
SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - United Kingdom
Eutrophication management strategy

The UK Environment Agency has issued a consultative report entitled "Aquatic eutrophication in England and Wales" which describes the causes and impacts of eutrophication, outlines a proposed strategy for assessing and managing eutrophication and seeks the views of interested parties on the proposed approach.

The Environment Agency defines eutrophication as: *"the enrichment of waters by inorganic plant nutrients which results in the stimulation of an array of symptomatic changes. These include the increased production of algae and/or other aquatic plants, affecting the quality of the water and disturbing the balance of organisms present within it. Such changes may be undesirable and interfere with water uses."*

===== Phosphorus sources =====

The report indicates the % contribution of the main sources of phosphorus entering surface waters in the UK:

- agricultural 43%
- human and domestic wastes in sewage 24%
- detergents 19%

The report estimates that 70% of total nitrogen input to inland surface waters is from diffuse sources (agriculture, precipitation and urban run-off, in order of decreasing magnitude).

The report underlines the magnitude of nutrient inputs to surface waters in the UK, related to high population density and agricultural activity: the UK has the third highest phosphorus loading to surface waters of the EU/EFTA nations.

===== Measuring eutrophication =====

The UK Environment Agency uses six "viewpoints" for measuring the state of the environment:

- land use and resources
- biological populations, biodiversity
- compliance with standards and targets
- "health" of environmental resources
- changes at long term reference sites
- aesthetic environmental quality

The report underlines the importance of assessing changes in water bodies' states over time (ie. measurements of changes from a baseline state estimated by "hindcasting").

For rivers, where a well established network of monitoring sites exists, trends in nutrient concentrations and loads can be established and relationships between dissolved oxygen concentrations and algal and plant growth indicate the impacts of eutrophication.

=====**Catchment approach to management**=====

The Environment Agency proposes a management strategy based on partnership and consultation of the different sectors involved in water management and use, and on a catchment approach.

Within each catchment area, the establishment of a Local Environment Agency Plan (LEAP) will include defining whether or not eutrophication is identified as a local priority. Where this is the case, a local Eutrophication Control Action Plan (ECAP) will define **actions regarding point sources and solutions to deal with diffuse sources such as changes in farming and forestry practices.**

=====**Phosphorus standards**=====

Ecological targets, taking into account a "reference" condition and corresponding to the **optimal chemical and biological quality that could be expected in a given water body**, are considered to be the long term tool for assessing eutrophication status. This approach will be a requirement of the EC Water Framework Directive.

Pending the development of such target systems, the Environment Agency proposes **interim standards for phosphorus in standing and running fresh waters:**

	Standing µg/l total P¹	Running µg/l SRP²
oligotrophic	8	20
mesotrophic	25	60

meso-eutrophic	-	100
eutrophic	85	200

1 – annual geometric mean total phosphorus

2 – annual mean soluble reactive phosphorus

The report indicates, however, that **such national standards should be applied with caution and should not prevail over site-specific standards** derived from scientific understanding of a particular water body. In particular, the attainment of phosphorus targets is likely to bring ecological benefits only in cases where phosphorus is limiting. The use of "hindcasting" techniques may assist in defining achievable targets for given sites but need to be studied carefully.

The above standards can be used for screening out actions which are unlikely to provide benefits. If the full range of available nutrient control techniques is not capable of bringing concentrations down to levels close to the adopted standard, then such control actions are unlikely to be justified.

Environmental Issues Series – Aquatic eutrophication in England and Wales. UK Environment Agency Consultative Report, December 1998.

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Document available at:

<http://www.environment-agency.gov.uk>

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SCOPE N°31 - 03/1999 - River management
Nutrient targets to control algae

The State of Montana wished to obtain indications relating aquatic dissolved nutrients (DIN, SRP) to algal densities. The State also wished to know whether total nitrogen and phosphorus would provide better management indicators, to obtain indications regarding management options for upstream nutrient point sources and to assess effects on *Cladophora* algae.

The Clark Fork River drains around 57,000 km² of western Montana. The study concerns the upper river, which has nine major tributaries and nine towns. Land use is mainly forest, agriculture and rangeland. **Benthic chlorophyll-a levels in parts of this basin routinely exceed 100 mg/m² (considered undesirable for water quality) and growths of the nuisance filamentous green alga *Cladophora* are occasionally abundant** in nitrogen limited upper sections.

===== 200 site model =====

A series of eutrophication models were derived from analysis of a data base from over 200 river sites from North America, Europe and New Zealand. Total nitrogen and phosphorus (TN, TP), dissolved inorganic nitrogen (DIN), soluble reactive phosphorus (SRP), their ratios, latitude, temperature, stream gradients and light were related to benthic chlorophyll-a (seasonal mean, maximum). Macrophyte development was not addressed.

