SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Nitrogen - Phosphorus ratios

Variations in nutrient-chlorophyll relations

Data on total nitrogen, total phosphorus and chlorophyll-a concentrations from 133 lakes were analysed to test predictions of nutrient limitation and nutrient-chlorophyll regression theories. Results were confirmed with independent data from other lakes.

Ordinary regression analysis of Chl-a, total P (TP) and total N (TN) gave the following equations :

$$\log_{10}\text{Chl-}a = -0.39 + 0.874 \log_{10}\text{TP} \ (r^2 = 0.69)$$
$$\log_{10}\text{Chl-}a = -3.131 + 1.445 \log_{10}\text{TN} \ (r^2 = 0.69)$$
$$\log_{10}\text{Chl-}a = -2.213 + 0.517 \log_{10}\text{TP} + 0.838 \log_{10}\text{TN} \ (r^2 = 0.81)$$

The best fit LOWESS regression curves suggest that there is a concentration of TP (around 100-125 µgP/l) above which increases in TP have nearly no effect and increases of TN a reduced effect (unlike for TP, there is no asymptotic value for TN). Low values of TN also have little effect.

======== No higher Chl-*a* values related to high TP ========

It is often widely suggested that **high TP concentrations (above the asymptotic value) are not related to increased Chl-*a* values** because of light limitation. However, the continuing (if slower) increase in Chl-*a* values related to higher TN concentrations suggests that this cannot be the correct explanation.

It has already been indicated by other authors that TN is nearly as closely related to Chl-*a* as is TP (Forsberg and Ryding 1980) or better related (Canfield 1983). In the data analysed, **TN had the same predictive power as TP but with a steeper slope.** Nonetheless, most work on freshwaters looks at TP - Chl-*a* relations with little or no concern for TN - Chl-*a* relations.

======== TN : TP ratios ========

It is to be noted that TN and TP ratios are log-log significantly correlated for the data analysed (r=0.71).

Analysis of the TN:TP ratios shows that **there is a clear region (23 < TN:TP ratio < 28, by weight) for which Chl-*a* values vary considerably with changes in nutrient concentrations** (TP and/or TN). At low (TN:TP < 15) and high (TN:TP > 35) ratios, Chl-*a* values are scarcely related to nutrient concentrations.

As might be expected from nutrient limitation theory, in lakes with very high TN:TP ratios (> 50), TP does indeed become more closely related to Chl-*a* concentrations than TN.

======== Variations in TN: Chl-*a* and TP:Chl-*a* relations ========

Various authors have previously underlined the **substantial variability in nutrient:Chl-*a* relations (eg. Smith and Shapiro, 1981) : regression coefficients vary to the extent of giving several fold differences** for predictions for individual lakes.

Various previous authors have also demonstrated that multiple regression analyses of other biological and physical factors do not explain much of the residual uncertainty.

The authors data analysis shows that the TN:Chl-*a* and TP:Chl-*a* regressions vary consistently with TN:TP ratios. **The authors indicate that these results show that the use of constant slope nutrient:chlorophyll models is inappropriate.**

They also indicate that, because of the nonlinearity of slopes, **it would be "very difficult at best" to develop a single multiple regression models to account for the widely changing behaviour of phytoplankton biomass and nutrient levels at different TN:TP ratios.**

An explanation of this variability is offered : **variation in phytoplankton species composition.** The TN:TP ratio at which Chl-*a* values vary most with nutrient concentrations (23-28 by weight) is close to the average cellular N:P ratio of algae (30 by weight, Shuter, 1978). Thus varying response could result from changes in phytoplankton species composition between species best adapted to differing TN:TP ratios.

"Unifying nutrient – chlorophyll relationships in lakes". Canadian Journal of Fisheries and Aquatic Sciences, vol. 46, number 7, 1989. Pages 1176-1182.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Florida

Assessing factors limiting algal growth

Spring/summer samples from a number of sites in three Shallow Florida lakes and along 46 km of a low-flow river were analysed for different forms of phosphorus and nitrogen (total, dissolved, biologically available), for chlorophyll-a and Secchi disc transparency, and using nutrient enrichment bioassays.

The "Redfield ratio" of 106:16:16:1 (by atoms) for carbon: nitrogen : silicon : phosphorus is derived from the largely constant ratio found in marine particulate matter by Redfield *et al.* 1963. This ratio is generally thought to be applicable to freshwater algal systems, except for the silicon requirements of diatoms which are approximately twice those of marine organisms. By extension, freshwater literature often considers that TN:TP ratios (measured total nitrogen: total phosphorus) > 16:1 indicate that phosphorus is the limiting nutrient for algal growth. To test this hypothesis, samples from four Florida surface waters were studied :

- **Lake Apopka,** 124 km 2 : hypereutrophic, mean TP 203 µg/l, mean TN 5110µg/l, TN:TP = 56:1.
- **Lake Okeechobee,** 1732 km 2 : five distinct ecological zones sampled mean TP 58-127µg/l, TN 1180-1342 µg/l TN:TP from 23 – 52.
- **Lower Saint Johns River,** 46 km reach, residence time 3 - 8 weeks : mean TP 75 µg/l, mean TN 1200 µg/l, TN:TP = 35
- **Anderson-Cue Lake,** oligotrophic : nutrient levels similar to rainwater.

======== TN:TP ratios wrongly predict P limitation ========

Use of the TN:TP ratios for these waters suggest that they are phosphorus limited, but this proves not to be the case.

Nutrient enrichment bioassays indicate that Lake Apopka, Lake Okeechobee and the lower Saint Johns River are in fact limited by nitrogen and/or light. The generation of algal growth in Anderson-Cue Lake requires not only the addition on both nutrients, but also trace metals.

Comparison of dissolved available nutrients (DIN Dissolved Inorganic Nitrogen : Soluble Reactive

Phosphorus SRP) ratios predict that Lake Apopka, Lake Okeechobee and the lower Saint Johns River are nitrogen limited, thus proving to provide better indicators than TN:TP ratios.

The authors note however that SRP measurements do not take into account stored cellular phosphorus, which can often be accumulated by algae in sufficient quantities to support several cell divisions. **DIN:SRP ratios >16 can thus also give a false indication of P limitation.** Nitrogen can also be stored in cells, but storage is limited and quantitively less significant than P storage (Reynolds, 1984).

