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# SCOPE NEWSLETTER

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## Public Policy

**Europe** p2

### **EU Commission presses for water quality**

*The EU Commission is maintaining legal pressure on Member States to implement EU water quality legislation, and in particular Directives requiring nutrient removal from sewage works and control of agricultural nutrient releases. A UNESCO report meanwhile suggests that Belgium has the most polluted rivers in the world, through the absence of adequate sewage treatment and agricultural manures.*

## Phosphorus recycling

**Belgium** p4

### **Struvite recovery from manure**

*A full-scale pilot struvite recovery plant is operational in Belgium, with a capacity of 15,000 tonnes/year of manure (1,500 tonnes of struvite per year)*

**Kawasaki City Japan** p4

### **P-recovery from sewage-sludge incineration ash**

*Kawasaki City has developed a technology for recovering phosphorus and aluminium contained in the ashes of sewage sludge.*

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### **Published patent**

*Furnace extraction of phosphorus from sewage sludge incineration or carbonisation ash*

**Analysis** p7

### **Total phosphorus in manures**

*Total phosphorus content of animal manures is an important issue in nutrient management, but methods of assessing this currently used are both problematic and unreliable. This paper suggests a more simple analysis procedure.*

**Bio P-removal** p8

### **Magnesium makes bio P-removal reliable**

*Soluble magnesium addition renders biological P-removal from sewage more efficient and reliable, which may offer relevant opportunities for the design of struvite recovery processes.*

**Conference announcement** p17

### **Sustainable land application**

## Water quality

**Estonia** p8

### **Modelled and observed river nutrient loads**

*First results of a GIS modelling study of nutrient loads to the Emajõgi and Võhandu rivers (Lake Peipsi) show results close to observed nutrient loads for three 5-year modelling periods between 1985 and 1999*

**Germany** p10

### **Impacts of nutrient removal on river quality**

*An analysis of effects of sewage nutrient removal on the Ruhr River shows that significant further investment is still needed, that this should improve ammonia-nitrogen levels relevant for drinking water extraction and nitrogen discharges to the North Sea, but that neither the considerable reductions in phosphorus loadings already achieved nor the small remaining reductions will probably prevent algal blooms*

**Ontario** p11

### **Combined effects of light and nutrients in a P-limited lake**

*A 12 week enclosure experiment assessed the combined effects of different levels of light and of nutrient addition (P, N) on phytoplankton and total biomass and their carbon:nutrient ratio.*

**Coastal waters nutrient over-enrichment** p12

### **“Estuaries” special issue: 18 papers from NAS Symposium**

*Most of the USA’s coastal waters have been degraded by nutrient over-enrichment, with nitrogen releases causing the most damage. Point source nutrient releases have been effectively addressed, in particular by sewage treatment, in many cases, but nitrogen emissions continue to be a major issue, and a generalised and increasing problem worldwide.*

**Southern Ocean** p15

### **Iron limitation of marine algae**

*Iron addition to Southern Ocean waters proved to significantly stimulate phytoplankton development, showing that iron limitation effectively controls marine algal growth in these waters in summer.*

**Conference announcement** p17

### **Eutrophication of waters from diffuse sources.**

### Public Policy

#### Europe

#### EU Commission presses for water quality

In SCOPE Newsletter n°46 <http://www.ceep-phosphates.org/scope/articles/scope46/SCOPE46.pdf> we reported EU Commission action against Austria, Belgium, France, Greece, Italy, Luxembourg, The Netherlands, Portugal, Spain and Sweden for inadequate implementation of EU water quality Directives, in particular the Urban Wastewater Treatment Directive 91/271 .

In January 2003 and April 2003 the Commission announced **further actions against 10 Member States**, this time Belgium, Denmark, France, Germany, Ireland, Italy, The Netherlands, Portugal, Sweden and the UK.

#### Obligation to treat urban sewage

**Belgium and France are both facing actions concerning inadequate implementation of the *Urban Wastewater Treatment Directive 91/271***, adding to actions already underway against Greece, Spain and Sweden – see *SCOPE Newsletter n°46*). For Belgium, this concerns “*the lack of a general implementation in the Brussels and Wallonia regions*”. And for failure to adequately designate “sensitive areas”. France has failed to provide information about implementation of this Directive, in particular designation of sensitive areas.

**Belgium, meanwhile, is flagged up as having the dirtiest water in the world** according to a report published by UNESCO in March 2003, the UN’s first *World Water Development Report*, ranking below India, Jordan and nine African states who appear as the other nations with dirtiest water. The OECD is quoted as saying that “*raw sewage still pours untreated into Belgium’s rivers where it mixes with manure from intensive livestock farms*”. Brussels, Belgium and Europe’s capital, hopes to complete its sewage works ... in 2005.

### Nutrient removal

**The *EU Urban Wastewater Treatment Directive 91/271* required sewage to be collected and treated**, with nutrient removal in all conurbations of 10,000 pe = around 6,000 population discharging into “sensitive areas”, defined as any water potentially subject to eutrophication by 1998, **with “appropriate treatment” also for smaller conurbations**. Many Member States are well behind this schedule, but the EU Commission and the EU Parliament have both stated their determination to obtain implementation of this Directive, including in the new Member States (Accession States have signed agreements to implement by 2010-2015). This should essentially resolve the issue of nutrients in sewage.

The European Court of Justice also declared (April 2002) that **Italy has failed to fulfil its obligations under Directive 91/271** by not adequately treating water flowing into rivers upstream of the Po Delta and Adriatic coast, which are classified as nutrient “sensitive areas”, in particular with the absence of sewage treatment for the city of Milan. The Court considered that, although Milan is not itself in a “sensitive area”, the rivers into which it discharges flow into such areas, and so Milan is subject to “sensitive area” nutrient removal requirements.

**Belgium, Denmark, Germany, Ireland and Sweden are accused of failing to adequately implement the *Bathing Water Directive 76/160***, both for failure to ensure that bathing water respected the standards set by the Directive and for inadequate sampling.

Portugal and France face action concerning failure to implement the *Drinking Water Directive 80/778*, The Netherlands under the *Dangerous Substances in Water Directive 76/464*, the UK under the *Freshwater Fish Directive 78/659* and Ireland under the *Groundwater Directive 75/440*.

### Nitrates

**Germany, UK and France face action concerning failure to implement the *Nitrates Directive 91/676***. For Germany and the UK this concerns implementation, in particular inadequate designation of “nitrate vulnerable zones”. France

has already lost a European Court of Justice case concerning nitrate pollution of surface waters in Brittany used for drinking water supply. The EU Commission is now taking further action under the Nitrates Directive, because of the absence of an effective action plan to reduce nitrate pollution in Brittany. If France fails to comply, the Commission may then refer again to the Court and request that fines be imposed.

**These numerous and varied actions show the continuing determination of the EU Commission to obtain implementation of EU water quality legislation by Member States**, in particular to resolve the issue of nutrients in sewage and (Nitrates Directive) to limit the impact of nutrients from agriculture.