Percentages of cases where chlorophyll-a levels exceeded 50, 100, 150 and 200 mg/m² were calculated for different nutrient ranges.

===== Total nitrogen levels best indicator =====

Total nitrogen and total phosphorus were found to offer the best correlation with chlorophyll-a.

Relations between season mean values of dissolved nutrients (DIN, SRP) and benthic chlorophyll are characterised by an extremely high variance, so that **dissolved nutrient levels explain only a very low proportion of observed chlorophyll-a variations** (although a closer relationship was shown for the Clark Fork River data than for the general data base).

Regression model results on the general data base showed that control to 275 µg/l of total nitrogen would generally yield acceptable chlorophyll-a levels (mean 100 mg/m², maximum 150 mg/m²). If TP is taken as the variable, similar results would be obtained with TP up to 35 µg/l and TN at 252 µg/l.

A probabilistic method suggests that both seasonal mean and maximum chlorophyll-a levels will be below 100 mg/m² if total nitrogen is below 200 µg/l or TP below 50 µg/l. **The plots confirm that there is a clearer relationship between TN and chlorophyll-a than for TP.**

Finally, a reference station approach was used, looking at nutrient levels at six sampling stations in the Clark Ford River basin where acceptable levels of benthic algae are found. Target nutrient levels were then calculated as the mean summer TN and TP concentrations from five years sampling at these sites. This gave values of 318 and 20.5 µg/l respectively for TN and TP.

To conclude, the authors suggest that maintaining mainstream total N and total P levels below 350 and 30 µg/l respectively should correspond to benthic algal chlorophyll-a density below nuisance levels of 100 mg/m² in most streams.

The authors underline that these targets may not be applicable in all river systems and that targets should always be fixed on the basis of objective local criteria.

The use of TN and TP targets (rather than DIN and SRP) offers the advantage of easier linking with land use practices (for which nutrient input to water is generally measured as TN and TP), thus facilitating efforts to control non point sources.

===== Management control options =====

The authors were unable to develop models to provide management scenarios likely to both lower algal biomass and also reduce *Cladophora* dominance. This is because the low total nitrogen levels considered necessary for chlorophyll-a limitation imply nitrogen limitation, which can correspond to *Cladophora* development.

Regarding nutrient point source management, under normal summer baseline flow conditions, 100% removal of nutrient inputs from one source and a 7 mg/l total nitrogen (TN) limit at another less important source further upstream would suffice to ensure TN levels lower than 350 µg/l throughout the basin. **Further nitrogen loading requirements would be necessary** if target TN levels are to be achieved during critical summer low flows. The authors indicate that the management strategy could also include actions to increase flows during periods of low flow to increase dilution.

"Developing nutrient targets to control benthic chlorophyll levels in streams: a case study of the Clark Fork River", Wat. Res. vol. 31 n° 7, 1997.

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Agriculture

Phosphorus loss from fields by leaching

This paper offers a summary of available literature concerning phosphorus leaching and sub-surface run-off in agricultural soils, particularly in agricultural drainage systems. Current research shows that in a number of cases, phosphorus levels in drainage water exceed surface water phosphorus targets.

The realisation that transport of phosphorus from agricultural soils to surface waters is of significant environmental concern dates from the early 1970's (Ryden *et al.*). Despite considerable research into this area, **non point source pollution of surface waters by agriculture remains a major problem today** (Foy and Withers, 1995; USEPA, 1994; Sharpley *et al.*, 1994).

Systems have been put forward to identify agricultural fields which are most vulnerable to P loss (Phosphorus Index : Lemunyon and Gilbert, 1993; Sharpley, 1995) and models developed to simulate the effects of changing soil and crop management (Sugiharto *et al.*, 1994). **Most of this work, however, has only concentrated on P transport by surface erosion and surface run-off.**

Phosphorus, from mineral fertilisers, manure, sewage sludge and other soil amendments, tends to **accumulate in agricultural top-soil by binding to the more erodible soil components:** clays, organic matter, oxides of iron and aluminium. This paper examines how phosphorus is lost from soils by leaching and sub-surface run-off (movement in shallow, perched, ground water towards nearby streams) and shows that this phenomenon can be significant in certain circumstances, particularly where artificial drainage is accelerating water movements.

Ryden *et al.* indicated (1973) that "*losses of P to subsurface and ground water run-off, although of little significance from an agricultural standpoint, may under certain conditions constitute a significant loss of P from agricultural watersheds in terms of the P enrichments of surface waters... losses of P in subsurface run-off can be similar or even greater than those in surface run-off*". Ryden *et al.* cited eight studies in which dissolved inorganic P in subsurface run-off in drainage systems exceeded 0.01 – 0.05 mg/l.

