
SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - Germany

Deviations from the OECD phosphorus/chlorophyll model

Three shallow soft-water reservoirs in the Wupper River catchment area (Rheinische Schiefergebirge) were studied to assess the possible reasons for chlorophyll levels not corresponding to the OECD model.

This model (Clasen 1981) suggests that chlorophyll-a levels are linearly related to total phosphorus levels. Whilst such a relationship can be found for some reservoirs in this area, the three reservoirs studied gave the following results.

mg/m ³	chl.-a	total P
Brucher	4.4	55
Wupper	8	30
Lingese	22.6	58

===== Fish populations and large daphnids =====

Significantly different balances of both fish and zooplankton grazer populations were identified in the three reservoirs :

- **Brucher** zooplankton was dominated by large red coloured daphnia and diaptomids, whilst fish population was very reduced with no re-stocking
- **Wupper** contained a varied zooplankton population of medium size grazers. The fish population was also varied with cyprinids of large adult size regulated by pike and zander.
- **Lingese**, on the other hand, had a zooplankton community dominated by small rotifers. The cyprinid fish population was very dense with many individuals of small size.

After considering other variants (light, temperature, other nutrients, etc.) the study concluded that a

healthy zooplankton population is the key factor for limiting algal development in these reservoirs, and that large daphnia play a particularly important role because of their grazing efficiency. Overstocking with cyprinid fish prevents the development of such a zooplankton grazing community.

===== Using particulate organic nitrogen for zooplankton assessment =====

The study also looked at possible experimental methods for assessing zooplankton communities. Results were compared between microscope population counts and netting with different meshes.

The use of particulate organic nitrogen (PON) measurements after netting with a 780µm net was suggested as giving a reasonable estimate of the numbers of medium-large zooplankton grazers, and thus the **zooplankton community's grazing efficiency**. Mean PON $>$ 780µm measurements in the three reservoirs studied were, for example, 6.2µg/l in Brucher, 0.1µg/l in Wupper and zero (undetectable) in Lingese.

No algae were ever found in the 780µm net hauls but results need to be corrected by ensuring that carnivorous zooplankton (eg. *Leptodora*) are not present.

"Derivations from OECD predictions in softwater reservoirs: effects of the zooplankton structure". Arch. Hydrobiol. 138-3 1997.

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SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - USA

Estuarine ecology - Copepod grazing affected by toxicants

The short term effects of very low copper concentrations on the grazing behaviour of three copepod species were compared to long term toxicity. Significant reductions in algal grazing were shown to result from sublethal copper levels comparable to those often found in estuaries situated near industrial areas.

Two estuarine copepods (*Acartia tonsa* and *Acartia hudsonica*) and one nearshore marine copepod (*Temora longicornis*) were used for these assays. Both water and organisms were collected from the Mullica River estuary near Tuckerton, New Jersey, USA.

As a first stage, acute toxicity was studied, using 72 hour exposure to copper concentrations in the range pCu 13.1 – 9.51 (ie. 1 part copper per 1013.1 to 1 part per 109.51). This showed that significant mortality resulted only from copper concentrations above approximately pCu 9.8 – 9.5 for both *Acartia tonsa* and *Temora longicornis*.

===== Significantly reduced algal grazing =====

Nine different feeding experiments were then carried out using the three copepods. Bottles containing the copepods were suspended in the estuary or placed in controlled incubators designed to imitate natural conditions (light, temperature). The copepods were first exposed to different copper levels without food for 24 hours, then fed the estuarine diatom alga *Skeletonema costatum* for 2 hours. They were then immediately filtered out, washed and frozen. Analysis for pigments (chlorophyll-a and pheopigment-a) was used as the indicator of food uptake.

Grazing rate was found to increase in copper concentrations in the range pCu 12 – 11, but to significantly decrease at concentrations above pCu 10.1 – 10 (pCu 11 for *Acartia hudsonica*). These concentrations are comparable to those found in estuaries near industrial areas (pCu 12 – 10, Stearns & Sharp 1994), whereas unpolluted estuarine and coastal waters normally have copper levels around pCu 13.

The authors conclude that **levels of copper occurring in coastal waters around industrial countries**

can have significant detrimental effects on the rate of algal grazing by copepods, with consequent deterioration of copepod egg production and destabilisation of population dynamics.

"Sublethal effects of cupric ion activity on the grazing behaviour of three calanoid copepods", Marine Pollution Bulletin vol. 34, n° 12, 1997.

A. Sharp and D. Stearns, School of Civil and Env. Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0355, USA.

SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - Canada

Motor boats and phosphorus

Two similar shallow lakes in the Whiteshell Provincial Park, Manitoba, Canada, were studied to assess the changes resulting from intensive use by motor boats.

