SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Australia

Most river P from soil erosion

The Australian National Eutrophication Management Programme (NEMP) has published a statement representing the agreed scientific consensus on sources and transport of phosphorus to inland surface waters. The aim was to provide managers with generally accepted guidelines for identifying action priorities. This statement is summarised below.

The statement was the conclusion of a joint workshop convened by NEMP (National Eutrophication Management Programme) and Environment Australia. The findings of the workshop have recently been published as an "occasional paper" by the Land and Water Research and Development Corporation.

The scientists at the workshop concluded that although phosphorus is a natural element in water, and essential for animal and plant life, levels currently reaching many rivers are too high.

Agricultural fertilisers and agricultural effluent have for a long time been considered the main sources of phosphates in rural environments, typical of many Australian rivers. Point sources such as sewage, intensive livestock production, irrigation and stormwater collection systems can be the major source in urban areas. Overall, **diffuse sources of phosphorus are the dominant component in most Australian catchments.**

========= Soil erosion main source =========

However, only in certain local circumstances (intensive agriculture, urban areas, poorly adsorbing sands) are the above sources the main input to rivers: **most phosphorus in Australian catchments derives from soil erosion, in particular caused by water.**

Transport of phosphorus from diffuse landscape sources can occur in both dissolved and particulate form.

Storms are the cause of most of the transport of phosphorus from land to rivers, when soil is eroded from hill-slopes, from the beds and banks of gullies and streams. Heavily grazed lands, irrigated areas, intensive livestock farms and horticultural areas are particularly at risk.

In the Murray Darling Basin, for example, gullies are widespread. The phosphorus associated with soil particles in these gullies is generally from natural sources and not from fertiliser use. Although much of the soil erosion which caused gully formation occurred several decades ago, active gullies continue to input phosphorus to rivers.

In river systems such as the Murray- Darling Basin, most of the diffuse-source phosphorus input comes from gully erosion and stream bank collapse of readily dispersible soils. **It is very likely that most of the phosphorus is "native" phosphorus coming from subsoils as a result of weathering of naturally occurring phosphorus containing rocks.**

The message to river managers is that the priority must be to reduce soil erosion, and in particular to stabilise gullies and stream banks. Gully stabilisation can often be combined with farm land improvement. Stream bank stabilisation can be achieved by physical management, by riparian vegetation and by limiting livestock access to stream banks. Other management practices, such as reduced or contour tilling or buffer strips can also slow down soil erosion towards rivers.

Nonetheless, fertiliser run off should not be overlooked in some cases, such as coastal plains and irrigated field areas. Fertiliser phosphates are soluble and so more readily available to algae than phosphorus bound to soil erosion particles.

The "occasional paper" explains phosphorus transport mechanisms in different soil types and summarises case studies from a number of Australian catchments. The paper concludes that **management practices developed for phosphorus control in the Northern Hemisphere will have only limited success in Australia, because of the high proportion of surface water phosphorus which comes from soil erosion, soil macropore and sub-soil transport in gullies.**

LWRRDC (Land and Water Resource Research and Development Corporation) Occasional Paper 16/98 "Phosphorus in the landscape: diffuse sources to surface waters", published following the NEMP May 1997 workshop; and LWRRDC "Rivers for the future" magazine, n° 8, summer 1999.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Lot River, France

Nutrients, sewage treatment, algal growth

For 57 reaches (total 297 km) of the lower Lot river (from Entraygues to the Garonne river confluence), data was collected and behaviour modelled for flow, light, temperature, nutrient concentrations and inputs (point and diffuse), phytoplankton biomass and zooplankton grazing. The model established was then used to assess the impact on algal biomass of scenarios for sewage treatment.

The portion of the Lot considered has 10 affluents and 66 sills, constructed to facilitate navigation, many with lateral canal systems and hydroelectric installations. The river can be considered to be of the Mediterranean type, with heavy autumn and winter precipitation and a hot dry summer. The August flow often naturally falls below 10 m^3/s compared to an annual mean of 150 m^3/s. Dams built above Entraygues are intended to maintain summer flow above 16 m^3/s. However, the series of sills in the lower river generate high residence times and low flow rates in certain reaches, leading to algal growth problems. Chlorophyll levels can reach 60 µg/l and cyanobacterial blooms *(Microcystis*) occur.

A **model of algal growth** was developed on the basis of water monitoring from July – October 1991 and 1992, and from available river board data (Agence de l’Eau Adour Garonne). Monitoring was carried out with two samples taken a few kilometres apart in order to "frame" a water mass, and then repeated as it moved along the river (movement calculated from flow rate data and morphology).