The EU has also now published **Guidelines for implementing the *Water Framework Directive 2000/60***, including instructions as to how to implement aspects regarding: analysis of pressures and impacts, identification of water bodies, identification of “heavily modified” water bodies (not subject to the obligation to reach “good water quality” by 2015), ecological assessment of transitional and coastal waters, selection of network and process, monitoring, public participation, GIS, assessment of rivers and lakes, planning process on wetlands. The Water Framework Directive takes the various existing water quality Directives, in particular the urban Wastewater Treatment Directive, as the minimal starting point for implementing water quality and management on a catchment basis.

### **Sewage sludge spreading**

**Switzerland** has now banned the spreading of sewage sludge on farmland, with effect from 1<sup>st</sup> May 2003. The ban initially concerns land used for growing vegetables and animal fodder, and will be extended to all farmland in 2006. Some 60% of Swiss sewage sludge is already treated, and the regulation is expected to result in a further 80,000 tonnes per year being incinerated.

UN World Water Development Report  
<http://www.un.org/Pubs/whatsnew/e03107.htm>

EU Press Release 4 April 2003 “Commission pursues legal action against France and the United Kingdom over EU water laws” IP/03/494  
[http://europa.eu.int/rapid/start/cgi/guesten.ksh?p\\_action.gettxt=gt&doc=IP/03/494|0|RAPID&lg=EN&display](http://europa.eu.int/rapid/start/cgi/guesten.ksh?p_action.gettxt=gt&doc=IP/03/494|0|RAPID&lg=EN&display)

Switzerland sewage sludge spreading ban:  
<http://www.umwelt-schweiz.ch/buwal/de/news/artikel/20030325/00985/index.html>

EU Press release 21/1/2003” Commission pursues legal action against eight Member States over EU water laws” IP/03/84  
[http://europa.eu.int/rapid/start/cgi/guesten.ksh?p\\_action.gettxt=gt&doc=IP/03/84|0|RAPID&lg=EN&display](http://europa.eu.int/rapid/start/cgi/guesten.ksh?p_action.gettxt=gt&doc=IP/03/84|0|RAPID&lg=EN&display)

EU Court of Justice decision against Italy concerning protection of nutrient sensitive areas, 25 April 2002  
<http://www.curia.eu.int/en/actu/communiques/cp02/aff/cp0237en.htm>

EU Water Framework Directive:  
[http://europa.eu.int/eur-lex/pri/en/oj/dat/2000/l\\_327/l\\_32720001222en00010072.pdf](http://europa.eu.int/eur-lex/pri/en/oj/dat/2000/l_327/l_32720001222en00010072.pdf)

### Phosphorus recycling

#### Belgium

#### Struvite recovery from manure

The Fraunhofer Institute for Chemical Technology (ICT), Germany, has developed a process to treat pig manures involving a methane-producing digestion stage followed by solid/liquid separation. The solid fraction is used for compost production, whilst the liquid fraction is **membrane treated** allowing a **high-quality phosphate solution** to be produced, from which struvite can be precipitated, for resale as a fertiliser.



The process was presented at the *Second International Conference on Phosphorus Recovery* in March 2001 and a full-scale pilot is now operational in Peer, Belgium, operational since January 2003, treating 15,000 tonnes of pig manure per year (photo below). Around 100 kg of struvite (magnesium ammonium phosphate = MAP) are recovered from 1 tonne of manure.

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Photo with permission: Mark Adriaensens

#### Kawasaki City Japan

#### P-recovery from sewage-sludge incineration ash

Japan is totally reliant upon imports for phosphorus ores, 80% of which are used in the production of agricultural fertilizers. Kawasaki City collects sewage sludge from four sewage treatment facilities in the city, and disposes of it through incineration. Approximately 14 tons/day of ashes are then produced from the sludge. The ashes are rich in phosphorus, the content of which is expected to increase as sewage disposal technologies are improved. Thus, it is of great importance with respect to the recycling of natural resources to recover phosphorus from sewage ashes.

Kawasaki City has therefore investigated methods for recovering phosphorus from sewage ashes and found that, **if an alkaline solution is added to sewage ashes, phosphorus and aluminium can be selectively eluted** to the solution. Phosphorus and aluminium can be separated from the solution through solvent extraction.

**The extracted phosphorus will be used as a material for fertilisers**, and the aluminium as a material for flocculants used in the removal of phosphorus from sewage.

#### Experimental results

We added nitric acid to sewage-sludge ashes in order to separate contained phosphorus and aluminium in the solution. The contents of these elements moved to the solution were compared with those separated in

an alkaline solution of sodium hydrate. The sewage-sludge ashes were added to water, then mixed with the acid or alkali for one hour at room temperature in order to perform element extraction. The table shows the contents of each filtrate: the concentration of P and Al eluted to the alkaline solution was half that in the acid solution. However, unlike in the acid solution, **heavy-metal elements did not move into the alkaline solution**, while Al and P were selectively extracted.

### Al and P contents in acid and alkaline solutions

	Al (mg/L)	P (mg/L)
Acid solution	3,000	5,100
Alkaline solution	1,900	2,200

**Methods were then investigated for eluting only aluminium from the alkaline solution** containing P and Al. Among various solvents, di-(2-ethylhexyl) phosphate (D2EHPA), a phosphate ester, was identified. Because D2EHPA forms an emulsion in alkaline solutions, the solvent cannot be separated from water under normal conditions. If the pH is too low, the extraction of aluminium becomes very difficult. To ensure successful separation, the pH of the solution was adjusted, and aluminium was eluted to a D2EHPA/kerosine solution, so that the solvent formed a clear layer readily separable from the (aqueous) alkaline solution. The solvent fraction was then reverse-eluted with sulphuric acid and then this solution was allowed to stand. Aluminium was then successfully collected in the form of aluminium sulphate.

**Meanwhile, phosphorus was precipitated from the alkaline solution in the form of hydroxyapatite (calcium phosphate)** by first removing sulphate ions through the addition of calcium chloride, and then adding calcium hydroxide to control the pH.

### **Developed process**

The final process developed is thus as follows. An alkaline solution is added to the sewage-sludge ashes in order to leach phosphorus and aluminium. Then the solvent di-(2-ethylhexyl) phosphate (D2EHPA) is added to this alkaline solution and aluminium is transferred (eluted) into the organic solvent fraction. The organic solvent fraction is then separated from the alkaline (aqueous) solution, and sulphuric acid is added to the solvent fraction in order to recover

aluminium in the form of aluminium sulphate. A calcium source is added to the alkaline aqueous fraction in order to recover phosphorus in the form of calcium phosphate.

**The D2EHPA solvent and sulphuric acid can be recycled in the process.** The recovered aluminium can be used as a flocculent in waste water treatment.

### **Recovered phosphorus**

**The recovered phosphorus compound was 100% citric-acid soluble**, and contained phosphoric acid by 37%. With respect to toxic heavy metals specified by the Fertilizer Control Law, the contents of Cd and As were below the standards, while Ni, Cr, Pb, and Hg were not detected in the available chemical analyses. Thus, the recovered phosphorus compound was of sufficient quality for use in plant-friendly fertilizers, and is an alternative to phosphorus ores.

Assuming that the daily production of 14 tons of sewage ashes contains approximately 6.1% phosphorus, 2.2 tons/day of hydroxyapatite (calcium phosphate) and 0.9 tons/day of aluminium sulphate will be recovered from the ashes. Kawasaki City is pushing forward with a recycling plan utilising sewage-sludge ashes.