The two lakes are similar in depth, temperature, watershed geology and vegetation and both had little external pollution. Brereton Lake, on the one hand, has significant motor boat use, including a water ski club, whilst motor boats are not allowed on Lyons Lake.

Water samples were taken in the spring and autumn from both lakes and a number of criteria compared.

===== Turbidity and phosphates =====

Turbidity was higher in Brereton Lake both in spring and in autumn. However, whilst turbidity decreased in Lyons Lake during the summer (probably by settling of particles brought in with the spring snow melt), it rose in Brereton Lake.

The same phenomenon was noted for both total P and ortho-P in the lake waters. Ortho-P in Lyons Lake fell from around 0.01 mg/l in the spring to around 0.005 mg/l in autumn, whereas levels in Brereton Lake rose from around 0.017 to around 0.021 mg/l.

Visually, Lyons Lake contained nearly 1m of submerged plant growth and little surface algae. Brereton Lake, on the other hand, had developed by the autumn **significant growths of surface algae and a slight water odour.**

The authors indicate that a 10 hp (horse power) motor boat mixes water down to a depth of 1.8m, increasing to 4.6m for a 50 hp motor, and that certain water ski boats are significantly more powerful than this, reaching 300 hp.

In general, the phosphorus entering a lake will accumulate in the top layers of the lake sediments. This takes place particularly through the spring and summer as a result of stratification and of assimilation by plants and algae which subsequently die and sink to the lake bottom. **Mixing by motor boats will**

recirculate this sediment phosphorus back into the water, increasing P levels and enabling algal growth. Motor boat mixing and algal growth both increase turbidity.

The authors conclude that motor boat activity may have significantly increased aquatic phosphorus levels and thus may have effectively switched Brereton Lake to the early stages of eutrophication problems.

"The effects of motor boats on water quality in shallow lakes", Technological and Env. Chemistry, vol. 16, 1997.

D. Nedohin and P.Elefsiniotis, University of Manitoba, Dept. Civil and Geological Engineering, Winnipeg, Manitoba, Canada.

SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - Australia

Sources of phosphorus input

The Suma Park Reservoir is the main water supply for Orange City, New South Wales. It has a history of nuisance algal blooms, with up to 70,000 cells/ml of cyanobacteria being recorded. The only other reservoir in the catchment, spring Creek, has also recorded blue-green algal problems.

A two year study of the catchment was launched in 1995 to assess the causes of and possible solutions to this problem. This concentrated on origins of phosphorus input, since P levels in the reservoirs had been identified as being above those estimated low enough to control algal growth (10µg/l). winter total P concentrations in Suma Park Reservoir varied from 70 to 490µg/l in deep water and 60-100µg/l in surface water.

Several hundred water samples were collected and analysed from 12 sites on the main tributaries and in the reservoirs from August 1995 to January 1996. Further samples were taken during storm flows. Samples were analysed for total P, reactive P and suspended solids. Rainflow and water flow velocities were also measured.

===== High phosphorus levels =====

The results confirmed that all the watercourses and reservoir sites in the catchment showed high P levels (total P > 50µg/l). Examination of these results, however, suggested that this was **not due to anthropogenic sources** :

- there was no significant variation in P concentration with stream length
- no significant variation appeared with point sources, in particular of the concentration up and downstream of Lucknow, the catchment's main urban centre
- the lowest P levels were found at the lower end of Brandy Creek, which flows through the most intensively farmed area of the catchment

The authors conclude that the primary source of phosphorus in the catchment's waters, and in

particular in the reservoirs, is the subsoil. This is made up of tertiary basalt and ordovician igneous rocks, which can contain up to 1% phosphate.

===== Primary phosphorus input is from soils =====

This phosphorus, bound up with fine suspended sediment, is believed to be transported to the waterways from unfertilised subsoil by gully and bank erosion. It is then released from suspended and bottom sediments and becomes bioavailable.

The paper concludes that strategies for reducing algal bloom problems should focus in the short term on better water management in the reservoirs (rather than P limitation) and in the long term on **reducing erosion and sediment transport in the catchment.**

"Phosphorus inputs to a reservoir in Orange, New South Wales" Water, July-August 1998.

Mosharel H. Chowdhury and Dr. Dhia Al Bakri, Orange Agricultural College, University of Sydney, PO Box 883, NSW 2800.

SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - River Wey, England

Sediments - River water

Phosphorus dynamics

Water and sediment chemistry were measured, over different seasons, at 6 sites upstream and downstream of a significant point source pollution (sewage works outflow) on the river Wey in Southern England. Results were compared with a laboratory fluvium channel and mathematical models of phosphorus dynamics were established.

