carbonate precipitation.

Following these trials, **a full scale installation was authorised for the factory site and completed end 2005**, with two 43 m3 HARDtac reactors, removing 43 tonnes of phosphorus per year in a form which can potentially be recycled as fertiliser.

"Phosphorus removal using novel crystallisation technology", Water Science & Technology, vol. 35, n°12, pages 169-175, 2006. www.iwaponline.com/wst

Phosphorus removal from soy protein wastewater using novel crystallisation technology", Water Science & Technology, vol. 55, n° 10, pages 29-36, 2007

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Japan

Oranges and P-recovery

Lab scale studies show that a gel product based on orange juice waste, after zirconium addition, provides an effective and reusable ion-exchange gel for P-removal from livestock waste waters, and that the phosphate can be released for possible P-recovery for recycling.

The work is based on a bio-waste material generated in orange juice factories, which contains around 10% pectin. This is saponified by treatment with calcium hydroxide (see Dhakal et al, 2005) to produce a gel (Saponified Orange Waste = SOW gel).

Around 100g of orange juice waste was mixed with 8g $Ca(OH)_2$, stirring for 24 hours, filtered, then dried at 70°C for 48 h to produce a gel. This gel was then loaded with zirconium ions Zr(IV), at c. 0.7 mol/kg.

P-removal

The zirconium-loaded gel was tested for P-removal capacity at different pH in thermostated (30°C) shaken beaker experiments, over times up to 24 hours, in pure phosphate solution made from phosphoric acid neutralised using NaOH. 25 mg SOW was mixed in 15 ml of phosphate solution, at 20 – 260 mgP/l. Optimal pH for P-removal was pH 3. P-removal from 0.2 mM phosphate solution was >85% over the pH range1-9, and near 100% in the range pH 2-4.

The effects of other ions on P-removal from 0.2 mM phosphate removal were tested: chloride 0.56 mM, carbonate 0.33 mM, sulphate 0.42 mM. **This showed very little change in P-removal rate in the presence of such ions** for pH < 8. The adsorption isotherms for phosphate were established.

Other ion exchange resins

The P-removal adsorption was compared to that of two commercially available adsorbents (ziroconnium ferrite, zirconium-loaded Muromac XMC 3614). The zirconium-loaded orange waste gel (Zr-SOW gel) showed P adsorption capacity of 57 mgP/g, better than either of these commercial adsorbents (13 and 43 mgP/g respectively). From literature data, certain mesostructured materials such as zirconium sulphate surfactant may have higher P-adsorption capacity than the Zr-SOW gel, many are also significantly lower.

Elution and P-recovery

A 200 mm high, 8 mm interior diameter glass column maintained at 30°C was used for continuous phosphate adsorption tests. The column was charged with approx. 150 mg Zr-SOW gel which had first been soaked in deionised water to swell.

In a first series of experiments, a pure solution of 20 mg/l phosphate solution at pH 7 was percolated through the tube at a flow rate of 5 ml/hour. Some phosphate began to come through the column after percolation of 55 bed volumes (breakthrough) and the column continued to adsorb significant phosphate up to around 800 bed volumes.

To elute the phosphate, the column was first washed with deionised water to remove any unbound phosphate, then percolated with 0.2 M sodium hydroxide NaOH at the same flow rate as above**. This enabled recovery of a solution of phosphate around 8x more concentrated than the original percolated solution**, with elution of around 95% of the adsorbed phosphate. Such a concentration in a relatively clean elution solution would provide a good basis for a P-recovery process.

Real wastewater

The Zr-SOW gel column was tested using real effluent from an experimental livestock station (Saga, Japan). The effluent was percolated as received, that is pH 3.2 and 38 mgP/l). With up to nine cycles, a good performance of P-adsorbtion and elution was observed. **Throughout the column experiments, no significant zirconium leakage occurred**.

"Removal and recovery of phosphorus from water by means of adsorption onto orange waste gel loaded with zirconium". Bioresource Technology, 99 (2008), p 8685-8690.
http://www.sciencedirect.com/science/journal/09608524

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Phosphorus flows

Phosphate resources

Global phosphorus flows

Two 2008 papers examine in detail the overall flows of phosphorus in the world, looking at both natural processes, farming and industry, and also assess the different uses and pathways for the part of these cycles which originates with industrial phosphate production (mined phosphate rock). These papers add to the information presented at the Vancouver 2009 Nutrient Recycling Conference, see *SCOPE. Newsletter* n°

Phosphorus is one of the most common elements on Earth, yet only a very small part is available to natural systems or to man, making it an essential and essentially non renewable resource. The total amount of phosphorus in the world's oceans is estimated at 27 - 840 billion tonnes (mostly in ocean sediments) and in soils at 90,000 – 200,000 MTP (million tonnes of phosphorus).

Phosphorus in agriculture

Total phosphorus annual inputs to cropland are estimated at 23 MTP with removals in crops of 13 MTP and losses in erosion and runoff from cropland of 20 MTP, and a total annual loss from cropland plus pastures of 37 MTP.

Industrial production of phosphates (mining of phosphate rock) is estimated at 19.5 MTP, of which the authors estimate 78% is used in mineral fertilisers and 6% in animal feed supplements. For comparison, the authors estimate natural inputs of available phosphates to land ecosystems worldwide (weathering of phosphate minerals, in particular apatite) at around 13 MTP.

World mineral fertiliser consumption was approximately 14 MTP in 2003-2004, slightly higher than the estimate of phosphorus removed in crop harvests (12.7 MTP, of which approximately 2.9 MTP was consumed in fodder crops fed to animals).

Phosphorus reserves and consumption

World phosphate reserves, that is which could be extracted at prices similar to at present, are estimated at 2400 MTP. The "reserve base", that is which could be extracted using current industrial practices, at 6500 MTP. Compared to the current phosphate mining rate of 19.4 MTP/year, this would mean several hundred years of reserves. However, **current mining rates are 30% lower than in the late 1980s and are expected to rise again in the future with an increasing demand for mineral fertilisers to ensure world food production**, thus shortening the horizons of reserves.

The quality of available phosphate rock reserves is already deteriorating, and P content of ores fell from 32.7% in 1980 to 29.5% in 1996. This will progressively put pressure on both price and supply.

Animal and human wastes

Phosphate use in detergents is estimated by the authors to be 0.86 MTP/year. The authors state that "*it is acknowledged that limiting or banning household consumption of P-containing detergents would not lead to a significant or perceivable improvement in eutrophication*". Phosphorus in farm animal wastes worldwide is estimated at 16 – 20 MTP and phosphorus in human body wastes (faeces and urine) at around 3.3 MTP (of which approximately half is in rural areas, half in urban areas). **Phosphorus recycled** to cropland through crop residues are estimated at 2.2 MTP, and in human and animal wastes at around 4 MTP.

In their second paper, the authors also present a **detailed breakdown of the phosphorus industry** into different product types and production methods, as well as presenting figures of phosphorus rock production and of P consumption by area of the world and by country. A model of industrial flows of phosphorus worldwide is developed using CONSEQUENCE (CSQ). This concludes that:

- **74% of P in mined phosphate rock is used in fertilisers**,
- **19% goes to losses** (in mining, processing) and other uses,
- **7% in total to animal feeds, detergents and other industrial applications**.

"Global phosphorus flows and environmental impacts from a consumption perspective" and "Global phosphorus flows in the industrial economy from a production perspective", Journal of Industrial Ecology, vol. 12, n°2, pages 229-247 and vol. 12, n°4, pages 557-569, both 2008
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