*Information from and article in "Water 21" December 2001*

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## Japan

### Published patent

US Patent 6,022,514 published 8<sup>th</sup> February 2000 presents methods for recovering phosphorus from sewage sludge by heating either sludge incineration ash with a carbon source or carbonised sludge (after heat treatment at 400-700°C) in a furnace (1,000 --1,250 °C).

The patent authors indicate that sewage sludge incineration ash can contain a significant amount of phosphorus: **13% P<sub>2</sub>O<sub>5</sub> for polymer coagulated sludge to 22% P<sub>2</sub>O<sub>5</sub> for sludge from sewage works using lime for phosphorus removal.** After

phosphorus recovery by the patent proposed method, the P<sub>2</sub>O<sub>5</sub> content of the ash is reduced to 4.4 – 7.2 %<sup>(1)</sup>, a level which the authors indicate is compatible with use of the material in the cement industry.

(1) The *patent text* refers to phosphorus content but the tables and the numbers quoted suggest that this is in fact expressed as % weight P<sub>2</sub>O<sub>5</sub>.

The authors cite previous Japanese Unexamined Patent Publications (n<sup>o</sup>s 7-251141 and 9-77506) which present **methods for recovering phosphorus from sewage sludge incineration ash by acid treatment** (to dissolve the phosphorus into phosphoric acid) followed

by organic solvent extraction (to separate the phosphoric acid from the process acid), and n<sup>o</sup> 9-145038 in which sludge incineration ash is melted at around 1,400°C with an added carbon source allowing phosphorus to be vaporised and recovered. The presented patent aims to avoid the complexities of solvent extraction and the very high temperatures (and so energy consumption) of the latter method.

The *presented patent* involves using either sewage sludge incineration ash or carbonisation of the sludge after drying at 400 – 700 °C. The ash or carbonisation product is then heated in an oxygen-free furnace at 1,000 – 1,250 °C, either with a carbon source (in the case of incineration ash) or using the carbonised sludge organics as an internal carbon source (in the case of the carbonised sludge).

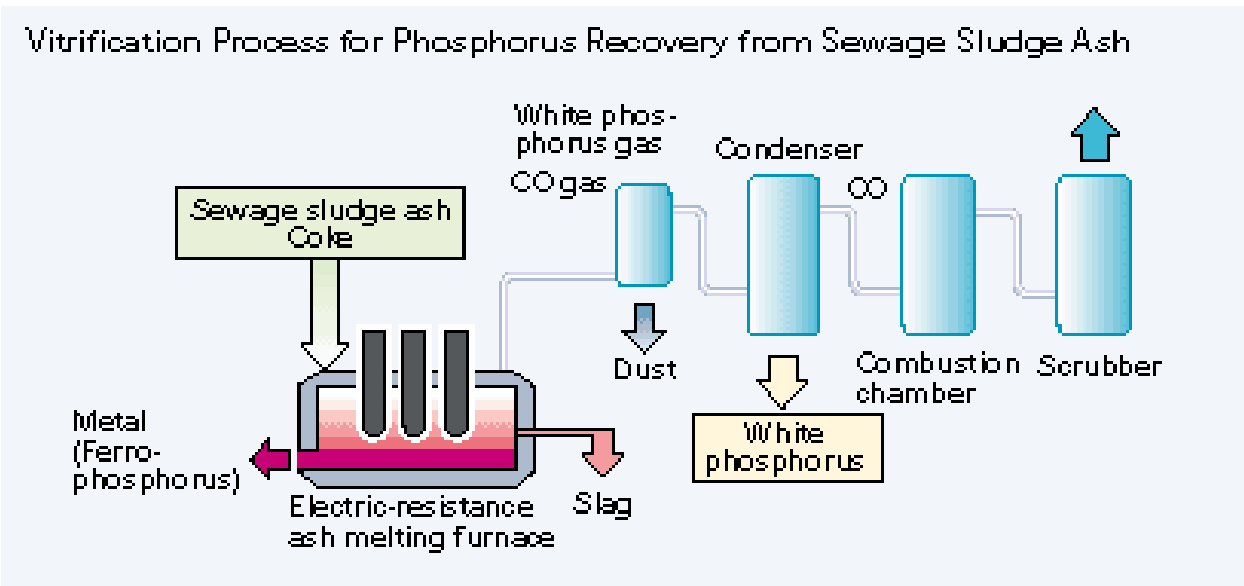
This furnace treatment causes vaporised phosphorus to be released which can be recovered either as elemental phosphorus by condensation in water, or as phosphoric acid by oxidation to phosphorus pentoxide which is then brought into contact with water (these are the classic pathways for harvesting phosphorus from the industrial furnaces using mined phosphate rock).

Where the carbonisation pathway is used, the exhaust gas from the carbonisation process is combustible (containing hydrogen, methane and other hydrocarbons) and can be used to supply energy to heat the carbonisation process. The carbonised sludge at 400 – 700 °C can then be fed directly to the phosphorus recovery furnace, thus reducing the energy input necessary to heat this to 1,000 – 1,250 °C.

**The published patent text includes brief presentations and results for four experimental tests** each using 100g – 200 kg of dried sewage sludge or sewage sludge incineration ash. For two of these, the phosphorus concentration of the phosphoric acid produced is indicated, at 17 and 12.5 %.

US Published Patents can be **consulted on the web** at <http://www.uspto.gov/patft/index.html> (request “patent number search” then enter “6,022,514” in the “query” box or use NKK in text search).

Further information in NKK Press Release <http://www.jfe-holdings.co.jp/en/release/nkk/40-7/art02.html>



### Analysis

#### Total phosphorus in manures

Manures are rich sources of phosphorus, containing complex mixtures of organic and inorganic, soluble and insoluble phosphorus compounds. Much of the organic phosphorus can be associated with plant cellular material which is resistant to digestion processes, having already come through the animals own simple or more complex (ruminant) digestion processes.

However, to **measure the total phosphorus in the manure** it is necessary to break down all the forms present to soluble inorganic phosphate, which can be then measured known techniques. The standard method for doing this at present is aqua-regis digestion of the manure, followed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy).

The aqua-regis digestion requires mixing with 15.5 molar nitric and 10.3 molar hydrochloric acid in a 1:3 ratio, then boiling for 3 hours under reflux. This is potentially hazardous, and requires constant operator supervision. As well as these practical difficulties, the method is known to give erratic phosphorus recovery rates, added to which the ICP-OES method is also documented as giving unreliable results at low phosphorus concentrations.

#### Autoclave digestion and reagent use

**The authors developed and tested a simpler process** for assessing the total phosphorus in manures. This was then tested and results obtained compared with those using the aqua-regis method, both for known and for randomly labelled replicate samples of four different types of manure: broiler chicken litter, layer chicken manure, cow manure, pig slurry and a certified reference material consisting of ground hay.

The new method involved adding potassium persulphate and sulphuric acid to the manure sample, digesting in an autoclave at 776mm mercury pressure 120°C for one and a half hours, then determination of soluble phosphorus using the molybdate-blue reagent addition method.