The river Wey is a lowland river with particularly hard water (Ca concentrations of up to 3.9 mmol/l) with a flow of 0.3 – 0.8 m³/s, increasing to over 3 m³/s in winter when the river is in spate. Total phosphorus (TP) concentrations upstream of the sewage works outflow are in the range 2 – 8 µmol/l).

The Alton sewage treatment works (>10,000 pe.), with a discharge flow of 0.1 – 0.15 m³/s, increases total phosphorus levels very considerably to 30 – 80 and periodically over 200 µmol/l.

===== Phosphorus removal to sediments in spring and summer

=====

Measurements at four points from 0 to 6 km downstream of the sewage treatment works showed that **significant amounts of the phosphorus in the discharge was being removed from the water to sediments in spring and summer :**

<u>Total phosphorus in river water (µmol/l)</u>		
	Immediately downstream of STP outflow	average 2-6 km downstream
spring	36.9	20.2
summer	83.0	48.6
autumn	73.7	53.7

This corresponded to increases of phosphorus and calcium contents of the sediments from the winter

through to the summer.

Sediment phosphorus levels fell again in the autumn and winter, as the river bed was scoured by high flows. In the winter, when the river was in spate, total phosphorus levels did not fall as the water moved downstream from the sewage works outflow.

=====**Mechanisms of phosphorus removal**=====

The river water is generally supersaturated with regard to calcite, so that some of the loss of water phosphorus to sediments can be explained by coprecipitation of calcium phosphates with calcite. Changes in the calcium content of the water suggest that only a part (and at most 53%) of the phosphorus reduction is a result of this mechanism. Other processes such as sorption to clay particles, biological assimilation and settling of suspended particles must account for the remaining uptake of phosphorus by sediments in spring ñ autumn.

Mathematical models were established for these different effects and tested and calibrated using a laboratory fluvarium channel. Data simulated by the model for phosphorus take-up by the river bed sediments corresponded closely to those measured in the field (outside the winter period, when the sediments were releasing phosphorus by scouring).

"Phosphorus dynamics in a lowland river". Wat. Res. vol. 32 no. 6 1998.

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SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - Science

New territories of water pollution

New areas of knowledge currently opening up regarding water pollution (pharmaceutical drug contamination of waters, levels of accumulated toxins in sediments) pose significant concerns regarding human health implications, but also raise questions about possible effects on the ecological community and on fish and zooplankton populations.

Now that analysis methods have evolved to allow their detection, pharmaceuticals are being found in both surface water and in drinking water in concentrations of 1 – 100 nanograms/l.

Widespread and variable pharmaceutical drug contamination

The cholesterol lowering drug clorifibric acid has recently been detected in Switzerland in various waters, ranging from rural mountain lakes to rivers flowing through urban areas. This product is not manufactured in Switzerland, so the source would seem to be its presence in sewage, resulting from human use. This drug was found by accident, because of its resemblance to the herbicide Mecoprop, studied by Drs M. Müller and H-R. Buser of the Swiss Government research institution. Concentrations found are comparable to persistent pesticides such as Lindane. (Env. Sci. and Technology, Jan. 1st 1998).

Clofibric acid has also been found for example in Berlin tap water at levels up to 2 ppb (T. Heberer and H-J. Stan, Berlin Technical University, to be published in Int. J. Env. Analytical Chem).

When T. Ternes, working with the municipal water research laboratory in Wiesbaden, Germany, looked for traces of 60 common pharmaceutical drugs, he found 30 of them, not only in raw and treated sewage but also in streams and rivers. Concentrations in the natural environment were generally in the parts-per-trillion range but reached 3 ppb for some drugs. **Residues of drugs detected included lipid-lowering drugs, antibiotics, analgesics, antiseptics, beta-blockers** (to be published in Water Research). There is virtually no literature regarding the potential health and environmental consequences of such widespread exposure.

===== Estrogens and antibiotics =====

There is particular concern about estrogen-like drugs. S. Synder of Michigan State University has found concentrations of human and pharmaceutical estrogens of up to 20 ppt in sewage works outflow. **This would be sufficient to affect fish reproduction.**

Antibiotics also raise concerns, A. Hartmann of the Swiss Federal Technology Institute has found 0.5µg/l concentrations of fluoroquinolone antibiotics in sewage plant outflow. **These levels may be sufficient to potentially develop bacterial resistance.**

In the past, the assessment of pharmaceuticals has concentrated on health effects, with little attention being paid to the risk of ecological impact or to biodegradability. The appearance of methods enabling detection at low concentrations and the discovery of generalised environmental contamination may lead to changes in this approach.