===== Certain soils liable to P leaching =====

As early as 1933, Bryan, working with deep, sandy soils in Florida, showed that available P 90 cm down in soil under heavily fertilised citrus groves was 48 mg/kg, compared to 6 mg/kg in virgin soil.

Humphreys and Pritchett, 1971, showed that 6-10 years after applying superphosphate fertiliser for the production of slash pine (*Pinus elliottii*), the fertiliser had leached down to at least 50 cm in very sandy soils. This leaching was reduced in finer-textured soils and soils with higher aluminium concentrations.

Fox and Kamprath (1971) showed that phosphorus leaching also occurs in coarse mineral soils with high organic content and in organic soils, presumably because of low soil concentrations of the constituents mainly responsible for P retention: clays, oxides of iron and aluminium, carbonates. **Leaching losses from organic soils was shown to depend on sesquioxide content** (20% P leaching in high sesquioxide conditions, and up to 80% leaching where sesquioxides were below 850 mg/kg).

P leaching has also been shown to occur where phosphorus fertilisers are continuously applied in excess of crop requirements (Schwab and Kulyingyong, 1989; Knudsen and Beagle, 1996).

===== P leaching and manure application =====

The above studies show that P leaching can occur in certain types of soils (deep sandy soils, organic soils) or after long-term over-application of mineral fertilisers. **The most common cause of P leaching is probably, however, the continuous application of organic wastes (manures, sewage sludge)**. This is, in particular, the result of basing manure application levels on crop nitrogen needs, which generates significant over-application of phosphorus.

Studies cited indicate the possibility of P leaching related to long-term application of poultry litter, cattle manure and pig wastes.

Sommers *et al.* studied the effects of 11 years of **application of municipal wastewaters** on two soils and noted significant leaching in a sandy loam but only limited downward movement of P in a clay loam.

In one study in Holland (Breeuswma *et al.*, 1995), more than 40% of areas sampled had total P concentrations in groundwater of > 1 mg/l. This was associated with intensive spreading of dairy, pig and poultry wastes as well as high mineral fertiliser use. Breeuswma *et al.* estimated that leaching losses of P > 0.43 kg/ha would cause groundwater to exceed 0.15 mg/l total P.

===== Agricultural drainage accelerates P leaching =====

The paper summarises 25 studies relating concentrations of P in drain run-off to fertilisation and soil type.

Soluble phosphorus in subsurface drains reached levels of 0.2 mg/l in several cases. In one study (Culley and Bolton, Ontario, 1983) 25% of watershed total P and 50% of ortho-P were estimated to come from subsurface drainage.

In general, the studies summarised show that the highest levels of P are found in drainage ditches fed both by subsurface and surface run-off.

Three recent research projects in Delaware, Indiana and Quebec are reviewed. These studies each look at the effects of long term intensive animal manure application combined with agricultural drainage.

Most of **Delaware's** 270 million broiler chickens are produced in Sussex County, which has around 100,000 ha of cropland. P levels in soils in this area are now rated as optimal (29%) or excessive (53%). Sallade and Sims (1997) found dissolved P levels in drainage ditches ranging from <0.01 – 0.82 mg/l.

===== Winter P release =====

Various studies in Delaware have shown that P solubility tends to increase during saturated soil conditions, generally occurring in the winter and spring. This will increase the potential for P transport at these periods.

Indiana counts around 4.3 million farmed pigs in increasingly intensive operations. Research by Provin *et al.* (1995) has aimed at examining the link between soil P tests (Bray P1) and leaching potential. Cumulative water soluble P in soils correlated well with Bray1 so this test gives a reasonable indication of likely losses to drainage waters. The prediction ability can be further improved by taking into account other measurable soil properties such as exchangeable Ca.

Recent research at 27 sites in the **Saint Lawrence lowlands, Quebec**, showed total P concentrations in subsurface drains from 0.01 – 1.17 mg/l. The research has shown that leached P concentrations are often much higher during rain occurring after a long dry period, and can be related to conditions facilitating rapid penetration of water (soil crevices or pores), thereby emphasising the importance of P mineralisation. Highest levels were recorded after autumn applications of pig manure.

===== Further research =====

The authors identify four areas for further research:

- how to identify fields and watersheds where subsurface P run-off is likely to be significant?
- how to improve soil testing to improve subsurface run-off management?
- how to improve understanding of the hydrologic pathways of subsurface run-off and P leaching?
- what actions can reduce subsurface run-off and how will they impact agriculture?