Different concentrations of sulphuric acid were tested for the digestion phase, suggesting that the lowest concentration used (2 molar sulphuric acid, giving a sample pH of 1.8) was largely adequate. Tests for different levels of persulphate addition for the digestion phase showed that 0.3g addition of persulphate to 40ml liquid samples was adequate for the manures, 0.6g persulphate was necessary for the hay sample (undigested plant material).

**The total phosphorus analysis results using the new persulphate method were significantly higher than for the traditional aqua-regis method for all the manure samples** (similar for the hay sample). For the hay, the results of both methods were lower than the certified phosphorus content of this material – the authors suggest that this may be because of silica content in the grass interfering with the molybdate-blue reagent reaction.

The authors conclude, from the randomised sample analysis results, that the new persulphate/molybdate-blue method **gives reliable and accurate estimations of total phosphorus** in manures, though further work is necessary regarding results for hay. The new method is considerably simpler, not requiring constant operator surveillance during the digestion phase (3 hours in the existing aqua-regis method) and using considerably less hazardous chemicals.

*“A rapid and simple technique for digestion and determination of total phosphorus in animal manures and herbage”, Commun. Soil Sci. Plant Anal. N°33 (9&10), pages 1577-1587, 2002.*

<http://www.dekker.com/servlet/product/productid/CSS>

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### Bio P-removal

#### Magnesium makes bio P-removal reliable

The authors tested the effects of adding soluble calcium (30-90 mg Ca/l) or magnesium (10-20 mg Mg/l) to a bench-scale biological sewage phosphorus removal plant (EBPR) over periods of 50 – 220 days. Influent phosphate (total) varied from 7.7 to 11 mgP/l.

Calcium addition improved bio-P removal performance only slightly (mean P-removal increased from 85 to 90%) and did not resolve problems of performance fluctuation (standard deviation of P-removal reduced only from 20% to 15%, inadequate to ensure reliable effluent P concentrations below 1 mgP/l).

On the other hand, **magnesium addition considerably improved both average P-removal (from 85% to 97%) and above all P-removal reliability** (standard deviation reduced to 4%, enabling 80% P-removal to be achieved nearly all the time).

The authors carried out various analyses (EDXS, STEM) which clearly show that the additional magnesium is being retained in the biological production of polyphosphate granules, within the context of the biological P-removal process. The intracellular polyphosphate granules were based on calcium (Ca), magnesium (Mg) or potassium (K) or combinations of these different cations. Analysis showed that in all the experiments (Ca addition, Mg addition, no cation addition), Mg and Mg+K based granules were the most

common types. During the magnesium addition experiments, more than 50% of the polyphosphate granules were Mg+K based and the calcium content of the granules was significantly lower.

#### Magnesium uptake and release

The authors refer to previous research which shows that soluble magnesium and potassium are both taken up and released during soluble phosphate uptake and release in bio-P processes, whereas calcium-based polyphosphate granules are more stable with calcium not being released during soluble phosphate release phases.

This work suggests interesting roads to explore in the **design of processes for the recovery of phosphate for recycling as struvite** (magnesium ammonium phosphate MAP). Magnesium addition could be used to both improve the efficiency and stability of the bio-P phosphorus removal process, and then be “re-used” on release of soluble phosphorus to contribute to struvite precipitation (which usually requires in any case the addition of soluble magnesium).

*“Stability of enhanced biological phosphorus removal and composition of polyphosphate granules”. Water Research vol. 35, n° 13, pages 3190-3196, 2001.*

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## Water quality

### Estonia

#### Modelled and observed river nutrient loads

Lake Peipsi is a 3,555 km<sup>2</sup> shallow lake (maximum: depth 15 metres) with a 44,000 km<sup>2</sup> catchment shared by Russia, Estonia and Latvia. Population in the catchment is sparse, with only two cities exceeding 100,000 inhabitants (Pskov

in Russia 198,700 and Tartu in Estonia 100,500 inhabitants). Dominant land cover is deciduous, coniferous and mixed forest, interspersed with farmland.

Nutrient emissions to the Estonian part of the lake catchment were modelled for three five-year periods covering 1985-1999. Emissions were modelled for diffuse sources (mainly agricultural activity) and for

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point sources (mainly sewage works and industry, discharging directly into surface waters).

Diffuse emissions were estimated from data covering fertiliser use, livestock numbers and nutrient excretion coefficients per type of animal, crop yields for each crop type, coefficients for nutrient export per mass yield for different crops, land cover, population numbers and connection to different types of sewage works.

Hydrological flows between and residence times in various storage compartments were also modelled using generic maps of soil types, land cover, aquifer and meteorological data, resulting in estimates of direct runoff, shallow groundwater and deep groundwater.

### Point and diffuse emissions

These different models were then combined to **model nutrient transfer and retention** through the hydrological system (soil, groundwater, channel network).

The modelling gives the **estimates of total point and diffuse emissions** (soil surface surpluses) shown in the table below, with the city of Tartu being alone responsible for around one third of point emissions.

Measurements of water nutrient concentrations and of discharge rates (water flows) were available for a number of sampling points from previous studies (Tallinn Technical University). From these, **nutrient loads being carried by the water were calculated,**

by interpolating measured nutrient concentrations to give daily results and multiplying by measured daily discharge.

**Modelled phosphorus and nitrogen loads** for the Emajõgi River at Tartu, the main Estonian tributary to the Peipsi lake (average discharge 68 m<sup>3</sup>/s), coincided reasonably well with observed loads, Simulated loads for the Võhandu River at Räpina, a smaller river (mean discharge 8 m<sup>3</sup>/s) proved higher than observed loads for the period after 1990. The better model performance for the larger Emajõgi catchment probably results from “averaging out” of temporal and local variations in nutrient discharges, related in particular to seasonal spate flows. In general, the decrease of riverine nutrient loads due to the collapse of agricultural economy in Estonia after the independence could be simulated by the model.

**The study provides evidence of the validity of GIS-based modelling of nutrient emissions and loads.**

*“Modelling nutrient fluxes from diffuse and point emissions to river loads: the Estonian part of the transboundary Lake Peipsi/ Chudskoe drainage basin (Russia / Estonia / Latvia)”, Session 9-2, IWA Conference on Diffuse Pollution 30 September – 4 October 2002, Amsterdam*

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<u>Annual emissions:</u>	<u>Point sources</u>		<u>Diffuse sources</u>		<u>Total</u>
<b>Phosphorus (tonnes P)</b>					
1985-1989	309	2%	18 443	98%	18 752
1990-1994	295	3%	8 259	97%	8 554
1995-1999	255	7%	3 209	93%	3 464
<b>Nitrogen (tonnes N)</b>					
1985-1989	1 029	1%	88 800	99%	89 829
1990-1994	990	2%	43 919	98%	44 909
1995-1999	882	3%	29 964	97%	30 846