===== Toxins in sediments =====

The six year UK government project "Land Ocean Interaction Study", looking at British pollution of the North Sea, has identified **significant deficiencies in the way water pollution is monitored.**

Firstly, only certain pollutants, such as nutrients and metals, are measured regularly. The lack of monitoring of other substances, in particular organic compounds, may give a misleading picture.

Secondly, **river sediments are rarely sampled.** This study, looking at both floating and river bed particles, found concentrations of toxic chemicals thousands of times higher than those monitored in water. Chemicals discovered included pesticides and organic industrial products.

For example, phtalates, which are estrogen imitating chemicals used in plastics, were found in every sediment sample taken in the Humber river.

Toxic substances in sediments not only pose risks to organisms and plants living on the river bed but can also be flushed into the river water during storms and floods.

"Drugged waters" by Janet Raloff, Science News, vol. 153, 21st March 1998.

"Muddy waters" by Fred Pearce, New Scientist, 16th May 1998.

SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - Landscapes

Buffer vegetation for nutrient removal

Bands of natural vegetation left, or more generally reconstructed, along watercourses can act as very effective buffers removing nutrients from surface and subsoil water and preventing them from reaching the river system.

Although the value of buffer zones in preventing non point source nutrient pollution is now widely recognised, few studies have attempted to accurately identify the mechanisms of nutrient removal functioning or to assess the factors influencing the nutrient removal efficiency of such buffers. Furthermore, **the majority of literature available concerns nitrogen removal, with few figures developed for phosphate removal.**

===== 100% N removal =====

Where measurements have been carried out, 20 – 30 metre bands of riparian forest vegetation have been shown to achieve near 100% N removal, both through uptake by vegetation and through denitrification (permanent removal of nitrogen to the atmosphere). Widely varying rates are reported under differing conditions. However a significant part of the nitrogen removal generally occurs in the first few metres of the buffer zone (edge effect), due to higher carbon availability and plant growth (access to light) in this area. The soil/watercourse interface is also an important area for nutrient retention.

A width of 30 metres is suggested as sufficient to generally ensure near 100% nitrogen removal, with 7 – 20 m being able to offer similar results in the case of dense vegetation.

Removal rates are related to retention times of subsoil water within the buffer zone's underground root system. Because subsoil water flows are generally oblique to the watercourse, these times can be relatively long : for example, 5 – 190 days in a 17m buffer zone alongside the Thames (Haycock and Pinay, 1993).

Forest vegetation is more effective at nitrogen removal than, for example, grassland, but up to 20 years may be necessary to establish a mature forest system.

===== Water levels and hydraulics =====

Nitrogen removal is maximised if the forest roots reach water and the soil is partly water saturated. Low oxygen levels in wetland soils create a demand for nitrates as an electron acceptor, resulting in denitrification and N removal rates significantly higher than rates of plant uptake. This poses problems in areas where modifications of the watercourse have led to a lowering of the water table.

Variations in water levels are also important. Riparian forest is adapted to these natural variations and requires them if it is to develop effectively. Water level variations also ensure varying oxidation in soil, which contributes to nutrient uptake and denitrification, and enable the deposition of sediments in the riparian zone.

Riparian vegetation is also very effective at retaining sediments. Restoring 10% of a watershed's surface area to wetlands can ensure retention of more than 70% of sediments. Sediment retention is largely permanent with vertical accretion rates in riparian areas reported in the 0.13 – 1.5 cm/year range.

===== Phosphorus removal and transformation =====

Phosphorus removal rates may be significantly lower than those for nitrogen. One study suggests 30% P removal in a strip achieving 68% N removal. In this case calcium (39%) and magnesium removal (23%) were also measured. (Lowrance et al, 1984).

However, **vegetation buffers transform phosphorus from soluble inorganic phosphates to particulate organic forms through plant uptake and assimilation** (Johnston 1991). **This significantly reduces bioavailability. Furthermore, buffer strips tend to retain phosphorus during the growing season and release it during the winter which also considerably reduces the potential impact on surface water quality** (in winter, surface waters are not subject to eutrophication problems and high flow rates can wash nutrients downstream).

A Swedish study suggests that a mixture of low forest (brush) and grassland is more effective in retaining phosphorus than either forest or grassland buffer strips (Vought et al, 1994).

===== Landscape and wildlife =====

Creation and protection of riparian vegetation zones is proportionally most effective along headwaters of a water shed : flow rates are much lower here, whilst most of the downstream water originates in headwater streams.

The lack of precise information regarding buffer strip nutrient removal efficiencies suggests that their definition should be largely based on landscape and wildlife criteria, for which they can have a very high value.