========= Nutrient inputs =========

The model developed also takes into account:

- sedimentation, estimated as a function of water velocity and depth
- release of nutrients from sediments light (meteorological data)
- water temperature
- light extinction, estimated as a function of depth and of chlorophyll concentration
- phytoplankton, calculated as overall biovolume, ignoring species variations
- internal nutrient storage in phytoplankton and nutrient excretion
- nutrient concentrations: P-PO 4 , N-NH 4 , N-NO 3

- dead organic matter
- nutrient inputs - point loads: estimated by multiplying the shore population of each reach by average P, N and BOD values, adding industrial sources, and weighting by estimated sewage treatment efficiency (presence or absence of treatment plants, % connection, % removal of P, N, BOD)
- nutrient inputs – diffuse sources: estimated for each reach from ground use and nutrient export coefficients (Pallo, 1993)
- loss of phytoplankton through sinking, considered as related to turbulence and estimated by water velocity
- zooplankton grazing, estimated by a constant predation factor applied to reaches with high grazer densities

========= Loss of biomass in deep reservoirs =========

The model simulates changes in summer algal biomass and nutrient levels ($P\text{-}PO_4$, $N\text{-}NH_4$, $N\text{-}NO_3$) along the stretch of river studied (57 reaches). After calibration, the model simulations correctly reproduce evolution of these variables for a broad range of low river flow rates (9 – 94 m^3/s).

Maximum biomass is reached in the middle reaches studied. The biomass produced upstream is proportional to available nutrients. Downstream, on the other hand, in deeper reservoir reaches, light does not penetrate into much of the water column and so algal respiration exceeds production. The reduction of phytoplankton biomass in lower reaches is accentuated by sinking (due to lower water velocities) and by zooplankton grazing.

Nutrient concentrations are low in the middle and lower reaches, due to consumption by algae, despite sources in the lower reaches. Comparison of predicted and measured nutrient levels suggest that **point source inputs entered in the model are probably underestimated.** This may be explained by tourist numbers increasing summertime populations and sewage outflows well above the annual average levels.

========= Sewage treatment scenarios =========

The model developed was used to assess different scenarios for sewage treatment and nutrient inputs:

0: average **current situation**
1: improved sewage treatment – **application of the EC Urban Waste Water Treatment Directive 91/271**

1.1 – to conurbations > 10,000 pe.
1.2 – extension to conurbations > 5,000 pe.
1.3 – extension to conurbations > 2,000 pe.

2: **malfunction** of existing sewage treatment
3: **doubled N and P inputs** in lower reaches and stratification of deep reaches

The EC Directive 91/271 requires (in sensitive areas) that the population of conurbations > 10,000 pe. be connected to sewage treatment with at least 70% nitrogen and 80% phosphorus removal. This should be compared with the present situation of only one third connection to sewage works and mean sewage works efficiencies of 36% for nitrogen and 20% for phosphorus removal.

The **application of the EC Directive** to conurbations > 10,000 pe. (scenario 1.1, affecting five sewage works) brings a **considerable decrease in algal biomass** in reaches below Toirac (reach 13), perceptible as far as Fumel (reach 50). Scenarios 1.2 and 1.3 (conurbations of > 5,000 and > 2,000 pe.) affect respectively one sewage works and one further effluent but do not bring significant further improvements.

Scenario 2, malfunction of existing sewage works, makes practically no difference compared to the present situation, probably because of the very low current connection to and efficiency of waste water treatment.

The third scenario (3) attempts to reflect nutrient levels which proved higher in observed data than those predicted by be model: it assumes bursts of nutrient release from sediments resulting from stratification in the river, as well as higher point inputs. This scenario predicts algal peaks in two lower reaches (Le Temple, reach 54, and Villeneuve, reach 55) which may explain blooms noted in later years (but not in 1991 or 1992 which were relatively rainy summers with higher than average flow rates).

"A model of phytoplankton development in the Lot river (France). Simulations of scenarios." Wat. Res. vol. 33, n° 4 1999. Pages 1065-1079.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Mediterranean

Nutrient transport in the Rhône river

The nutrient input (nitrogen, phosphorus, silicate) of the Rhône river to the Mediterranean Sea was assessed for the year June 1994 – May 1995 using a combination of nutrient concentration measurements and flow data.

The Rhône is the main river flowing into the western basin of the Mediterranean, with an average annual flow rate of 1690 m^3/second, compared, for example, to 200 m^3/s for the Ebro or 234 m^3/s for the Tiber.

The Rhône's input thus has a direct influence on primary production in the Golfe du Lion where 50% of primary production can be attributed to river inflow and associated land runoff.

Total nitrogen input from the Rhône is calculated by the authors as 115,000 – 127,000 tonnes N/year with:

- 92 - 96,000 tonnes N as nitrate (around 80%)
- 1,300 - 1,500 tonnes N as nitrite
- 6,300 - 6,700 tonnes N as ammonium
- 9,700 - 9,800 tonnes N as dissolved organic N
- 5,300 - 12,700 tonnes N as particulate N

Total phosphorus input to the Mediterranean from the Rhône is calculated as 6,500 – 12,200 tonnes P, of which only 25 – 45% is soluble, the remainder being particulate.