**Germany**

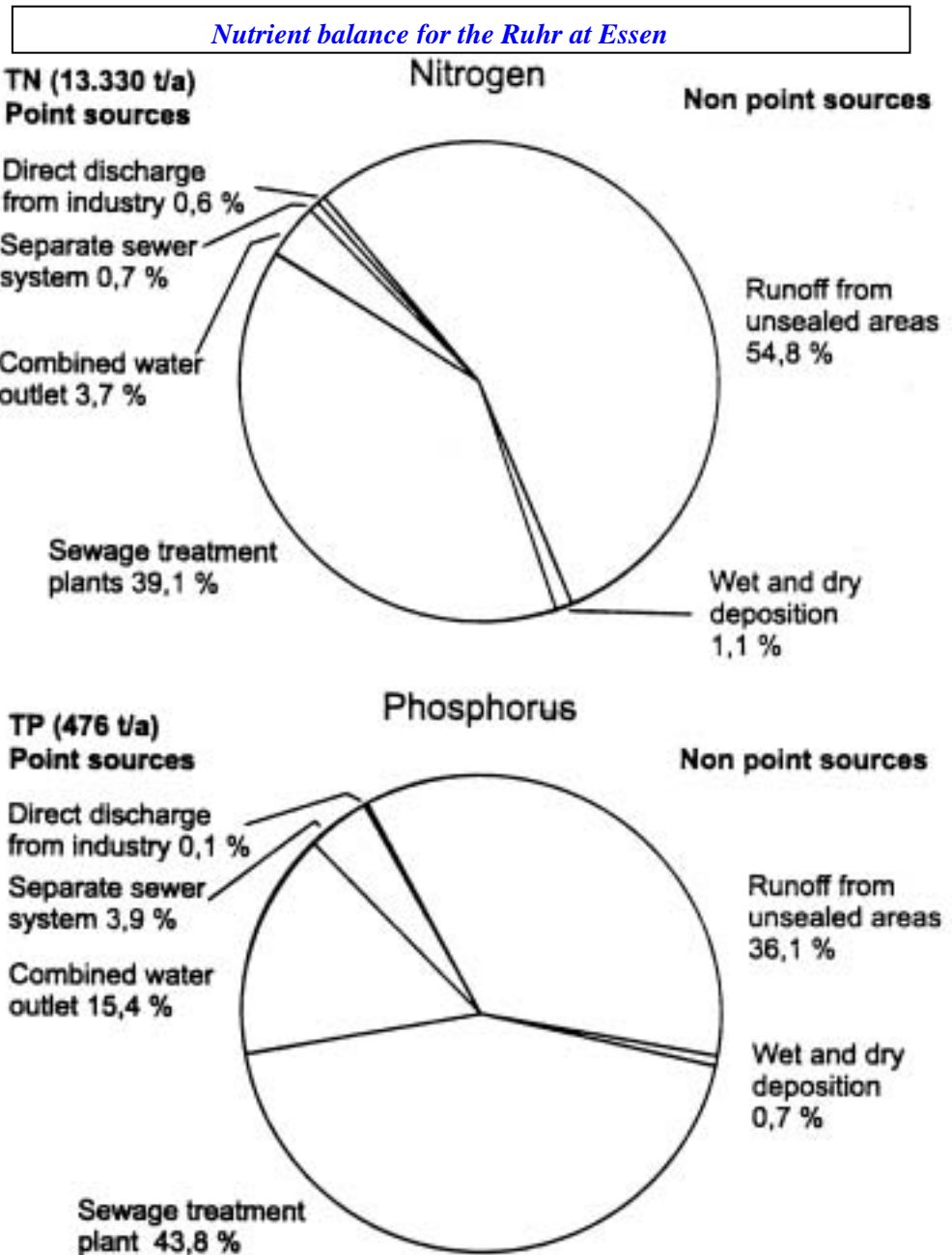
**Impacts of nutrient removal on river quality**

The 217km long Ruhr river drains an industrial and highly populated (2.2 million inhabitants) lowland catchment of 4,500 km<sup>2</sup> in Germany, discharging an average 80 m<sup>3</sup>/s into the Rhine of which it is a tributary (the Rhine then discharges into the North Sea). The river supplies, via artificial groundwater recharge, drinking water for 5 million people and a total of 560 million m<sup>3</sup> per year of water for domestic and industrial (cooling) uses.

By 2001, considerable investments had already been made in the past in sewage collection and treatment, with an **estimated 96% connection of the population to a total of 92 sewage works** (total capacity 3.7 million pe.), plus some 500 stormwater works. At low river flows, 20-30% of the river flow can consist of sewage works discharge.

The middle and lower Ruhr includes 5 dams with residence times in dry weather periods of 1-5 days and these have been and still are subject to algal blooms. **Total phosphorus had been reduced from around 0.8 mgP/l in the 1970's to below 0.2 mgP/l by the mid-late 1990's**, with over this period both the move to P-free laundry detergents in Germany and the implementation of nutrient removal in the river's sewage works (1996 requirements set at: 2 mgP/l in discharges from sewage works of >10,000 pe. And 1mgP/l for those > 100,000 pe.)

**Ammonium-nitrogen concentrations in the river have also been divided to around one third of their 1970's value over this period by investments in sewage treatment (nitrification).** This parameter is considered very important for drinking water extraction (by bank filtration).



Nitrate-nitrogen levels in the river, on the other hand have not significantly decreased over this period (1970's to late 1990's), showing an increase for annual average nitrate concentrations in the 1980's and a return to 1999 to levels near those of 1970-1975, but still a higher level for winter low river flow nitrate concentrations in the late 1990's than in the 1970's. This is attributed by the authors to nitrogen fertiliser use in agriculture.

Investments in sewage treatment over the period 1948 -1999 were estimated to have totalled 2.4 billion €(1995 price index).

### Sources of nutrient loadings

Nutrient balances calculated for the Ruhr showed, predictably, the considerable importance of the sewage works contribution. For phosphorus (total load = 476 tP/year), over 60% came from point sources (44% from sewage works discharges). For nitrogen (total load = 13.330 tN/year), 44% came from point sources.

The authors estimate that, by 1999, EU Urban Wastewater Treatment Directive (91/271) requirements for nutrient removal were met to only 52% with some 1.12 billion € investment remaining necessary to achieve 100% compliance (in particular nitrogen removal and nutrient removal installation, stormwater collection). This is expected to result, by 2006, in further 25% reductions in emissions from sewage works and stormwater releases for nitrogen, and 10% for phosphorus.

This improvement in nitrogen removal is expected to significantly improve the situation for drinking water extraction (ammonia-nitrogen concentrations in the river never exceeding 1 mg/l). Regarding nitrate-nitrogen, the reduction is not expected to improve the Ruhr water quality, given the loadings from non-point sources, but will contribute to the overall wider objective of reducing nitrogen loadings to the North Sea (via the Rhine discharge).

Because the reductions in dissolved phosphorus levels in the river (of the order of 1/10) already achieved over the last two decades have not produced significant effects on algal blooming and eutrophication

symptoms (chlorophyll concentrations), the further expected reduction of -10% is not expected to have significant effects.