"Phosphorus loss in agricultural drainage: historical perspective and current research", J. Environ. Qual. 27, 1998.

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Measurement techniques

Soluble Reactive Phosphorus greatly overestimates ortho-P

Soluble Reactive Phosphorus (SRP) is often equated with the free ortho-Phosphate ion. The author shows, however, that the standard molybdenum method used to measure SRP can both hydrolyse organic phosphate compounds and displace phosphates from colloids. Analysis of lake water samples showed that the free ortho-P ions actually represent only a small fraction of the SRP concentration measured.

SRP is generally determined using molybdenum in acid conditions ($\text{pH} < 2$) to produce phosphomolybdic acid, which is then reacted with vanadium, ascorbic acid or SnCl_2 to produce molybdenum blue. The acidity and the presence of transition metal ions can potentially contribute to the hydrolysis of organic phosphorus compounds.

The author used weak ion exchange chromatography to estimate **the extent to which certain organic P species are susceptible to hydrolysis under the conditions of the standard SRP test.** The study examined both commercially available organic phosphorus compounds (representative of those found in the environment) and native P species isolated from an eutrophic lake water sample.

===== Varying susceptibility to hydrolysis =====

Certain compounds (tripolyphosphate, DNA, RNA, inositol hexaphosphate) were resistant to hydrolysis (<2% hydrolysis under the SRP test conditions). Others were hydrolysed to a limited but significant extent (7 – 37%): c-AMP, myo-inositol 2-monophosphate, phosphorylchlorine chloride). 5'-AMP, finally, underwent near 100% hydrolysis.

===== Very little of the SRP in lake water samples was in fact free Ortho-P =====

Natural water samples were collected from Ryan's 2 Billabong, a shallow eutrophic oxbow lake near Albury, Australia. P species fractions were separated using weak ion chromatography.

Overall, very little of the measured SRP in these samples proved to be free ortho-P.

Somewhat less than half the SRP measured was the result of hydrolysis of (unidentified) organic P species, whilst the majority of the measured SRP was associated with a fraction which adhered strongly to ion-exchange resin and could only be eluted at very high pH.

The author suggests that this latter fraction may consist of labile P compounds associated with small organic or inorganic colloids.

Although the eutrophic billabong water samples studied may represent an extreme case, the author concludes that SRP cannot be equated with free ortho-phosphate.

"Reactive organic phosphorus revisited", Wat. Res. vol. 32 n° 8, 1998.

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - France

Variation in sediment phosphorus bioavailability

Physical and chemical properties and bioavailability of phosphorus associated with sediment particles were measured in different flow conditions and at different places in the 33 km² watershed of the Redon river, which flows into the French side of Lake Geneva.

This watershed is mainly made up of glacial rock formations, so that its sediments have relatively similar mineral properties. The watershed is mountainous upstream, rising to 1540m, flowing down into an area of gentle slopes covered mainly by pasture land, and urbanised near its exit into Lake Geneva. Particulate phosphorus runs off into the upstream watershed from cultivated land and forests, and soluble phosphorus enters the river from sewage discharges downstream.

Samples were collected from a variety of sites in the watershed, including river bottom sediment, ditches draining forested areas, ditches in intensively cultivated areas, inlet and outlet of a marshland receiving agricultural run-off and parent watershed soils.

The characteristics of the phosphorus associated with particles from these different sites were assessed using different chemical extraction methods, using a bioassay method to evaluate bioavailability, and using an isotopic tracer to determine the ability of the sediment particles to fix and exchange phosphorus with water.

===== Increasing bioavailability and decreasing fixation

=====

Sediment total P increased towards the river outflow, from 393 mg/Kg upstream, through 562 – 700 in agricultural drainage networks, to 680 – 741 mg/kg in the lower river. **Bioavailability of phosphorus in particles increased significantly more, however, being 1.5 – 2 x higher at the river outflow.** Similarly, the P fixing ability of the sediments decreases significantly.

The total phosphorus content of the particles was thus not a good indicator of phosphorus bioavailability.

Total phosphorus in the agricultural soils (800 – 830 mg/Kg) was considerably higher than that found in the river sediments.

===== Positive effects of marshland =====

The total and organic phosphorus levels in particles upstream and downstream of an area of marshland were shown to be similar (total phosphorus 708 mg/Kg upstream and 781 mg/Kg downstream). However, **the bioavailable phosphorus dropped significantly with the passage through the marshland and the phosphorus fixing capacity increased considerably** (reaching the highest level of all sample sites). This was probably a result of increased calcium carbonate, iron and organic matter levels in the sediment particles.