SCOPE editor’s note: It is interesting to compare this figure with an estimate of total phosphorus in sewage in the Rhône catchment. We assume 0.7 kg/year/habitant P from human sources (published figure) and 0.35 kg/year/h P in detergents (1996 consumption, France only). The population of the Rhône catchment in France is 9 million (Agence de l’Eau) and approximately 3 million in Switzerland. ***Total sewage phosphorus load (before sewage treatment) would thus be approximately 11,500 tonnes.*** *(By comparison with estimated soluble in the Rhône), this suggests that 60-80% of sewage P load is removed either in water treatment and/or in river sedimentation.*

The particulate P in the Rhône was found to be:

- 5 - 34% iron bound
- 43 - 56% calcium bound
- 6 - 28% acid soluble organic
- 11 - 13% NaOH soluble organic

The high particulate fraction of the phosphorus input leads to a significant variation in results between the different calculation techniques (evaluation of total water flow rate or solid flow rate).

Total silicate input is calculated as 135,000 – 139,000 tonnes Si / year.

The authors estimate that the Rhône's mean annual nitrate concentration has increased by around 50% over the last two decades.

They estimate that the Rhône represents around 10 – 20% of the total N and **2 – 6% of total P input to the Mediterranean Sea** and that this nutrient load is significant with regard to the Mediterranean's nutrient balance and primary production.

"The input of nutrients by the Rhône river into the Mediterranean Sea: recent observations and comparison with earlier data". Hydrobiologia 373/374, 1998, pages 237-246.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - USA

Ecosystem ascendancy and nutrient dynamics

Ecosystem ascendancy dynamics were employed to look at flows of carbon, nitrogen and phosphorus between the different compartments of the Chesapeake Bay ecosystem. Amongst other conclusions, it appeared that in summer the overall ecosystem was N limited, but that the nekton were nonetheless P limited. In winter and spring, limitation was mainly related to cycling of both N and P between bacteria, microflagellates and dissolved organic P. In autumn, no clear pattern appeared.

It is now generally recognised that different compartments of an ecosystem can be limited by different factors or combinations of factors. Thus, **where primary production may be limited at a given time and context by one particular nutrient, other compartments of the ecosystem may be limited by other factors.** Network ascendancy, developed from information theory, involves examining the dynamic exchanges of different factors between different ecosystem compartments, as well as sources and sinks.

This paper reports results of a decade long study of the Chesapeake Bay, USA. The authors evaluated the magnitude of exchanges of N, P and C along 122 pathways (between 36 ecosystem compartments), as well as 55 exogenous flows of carbon and external nutrient inputs.

========= Carbon and nutrient cycles =========

Relatively separated carbon cycles were found within on the one hand the planktonic compartments, and on the other the benthic and nektonic compartments. Transfer between these cycles was mainly through sessile and nektonic filtering organisms. The "microbial loop" for carbon proved non-existent, **bacteria acting essentially as sinks transferring carbon out of the system.**

Nutrient pathways were evaluated by assuming that net production from a given compartment has a fixed nutrient:C ratio characteristic of the donor species.

Nitrogen was found to be much more actively cycled within the system than carbon. Some 50,000 simple nitrogen cycles were enumerated, compared to only 61 for carbon. Bacteria were very active in cycling nitrogen, to some extent returning it to available forms in the water, but mostly cycling it within sediments.

======== Nitrogen limitation ========

It can be shown that the element available to a given ecosystem component at the lowest levels, compared to stoichiometric needs, will be the element which moves slowest through this component.

Marine systems, such as the one studied, are generally thought to be "nitrogen limited". **The phytoplankton and benthic algae in Chesapeake Bay do indeed appear to be nitrogen limited over the year, but this is not the case for the heteroptrophic ecosystem compartments.**

One noticeable feature, is that **all the nekton compartments prove to be P limited, as are the two planktonic bacterial compartments.** This property may be due to the large relative needs of vertebrates for phosphorus for bones, and of bacteria for ATP/ADP. Sediment bacteria, close to abundant P supplies, tend however to be nitrogen limited, as reduced N is in short supply in the sediments.

Other findings are more difficult to explain, for example P limitation of meiofauna and crustacean deposit feeders, or carbon limitation of the blue crab.

======== Seasonal variation ========

These overall patterns persist throughout the seasons, with some variations. In autumn, the phytoplankton, ctenophores and oysters become carbon limited, which corresponds to the reduction in light available for photosynthesis.

However, despite the relative stability of specific pathway limitations throughout the year, the overall network limiting flows of the ecosystem change considerably between seasons.

In summer, nitrogen is indeed the general controlling factor and overall limitation of the ecosystem can be traced back to the rate of cycling of nitrogen between particulate nitrogen in the sediments and fixed bacteria. Although NH_4 may be plentiful in the sediments, organisms may still be limited by the availability or reduced nitrogen.