The authors suggest that the comparison of biologically available nitrogen (essentially DIN plus urea) to BAP biologically available phosphorus (SRP plus cellular phosphates, which can be hydrolysed by enzymes – Newman *et al.* 1994) would provide a better indication of nutrient limitation. For comparison, concentrations of the various forms of phosphorus (different availability) in Lake Okeechobee are given :

µg/l	***SRP***	***BAP***	***TP***	***TN:TP ratio***	***BAN:BAP ratio***
Lake Okeechobee					
Zone 1	*46*	*114*	*127*	*23*	*17*
Zone 2	*27*	*34*	*94*	*28*	*11*
Zone 3	*15*	*20*	*68*	*44*	*9*
Zone 4	*12*	*21*	*58*	*52*	*9*

========= Wollenweider model =========

The accuracy of total phosphorus concentrations for predicting chlorophyll-a levels were tested. Relatively low predictability was shown (R^2 = 0.59). **A better fit was found for the regression of chlorophyll-a on total nitrogen** (R^2 = 0.77), similar to that found using both TP and TN (R^2 = 0.81).

The authors emphasise that **using total nutrient level regressions to model chlorophyll levels is based on correlated not causal factors** and that many lakes do not fit the predicted patterns.

In the case of the Florida waters, assessment of nutrient limitation is confused by rooted macrophytes which compete with phytoplankton for available nutrients. Water depth, light limitation and wind induced water column mixing (which can suspend benthic algae and sediment nutrients) also render the assessment of trophic status more difficult.

The authors conclude that they have shown that **TN:TP ratios give false predictions of limiting nutrient status.** However, measurements of biologically available nutrients or nutrient limitation bioassays, which provide information on current nutrient limitation, must also be interpreted in a historical perspective. Managers must evaluate and use many sources of information to define policies to control and prevent undesirable algal and macrophyte problems.

"Assessing nutrient limitation and trophic state in Florida lakes". In Phosphorus Biogeochemistry in Subtroipical Ecosystems, CRC/Lewis Publishers 1999, pages 321-339.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Belgium, River Meuse

Grazers can sometimes control algae in rivers

There is a certain amount of experimental evidence of zooplankton control of algal development in lakes, where grazing can lead to clear water phases even in eutrophic lakes and can modify phytoplankton species composition. Such grazing is particularly associated with larger zooplankton species, which are generally absent from rivers (because of short residence times). This study shows, however, that zooplankton control of algae can nonetheless also occur in rivers.

The site studied, La Plante in Belgium, is situated 537 km from the source of the Meuse river and 348 km from confluence of the Meuse and the lower Rhine. Phytoplankton, zooplankton and grazing measurements, as well as physical (flow, temperature, light) and chemical parameters (water nutrient concentrations) were measured during the spring and summer over a three year period (1994-1996).

At the point studied, the Meuse is on average 100m wide and 3.95m deep, with alkaline, nutrient rich waters. **Total phosphorus varied during the three years studied from 27 – 428 µgP/l with annual averages of 133 – 226 µg/l.** Total nitrogen varied from 2.3 – 16;3 mgN/l, with annual averages of 3.6 – 4.3 mgN/l.

Flow varies from up to 500 m^3/s down to below 50 m^3/s with low flows of below 100 m^3/s occurring in spring and summer.

========= Variations is phytoplankton and zooplankton populations =========

The study provides considerable data on algal and grazer species variation, populations and seasonal variations. Changes in algal biomass and species composition observed each spring were probably influenced mainly be decreasing flow and increasing light and temperature. The spring development of zooplankton appeared to depend on weather conditions, probably occurring in response to downstream transport resulting from flow and to temperature variations.

The most abundant spring zooplankton were *Brachionus calyciflorus* and *B. angularis*, rotifers widely considered to be generalists.

Maximum daily filtration rates of 113%/day were achieved when rotifer densities reached several thousand per litre. **Such high filtration rates have rarely been reported from rivers.**

Grazing rates during the spring algal bloom ranged from 0.5 – 2.15 gC/m^2/day. In most cases, **this was sufficient to reduce algal biomass by a factor of 10 within two weeks** and approached or even surpassed the algal net production rate.

Even higher grazing rates were noted in summer, at the same time as a shift towards larger species of algae and a decline in algal biomass. These changes occurred after increases in grazer biomass and species diversity, and probably resulting from selective grazing of the smaller algal species.

The **zooplankton grazing effectiveness was very size specific,** depending on the relative size composition of both the algal and grazer communities, rendering simple model simulation of grazing impossible.

The authors suggest that **the algal community composition in large rivers can, at times, be effectively controlled by grazers,** but that this occurs when physical restraints are reduced (low flow, high temperature) and when availability of edible algae allows high grazer biomass.

"Can a community of small-bodies grazers control phytoplankton in rivers". Freshwater Biology n° 39, pages 9-24, 1998.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Lake Mendota, Wisconsin

Factors affecting summer algal density

Lake Mendota is a eutrophic 24m deep lake in Winsconsin with a 604 km^2 rural watershed. The principal phosphorus loading is from agricultural run-off in the main tributary rivers.

Over the period 1976 – 1995, data were collected for summer water clarity (Secchi disk depth visibility), indicative of algal development ; phosphorus loadings ; spring in-lake phosphorus concentration ; daphnia species distribution, size, density and biomass ; lake mixing index (Schmidt stability – indicative of temperatures and wind). Lake water mixing is lower during high spring and summer temperatures.

Total phosphorus in the lake water in spring varied during the twenty years from 70 – 160 µg/l with no definite long-term trend.

The deep water in the lake is generally anoxic by early July, so zooplankton counts through a vertical net sweep were corrected to give densities in oxygenated water zones only.

========= Daphnia densities =========

The main zooplankton grazer species present in the lake were almost always *Daphnia pulicaria* and *Daphnia galeata mendotae*. *Daphnia* biomass was generally greater in years when *D. pulicaria* dominated. *D. g. mendotae* dominated most spring clear water periods, probably because of relatively high predation by fish (cisco, yellow perch, white bass). *D. pulicaria* dominated in years with lower fish predation.