===== Modification of particles during transport =====

The authors suggest that the properties of sediment associated phosphorus, and in particular its bioavailability, depend not only on the sediment particle origin, but strongly on changes occurring during transport through the watershed. In particular, during periods of low flow, **interactions occur with sources of soluble phosphorus (eg. from sewage)**. This means that spates following low flows will cause sediments to release soluble phosphorus.

For the Redon river, such releases of phosphorus are important: **storm spates following dry periods (mainly summer storms) contribute 40% of exported particulate phosphorus**. The authors suggest that this phosphorus is likely to be relatively bioavailable, further increasing the impact of these releases. They also note that these often occur in the spring and summer when the receiving lake is susceptible to algal development.

"Physico-chemical properties and bioavailability of particulate phosphorus of various origin in a watershed of Lake Geneva", Wat. Res. Vol 32 n° 2, 1998.

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - C/P stoichiometry

Food chain production is phosphorus dependent

Large indoor mesocosms containing algae, microbes and herbivores were used to study food chain response to increased energy input (light). Although the mesocosms with more light showed increased algal growth, this was not transmitted up the food chain and herbivore populations actually showed decreased development.

Two large stainless steel indoor mesocosms (11m high, 0.86m diameter) were used for two runs, with the assignment of the mesocosms being inversed for the second run. Temperature was controlled at 20°C in the upper 2.5m and 10°C below that. Light was supplied with high wattage, near daylight spectrum lamps with constant 24 hour illumination. Incident light levels were 60 and 400 $\mu\text{E}/\text{m}^2/\text{s}$.

The experiments were started by filling the mesocosms with 5 μm filtered water from a Minnesota lake, so that **the water contained the natural microbial community.**

Initial phosphorus levels in the experiments were 0.72 and 0.5 $\mu\text{gP}/\text{l}$, corresponding to the state of the lake's water. Nitrogen was increased artificially by fertilisation (using NH_4NO_3) to 500 $\mu\text{gN}/\text{l}$ to avoid nitrogen limitation.

Phosphorus limited cultured algae *Scenedesmus acutus* were added on day zero and zooplankton herbivores *Daphnia hyalina* on day 4. Initial algal and zooplankton densities are not indicated in the paper. Runs lasted 26 days. Throughout the runs samples of seston, bacterial population, algae and zooplankton were taken to assess biomass/numbers and particulate carbon and phosphorus were also measured.

===== Increased seston carbon and algae, but decreased zooplankton =====

Increased seston carbon and decreased zooplankton biomass in the high-light mesocosms were both statistically significant. **Increased algal biovolume** was apparent at a statistically nearly significant level ($p=0.08$). Total seston carbon closely matched algal biomass, but bacterial biomass and heterotrophic bacterial numbers showed no significant relationship to increased light. **The main seston chemistry**

effect of the increased light was to increase algal carbon.

The decrease in zooplankton was statistically significant both in terms of numbers (individuals/litre) and biomass. Assuming low mortality (since there were no predators present), this indicates that the increased seston carbon and algal development was not passed on to secondary production.

This experiment alone cannot exclude the possibility that the lower Daphnia growth may be a direct result of increased light on grazing behaviour or efficiency, but previous experiments has shown that light does not affect grazing (Buikema 1973).

===== High carbon/phosphorus ratios and lower secondary production =====

It is known that the chemical make up of consumer species varies less than that of primary producers, and in particular that consumers often have a higher nutrient/carbon ratio. Thus ecosystems with low carbon/phosphorus ratios are well balanced to the needs of secondary producers. This is true both for terrestrial and aquatic food chains.

In particular, it has been shown that **algae with high carbon/phosphorus ratios provide a poor quality food for herbivores** such as Daphnia (Sterner 1993).

These mesocosm experiments demonstrate that this can result in a higher energy input to a phosphorus limited system not being transferred up the food chain, or indeed resulting in lower secondary production.

The authors indicate that such phenomena could prove important in the context of global warming and increasing atmospheric CO₂. Anticipated increases in primary production may not result in increases in secondary production.

"Carbon: phosphorus stoichiometry and food chain production", Ecology Letters 1 - 1998.

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Estuaries

Nutrients and grazing

Macroalgal development in coastal ecosystems can be limited by bottom up processes, such as nutrient loading (in particular, anthropogenic nitrogen) and by top-down processes (zooplankton grazing either reducing algal biomass or changing community composition).