An essential point is that of reestablishing suitable hydrologic conditions : preventing lowering of water tables, ensuring that wetlands stay wet, and maintaining natural variations in water levels and flow rates.

"The effectiveness and restoration potential of riparian ecotones for the management of nonpoint source pollution, particularly nitrates", Critical Reviews in Env. Science and technology 72(4) 1997.

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SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - UK

Variations in ecological community response to nutrients

Indices based on measurements of the photosynthetic community have been developed as indicators of eutrophication. The author emphasises, however, that it is difficult to demonstrate that changes in the ecological community are related to nutrient inputs and that other factors can have important effects.

Biological monitoring techniques for assessing the impact of organic pollution have been developed into quite sophisticated multivariate tools, essentially based on invertebrate community indices. **It is generally accepted, however, that these indices do not reliably reflect eutrophication,** and community indices based on measurements of the photosynthetic community have been developed (eg Mean Trophic Rank index, based on the macrophyte community, Holmes 1995, and Trophic Diatom Index, based on the diatom community, Kelly & Whitton 1995, Kelly 1997).

Other models have been constructed which relate point nutrient load changes to final river concentrations (Whitehead et al. 1997). Predictions of the resulting ecological changes, however, have proved difficult, even for lakes, where eutrophication and restoration processes have been widely studied. Rivers provide even more difficult systems to model.

===== Impact of factors other than nutrient load =====

The author suggests that it is misleading to use phytocommunity indices as a proxy indicator of eutrophication. Other factors, and in particular other components of sewage works discharges, affect flora and algae. *Potamogeton pectinatus* can develop in organically polluted water because of increased silting, and *Rhynchostrigium riparioides* and *Amblystegium riparium* were seen to develop downstream of a paper mill with a high BOD effluent which was low in nutrients.

It is not possible to consider nutrients in isolation in a lowland river. The effects of organic pollution, reduced oxygen concentrations, ammonia and suspended solids must also be taken into account.

On the other hand, at very low aquatic P concentrations, although P may be limiting in absolute terms, it

is often pH that represents the primary gradient affecting community structures of organisms adapted to low nutrient levels.

===== Upper limit of sensitivity =====

Studies of lakes suggest that there are **four distinct levels of response to reductions in phosphorus loadings**:

- I. initial limited reductions in P loading : no biomass response to P reduction
- II. limited reductions in P loading : physiological or behavioural response
- III. significant P loading reduction : biomass reduction but no floristic change
- IV. considerable reduction in P loading : biomass reduction and floristic change

The principles of this model can also be applied to rivers. Reduction of P loading will only modify the ecological community if the reduction is large enough to reach level III or IV. The author suggests that this will rarely be the case in UK rivers with water quality class 2 or below.

===== Nitrogen and phosphorus =====

Where improving sewage treatment leads to a reduction in P load falling into the levels I or II of the above model, other factors such as nitrogen or carbon may affect ecological community response.

A survey of UK rivers found 20% of sites with N:P ratios below 10, suggesting that nitrogen may be limiting. These sites often corresponded to rivers targeted for sewage works nutrient removal under the EC Urban Waste Water Treatment Directive.

Phosphorus removal in sewage works will usually bring with it reductions in nitrogen loads, but also reductions in suspended solids and biological oxygen demand. Community-based indices remain a valuable tool as rapid and cheap indicators of ecological status, including eutrophication, but care has to be taken to not simplify interpretation by assuming that observed ecological responses are due only to nutrient loadings.

"Use of community-based indices to monitor eutrophication in European rivers" Environmental Conservation 25 (1) 1998.

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SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - USA

Guide to nutrient removal technologies

"Biological and chemical systems for nutrient removal" is a special publication (1998) of the Technical Practice Committee of the Water Environment Federation (WEF). It is intended to provide background information through a review of operating procedures, research and practical experience.

The 400 page book includes a brief look at :

- nutrients, their effects on the environment and control policies
- analytical techniques for measuring phosphorus and nitrogen
- design of chemical phosphorus stripping
- design of biological phosphorus removal
- design of biological nitrification/denitrification
- process models for biological nutrient removal
- aquatic systems for nutrient removal (ponds, wetlands)
- testing and evaluation of nutrient removal systems
- costs of nutrient removal with chemical or biological systems

A number of figures are given regarding phosphorus in waste waters and phosphate removal.