Over the study period, *Daphnia* biomass varied from near zero to 487 µg/l, with averages of 236µg/l in June in *D. pulicaria* dominated years and 127 µg/l in *D g. mendotae* years, falling respectively to 66 and 14 µg/l in August..

20 cm Secchi disk depths fell to an average of 1.92m in August in *D. pulicaria* years and 1.44m in August in D. g. mendoatae years.

========= Modeling algal growth =========

The different factors tested as predictor variables for algal development were phosphorus loadings, April in-lake phosphorus concentrations, *Daphnia* biomasses and lake stability. These factors varied considerably, but independently (non significant correlation coefficients).

Significant relationships were found between July - August mean Secchi disk depth (indicator of water clarity, and so of algal development) and April in-lake phosphorus concentration, midsummer *Daphnia*, lake mixing.

June Secchi depth is, however, governed mostly by May and June *Daphnia* biomass. Loss of water clarity occurred in only two years, and was probably the result of high fish zooplankton predation in one year and of an unusual spring (inedible) blue-green algal bloom *(Aphanizomenon flos-aquae)* in the other year.

In years with early spring warming, water clarity can occur early (in May rather than June), leading to declines in Daphnia populations and subsequent algal development in summer.

External phosphorus loadings were not a very effective annual predictor variables, because much of the lake's phosphorus availability in any one year comes from internal loading, which is related to mixing.

The authors conclude that summer water clarity is essentially governed by in-lake phosphorus concentrations, related mainly to lake mixing, and *Daphnia* grazing.

"Summer water clarity responses to phosphorus, Daphia grazing and internal mixing in Lake Mendota". Limnol. Oceanogr. 44(1), pages 137-146, 1999.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - China

Health impacts of water pollution

China faces a range of serious water quality problems, with significant health impacts.

Widespread contamination of surface and drinking waters by pesticides and nitrates results in regional diseases such as gastric illnesses and cancers in areas with intensive irrigated agriculture.

The discharge of **30 billion tons/year of sewage - 97.3% of which is untreated** - results in 1.5 million cases of acute schistosome infections/year, as well as the common occurrence of hepatitis A, diarrhea, para-cholera and typhoid.

The rapid development of small industries in rural areas (Town and Village Industries = TVIs) is accentuating industrial pollution problems, as these installations generally operate without any waste water treatment.

Pollutants generated include heavy metals, cyanide and phenol.

========= Nitrates and pesticides =========

China currently feeds some 1.2 billion people from only 133 million ha of arable land. This has led to a rapid intensification of agriculture, with considerable use of mineral fertilisers and a wide range of pesticides.

The average rate of application of mineral fertiliser nitrogen application in China (Sun 1995) was 191.6 kg/ha, which is around 3.55 x the world average. The P:N ratio for mineral fertiliser application was however roughly half the world average.

90% of rural populations rely on shallow water tables (0.2 - 10m depth). The quality of these resources has deteriorated rapidly. **There are a number of reported cases of groundwater nitrate levels well above the WHO guideline** for drinking water (10 mg/l NO_3-N) : Yuanmingyuan, Tai-hu lake, Matan - Lanzhou City (291 mg NO_3-N), Ganshu, Beijing, Fujian, Zhejiang.

One survey found nitrates in excess of norm levels in 37 out of 69 groundwater resources tested.

Pesticides are applied at an average of 2.82 kg/ha active ingredient. As a result, significant concentrations occur in rivers and lakes, and even offshore. Concentrations of up to 80 µg/l of HCH have been reported, with, for example, 3.89 µg/l in Tai-hu Lake.

Concentrations of **DDT, HCH, Alachlor, Dimehypo, Delachlor, Aldicarb, Aldicarb sulfoxide, and Aldicarb sufone** have also been found in groundwater, leading in some cases to the closure of drinking water wells.

One study looking at the use of Pentachlorophenolate to eradicate the snail *Oncomelania* (intermediate host of shcistosomiasis) showed concentrations of up to 6.8mg/g in foods, 7.3 g/l in milk and 257 mg/g in human body fat in areas using the pesticide. The rate of cancer mortality in these areas was 2 - 3 times higher than control areas, although this may have been influenced by other factors.

Eutrophication of rivers and lakes is also a widespread problem, with numerous cases of toxic algal blooms. These can result in health problems, including a risk of liver cancer. Eutrophication in China is a consequence of excessive use of fertilisers, discharge of untreated sewage, animal manures and industrial waste waters.

======== 2.7% of sewage treated ========

Almost all monitored urban river sections in China in 1994 failed to meet designated quality standards (131 out of 135). Moreover, 52 of these urban 135 river sections failed even to meet the lowest quality standard.

Most urban pollution is linked to organic loads. In 1995, only 100 sewage works were operational across China. **Only 2.7% of China's 30 billion tons/year of urban sewage are treated before discharge.**

The result is significant health risks, with only 6 of China's 27 largest cities providing drinking water which meets government standards. 1.5 million people contract schistosome infections annually, and the incidence of typhoid fever is 10.6/100,000.

Pollution from sewage is compounded by intensive cultivation of vegetable plots and small-scale poultry and other animal rearing installations in cities.

Even larger quantities of industrial waste waters are produced (approx. 15 x sewage volumes), and these are also largely untreated. Small rural industries (Town and Village Industries) pose a particular problem, with a rapid increase in industrial production and virtually no waste water treatment. Specific problem industries include paper and pulp mills, chemical industries, metal treatment, dyeing and leather tanning plants.

"Agricultural diffuse pollution from fertilisers and pesticides in China". Wat. Sci. Tech. Vol. 39, n° 3, pages 25-32, 1999.

Yong Li, Dept. Environmental Science, Institute of Soil Science, CAS, Nanjing 210008, China. Jiabao Zhang, Dept. Soil Physics, Institute of Soil Science, as above.

World Resources Institute dossier "Water pollution and human health in China" : http://www.wri.org/health/prcwater.htm.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Baltic Rivers

Underestimation of diffuse sources

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Baltic Lakes

Phosphorus forms in sediments and release mechanisms

This study compared the chemical form and vertical distribution of bound phosphorus in sediments from two Baltic lakes, one oligotrophic and one eutrophic. Conclusions were drawn regarding phosphorus release mechanisms from sediments and regarding mechanisms for long-term P burial in the different lakes.