This study compared algal and zooplankton populations (composition, number, changes), primary production and zooplankton grazing rates, and nutrient loading, in three estuarine subwatersheds of the Waquoit Bay, Cape Cod, Massachusetts:

Estuary:	Child's River	Quashnet River	Sage Lot Pond
Nitrogen load kgN/ha/year	HIGH 624	MEDIUM 520	LOW 64
Open water area (ha)	13	19	13
Residence time (days)	1.1	0.3	2.2
Depth (m)	1.1	0.5	0.9

Evaluations of macrophyte biomass, macroalgae and zooplankton were carried out from spring through to autumn of 1994 and 1995. Field grazing experiments were carried out in floating field cages during the summer and early autumn of 1993 and 1994.

===== **Field measurement of grazing rates** =====

For these grazing experiments the macroalga *Cladophora vagabunda* was used, because of its abundance in all three estuaries and because previous experiments had shown it to be a preferred food of several zooplankton species. The zooplankton amphipods *Microdeutous gryllotalpa* and *Cymadusa compta* and the isopod *Idotea baltica* were studied: *M gryllotalpa* because it was the most abundant grazer in all three estuaries, the other two species to compare larger zooplankton (up to 15 and 20mm respectively).

Grazing rates were measured using 9 x 9 x 9 cm 500µm mesh cages, with four cages suspended in each estuary, each with 500 mg (rinsed wet weight) of *Cladophera vagabunda* and with different initial grazer populations (control = no grazers, 15 *Microdeutopus gryllotalpa*, 10 *Cymadusa compta*, 5 *Idotea baltica*). Seven such experiments were each run for four days.

===== Algal growth and nitrogen load =====

C. vagabunda grew in almost all of the control cages (except early autumn runs and one case in the low nitrogen estuary) and **growth rates were clearly related to the estuary nitrogen loads**: around 0.1%/day in the low nitrogen water to around 5.4%/day in the high nitrogen water.

The average % nitrogen in the dry weight of the algae at the end of the experiment also varied between the estuaries : it was around 1% higher in the high nitrogen water than the low nitrogen water. This is consistent with other studies in these estuaries which indicate 3.9% nitrogen in *C. vagabunda* collected from the high nitrogen estuary compared to 3.1% in the low nitrogen estuary.

Algal carbon content, on the other hand, did not vary significantly.

The high nitrogen-content algae would be expected to provide a better food source for zooplankton (high N:C ratio). Other studies had already shown that algae from the high nitrogen estuary were a preferred food and/or were grazed faster by different species than those from the low nitrogen estuary.

===== Grazing rates and eutrophication =====

The field experiments showed that grazing rates increased with grazer size, reaching an average of 7.3 mg/individual/day for *I. baltica*. For the two larger grazer species, grazing rate was significantly higher with higher water nitrogen levels (roughly 2x higher), presumably because of the improved food quality of the algae (high N:C ratio, as indicated above). The grazing rate of *Microdeutopus gryllotalpa*, however, did not vary significantly between the three estuaries.

Overall, the increase in grazing rates with higher nitrogen were exceeded by the greater increase in *C. vagabunda* growth rates, so that experimental end weights of algae were consistently higher in the cages in estuaries with higher nitrogen loading.

In most of the experiments, however, *C. vagabunda* was effectively controlled by the densities of zooplankton in the cages. Whilst algal weight generally increased in the control (no zooplankton) cages (with the exceptions indicated above), it generally decreased in cages with zooplankton. An exception was the grazer *M. gryllotalpa* in the high nitrogen estuary which was unable to control algal growth (increases in *C. vagabunda* weight of up to 10%).

===== Estimating primary production and predicting grazer impact =====

As a second stage, the study makes estimations of total *C. vagabunda* production and total grazing, on the basis of total biomass and growth rate estimations, in the three estuaries. These estimates are based on observations of the algal canopy biomass and thickness (light limitation slows or prevents growth), on field measurements of zooplankton species density and on experimental measurements of grazing rates for different zooplankton.

These estimations suggest that there is a potentially significant mid-summer impact of grazers on macro-algae in estuaries subject to lower nitrogen loads.

It was noted that there were only half as many grazers in the medium nitrogen estuary than in the low nitrogen water, and only a half as many again in the high nitrogen estuary. This is thought to be the consequence of hypoxic events and to the change in macroalgal canopy structure: in dense canopies, only the upper 6-10 cm are available habitat for grazers as the canopy becomes anoxic below this depth. Changes in algal community (substitution of macroalgae for eelgrass in high nitrogen conditions) may also deteriorate food quality and make zooplankton more vulnerable to predation.

Grazer abundance increased in all three estuaries through to a July-August peak, corresponding to the period when algal abundance would be expected to be at its highest. In fact, however, biomass surveys indicated no net increase in macroalgal biomass in the summers of 1991, 1992, and net decreases in the summers of 1994, 1995.