In winter and spring, the key controlling mechanism seems to be the "microbial loop". As indicated above, carbon is not cycled, but nitrogen and phosphorus are, between dissolved organic phosphorus (DOP), free bacteria and heterotrophic microflagellates. The DOP pool is most sensitive to microcflagellate excretion and the bacteria are mainly P limited; the microflagellates, on the other hand, are N limited and receive most of their nitrogen from the free bacteria. The phosphorus ingested by the microflagellates is somewhat in excess of their needs and is excreted, effectively fertilising the growth of the P-limited bacteria, their prey. The overall ecosystem limitation thus depends on this bacteria –

microflagellates co-dependency, which itself is limited by both N and P.

In autumn, it is not possible to identify a cycle which defines overall ecosystem limitation. Phytoplankton become carbon (photosynthesis) limited and benthic primary production becomes sensitive to external N inputs. Much of the rest of the ecosystem is essentially sensitive to external P inputs. **Thus in autumn, the system compartments are each differently dependent on external inputs (light, nutrients): all metabolic demands are declining, and the system is in collapse rather than control.**

The authors conclude that the assessment of the role of chemical nutrients in ecosystems requires adequate quantification of the whole system status. **They underline the importance of the dual nutrient feedback control mechanisms** identified in Chesapeake Bay. These internal control systems enable the whole ecosystem metabolism to be maintained and stabilised.

"Nutrient controls on ecosystem dynamics: the Chesapeake mesohaline community. Journal of Marine Systems 19, 1999. Pages 159-172.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Nutrients, zooplankton and algae

Top-down or bottom-up control ?

Algal response to increases in nutrients and in zooplankton populations were tested in 20l carboys suspended in the oligotrophic Flathead Lake, Montana, USA. Algal growth was stimulated by addition of N and P, in some cases by addition of N only, but not by addition of P only. Addition of zooplankton at ambient (oligotrophic) nutrient concentrations did not reduce chlorophyll production, but restoration of natural zooplantkon population concentrations did prevent increased algal development at increased nutrient levels.

The experiments reported were carried out to assess the implications of decreases in zooplankton abundance in the lake resulting from introduction of the invertebrate zooplankton predator *Mysis relicta*. Twenty litre carboys filled with natural ambient lake water and phytoplankton/zooplankton communities were used for four triplicated 5-day experiments in July and October 1987 and in May and August 1988. Zooplankton populations were unchanged or adjusted to around 50% of current lake densities, or to 4x or 7x these densities using a 280 µm sieve to remove or catch and add zooplankton. The authors indicate that these increased **densities are comparable to those found in the lake before the introduction of *Mysis relicta.***

The phytoplankton community was dominated by grazable species (diatoms, small flagellates, chlorophytes, chrysophutes, small monocellular coccal cyanobacteria). Zooplankton mortality was low (never exceeding 15% over the duration of the experiments), so that there were no obstacles to grazing effects.

======== N and N+P response ========

The ambient nutrient concentrations in the lake water used for the experiments varied as follows:

- P (soluble reactive P): non detectable - 0.5 µgP/l
- N (NH_4^+): non detectable - 4.9 µgN/l
- N (NO_3^-): non detectable - 5.8 µgN/l

Simultaneous addition of N and P (to 140 µgN/l and 60 µgP/l) caused significantly increased chlorophyll production (algal development) in all four series of experiments. Addition of only N caused statistically significant algal development in the October experiments, whereas **there was no significant response to the addition of P only in any of the experiments.**

======== Zooplankton control of algal growth ========

Changing zooplankton population densities in the ambient nutrient level carboys had no significant effect on **production to be held below the "control" level** (ie. no nutrient addition, ambient zooplankton densities). In this latter case, chlorophyll concentrations after 5 days were brought down to around 2.5 µg/l compared to 3 µg/l in the "control" and around 4 µg/l for the carboys with nutrient addition and without increased zooplankton.

Initial ambient zooplankton densities varied as follows:

Individuals per litre:

- Caloid copepods 3 - 11.9
- Cyclopoid copepods 3.6 - 5.2
- *Daphnia thorata* 0.1 - 4
- *Bosmina longirostris* 1 - 2.3

The authors conclude that, at current ambient lake nutrient levels (oligotrophic), zooplankton densities make little difference to algal development, probably because densities are so low that grazing pressure is not a major influencing factor. The authors therefore suggest that current management practice of Flathead Lake should concentrate on nutrient abatement (bottom-up control).

In the case of higher nutrient levels (eutrophic waters), top-down controls become more important. In particular, **the experiments show that increasing zooplankton densities can enable control of algal development despite nutrient enrichment with densities of zooplankton comparable to those found in natural ecosystems** (where predation or other factors have not reduced zooplankton populations).

"Role of nutrients and zooplankton in regulation of phytoplankton in flathead Lake (Montana, USA), a large oligotrophic lake." Hydrobiologia 373/374, 1995. Pages 755-763.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Freshwater ecology

Phytoplankton control at high nutrient levels

This paper examines both literature field data and mesocosm experimental results regarding daphnia control of edible phytoplankton. Stable control of phytoplankton at high nutrient levels is generally observed, whereas standard arithmetical predator-prey models would predict large population fluctuations.

Several hypotheses are suggested as possible explanations of this difference between model predictions and real ecosystem behaviour.