The lakes studied are in the Northern German lowland Baltic lakes region. **Lake Stechlin** is one of the last oligotrophic lakes in this region, with an area of 4.25 km^2 and a maximum depth of nearly 70m. The whole water body has permanently oxic conditions.

Lake Feldberger Haussee (1.3 km^2, max. depth 12m), on the other hand, was originally slightly eutrophic and was then heavily polluted by sewage inflow. Following sewage diversion in 1980, quality has gradually improved, but total phosphorus concentrations are still over 100 µgP/l and oxygen depletion often occurs in the deeper waters.

========= Similar sediments despite differing trophic states =========

Sediment cores were taken from depths of 32m in Lake Stechlin and 8.5m in Lake Haussee, in spring and summer. Samples of the sediment cores from different depths were separated and analysed for organic matter, $CaCO_3$, Fe, Al, Mn, Ca and different forms of phosphorus, in the interstitial water and in the sediment particles. Differently bound phosphorus forms were assessed as soluble reactive phosphorus (SRP) and total phosphorus (TP), by using a progressive sequence of extractions with 1M NH_4Cl, 0.11M $Na_2S_2O_6$, 1M NaOH, 0.5M HCl and $K_2S_2O_8$.

The overall composition of the sediment, and in particular the proportion of organic matter, proved relatively similar in the two lakes. The soluble P concentration in the interstitial water was however significantly higher in the eutrophic Lake Haussee.

========= Importance of Fe- and Mn- bound phosphorus in

oligotrophic conditions ========

The proportion of NH_4Cl extractable P in both lakes decreased in deeper sediments, where the pH was lower. During the NH_4Cl extraction, relatively large amounts of Ca were mobilised, suggesting that a significant proportion of the NH_4Cl extractable P is **loosely adsorbed to calcite.** The proportion of such loosely adsorbed P in Lake Haussee (4-8% of total P) was higher than in Lake Stechlin (1-3%).

Reductant soluble ($Na_2S_2O_6$ extracted) P was considerably higher in Lake Stechlin than in Lake Haussee (1.29 gP/kg n the top 1cm of sediment, compared to 0.32 gP/kg in Lake Haussee). The amounts of Fe and Mn extracted were also higher in Lake Stechlin. $Na_2S_2O_6$ extracted P levels were higher near the sediment surface and made up 54% of total P in the top centimetre of Lake Stechlin sediment. This is related to the oxic conditions occurring at the sediment surface in this oligotrophic lake.

It is suggested that **burial of Fe- and Mn- bound P, involving moving into anoxic conditions, is the main mechanism for phosphorus release in the sediments of Lake Stechlin.**

NaOH extractable P was higher in Lake Haussee, as were the amounts of extracted Al. This corresponds to higher levels of Al- and Fe- bound phosphorus in the eutrophic lake.

======== Importance of $CaCO_3$- bound phosphorus in eutrophic conditions ========

In the Lake Haussee sediment, some 32% of total phosphorus is bound to calcium carbonate ($CaCO_3$), compared to only around 14% in Lake Stechlin, despite similar $CaCO_3$ levels in the sediments. **This suggests that co-precipitation of phosphorus with autochthonous calcite precipitation increases the P-binding capacity of the sediments.**

In Lake Haussee, the level of labile organic phosphorus at the sediment surface decreased rapidly with depth.

======== Differing phosphorus mobilisation between the two lakes ========

The authors conclude that whilst the quantities of dissolved, loosely adsorbed, metal oxide- and calcium carbonate- bound phosphorus are higher in the sediments of the eutrophic lake, the Fe- and Mn- bound (reactant soluble) fraction was considerably higher in the oligotrophic lake.

The mobilisation of recently deposed labile organically bound phosphorus is the driving mechanism for sediment phosphorus release in eutrophic conditions, whereas release from Fe and

Mn (due to burial leading to anoxic conditions) is the main mechanism in oligotrophic conditions.

Co-precipitation of phosphorus with calcite is an important mechanism in both conditions. Since this process takes place faster in eutrophic conditions, it can be a significant self-cleaning mechanism, thereby permitting long-term removal of phosphorus from the lake water.

"Phosphorus binding forms in the sediment of an oligortophic and an eutrophic hardwater lake of the Baltic Lake district (Germany)". Wat. Sci. Tech. Vol. 37, n° 3, pages 51-58, 1998.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Surface Water Management

Phosphorus in sediments

This paper provides an overview of current knowledge regarding phosphorus cycling mechanisms within sediments and discussions the implications for surface water management and for global environmental cycles.

For a number of lakes, it has been shown that **internal P loading by release from sediments can equal or exceed external nutrient inputs.** The retention of phosphorus in surface waters, by immobilisation, burial and infiltration to deep sediments, has a major impact both on the quality of the surface water and ultimately on the transport of phosphorus into the sea. It is generally recognised that it is phosphorus availability which limits marine productivity over geological time scales.

========= Sediment retention mechanisms =========

Sediment nutrient retention results mainly from the **deposition of particles on the sediments** as dead or decaying phytoplankton (primary production). In some waters, however, the deposit of inorganic phosphorus precipitants can be of significant importance (deposit of calcium carbonate particles, adsorbtion on ferric (oxi)hydroxide surfaces).

Within the sediment, a number of **microbiologically and chemically induced transformations** take place as well as in-sediment transport through sediment mixing and accumulation and water percolation. Over the long term, the accumulation of nutrients in the sediments will be equal to the net sediment accumulation rate (m/year) multiplied by the average nutrient content. Over the shorter term, high P loadings result in the binding on iron in the sediments, and this phosphorus can readily be released back into the water when P loading is reduced or with changes of redox state in the sediment.

Long term retention of phosphorus in the sediments therefore depends on three mechanisms : net deposit of particulate P, early diagenetic cycling and transformation of reactive P compounds in the sediment surface layer, burial of non mobilisable P compounds in deeper sediment layers.

========= Case studies =========

The paper examines four cases where phosphorus sediment mechanisms have been studied, each related to

nutrient inputs from the river Rhine :

- Lake Veluwemeer, Holland
- Ijsselmeer, Holland
- The Western Dutch Wadden Sea
- The German Bight in the North Sea.