*"Nutrient removal in the river basin of the Ruhr – a German case study", Water Science and Technology, vol.44, n°1, pages 15-24, 2001.*

*H. Bode, Executive Technical Director, and R. Klopp, Head of Chemical and Biological Laboratory, Ruhrverband (Ruhr River Association, responsible for water management in the river basin), Kronprinzenstrasse 37, 45128 Essen Germany info@ruhrverband.de*

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## Ontario

### Combined effects of light and nutrients in a P-limited lake

The experiment was carried out from 1st June to 12th August (12 weeks) in Lake 239 of the Experimental Lakes Area, South West Ontario (around 94°W, 49°N, altitude 380m). The lake has been described elsewhere as it has been the subject of extended study (Schindler et al. 1996). The lake is relatively deep (3-30m). Mesocosm enclosures of 25m<sup>3</sup> (8m deep, 2m diameter) made of clear polyethylene and closed at the bottom were used, filled with water pumped from 1.5m depth in the lake from which zooplankton (grazers) were removed by 125µm filtration.

3 different levels of light intensity x 3 levels of nutrient addition (9 combinations) were tested, with 2 replicates for each one. Light levels were 100%, 50% and 25% of natural ambient light, achieved by partial shading. Nutrient addition levels were 1x, 2x and 4x addition of inorganic P at the rate of 5µmolesP/m<sup>2</sup>/day (this being approximately the loading rate of the Experimental Lakes). Inorganic nitrogen was also added with a molar N:P ratio of 75x in order to ensure that the system remained P-limited.

Nutrients were added every 2-3 days and at the same time the water in each enclosure was mixed (throughout the enclosure depth) and 2% of the enclosure volume was replaced by ambient lake water, to simulate lake water renewal. This frequent nutrient addition was considered as

semi-continuous and so close to real nutrient loading conditions.

Every 5-6 days each enclosure was sampled with analysis of water characteristics (dissolved nutrients, chlorophyll<sub>a</sub>) and of particulate C, N and P, seston and algal biomass, nutrient ratios, and of phytoplankton communities. Radioactive labelled carbon was used to assess the fixation of dissolved inorganic carbon (DIC) into biomass and its subsequent release as dissolved organic carbon.

### Nitrogen concentrations

Soluble reactive phosphorus (SRP) levels in the enclosure water were not significantly related to nutrient enrichment levels, and nor was dissolved nitrate (NO<sub>3</sub>-N), whereas NH<sub>4</sub>-N was significantly higher in the high nutrient addition enclosures. **This is indicative that the enclosures remain P-limited in all cases** (phytoplankton sequester all added P). The increase in NH<sub>4</sub>-N in the high nutrient addition enclosures may be related to increased populations of zooplankton in these enclosures (through excretion).

### No effect on chlorophyll or biomass

**The different light intensities and levels of nutrient enrichment showed to have no apparent effect on either chlorophyll<sub>a</sub> (indicator of algal development) nor on total biomass.**

Higher light intensities did result in significantly increased total seston phosphorus (with 60% or more of seston biomass being bacteria). Higher light intensities also increased the C:P ratio in phytoplankton (algae). Both these effects could be expected, as they are indicative of higher primary production with higher light intensity.

**There were no significant correlations between treatments and seston community structure, but nutrient enrichment did result in a significant but moderate increase in the biomass of larger zooplankton.**

The authors explain in introduction that it is increasingly considered necessary to consider the “balance” between energy and nutrient inputs into

systems in assessing possible ecosystem effects, and not just the levels of nutrient inputs.

They suggest that their results support certain aspects of the light:nutrient hypothesis but that further research is required.

**The study results show that in these enclosures the natural lake biocommunity (algae, bacteria, zooplankton grazers) was able to adapt to increases in nutrient enrichment**, both at natural and at reduced light intensities, without showing significant ecosystem modifications (such as algal development).

*“Effects of light and nutrients on plankton stoichiometry and biomass in a P-limited lake” Hydrobiologia 481, pages 101-102, 2000*

<http://www.kluweronline.com/issn/0018-8158>

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### Coastal waters nutrient over-enrichment

#### “Estuaries” special issue: 18 papers from NAS Symposium

“Estuaries”, the bimonthly journal of the Estuarine Research Federation <http://erf.org/>, has published (2002) as a special issue 18 papers from the US National Academy of Science symposium “Nutrient over-enrichment in coastal waters. Global patterns of cause and effect” (2000). These papers cover the question widely including trends in nutrient sources (including atmospheric nitrogen deposition), impacts (on eg. algal blooms, salt marsh ecology, coral reefs), policy and economic issues, positive impacts of nutrient enrichment (fishery productivity), science developments.

Howarth *et al.* set the picture stating that 60% of US coastal rivers and bays have been moderately to severely degraded by nutrient over-enrichment, with increases in both nitrogen and phosphate

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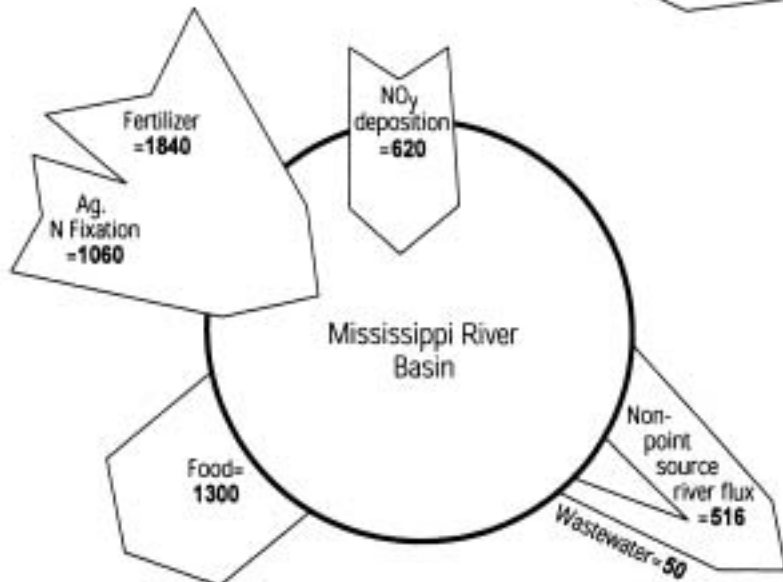
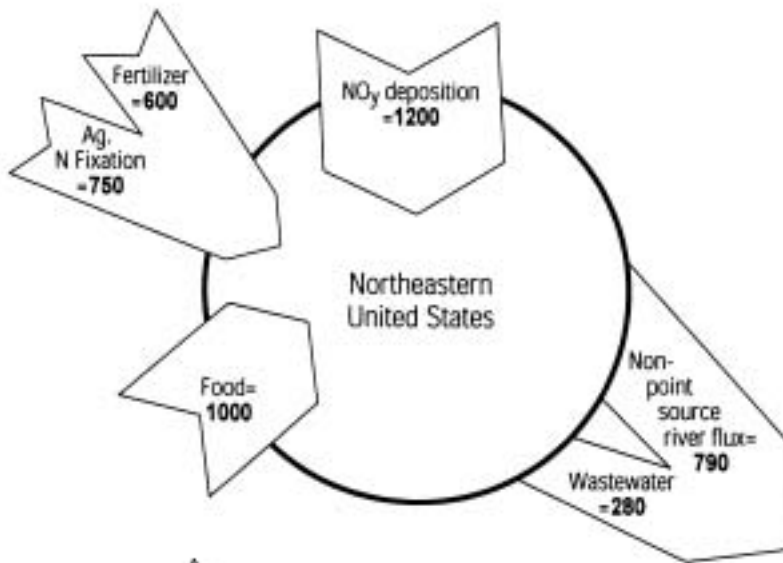
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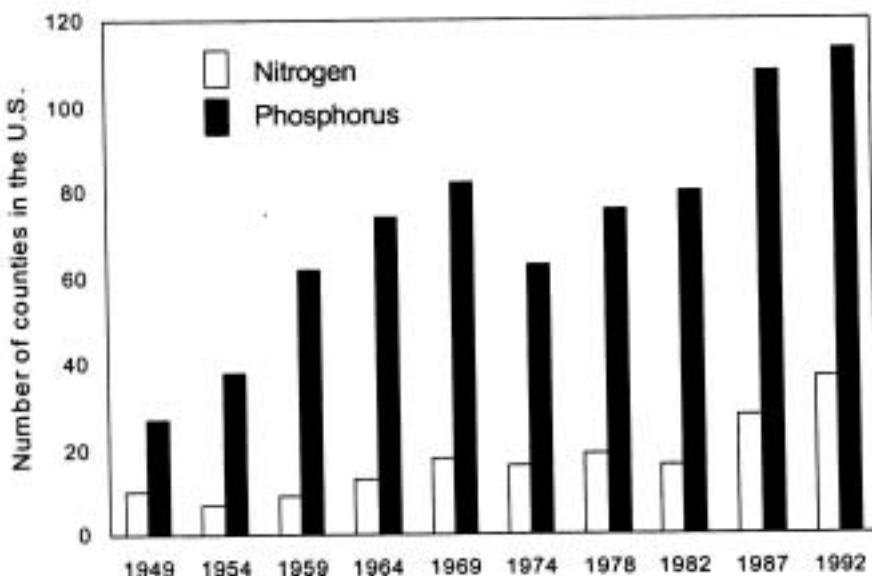
## SCOPE NEWSLETTER