McCauley and Murdoch (1990), reviewing field data, concluded that **daphnia and algal populations are generally stable** (with low amplitude cycles) at both low and high nutrient concentrations. Populations are stable up to an algal carrying capacity (K) of at least 3 mgC/l (this is defined as the maximum potential biomass of edible algae in summer, in the absence of competitors and grazers, and is used as an indicator of nutrient levels).

Watson *et al.* (1992), analysing data from >100 northern temperate lakes, showed furthermore that the **populations of edible algae increase by only 1.8x for a 10-fold increase in phosphorus levels.** Inedible algae populations, on the other hand, increase six-fold over the same range (ie. inedible algae increase from 0.05 to 0.3 mgC/l as K increases from 0.3 to 1.2 mgC/l. 20-25% of algae in these lakes are estimated to be edible.)

======== Predator-prey models ========

The authors model calculations are based on field data from four natural lake environments, calculated values for a fifth, and data from a series of experimental tanks at Santa Barbara and Calgary.

- the four lakes were: Lake Maarsseveen (Koning and Dorgelo, 1982), Hall Lake (Taylor, 1981), Lake Constance (Lampert and Schober, 1978) and Lake Washington (Edmondson and Litt, 1982)
- calculated values concerned Eglwys Nynydd Reservoir (based on George and Edwards, 1974)
- the Santa Barbara tanks contained a single edible alga species *Chlamydomonas reinhardii* and the zooplankton grazer *Daphnia pulex* in nutrient rich water (K > 3 mgC/l). In these systems, tanks

without Daphnia moved to become a "pea soup" of edible algae.

- b the Calgary tanks contained a mixture of edible and inedible algae with *Daphnia pule*x.

======== Modelling and algal population stability ========

Basic models of predator-prey population dynamics predict extreme instability in a nutrient rich environment where predation suppresses prey populations below carrying capacity. This is known as the **"Paradox of Enrichment"** and large amplitude cycles are predicted as the prey is periodically suppressed by predation, "escapes" to carrying capacity, is caught up and suppressed again. **This does not, however, appear to actually occur in many ecosystems, and in particular for daphnia / edible algae in nutrient enriched waters.**

Evidence from mesocosms containing only one species of algae and of Daphnia suggests that the stability is inherent to the predator-prey relationship, and is not the result of other factors (competition between species, predation of Daphnia by fish, refuges for algae …)

======== Stable algae control by Daphnia ========

In the natural and experimental systems studied **Daphnia proved able to suppress edible algal populations to well below the limits set by nutrient resources, even in nutrient rich systems.** In the Santa Barbara tanks, for example, the biomass in tanks containing Daphnia are around 1% of that reached in the absence of Daphnia.

Also, Daphnia is strongly food-limited. Daphnia egg clutches in cultures can reach 20 – 30 eggs, but in both the natural and experimental systems, the average clutch is < 1 egg, and even in recruitment drives reaches < 2 eggs.

The authors test four hypotheses for mechanisms which could explain this **stable limitation of algal populations:**

- increased abundance of inedible algae interfere with Daphnia grazing
- Daphnia death rate increases with nutrient enrichment
- Daphnia death rate increases with Daphnia density
- Daphnia grazing rate varies with Daphnia density

All of these hypotheses are rejected, because models using them would predict much higher algal biomass than observed at high nutrient levels. Observations also show that Daphnia death rates do not increase with Daphnia density or nutrient levels.

The authors suggest three other mechanisms which could contribute to stability and merit further investigation:

- inedible algae absorb nutrients reducing their availability to edible species
- limited spatial movement of algae enhances stability through a combined effect of many local populations (meta-populations)
- variation between the Daphnia individuals present contribute to overall stability

"Plankton abundance and dynamics across nutrient levels: tests of hypotheses", Ecology 79(4), 1998. Pages 1339-1356.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Nutrient cycling

Algal response to nutrients dependent on grazer N:P:C stoichiometry

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This comprehensive paper brings together conclusions from a number of recent papers concerning how differences in nutrient element stoichiometry (N:P:C) between algae and grazers in pelagic ecosytems affect consumer nutrient recycling (rate and ratio of elements cycled).

A.C. Redfield *et al.* in 1963 first demonstrated a characteristic elemental ratio between N, P and C in marine phytoplankton, showing that this left a "fingerprint" on the cycling of the major elements 0, N, P and C throughout oceanic and indeed biosphere food webs. This ratio was then shown to be relatively reliable in marine waters, whereas **algal nutrient ratios in fact vary widely in fresh waters.** Since then, there has also been considerable work indicating that the nutrient stoichiometry of grazers is often very divergent from the typical "Refield ratio". Ratios for three typical crustacean grazers are given as illustrations:

- *Acanthodiaptomus pacificus* 240C: 48N: 1P
- *Bosmina longirostris* 151C: 26N: 1P
- *Daphnia similis* 80C: 14N: 1P.