===== Detergent phosphates =====

Average USA waste water phosphate levels are indicated **before and after laundry detergent phosphate bans** :

<u>mg/l</u>	<u>before ban</u>	<u>after ban</u>	<u>difference</u>
total P	8	5.44	-32%
ortho-P	6.06	3.68	-39%

=====**Iron dosing**=====

For chemical P stripping using iron chloride dosed to the primary sewage treatment, **estimates of iron dosages** are given:

- to achieve outflow levels of 0.2 mg/l ortho-P :
molar iron/phosphorus ratio of 5
(calculated on the basis of [ortho-P inflow] - [outflow 0.2 mg/l])

Such iron chemical stripping is estimated to increase settling in the primary treatment as follows :

- TSS (suspended matter) removal increased from 50% to 75%
- BOD (oxygen demand) removal increased from 30% to 50% (both referring only to removal in primary treatment stage).

=====**Sludge increases and costs**=====

Where iron P stripping is applied as above, **primary sludge solids are estimated to be increased by a total of 94%** : 50% due to increased TSS removal plus 43% due to precipitation chemicals.

Costs are estimated for biological nutrient removal (BNR), on the basis of 370 such plants operating in the USA. **Actual capital costs of these BNR plants are considered to be comparable to capital costs of other new secondary treatment installations.**

Operating costs are estimated at US\$ 6.66 – 57.1 per 1,000 m³, with an average of US\$ 22.6. Running costs are strongly dependent on the availability of suitable organic carbon source to "feed" biological P removal.

Sludge P content is compared for sewage works with and without biological P removal. Conventional secondary biological treatment is estimated to achieve 10 – 30% total P removal, depending on BOD/P input ratio and operating conditions. This gives a waste activated sludge P content of 1.5 – 2.5 %. Biological P removal (85 – 95% P removal), however, will produce sludges with a P content of 2 – 7 %

=====**Struvite precipitation**=====

The fate of phosphorus in the anaerobic sludge digesters of biological nutrient plants is considered. Significant proportions of P may precipitate out at this stage of treatment : this proportion can reach 70% (eg. York River Plant, Randall et al. 1992), in particular as struvite.

=====**Wetland systems**=====

Artificial and natural wetlands are considered as effective nutrient removal systems for small sewage works. Phosphorus removal results from a combination of plant uptake, soil microbe uptake, soil particle retention and chemical precipitation within soil water.

It is estimated that a 71,000 m² wetland system should be able to ensure P removal from 10 down to 1 mg/l for a 1,000 m³/day influent loading.

This surface is approximately twice that considered necessary to reduce nitrogen from 30 to 5 mg/l and BOD from 80 to 15 mg/l.

"Biological and chemical systems for nutrient removal" Water Environment Federation special publication, 1998, ISBN 1-57278-123-8. Prepared by the WEF task force chaired by Movva Reddy. Water Environment Federation, 601 Wythe Street, Alexandria, VA 22314-1994, USA.

SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - Struvite recovery

Struvite crystallisation in anaerobic sludge digester effluent

P recovery can significantly improve the effectiveness of biological nutrient removal (BNR) by preventing phosphate release during sludge handling or anaerobic digestion. Struvite precipitation from the anaerobically digested sludge supernatant offers one route for achieving this.

Struvite crystallisation conditions were explored using the liquid from the dewatering section (belt press) of a 100,000 pe. sewage works equipped with nitrification, denitrification and anaerobic sludge digestion. This supernatant had Mg and Ca contents 10x higher than stoichiometric demand for struvite [struvite = MAP = magnesium ammonium phosphate = $MgNH_4PO_4$] or for hydroxyapatite [HAP = $Ca_5OH(PO_4)_3$] :

Chemical analysis of the supernatant used :

pH = 7.3

PO₄ = 18 mg/l

Mg = 53 mg/l

Ca = 184 mg/l

NH₄ = 220 mg/lCO₃ = 0HCO₃ = 1430 mgCaCO₃/l

An initial investigation was carried out on the ageing properties of this supernatant, with and without the addition of phosphate (as Na₃PO₄), in order to simulate the anaerobic supernatants of BNR processes. This showed a gradual increase of pH, probably due to loss of CO₂ to the air, and a fall in P levels. P removal levels after 3 days were 81% for a liquid with initially 164 mg/l PO₄ down to 53% for initial 18 mg/l PO₄.

Crystallisation of struvite but not of HAP

As a second stage, the supernatant curves of HAP and struvite at different calcium concentrations were evaluated for different synthetic phosphate concentrations and then compared with those found in the real effluent. This showed that **phosphate precipitation was occurring in the real effluent at a lower pH than for struvite in the synthetic solutions**, but at a higher concentration than for HAP (even at 200

mg/l Ca).

Ion analysis suggested that struvite is nonetheless being formed in the effluent, and that calcium salts are providing a seed crystal. This situation is thought to be related to magnesium and bicarbonate inhibition of HAP crystalliation.