===== Conclusions =====

The authors indicate that, for these estuaries, higher nitrogen loadings result in increased macroalgal biomass (3x), loss of eelgrass (*Zostera marina*) and a decrease in zooplankton herbivore abundance (4x lower).

They suggest that grazers (copepods and amphipods) at densities above 4 individuals/litre can play a significant role in controlling macroalgal development.

In the estuaries studied, the comparison of total production and grazing suggests that zooplankton do indeed control macroalgae in the low nitrogen estuary, causing summer algal biomass levels to be stable or even decrease.

In the high nitrogen loaded estuary, however, algal biomass and growth rates are too high, along with significantly reduced grazer populations. The consequence is that grazing is no longer capable of controlling algal biomass.

*"Relative importance of grazing and nutrient controls of macroalgal biomass in three temperate shallow estuaries",
Estuaries vol 21, n° 2, June 1998.*

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SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Scotland

Limits to sewage sludge disposal

139,000 ha of land around Edinburgh, Scotland, were studied to determine the area potentially suitable for sewage sludge spreading: agricultural land with limited slope, suitable soil properties including heavy metal retention, and without risk of water pollution. The resulting area was compared with a projected 70% increase in sludge quantities produced by the Edinburgh area's waste water treatment plants.

Sludge quantities produced by the 750,000 population of the Edinburgh area is expected to reach 21,800 tonnes dry solids/year by the end of the year 2000.

===== Sewage sludge increases =====

As a result of application of the Urban Waste Water Treatment Directive 91/271, sewage sludge production is expected to increase by 2005 by an average of 50% over the EC as a whole and over the UK, Furthermore, marine disposal of sewage sludges is no longer possible as from the end of 1998.

Sewage sludge is a valuable organic manure, providing recycling of nitrogen and (where sewage treatment processes leave it in an agriculturally available form) of phosphorus. It improves soil physical properties, in particular water retention capacity and structural stability.

However, these benefits of agricultural spreading have to be balanced against **potential long-term risks due to the addition of heavy metals and organic compounds such as polynuclear organic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)**. These substance persist in soils so that any addition above "natural" levels must be carefully monitored.

===== Defining potential spreading soils =====

Edinburgh is situated on the South shore of the Firth of Forth and the study examined an area of 139,000 ha situated to the South, East and West of the city.

Data were collected over this area concerning soil types (soil properties, morphology, analytical data) from existing soil maps and soil inventory points. Data were also assembled regarding the slope of land (calculated from altitude contours) and land use.

From these different data, the different areas physically suited for sewage sludge spreading were mapped according to the following criteria:

- slope < 15 degrees
- land use of arable or improved agricultural grassland
- not rocky
- reasonable soil depth, drainage and organic surface horizons.

On the basis of these physical parameters, 57.6% of the land area was potentially suitable for sludge spreading.

Risk of water pollution was then assessed, on the basis of soil hydrology types (which model water movement in the soil, soil properties and hydrology, including depth to aquifer). **Only 4.5% of the total area offered a low risk of both ground and surface water pollution.**

As a final selection criterion, the metal-binding capacity of soils was assessed, on the basis of pH, texture, clay content, organic matter and colour (a surrogate for oxide content). It was concluded that this property was closely dependent on pH. Current regulations suggest that sludge amended soils should be tested for pH only every 20 years, but the changes possible over this time could considerably alter binding capacities for many metals.

Comparison of soil baseline metal concentrations and EC recommended soil metal limits, for zinc, copper, nickel, lead and chromium suggest that sludge applications could not exceed around 25 – 30 years.

===== High land requirement =====

On the basis of predictions for sewage sludge production, the study estimates that sludge would need to be applied to 5.9% of potentially suitable land every year (application of 5 tonnes dry solids of sludge/ha/year).

This figure exceeds the area of land not at risk of polluting water.

In addition, sludge spreading has never before been implemented on such a large proportion of available land in the UK. Severn Trent Water, for example, currently use only 1% of suitable land each year.

"Sewage sludge recycling to agricultural land: the environmental scientist's perspective", J. Ciwem n° 11 April 1997.

W. Towers, P. Horne, Macauley Land Use Research Institute, Aberdeen, UK.

SCOPE NEWSLETTER

SCOPE N°31 - 03/1999 - Switzerland

Biologically induced phosphate precipitation

12 experiments were carried out to assess the kinetics of phosphate precipitation at different pH's (in the range 7 – 8.1) in mixed liquor taken from the aerobic phase of an enhanced biological phosphorus removal sewage plant.