Equally, many studies have looked at grazer nutrient recycling, generally for N in marine waters and for P in freshwaters, but rarely were both nutrients taken into account or their relative recycling rates looked at.

======== Grazer community changes nutrient limitation of algae ========

In the 1980's, papers began to appear suggesting differing cycling rates between N and P and indicating that the grazers *Daphnia* had a much lower P cycling rate when algal P:C ratios were low. In 1988 Elser *et al.* showed that the nutrient limiting algal growth shifted from P to N when the dominant grazer changed from *Daphnia* to copepods, as a result of fish population modifications. Three years later, data was published showing that *Daphnia* have a 2-3 times lower body N:P ratio than copepods.

========= Stoichiometry modelling =========

The authors review models of N:P and C:P stoichiometry effects on nutrient cycling and pelagic ecosystem balance.

Sterner (1990) developed a model to predict the N:P ratio of cycled nutrients as a function of algal N:P, grazer N:P and grazers' ability to retain a growth limiting nutrient. This model illustrated how **grazer N:P ratios affect the relative rate of release of these nutrients back into the water** by the grazers, thus in turn influencing the nutrient regime experiences by algae. **response to nutrients dependent**

Another set of models looks at C:P ratios. Starting with Osten and Ostgaard (1985), these models suggested that the rate of P recycling by grazers would fall with increasing C:P ratios. Olsen *et al.* indeed concluded from experimental data and the model that **for a C:P ratio > 370 *Daphnia* no longer cycle soluble P back into the water.** Urabe and Watanabe (1992) further indicated that P limitation of *Daphnia* development is likely in the natural environment. Elser and Hassett (1994) indicated that algal P:C ratios in many natural fresh waters systems will be lower than P:C ratios for most grazer species. This would significantly limit P cycling, and thus P availability for algae.

========= Dynamic modelling and algal state switches =========

Andersen (1997) extended the static models to look at the dynamic feedback effect that changing nutrient cycling would have on algal nutrient ratio, and thus again on grazer ratios and cycling. **In the case of algal P:N ratios below grazer needs, this will result in relatively lower P cycling, reducing P availability for algae, and thus further reducing algal N:P ratios.**

He concluded that **ecosystems could move between two distinct stable states,** either the different food web levels can adapt with nutrient elements being cycled indefinitely in a limit cycle, or one nutrient can become progressively scarcer, increasing pressure on grazers until they are driven to extinction. Movement between these states depends on given properties of the ecosystem's trophic dynamics (grazing, ingestion and assimilation rates).

When Andresen extended his model to include nutrients held in particles, detritus and bacteria caused the model to predict dynamic chaos The capacity of grazers to differentiate between such particles and algae will significantly affect the real behaviour of ecosystems.

========= Experimental evidence =========

The authors present a literature review and analysis of experimental evidence of differential release of nutrients by zooplankton. Firstly, evidence shows that grazers maintain nearly constant body nutrient ratios despite variations in food ratios. Secondly, other experiments reviewed show that **grazer nutrient release ratios are not constant,** but vary considerably in relation to food nutrient ratios. Statistical analysis of the different published experimental results also shows that zooplankton with relatively higher body ratios tend to cycle less P, resulting in lower P:N ratios in water.

======== Effects on algal growth and blue greens ========

Some evidence shows that **differential nutrient cycling can indeed affect algal growth,** but this would appear to be affected by other factors. In Castle Lake, California, for example, Elser *et al.* showed that the relative severity of N to P limitation of algae was correlated to estimated grazer N:P ratios in two out of three study years.

One interesting application of grazer stoichiometry effects may be on blue-green algae. Grazing by *Daphnia* or other high P:N ratio grazers, which cycle nitrogen relatively faster than P, may be to counter risks of blue-green development by decreasing relatively availability of P.

"The stoiciometry of consumer-driven nutrient recycling: theory, observations and consequences". Ecology n° 80(3), 1999. Pages 735-751.

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SCOPE NEWSLETTER

SCOPE N°33 - 09/1999 - Anaerobic liquors

CO_2 stripping with air for struvite recovery

Experiments were carried out to examine phosphate precipitation rates and forms from the supernatent of anaerobically digested biological nutrient removal sewage sludge. Precipitation was assessed during natural ageing of the supernatent and the inhibiting effects of Mg and bicarbonate ions were studied. Phosphorus recovery as struvite was then demonstrated using CO_2 stripping by aeration to increase pH only (no chemical addition) in a bench-scale batch fluidised bed reactor.

Sludge handling and digestion can pose problems in biological nutrient removal (BNR) water treatment plants, firstly because of struvite (magnesium ammonium phosphate) deposits, and secondly because of uncontrolled release of phosphates into supernatent (which is then recirculated to the BNR system, decreasing nutrient removal performance). This paper studies the phenomenon of phosphate precipitation in the digester supernatent and the **possibility of utilising struvite precipitation to recover phosphates for recycling,** thus resolving these two operating problems.