Bench tests simulate P recovery

Following these results, **a bench scale fluidised bed reactor was used to assess the possibility of struvite precipitation from a relatively low phosphate concentration liquid (<50 mg/l PO₄)** using only air stripping to remove CO₂ without chemical addition.

Air stripping raised the pH from 7.9 to 8.3 - 8.6 and enabled up to 80% P removal after around 4 hours. These results were better than those obtained by Fujimoto et al (1991), most probably because of the use of external seed crystals (quartz sand).

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

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SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - Country : USA

Poor availability of phosphorus in chemical sewage sludge

Experimental agricultural field trials were carried out to determine the availability to crops of phosphorus in different organic wastes : digested dewatered sewage sludge (DS), irradiated sewage sludge (IS), irradiated and composted sewage sludge (CS) and composted livestock manure. The sewage sludge used was from a works using iron precipitation for P removal.

Varying dosages of each waste were applied for two years using three crops (lettuce, beans and petunias), each replicated four times. Dosages of nitrogen and other minerals were maintained in excess so that phosphorus was the limiting factor for plant growth.

The authors note that literature suggests an average of 2.3 % P in sewage sludges in the USA, with 10 – 15% iron (dry weights) where P removal down to <1 mg/l in the sewage works outflow is required. The paper investigates the implications of this iron content on P availability to agricultural crops and soils.

===== Low extractability of P in sewage sludges =====

As a first stage, the total P and its NaHCO₃ extractability were evaluated for each waste (Olsen and Sommers 1982 method). NaHCO₃ extractability is considered a good representation of the availability of soil phosphorus for plants.

Total P content ranged from 1.2% to 3.6% in the prepared sludge, and from 0.36% to 0.64% in the manure. Iron content ranged from 6 to 24% in the sludge preparations.

However, NaHCO₃ extractable P was very low in the sludge preparations, ranging from 0.8 % to 5.6% of total P. In comparison, extractable P ranged from 31% to 69% in manure.

===== No crop uptake of sewage sludge P =====

Mature crop yield was found to depend little on applied phosphorus, probably because adequate P was in

any case present in the farm soil. Young crop uptake and growth, on the other hand, correlated well with NaHCO₃ extractable P (eg. first cut lettuce).

None of the three sewage sludge products proved capable of increasing crop growth or yield. **Non composted sludge (DS, IS) in fact reduced P uptake by first cut and mature lettuce, possibly by modifications to the physical growing conditions. The composted livestock manure, however, increased P uptake significantly.**

These results correlate well with analyses of extractable soil phosphorus. NaHCO₃ extractable soil P was actually lower after two years of application of the different sewage sludge products (55 – 61 mg/kg, not correlated to sludge application dosages) than its initial value (62 mg/kg).

The composted manure, on the other hand, significantly increased NaHCO₃ extractable soil P, from 62 mg/kg initially to 67-75 mg/kg.

The fact that the addition of sewage sludge, which contains small quantities of NaHCO₃ extractable P, does not increase soil extractable P is thought to be a result of available P in the soil reacting with the added sludge, thus reducing its bioavailability.

"Comparison of phosphorus availability with application of sewage sludge, sludge compost and manure compost", Commun. Soil Sci. Plant Anal. 28 (17 & 18) 1997.

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SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - Honk Kong

95% nutrient removal by immobilised algae

Microalgae are known to provide effective biological treatment systems for both raw and treated sewage, one of the limitations being the difficulty in settling and removing the algae after growth. For this reason, immobilised algae in polysaccharide matrices were tested.

Cultivated unicellular *Chlorella vulgaris* were inoculated into 4mm beads of the two common polysaccharide matrices : alginate and carrageenan, which were extracted from algal cultures.

Triplicated experiments were carried out to test the ability of the *Chlorella vulgaris* to remove nutrients (NH_4^+ and PO_4^{3-}) from primary settled sewage from Hong Kong's second largest sewage works at Shatin. Sewage water (300 ml) was mixed with : carrageenan immobilised algae, alginate immobilised algae, free algae and a control without algae. Algal densities in each case were around 1 million cells/ml. The flasks were then maintained at around 24°C and exposed to 16-8 hour light-dark cycles.

Nutrient concentrations, calcium concentrations, algal numbers, size and chlorophyll contents were monitored over a period of 5 days.

===== 95% ammonia removal =====

Both of the immobilised algae systems achieved 95% NH_4^+ removal after 3 days. The carrageenan system offered a faster and more regular response, with around 56% removal after one day. The free algae system achieved only around 50% removal after 3 days, reaching 85% after 5 days. The no algae system achieved only 32% removal after 5 days.