The authors note that **average P concentrations in the Rhine have been reduced from around 30µg/l in the late 1970's to 5 µg/l today.**

In **lake Veluwemeer,** sediment P retention occurs in the deeper part of the lake and is mainly associated with calcium compounds (50-60%) or iron and aluminium compounds (10-20%). Around 70% of the downward transport of P results from infiltration of dissolved P, and the remaining 30% from burial. Roughly 50% of the P in the sediment is not susceptible to reduction. When phosphorus loadings to the lake were reduced in 1979-1980, accompanied by increased flushing with water rich in nitrate and carbonate, the P concentration in the lake dropped rapidly and this was not offset by significant sediment release.

However, in **lake Ijsselmeer a rapid roughly 60% reduction in P loadings from 1982 resulted in only slight decreases in water P concentrations** until 1988 when they fell sharply. The relatively high sediment P retention in Ijsselmeer, despite low sediment iron concentrations, is thought to be related to sedimentation of the input river particle load and to continuous delivery of new sorption surface by the river Ijssel.

In the **Wadden Sea,** particulate organic matter is imported with the tides and deposited near the main land where it is mineralised during the summer when the temperature is higher.

In the German Bight, nutrients are transported to and deposited in the Skagerrak as a result of currents. Because this transport takes around a year, only aged organic materials are deposited and most are mineralised before arrival. Large amounts of P are released from the Skagerrak sediments in summer, when oxygen penetration to the sediment is near zero, by the reductive dissolution of iron : pore water concentrations of phosphorus can reach 700 µg/l.

======== Agricultural sources and lake management ========

The authors note that there is now considerable knowledge available concerning the mechanisms and dynamics of sediment nutrient retention and release. The number of scientific papers on this subject, particularly the **number of papers relating to lake restoration being published, is decreasing,** indicating that we now "know enough".

The authors note, however, that the considerable research over the last two decades has not resulted in new approaches to lake restoration. There have been few applications of sediment restoration techniques. The knowledge developed has, though, led to **more realistic expectations of lake restoration programmes.**

The authors indicate that it is increasingly recognised that **most of the nutrients of anthropogenic origin entering lakes and coastal waters originate from agriculture.** Management policies therefore need to be defined at the whole watershed level and take into account the transformations undergone by agricultural phosphorus inputs as they move through surface waters to the sea.

For the future, there is considerable interest developing into the **long term role of phosphorus in global productivity cycles.** Van Cappellen and Ingall (1996), for example, demonstrate that the redox dependent burial of phosphorus in ocean sediments provides a powerful forcing mechanism for balancing production and consumption of atmospheric oxygen over geological time scales.

The authors indicate the need for studies of **how phosphorus cycling affects the atmospheric carbon dioxide balance, and thus the greenhouse effect.**

"Phosphorus retention is sediments". Wat. Sci. Tech., vol. 37, n° 3, pages 31-39, 1998.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Grassland
Phosphorus leaching from farmland

Large monolith lysimeters (135 cm deep, 80 cm square) were used to measure reactive and organic phosphorus concentrations in leachate underneath farm grassland under natural rainfall conditions.

Four replicate lysimeters were used in each of four different soil types (silty clay, well drained clay-loam, sandy loam over chalk, sandy soil), with intact soil blocks installed in a field site at the Institute of Grassland and Environmental Research, North Wyke, Devon, UK.

They were managed as typical cut grassland with application of NPK fertiliser in accordance with UK Ministry of Environment guidelines. 25 kg/year/ha of phosphorus was applied as Triple Super Phosphate mineral fertiliser.

Natural rainfall was around 1100 mm/year and leachates were collected between November 1997 and June 1998.

========= Most leached phosphorus biologically available =========

The average total phosphorus concentrations in the different soils' leachates at 1.35m depth ranged from 61 - 152 µgP/l; high enough to present a significant threat to surface waters, and remained consistently high throughout the drainage year.

The percentage of total phosphorus present in leachate in an immediately biologically available form (molybdenum reactive P) varied from 68 - 86% between the different soil types.

The authors underline, however, that the "unreactive" fraction of total phosphorus is generally organic, and is thought to be potentially bioavailable after enzyme metabolism in surface waters. Further research is necessary to quantify the bioavailability of the organic fractions of leached phosphorus from grasslands.

The authors also measured the "Olsen-P" status of the soil ($NaHCO_3$ extractable phosphorus), which is generally used as an index of soil phosphorus status. There was no apparent correlation between Olsen-P in the soil and the concentration of phosphorus being leached.

======== Grassland P-leaching : a significant risk of surface water pollution ========

Farmed grasslands cover large areas of land in the UK and the authors conclude that, in contrast to traditional perceptions, phosphorus leaching from them can pose a significant risk to surface water.

Most past evidence regarding phosphorus leaching from agricultural land comes from plot-scale studies where sub-surface leaching has rarely been measured. The authors' direct measurements from large monolith lysimeters suggests phosphorus leaching of 51 - 152 µg/l, mainly in inorganic bioavailable form.

"Phosphorus leaching under cut grassland". Wat. Sci. Tech vol.39, n° 12; pages 63-67, 1999. B. Turner, Dept. Geography, Royal Holloway, University of

London, Egham, Surrey TW20 0EX, UK. P. Haygarth, IGER Soil Science Group, North Wyke, Oakhampton, Devon EX20 2SB, UK.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Baltic Sea nutrient reductions

Cost-effectiveness of wetland management

This study establishes a model for calculating the costs of nutrient reductions (N, P) in the 14 drainage basins (9 countries) surrounding the Baltic Sea, based on sources of atmospheric deposition and run-off, and on mechanisms for nutrient retention. Cost-effective routes are identified for achieving the 50% reductions in N and P set as objectives by HELCOM.

The nine countries surrounding the Baltic Sea are Finland, Estonia, Latvia, Lithuania, Russia, Poland, Germany, Denmark and Sweden, with a drainage area of 1.4 million km 2 and 75 million inhabitants. These countries signed in 1974 the Helsinki Convention, to monitor and protect the ecological quality of the Baltic Sea and a **Ministerial agreement to reduce nutrient loads to the Baltic (N, P) by 50%.**

This action is seen as necessary because of ecological damages resulting from eutrophication, including toxic algae and oxygen depletion near the sea bed. The ultimate effect is reduced cod stock and areas of sea bed without biological life (Wulff et al., 1990).