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Number of US counties where manure nutrients exceed potential plant uptake and removal, including pastureland application (in *Howarth et al*, adapted from Kellogg and Lander 1999).



Comparison of anthropogenic nitrogen inputs to nitrogen losses as food and riverine exports (kgN/km<sup>2</sup>/year), for the North Eastern USA and for the Mississippi River basin (modified from NRC2000, based on data in *Howarth et al* 1996).

discharges, but **“for most coastal systems nitrogen additions cause more damage”**. For most waters, nonpoint nutrient inputs are now the most significant, particularly for phosphorus, because of improved sewage treatment. By 1996, sewage was estimated to contribute only 12% of total US nitrogen releases to coastal waters.

Regional nitrogen budgets vary considerably in the USA (see diagram) but with both agriculture and atmospheric deposition playing important roles. **Nitrogen discharges in the US have been increased 4-8 times by human activity**, and are continuing to increase for reasons which vary from one region to another, including both intensification of agriculture and increased atmospheric deposition (related to fossil fuel burning). Phosphate discharges have been generally stable or small increases or decreases over the last 30 years, with increases in phosphate fertiliser use being balanced by reductions in point sources (improved sewage treatment).

Faeth and Greenhalgh explore the synergies between limiting nitrogen discharges and greenhouse gas emissions. **US farmers have dramatically increased fertiliser use since the mid-1960's**: +150% for nitrogen, reaching 11 tonnes by the 1990's, and +25% for phosphorus, reaching a peak of 5.1 million tonnes in 1979 before falling somewhat. US National Research Council analysis (1993) showed that around 40% of N and 60% of P applied in fertiliser in the USA is not taken up in crops.

**Agriculture is responsible, through methane and nitrous oxide emissions only (ignoring agricultural fossil fuel use and changes in soil carbon content), for about 12% of US greenhouse gas emissions**. The paper shows that changes in land use and tillage practices can contribute both to reducing greenhouse gas emissions and to reducing nitrogen discharges, with nitrogen emission reduction policies in some cases giving up to 25% reductions in agricultural greenhouse emissions.

**Anderson et al examine the relationship between nutrient enrichment of coastal waters and harmful algal blooms**. In many cases, algal blooms have been linked with nutrient over-enrichment, and have been reduced when nutrient

discharges have been limited. In other cases, harmful algal blooms (toxic algae, or nuisance algae producing foams, mucilage or other problems) have been linked to changes in the ratios between nutrients (N:P, N,P:Si or N,P:C) but the effects of changes in ratios appear to differ widely in different circumstances. In some cases, nutrient levels do not appear to be a contributing factor to harmful algal blooms. The author concludes that effects are highly species specific, and that the relationship between nutrient loadings and harmful algal blooms remains very poorly understood.

**Turner compared world commercial production of nutrients (in fertilisers, atmospheric releases, other products ...) to the Earth ecosystem's natural production: +0.03% for P, +0.41% for N, +0.73% for C (from Kaiser 2001)**. The author indicates that, on a molar basis, world N fertiliser use is 50 times higher than for P. This relatively high N loading results in N:P ratios increasingly higher than the Redfield ratio (biological requirements), leading to disruptions of the diatom – zooplankton – fish food web both more frequently and over wider areas.

**Conley et al. present experience from Denmark where an Action Plan decided in 1987 aimed to reduce total nitrogen loads to surface water by 50% and point source phosphorus sources by 80%**. For municipal sewage works, targets were defined in 1990 to reduce N discharges from 18,000 to 6,600 tN/year and phosphorus from 4,470 to 1,220 tP/year. This corresponds to biological N removal in all plants > 1,000 pe and P removal in all plants > 5,000 pe (down to 1.5 mgP/l). The Action Plan, including a recent extension, is estimated to have cost around 470 million € to the agricultural sector and 1,100 million € for domestic sewage treatment investments.

**This Plan has been successful for point sources, with reductions of 74% for nitrogen from sewage treatment plants and 90% for phosphorus**. By 1999, 81% of total N loads to surface waters came from agricultural sources, 11% from natural background loads, and only 8% from point sources. Diffuse sources of

phosphorus have also become the significant load to coastal waters.

Nixon and Buckley present a somewhat different viewpoint on nutrient enrichment, presenting evidence from a variety of sites, ranging from the Nile delta to Denmark, Scotland and the Baltic, showing that **increased nutrient inputs usually result in increased fish productivity, as increased primary production “feeds” up the food chain.** The authors emphasise that this does not remove the need for concern about nutrient over-enrichment, and that specific issues such as shifts in species of fish (from benthic to pelagic, for example) may occur, but that the economic consequences (positive) of increased fisheries productivity related to nutrient inputs to coastal waters cannot be ignored.

*Estuaries*, <http://estuaries.olemiss.edu/> vol.25, n°4B, August 2002, pages 639-900. Dedicated issue “Nutrient over-enrichment in coastal waters: global patterns of cause and effect”. Containing 18 papers, selected from the 49 papers and 11 oral presentations at the US National Academy of Science Symposium of the same title, Washington D.C., 11<sup>th</sup>-13<sup>th</sup> October 2000, see [http://erf.org/newsletter/W00\\_SCOR.htm](http://erf.org/newsletter/W00_SCOR.htm).