===== 94% P removal =====

Phosphate removal was more difficult to interpret due to the effect of calcium phosphate precipitation as well as algal uptake.

P removal was very rapid and effective in the immobilised algal systems, with 94% removal after

one day in the alginate system and both immobilised systems achieving 99% removal after two days. For comparison, the free algal system achieved only 50% removal after 5 days whilst P levels remained more or less constant in the no algae flasks.

Calcium concentration monitoring showed increases of around 50% in the carrageenan system and 60 fold increases in the alginate system. These increases were due to calcium ions present in the polysaccharide gels, in particular in the alginate where a high level of calcium is necessary for gelling. These ions bind with phosphates forming calcium phosphates. Because the gel strength of alginate relies on calcium ions, the presence of phosphates in the waste water will tend to cause release of the algae cells, a phenomenon which was confirmed for the alginate system after 3 days. Very limited cell leakage from the gels was otherwise observed.

The increased nutrient removal efficiency of immobilised algae, compared with free algae, was thought to be due to the constraints posed upon the cells by reduced light and differing access conditions to dissolved ions. **These conditions cause the cells to grow more and stock more nutrients (higher chlorophyll levels) before entering the phase of cellular reproduction.** The carrageenan gel also enhanced algal access to NH_4^+ ions.

The study concludes that carrageenan immobilised algae provide a potentially efficient system for nutrient removal whereas alginate gel is not suitable due to its lack of stability in the presence of phosphates.

"Wastewater nutrients (N and P) removal by carrageenan and alginate immobilised Chlorella vulgaris"
Environmental Technology vol.18 1997.

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SCOPE NEWSLETTER

SCOPE N°28 - 10/1998 - USA / Minnesota

Operating costs of P precipitation

Ferric chloride precipitation P stripping was tested full scale on a fourth of the capacity of the 950,000 m³/day Saint Paul, Minnesota, sewage plant. Costs were found to be much higher than expected due to the additional capital and operating costs required for sludge handling and disposal (54% increase in sludge solids).

Simultaneous P precipitation was installed using injection of ferric chloride and polymer at the head of the primary treatment tanks which covered around a quarter of the plant's total flow. The chemical precipitated waste water stream was then separated from the non precipitated stream throughout the rest of the sewage work's processes, including throughout the sludge thickening and incineration sections.

===== 1.5 : 1 molar chemical use =====

Influent phosphorus levels varied from 2.4 to 8.4 mg total P / l, with an average of 5.2 mgP/l. Ferric chloride had to be dosed at a molar ratio (to P) of 1.5 : 1 to ensure P stripping down to 2 mgP/l. The average P removal rate in the chemical treated stream was then 71% compared to 24% in the untreated stream. In addition, **polymers had to be used at doses of 1.3 mg/l in the primary injection plus 10-12 mg/l at the sludge conditioning stage.** These levels were higher than those estimated before running. This treatment, however, offered 8% better suspended solids removal and 16% better organic material removal (BOD).

===== Deterioration in sludge processing =====

The chemical stripping significantly deteriorated sludge treatment efficiency, increased operational costs and, by reducing effective capacity, increased capital costs.

Solids capture in the gravity thickeners fell from 90.4% to 81% so that the dry solids content of the sludge fell significantly from 7.4% to below 5%. In order to obtain acceptable thickening of the chemical precipitation stream sludge, a gravity thickener loading rate of 78 kg/day/m² was necessary, equating to around 2/3 the loading for the untreated sludge stream (even then quality was still lower). Capital costs for sludge thickening would thus be multiplied by a factor of 1.5.

Roll press dewatering of the chemical precipitation stream sludge also proved difficult. Increased polymer doses were necessary and the solids content was on average 2% lower (around 29% instead of around 31%). Feed rate to the roll presses was reduced from an average of 49.6 to around 39.7 dry tons/day, implying additional capital costs of around 25% to maintain treatment capacity.

The wetter sludge in the chemical precipitated stream implied a 40% increased fuel use in incineration (rising to 0,136 m³/day/dry kg).

===== 54% increase in sludge solids =====

The chemical precipitated sludge produced more ash during incineration, increasing operating problems and costs. The 54% increase in sludge solids resulting from ferric chloride P precipitation also caused an overall increase in incinerator ash generated. Arsenic, cadmium, chromium, copper, iron and lead were removed from the waste water and transferred to the sewage sludge and ultimately to the incinerator ash.

After one year's full scale operating experience, the paper concludes that ferric chloride P stripping is much more costly than anticipated because of increased sludge handling and disposal problems.

"Full scale comparison of primary treatment, solids handling and solids incineration with and without chemical precipitation for phosphorus removal".

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