======== Data collection difficulties ========

The authors underline the difficulties met in obtaining data concerning nutrient leaching and retention for many of the 14 catchment basins of the Baltic Sea. Estimates were therefore made of the basis of data available, mainly from Sweden.

The estimated total anthropogenic nutrient load to the Baltic Sea is estimated as **728,000 tons/year N** from within the Sea’s catchment, plus around 22,000 tons/year N atmospheric deposition from outside this basin; and **37,000 tons/year P.** These estimates fall within the range of other published figures.

Agricultural sources account for more than a half of nitrogen load and a third of phosphorus load. Sewage (from households and industry) accounts for nearly a third of nitrogen load and two thirds of phosphorus load.

Poland has the highest nutrient emissions, with a third of total nitrogen and a half of total phosphorus load.

======== Source reduction, land use and nutrient retention ========

To assess cost-effectiveness of nutrient reduction measures, these were divided into three different types of action :

- **source reductions,** including improved sewage treatment, catalysts in cars and ships, scrubbers at point sources, reductions in deposition of fertilisers and agricultural manures
- **land use measures,** including better manure spreading, changes in crops, tree planting
- **retention measures : restoration of wetlands as nutrient sinks.**

Wetland retention of nutrients is estimated at between 10% and 50% depending on type and location (Janson, 1994). **Restoration of natural wetlands is significantly more effective than creation of artificial wetlands.**

======== Sewage treatment and wetland restoration ========

The authors main conclusions are that improving sewage treatment and wetland restoration are the most cost-effective nutrient reduction measures.

To achieve 50% reductions, **costs for reducing nitrogen loads are roughly five times higher than those for reducing phosphorus loads. This is largely the** consequence of low marginal costs for phosphorus removal in sewage works.

At the 50% reduction level, for the most cost-effective hypothesis, roughly one third of the nitrogen load reductions come respectively from sewage treatment, agricultural measures and wetland restoration. Again for a 50% reduction, **around two-thirds of the phosphorus reduction come from sewage treatment** and about one fifth from wetland restoration.

If wetland nutrient retention capacity is reduced by 25% (for example by drainage and wetland destruction), the costs for achieving the 50% nutrient reductions increase by 35%.

======== Much higher costs for nitrogen reduction ========

Annual costs to achieve a 50% reduction in total nutrient emissions from the Baltic Sea catchment are estimated at 1,400 million Euro and 340 million Euro for nitrogen and phosphorus respectively.

If a 60% reduction from the Baltic catchment area is required, which would be necessary to achieve an overall 50% reduction for the Baltic Sea (because of inputs from areas outside the catchment), total costs would be multiplied by nearly three times.

If the objective of a 50% reduction from the Sea's catchment area is achieved by obliging each country to reduce its loads by 50% (rather than achieving a 50% total reduction distributed between different countries in the most cost-effective way), then total costs will by multiplied by around four times.

"Cost-effective nutrient reductions to the Baltic Sea". Environmental and Resource Economics n° 10, pages 341-362, 1997.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Wetlands

Long-term phosphorus assimilation capacity

Wetlands' phosphorus assimilation capacity and long-term response to phosphorus loadings are estimated from analysis of a North American wetland data base and of Everglades test sites.

Phosphorus inflow and outflow levels from the 126 wetlands in the North American data base indicate **low phosphorus outflow concentrations (35 – 50 µgP/l) for inflow loadings below a change point ranging from 0.4 to 1.4 mgP/m^2** (95% confidence limits).

These results were compared with observations of ecosystem changes in Everglades test sites along a 10 km P-loading gradient. Inflow was 2.7 mgP/m^2 annual average around the Hillsboro canal discharge, descending to the natural background level of 0.3 mgP/m^2 10 km downstream. Phosphorus metabolism and ecosystem condition were characterised by calculating phosphorus loadings and measuring water phosphorus concentrations, soil phosphorus accretion rates, phosphatase activity in water, N:P ratios in plants, changes in plant community structure, plant productivity and macroinvertebrate diversity.

======== Ecosystem differences above 1 mgP/m^2/year ========

Surface water phosphorus concentrations and soil P accretion rates are highly correlated and both decrease exponentially with distance from the nutrient inflow.

Water phosphorus concentrations were up to 100 µgP/l near the nutrient inflow, and above 60 µ mg/l in areas with a phosphorus loading of more than around 1 mgP/m^2/year : that is higher than the average baseline concentration of 43µg/l. in North American marshes, calculated from the data base Two biochemical indices, phosphatase activity in the surface water and N:P ratios in sawgrass *(Cladium jamaicense)* indicated that the **marsh vegetation was in effect phosphorus limited only where phosphorus loadings were below 1 mgP/m^2/year** (the Everglades wetlands are naturally P-limited).

Detailed measurements of community structure showed significant changes resulting from what is now nearly 30 years of nutrient input from agricultural run-off : the dominant vegetation varied from dense cattail grass *(Typha domingensis)* in the phosphorus impacted zone through mixed grasses to dominant slough and sawgrass in the unenriched areas. However, **the plant community changed little past the point 5.1 km downstream from the nutrient-rich inflow, beyond which phosphorus loadings were below the 1 mgP/m^2/year level.**

Sawgrass plant productivity was nearly double in the areas with loadings higher than 1 mgP/m 2 /year, but plant 1 mgP/m^2/year had maintained 18 out of 19 native macrophyte and slough species.

Macroinvertebrate densities and diversities were higher in nutrient loaded areas but were reduced to natural levels where phosphorus loadings were less than 1 mgP/m^2/year.

The authors conclude that a phosphorus loading of 1 mgP/m^2/year can be taken as a threshold which North American wetlands are generally able to tolerate over the long-term without significant ecosystem modifications and without loss of their phosphorus retention capacity.

======== Even P-limited wetlands can sustainably assimilate phosphorus ========

At loadings above this, wetlands will lose native species and become phosphorus saturated over a number of years. On the other hand, **even phosphorus limited wetlands seem able to sustainably retain phosphorus at loadings below around 1 mgP/m^2/year** without significant changes in ecosytem structure and function.