Biological activity was inhibited using formaldehyde and pH was adjusted using sodium hydroxide and hydrochloric acid. Initial soluble phosphate concentrations ranged from 0.68 – 1.46 mole/m³ and soluble calcium concentrations from 1.58 – 2.1 mole/m³. Magnesium concentrations, at around 0.6 mole/m³, varied from 0.19 – 0.56 x those of phosphates. Temperatures were held constant at various levels from 9.5 – 22.6 °C.

===== Effects of formaldehyde =====

After the inactivation using formaldehyde, no aerobic respiration could be detected. Liquor then left for 24 hours showed a clear decrease in soluble calcium concentrations, an increase in potassium, a slight increase in phosphates and no change in magnesium concentrations. It is concluded that the formaldehyde was having a destructive effect on the sludge flocs or micro-organisms, but that polyphosphates were not being hydrolysed (constant magnesium concentrations). Calcium ions were probably being immobilised by carbonate precipitation or other processes, such as absorption onto detergent zeolites.

===== pH and phosphate precipitation =====

pH was adjusted in the different experiments in the range 7 – 8.1, with both rapid increases/decreases and progressive changes being tested. The effects of pH changes on soluble calcium, phosphate and magnesium concentrations were studied.

In all experiments, the soluble phosphate concentration decreased with increasing pH and vice versa. Soluble calcium concentrations showed a strong positive correlation to changes in phosphate concentrations, whereas magnesium concentrations remained nearly constant. **It was thus concluded that soluble phosphorus removal was the result of calcium phosphate precipitation only** (not

struvite = magnesium ammonium phosphate precipitation).

No data is given for ammonium concentrations in the liquor used (taken from the aerobic phase of a pilot biological phosphorus removal plant, JHB mode with separate denitrification of return sludge). This is regrettable, as this parameter would influence the precipitation of struvite. Other literature sources report significant struvite precipitation from waste waters (eg. page 8, Scope Newsletter n° 30).

===== HDP and HAP =====

The removal of soluble phosphates was shown to be strongly dependent on pH and partly reversible. The ratio of change in soluble calcium concentration to change in phosphate concentration was clearly different between experiments with rapid changes in pH and those with slow, progressive pH changes (2.2 compared to 1.6 mole Ca/mole P).

The authors suggest that this may be explained by a two step precipitation of calcium phosphates:

- **formation of a surface complex of HDP hydroxydi-calcium phosphate $\text{Ca}_2\text{HPO}_4(\text{OH})_2$, occurring with rapid pH changes;**
- formation of HAP hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, occurring through transformation of HDP with progressive pH changes and at higher pH's where the solubility product of HDP is exceeded.

The formation of HDP was reversible if the pH returns to a lower value, whereas that of HAP was not reversible under the experimental conditions.

It is also noted that whereas the HDP complex was more easily formed at higher temperatures, HAP was more easily formed at lower temperatures.

===== Crystallisation conditions =====

A dynamic model was established for the crystallisation conditions for the two forms of calcium phosphates, HDP and HAP. Most parameters in this model could be accurately estimated, except the temperature dependence of HAP formation.

Regarding the formation of HDP, an exceptionally high solubility product was found ($10^{-22.6} \text{ M}^5$), significantly higher than literature values. Also HDP formation was shown to be exothermic. These results indicate that it was not a pure compound being formed, but **an amorphous mixed crystal**. The authors suggest that this may be related to the presence of inhibiting magnesium and carbonate ions.

One of the implications of this is that, in typical waste water conditions (concentrations of soluble calcium 1 – 2 mole/m³, pH 7 – 7.7), precipitation of the HDP complex will only occur at relatively high soluble phosphate levels: for example, around 25 mole P/m³ at pH 7.6 and 10°C or at pH 7.4 and 20°C.

Such high soluble phosphate concentrations are typically encountered after the anaerobic release phase of biological P removal.

===== Up to 40% partly reversible phosphate removal =====

Phosphate precipitation gave soluble phosphorus removal rates of up to 40%. For example, in experiment B1, phosphate concentration was reduced from around 1.1 to 0.7 mole/m³ after 4 hours by progressively increasing the pH up to 8.1 at a temperature of 15.8°C.

This phosphate removal was however partly reversible. For example, in experiment A2, phosphate concentrations were reduced from nearly 0.8 to around 0.65 mole/m³ during two abrupt pH increase phases to 7.7, but returned to around 0.77 mole/m³ when pH was returned to around 7 (total experiment time 7 hours).

The authors conclude that, when the solubility product for the HDP complex is exceeded, phosphates are irreversibly fixed as HAP calcium phosphates at a rate of 0.5 mole P per day.

"Kinetics of biologically induced phosphorus precipitation in waste water treatment" Wat. Res. vol. 33 n° 2 – 1999.

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