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### Southern Ocean

#### Iron limitation of marine algae

Since the late 1980's, scientists have suggested that iron may be a limiting nutrient in vast areas of the world's oceans, rather than phytoplankton growth being limited by dissolved nitrates and/or phosphates, or sometimes silicon. The “SOIREE” (Southern Ocean Iron Enrichment Experiment) has now provided large scale evidence that this is indeed the case.

**The late Dr John Martin (Moss Landing Laboratory) first succeeded in accurately determining low iron concentrations in the sea – not easy given the pervasive presence of iron in steel in ships, laboratory equipment, wires and so on! - showing that these were indeed low enough to be limiting, and suggested that iron supply to ocean waters could be related to climate change (by limiting phytoplankton CO<sub>2</sub> uptake).**

Experiments onboard ocean research vessels showed that adding iron to seawater could enhance

phytoplankton growth, and two in-situ experiments near the Galapagos islands in 1993 and 1995 then showed the effect in the sea.

The SOIREE experiment was designed to test the theory on a large scale, by adding iron to a 50 square kilometre area of ocean. **In February 1999 (summer), 1.7 tonnes of iron (in around 8.7 tonnes of iron sulphate FeSO<sub>4</sub>·7H<sub>2</sub>O) were added to the 50 km<sup>2</sup> “patch” of seawater over 7 days. The phytoplankton response to the increased iron concentrations was studied over a period of 12 days. The resulting bloom was seen in satellite imagery obtained 42 days after the initial fertilisation.**

The site studied (61°S, 140°E, in the Southern Ocean 2,000 km SW of Tasmania) does not receive iron in dusts from nearby continents. It was selected to be representative of large areas of circumpolar waters with high nitrate – low chlorophyll levels. The site had a mixing depth typical of these waters (50 – 70m), but relatively low horizontal current, resulting in low dispersion of the iron-fertilised patch of water.

#### Nitrogen and phosphorus levels

In the mixed surface layer at the site, nitrate and phosphorus levels were relatively high (around 25 and 1.5 μM respectively), dissolved silicate was somewhat less elevated (around 10μM), dissolved iron levels were low (around 0.08μM) and chlorophyll-*a* concentration was 0.25 mg/m<sup>3</sup>. Phytoplankton were dominated by pico-eukaryotes (50% of chl-*a*) with diatoms also present (20% of chl-*a*). Various physiological and biological observations were indicative of iron limitation.

#### Fertilisation

The waters of the 50 km<sup>2</sup> patch were fertilised by four additions of iron sulphate. The iron was diluted in seawater and added at approx. 15m depth. The four iron additions were calculated to add respectively 3.8 nM FE, 2.6 nM Fe and 2.5 nM Fe to the 50 km<sup>2</sup> patch (total iron added 8.7 tonnes of FeSO<sub>4</sub>·7H<sub>2</sub>O). At the same time, 500g of SF<sub>6</sub> were added to label the fertilised water and enable the movement and dilution of the “patch” to be monitored.

After iron addition, dissolved iron concentrations were comparable to those found in iron-rich zones of the Atlantic polar front, but after 2 days they decreased rapidly, probably as a combined result of

biological uptake and dispersion. Further iron was therefore added on days 3, 5 and 7. When the iron additions were stopped (after day 7), levels decreased to around 1 nM Fe and remained around this levels until the end of monitoring on the site (day 13).

### Algal response

A small but detectable increase in photosynthetic competence ( $F_v/F_m$ ) was measurable immediately after each iron addition, whereas phytoplankton development measured by chlorophyll-*a* levels only began to increase after days 3-4. Chlorophyll-*a* levels increased consistently over days 3-4 to 10-11 to a peak of nearly 120 mg chl-*a*/m<sup>3</sup>. Chlorophyll levels in a controls area of ocean outside the fertilised patch showed no significant increase over the same period.

However, biological indicators of iron limitation (slower rates of iron uptake, decreases in phytoplankton flavodoxin levels) did not decrease until days 5-7.

The rapid phytoplankton development following iron fertilisation resulted in an increase in chlorophyll significantly greater than that of phytoplankton carbon (cellular carbon/chlorophyll ratios halved over the 13-day study). **Overall, net phytoplankton growth more than doubled and phytoplankton carbon tripled.**

The phytoplankton development resulting from the fertilisation caused a species shift in species towards a diatom dominated bloom. This change will facilitate phytoplankton biomass increase, as these larger species are less susceptible to grazing.

**Satellite observations of the patch of ocean 42 days after the first iron fertilisation showed that the bloom was still present, with chlorophyll-*a* concentrations up to 3 mg/m<sup>3</sup> spread over a ribbon-shaped area of 1,100 km<sup>3</sup> of ocean. This suggested that a significant amount of the added iron had been maintained in the surface waters.**

### Carbon sink rate

Despite the increase in chlorophyll levels resulting from the iron fertilisation, carbon loss processes were not observed to increase significantly, although there was some development of small zooplankton grazers. Accumulation of phytoplankton carbon was estimated to account for around two thirds of iron increased primary production, suggesting that **around 800 tonnes of carbon were accumulated as a result of the addition of the 1.7 tonnes of iron Fe.**

However, the bloom continued to develop after the 13 days of monitoring (as indicated by the satellite observations after 42 days) and could thus have continued to contribute considerably to carbon accumulation.

The authors conclude that this experiment provides unequivocal evidence of the role of iron in controlling phytoplankton primary production in the Southern Ocean. It does not however provide proof that iron fertilisation would increase the rate of carbon fixation (CO<sub>2</sub> sink), because increased downward export of carbon particles from the productive surface layer was not assessed.

The authors suggest that the study site is representative of 75% of polar waters in the Australian-Pacific sector of the Southern Ocean in summer. The satellite observations following the study, in March, were at a period when light levels were already 50% lower than peak summer (December) levels, suggesting that algal growth may be iron-limited (rather than light limited) for up to 8 months of the year.

*"A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization". Nature, vol. 407, 12<sup>th</sup> October 2000, pages 695-702 and*  
[http://daac.gsfc.nasa.gov/campaign\\_docs/ocdst/soiree.html](http://daac.gsfc.nasa.gov/campaign_docs/ocdst/soiree.html)

*P. Boyd and other authors. Correspondence : Edward Abraham, National Institute of Water and Atmosphere, Greta Point, PO Box 14-901, Wellington, New Zealand*  
[e.abraham@niwa.cri.nz](mailto:e.abraham@niwa.cri.nz)

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### Conference announcement

#### Eutrophication of waters from diffuse sources.

The 7th International Conference on Diffuse Pollution and Basin Management (**DiPCon**) will take place 17-22nd August 2003, Dublin

<http://www.ucd.ie/~dipcon/dipcon.htm>

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### Conference announcement

#### Sustainable Land Application Conference



January 4-8, 2004  
Wyndham Palace Resort and Spa  
Lake Buena Vista

Objectives: Review fundamental and specific reactions of constituents in non-hazardous wastes (manures, biosolids, and effluents)

Improve understanding about contaminant reactions in soils, emphasizing the commonalities of reactions among wastes

Synthesize multi-disciplinary information and characterize the "state-of-the science"

Identify high priority and critical research needs

Promote interdisciplinary approaches to solving societal problems of waste disposal

## The SCOPE Newsletter

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

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

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

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