========= Supernatent parameters =========

The liquid from the dewatering section (belt press) of a 100,000 pe biological nitrification - denitrification sewage treatment works was used, with phosphate concentrations adjusted in some cases to simulate higher P levels in bio-P sludge lines. The supernatent had an initial pH of 7.3 and the following ion concentrations (mg/l):

PO_4 : 18	Mg: 53	Ca: 184

Experimental phosphate concentrations were adjusted to 18 - 180 mg/l.

========= Natural ageing =========

A first series of experiments were run to examine the precipitation of phosphates from digester supernatents over three days of natural ageing.

An increase in pH (to 8.3 - 8.5) and a decrease in phosphate concentration was observed. **Phosphate removal was 81%** from an initial concentration of 164 mg/l and 53% from 18 mg/l. Around 1/3 of the phosphate removal occurred during the first few hours, with levels then declining progressively.

This phosphate removal was thought to result from the increase in pH due to progressive CO_2 loss from the supernatent: CO_2 partial pressure changed progressively over the ageing time from an initial 30-40% (biogas) to 0.035% (air).

The molar depletion of different ions over the ageing period indicated that phosphate removal was due to struvite formation.

======== Supersaturation curves for calcium phosphates and struvite ========

Supersaturation curves for the different starting concentrations of phosphates were established by adding alkali and by air stripping of CO_2.

This demonstrated that the supernatent supersaturation curve existed at a lower pH than for struvite and at a higher pH than for calcium phosphates.

It was concluded that bicarbonate and magnesium ions are inhibiting calcium phosphate (hydroxyapatite) formation.

======== Fluidised bed struvite recovery reactor ========

On the basis of these experimental results, a bench-scale fluidised bed batch reactor was constructed to investigate **struvite precipitation by air stripping only** from supernatents with a phosphate concentration < 50 mg/l.

The reactor had an internal diameter of 58 mm and an expanded bed height of 300 mm. Upflow rates of 1.8 - 5 l/min were tested.

Air stripping for 56% of the time proved to be insufficient for effective phosphate precipitation, whereas continuous aeration (15 l/min) enabled phosphate removal of up to 80% (pH increase to 8.3-8.6) in 120 - 150 minutes.

Quarz sand (0.21-0.35 mm) was used as a seed crystal. Total phosphorus and soluble phosphorus concentrations in the reactor effluent were very similar, showing that **nearly all of the phosphates removed from solution were being precipitated in the reactor and not "lost" as fines** in the effluent. Also, there were no deposits formed on the reactor structure itself, showing that precipitation was only occurring within the solution on the seed crystals.

Ion balance analysis showed that all the phosphates precipitated were in the form of struvites.

========= Feasibility of P-recovery without chemical addition =========

The authors conclude that CO_2 stripping by aeration can be sufficient – without the addition of chemicals - to **enable effective phosphate removal and recovery as struvite from bio-P sewage works digester or sludge treatment supernatents.**

"Phosphate removal in anaerobic liquors by struvite crystallization without addition of chemicals: preliminary results", Wat. Res. vol. 31, n° 11, 1997. Pages 2929-2929.

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Comité Environnement Détergents

The French "Comité Environnement Détergents" officially presented, in Paris on 24th June 1999, the results of several years of research into the potential risk to the environment of detergents. The Committee's research programme was the result of an agreement between the French Environment and Research Ministries and the detergent industry and has involved over 50 experts and scientists and a steering committee grouping industry, regulators, environmental and consumer associations.

The Comité Environnement Détergents research programme has included:

- measuring the removal rate achieved for different detergent components in six sewage works of different configurations and types
- examining the feasibility of a "eutrophication test" using algal growth
- comparing concentrations of different detergent components likely to be found in rivers (using a detailed model of 800 river reaches) with concentrations liable to have an environmental impact (taking into account removal in existing sewage works)

========= Phosphorus removal in sewage works =========

A detailed study of the performance of six different sewage works was carried out in order to assess the removal rate for different detergent components (Cemagref, Groupement d'Anthony, report dated October 1996). The results for phosphorus removal are as follows:

Sewage Works	*Type*	*Load pe*	*Inflow P mg/l*	*Removal of P (%)*
Corbeil-Essonnes	*activated sludge + trickling filter*	*70,000*	*11.5*	*52% removal*
Nîmes	*bacterial bed + trickling filter*	*40,000*	*11.8*	*25% removal*
Vauciennes	*natural lagoon*	*620*	*19.1*	*65% removal*

Villeneuve Saint-Denis	*intensely aerated activated sludge*	*660*	*9.6*	*84% removal*
St-Thibaul-des-Vignes	*trickling filter*	*150,000*	*13.6*	*53% removal*
Bormes-les-Mimosas	*chemical*	*variable (seasonal)*	*10.4*	*87% removal*

The two sewage works using activated sludge treatment thus both achieved over 50% phosphorus removal. The study indicates that nearly 75% of French sewage treatment (% capacity pe.) currently uses activated sludge systems.