The actual long-term phosphorus assimilation capacity figure may vary from one site to another, perhaps within the range 0.4 - 1.4 mgP/m^2/year and this requires further investigation at other sites.

"Long-term phosphorus assimilative capacity in freshwater wetlands : a new paradigm for sustaining ecosystem structure and function" Environmental Science and Technology, vol.33, n° 10, 1999; pages 1545-1551.

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Italy

Phosphate recovery without chemical addition

This paper reports experiments carried out using a 9 cm diameter, 1m high, sand-seeded fluidised bed reactor used to precipitate a mixture of struvite and calcium phosphate.

Full-scale phosphate precipitation installation at Treviso, Italy.

Since writing of this paper, a full-scale installation has been constructed, due for commissioning this summer, after further testing using a 9 cm diameter/3m high pilot plant (carried out at Ancona, Italy). The full-scale installation will treat a third to a half of the digester liquors from the new Treviso biological nutrient removal (BNR) sewage works (100.000 pe.), near Venice, Italy, using the same air stripping process presented in this paper. The Treviso waste water plant uses an original system where sorted organic household refuse is mixed with BNR sewage sludge for fermentation/ digestion both to produce methane (approx. 2,000 m^3/day) and to provide fatty acids necessary to "feed" the biological nutrient removal process.

This paper presents experiments using a 1m high pilot fed with anaerobic digester centrifuge liquors from a biological nutrient removal wwtp at Ancona, Italy. **This pilot plant work follows laboratory studies already reported (see SCOPE Newsletter n° 33).** Phosphate precipitation was initiated by a **pH increase generated only by CO_2 stripping (by intensive aeration), without the addition of any chemicals.**

The feed liquors had the following average characteristics (mg/l) :

pH	***7.7***
SCOD	*1320*
PO_4	*139*
NH_4	*914*
Ca	*153*

Mg	*24*
HCO_3	*3550*

The fluidised bed column was filled with 3.3 kg of quartz sand (0.21 - 0.35 mm), giving a compressed bed height of 0.4m and an expanded height of 1m. Two reactor vessels ahead of the fluidised bed column (in the fluid recycling loop) ensured aeration and a return to equilibrium of excess dissolved air. The aeration rate was up to 50l/m and the liquor recycle rate was 0.23 m^3/h (approx. 4 x the reactor volume hourly). Injection into the fluidised bed used a heavy gravel layer in the base of the bed to disperse and mix the flow, rather than a system of nozzles or injectors.

The pH, ion concentrations and recycling rate (reactor contact time) were modified to assess the impact of these different parameters of phosphate removal efficiency and precipitation.

========= Struvite and calcium phosphate =========

Experiments were carried out using artificially increased concentrations of Ca and Mg in the digester liquors to study the balance **between struvite (magnesium ammonium phosphate MAP) and calcium phosphate (CP) precipitation.** The MAP/CP ratio in the precipitated phosphates, using real sludge digester liquors only, was around 2:3 and relatively constant on the sand granules from the bottom to the top of the reactor bed. Calcium enriched liquors produced 80-100% CP and magnesium enrichment 80-100% MAP. The authors conclude that the two crystallisations occur without competition.

========= 96.5 % P-removal =========

The mass balance of phosphorus was monitored by comparing total input P to total and dissolved P in the outflow fluids and estimates of P precipitated on the seed crystals. The mass balance could be account for all input P with an error of under 10%.

Phosphorus removal efficiency (total output P / total input P) was high, reaching 96.5%.

The loss of "fines" from the reactor was very low (crystallised phosphates not agglomerated to seed sand granules and leaving the reactor suspended in fluid) : an average of 1.7% of total input P, with a maximum of only 3.5%. This meant that a filter step was not necessary on the reactor outflow.Fines were measured as the difference between outflow total and soluble P.

======== Phosphate precipitation efficiency ========

The precipitation efficiency of the reactor (proportion of input total P fixed onto sand seed crystals) was relatively good, nearly always at least 70% (14 out of 17 runs).

This **efficiency was strongly pH dependent,** varying from 58.2% at pH 7.4 to 86.7% at pH 8.55. The percentage of fines did not, however, increase significantly with higher pH. A pH of around 8.2 was considered adequate for optimal operation.

Phosphate precipitation efficiency was also strongly related to contact time, which was calculated from the fluid recycling rate through the reactor, from fluid velocities within the reactor and from the mass/surface area of seed crystals present.

Mathematical equations were developed to predict efficiency as a function of pH and contact time (the latter estimated by the fluid recycling ratio through the reactor).

========= Recovered phosphates =========

The mass balance of the seed grains in the reactor, after 24 days operation, showed **11.9 – 12.6% PO_4 by weight (approx. 4% P),** around 5.3% Ca, 1.2% Mg and 0.9%NH_4 .

"Phosphate removal in real anaerobic supernatants: modelling and performance of a fluidized bed reactor". Wat.Sci. Tech. vol 38, n° 1, 1998.

P. Battistoni, Institute of Hydraulics, Engineering Faculty, Unviersity of Ancona, 60131 Ancona. P. Pavan, University of Venice, Dept. Env. Sciences, Dorsodura 2137, Venice. F. Cecchi, Dept. Chemistry, University of L'Aquila, L'Aquila. J. Mata-Alvarez, Dept. Chemistry and Engineering, University of Barcelona, c. Marti i Franque 1/6, 08028, Barcelona, Spain.

SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Holland
Conclusions and futures for P-removal

The waste water treatment group of the Dutch National Water Association (NVA) organised a symposium on the policy, technologies and sustainability aspects of phosphorus removal in Amersfoort on 2nd July 1999.

It is now five years since large-scale phosphorus removal in sewage works was introduced in Holland, and this conference aimed to draw conclusions from this experience. **A phosphorus removal level of 75% is required in Holland,** as a result of national implementation of agreements between Rhine and North Sea countries (OSPARCOM). Dutch phosphorus discharge limits are more stringent than those in much of Europe, as they are based on ten-day moving average concentrations, rather than annual averages.