The study shows that removal of surfactants in activated sludge sewage works is generally excellent (95% or higher). Removal rates for EDTA and NTA are very variable (these substances are used in P-free detergents in some countries, but not in France, where can nonetheless be present in small quantities from other sources). Borate is not removed at all in sewage works.

========= Environmental exposure =========

The main body of studies presented in Paris involved a comparison between model-predicted concentrations of various detergent components in 800 river reaches (within risk of environmental impact. **The model took into account the exact situation in each river reach regarding population (and thus detergent use, based on national averages) and sewage treatment (connection rate, type of sewage works, operating efficiency).**

The components studied were: LAS surfactants, ethoxylate surfactants, soap, **zeolite, cellulose polymers, acrylic polymers (these three substances are used in P-free detergents),** phosphates, phosphonates, perborate, perborate activator TAED, propylene glycol (solvent used in liquid detergents) and optical enhancers.

For each component, PEC (Predicted Environmental Concentrations) were compared with calculated PNEC (Probable No Effect Concentrations), the latter being estimated from the best available experimental toxicity data with a safety factor being incorporated.

The work so far was entirely based on modelling. Field samples should now be taken in river reaches to confirm the calculated results.

The only products for which the PEC exceeded the PNEC (ie. releases from detergents were **susceptible to have an effect on the environment) in average flow conditions were LAS surfactants, ethoxylate surfactants, soap and TAED activator.** These were also the main components susceptible to reach PNEC concentrations in more than a quarter of hydrological zones in very dry weather conditions.

Wherever PNEC concentrations are exceeded, the Committee concludes that this is **the result of inadequate connection to sewage treatment or exceptionally inadequate design or operation of**

sewage works. A very significant proportion of all components reaching rivers comes from sewage which is not reaching sewage works (populations not connected) or sewage works by-passes (resulting from under capacity or inadequate storm-water retention).

========= Eutrophication "test" ? =========

After consideration, the expert sub-committee of the Comité Environnement Détergents decided that **"with the current state of scientific knowledge, it is not possible to establish a PNEC for eutrophication effects".**

This is coherent with the European Union decision to reject the concept of a "CDV (critical dilution volume) eutrophication" in the EU laundry and dishwasher EcoLabel schemes (both of which authorise phosphate containing detergents).

The Comité Environnement Détergents had work carried out by Cemagref (Groupement de Bordeaux n° 8, report dated December 1995) into the feasibility of designing a standard bioassay test using freshwater planktonic algae to test substances' eutrophication potential. This report concluded that **any such test would have to use algae which had previously been phosphorus starved** or they would not react coherently to phosphate input. Such conditions could not be considered to reflect the situation in a freshwater ecosystem.

The Comité Environnement Détergents report indicates that, in very low flow river conditions, detergent phosphate would currently result in river concentrations above 50 µgP/l in 28% of reaches studied (the Committee indicates that this concentration is given in literature as indicative of rivers' potential trophic level). In these cases, the Committee indicates, **phosphorus reaching the river is the result of untreated sewage or of sewage works not adequately removing phosphorus.** The Committee states that to confirm such results would require constructing **"a model which includes all other sources of phosphorus and the positive implications of the progressive implementation of the urban waste water treatment Directive, and to verify results with field sampling".**

========= Lake Geneva and the Redon =========

The figures presented by the Comité Environnement Détergents complete those previously obtained by the French Environment Ministry Phosphorus Working Group (report dated 17th April 1986) and referred to in the Comité Environnement Détergents' Paris presentation. This report, looking at phosphorus inputs into Lake Geneva and into a small tributary of the lake, the river Redon, concluded that, at the time, **detergents contributed only 7% of total phosphorus inputs to Lake Geneva.** This assumed that 50% of municipal and industrial waste water phosphorus came from detergents, which would correspond to universal use of very high P detergents: the proportion of phosphorus coming from detergents would be significantly lower today.

This study also underlined the **importance of phosphorus release from lake sediments:** the potential quantity being comparable to the lake’s total anthropogenic phosphorus load. Lake sediment phosphorus is related to past phosphorus loads and ecosystem functioning.

A very detailed study was carried out of all the point sources along the Redon river. This study suggested that for this tributary of Lake Geneva, 16 – 20% of phosphorus in the river outflow came from detergents. This was considered to be unrepresentatively high because only one fifth of the Redon catchment’s population were connected to sewage treatment at the time.

This study concluded that **a change in use to P-free detergents in the basin would not lead to measurable differences in phosphorus concentrations flowing from the river into Lake Geneva.**

Report of the ***Comité Environnement Détergents*** *"A contribution to the evaluation of the environmental risks of different domestic laundry detergent components" dated 24th June 1999. Available from: AISD (Association des Industries des Savons et des Détergents), 118 avenue Achille Peretti, 92200 Neuilly sur Seine, France.*

Report of the French Environment Ministry ***"Phosphorus"*** ***Working Group, sub-group "Redon"****, 17th April 1986 "Studies of the Redon river and of phosphorus enrichment of Lake Geneva". Available on request from CEEP.*