The phosphorus reduction objective set by OSPARCOM in 1987 was 50%, this has been more than achieved with a 60% reduction in phosphorus flowing into Holland in the Rhine as well as a 60% reduction in Dutch point source emissions.

======== Chemical or biological P-removal ? ========

Technical and economic presentations were made of chemical P-stripping and biological nutrient removal by Ir. P. de Jong **(Witteveen & Bos).** He considered the operating costs of biological phosphorus removal to be somewhat lower and indicated that 40% of operators now prefer biological systems, partly on grounds of sustainability.

Ir. M. Bentwelsen (Hoogheemraadschap van Delfland) indicated that in 1996 around 80% of phosphorus removal was by chemical precipitation and 20% by biological nutrient removal. He stated that chemical P-removal increases sewage sludge production by 15% and increases the iron content of sludge solids from 8% to 20%. Costs of metal salts have fallen in recent years, so that the chemical P-removal costs are now around 6.1 Euros/ kgP. He nonetheless concludes that, because of sludge generation and of salt discharges, chemical P-removal will be phased out over the coming 20-30 years and be replaced with biological systems.

Other speakers also indicated that biological nutrient removal was gaining ground. **Ing. H. Ellenbroek (Waterschap Regge en Dinkel)** indicated phosphorus removal costs of 2.4 Euros/kgP removed by biological treatment, 3.5 Euros/kgP for combined biological + chemical removal.

======== Sustainability and phosphorus recycling ========

Dr. Ir. Klapwijk (Wageningen Agricultural University) presented Life Cycle Analysis work carried out for the Dutch water research board STOWA. This suggests that, if nutrient removal requirements are satisfied, sewage treatment represents a minor contribution to most environmental issues. Only 4.4 % of Dutch nutrient releases to the environment will come from sewage following the implementation of phosphorus and iron discharge limits.

He considers that biological phosphorus removal is more sustainable than chemical treatment. Sustainability can be further improved by reductions in energy consumption, stricter discharge limits (effluent polishing) and the recovery of phosphates for recycling as calcium phosphates or struvite.

Ir. Gaastra (Hoogheemraadschap Uitwatrende Sluizen) presented operational experience of phosphorus recovery as calcium phosphates at the Geestmerambacht sewage works. The recovered phosphates are now being recycled in the phosphate industry. He estimates costs as 4.5 - 5.5 Euros/kgP removed.

The symposium was concluded with a general discussion as to the relative costs of biological and chemical phosphorus removal and regarding possibilities for phosphorus recycling. **It was noted that the phosphate industry is actively supporting recovery for re-use.**

Source : H_2O, Tijdschrift voor watervoorziening en waterbeheer. 16 July 1999, No. 14/15 (32), pages 40/41 (in Dutch).

Symposium proceedings available (in Dutch) from Mr. Bommele, NVA bommele@vewin.nl

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SCOPE NEWSLETTER

SCOPE N°35 - 12/1999 - Berlin area

Full P-removal from sewage key to surface water restoration

This paper summarises measures taken to reduce eutrophication of surface waters in the Berlin area. This is important because these waters are used to replenish groundwater supplies and provide drinking water through bank filtration systems. The water bodies themselves are used intensively for navigation, commercial fisheries, leisure activities.

Berlin is located in a lowland area with many rivers and lakes covering approximately 6% of land surface. Average rainfall is around 600 mm/year and the natural groundwater recharge of around 200 mm/year is not sufficient to maintain groundwater levels.

Drinking water is extracted from underground as the area's sandy soil is efficient in eliminating bacteria and viruses. Wells at depths of 70 - 170 m extract water that has filtered through the ground for around 2 months, either from natural groundwater or from artificial groundwater refilling.

This **bank filtration of surface water** has been shown to eliminate or degrade many contaminants, the best safeguard against the passage of undesirable substances is to provide high quality surface water. The organic substances present in eutrophic surface waters can impair the quality of bank filtered water, in particular due to volatile substances produced by algae.

======== Ambitious nutrient reduction strategy ========

This has led the Berlin area to **implement an ambitious strategy aimed at achieving low nutrient concentrations in surface waters.**

Targets of 0.07 - 0.08 mgP/l in rivers (Havel, Spree) and around 0.04 - 0.06 mgP/l total P for the major Berlin lakes (Tegel, Schlachtensee, Krumme) are considered necessary to avoid nuisance levels of algae.

The author indicates that the achievement of these targets in the rivers will require not only management of sewage works discharges, urban stormwater and industrial discharges, but also limitation of diffuse agricultural sources. The latter would necessitate buffer strips along rivers, reducing fertiliser use and reducing tile drainage - but these are sensitive political issues.

======== The need for advanced phosphorus removal from sewage ========

The achievement of nutrient reduction objectives for the Berlin lakes necessitate advanced phosphorus removal installations in sewage works, as well as ensuring full connection of households to sewage networks, avoiding sewage works overflow (ensure adequate capacity) and optimal management of urban stormwaters.

Berlin Wasserbetriebe's investments in improved sewage treatment since the reunification of Germany will total around 12 billion DM (1992 - 2004).

The Wassmansdorf sewage treatment plant was commissioned in 1994 and treats sewage from 1 million person equivalents achieving 0.05 mg/l phosphorus discharge by biological methods only.

======== P-stripping of lake inflow ========

For Lake Tegel, one of the city's larger lakes (4 km^2, surrounded by wells extracting a mixture of groundwater and bank filtered water to supply 700,000 people), a water treatment installation has been built on the lake's inflow. This plant treats 100 million m^3/year, flushing the lake approximately three times per year with treated surface water. The plant reduces phosphorus input concentrations from around 5 mg/l to below 0.02 mg/l using a four step chemical P-stripping process : precipitation - coagulation - flocculation, sedimentation, post-precipitation and flocculation - filtration.

This has enabled a concentration of 0.02 mg/l total P to be achieved in the lake's water.

Berlin's strategy is to improve surface water, to enable quality drinking water to be reliably and ecologically supplied by filtration through soil. **This necessitates action on diffuse nutrient sources, stormwater management, prevention of combined sewer overflow, full connection of households to sewage works and efficient nutrient removal in sewage works.**

"Improvement of the surface water quality in the Berlin area". Wat. Sci. Res. vol. 38 n° 6 pages 191-200, 1998.

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