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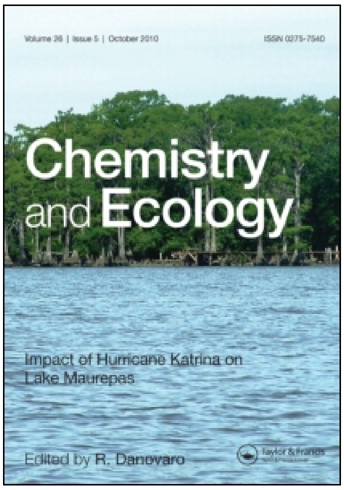

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Internal eutrophication: How it works and what to do about it—a review

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Internal eutrophication: How it works and what to do about it – a review

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In the 1980s and 1990s, it became increasingly clear that changes in external nutrient loads alone could not entirely explain the severe eutrophication of surface waters in the Netherlands. Nowadays, 'internal eutrophication' has become a widely accepted term in Dutch water management practice to describe the eutrophication of an ecosystem without additional external input of nutrients (N, P, K). This review surveys the principal mechanisms involved in this process. It also discusses possible remedies to combat internal eutrophication.

Keywords: Alkalinity; Anaerobic decomposition; Biomanipulation; Internal eutrophication; Nitrate; Phosphate; Sulphate

1. Introduction

In the Netherlands, the term internal eutrophication ('*interne eutrofiëring*' in Dutch) has become popular through publications by Roelofs and co-workers since the late 1980s [1–8]. Most of these publications were written in Dutch and described the eutrophication of surface waters in Dutch peaty lowlands as a result of changes in water quality without additional external supply of nutrients (N, P, K). Their ideas were based on the observation that water quality had deteriorated considerably, even in nature reserves, although in many cases no significant increase had occurred in the external nutrient loads [1, 3, 5]. Initially, this idea was received with great scepticism. However, as it became increasingly clear that changes in external nutrient loads alone could not possibly explain the eutrophication of the surface waters in the Netherlands, even in areas where external nutrient loads had been considerable, this idea gradually became accepted during the 1990s. Nowadays, internal eutrophication has become an accepted concept in Dutch water-management practice, as well as among fellow scientists, who have shown increasing interest in this theme.

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This review presents a brief overview of the mechanisms involved in the process called internal eutrophication, which we define as the eutrophication of an ecosystem without increased external input of nutrients (N, P, K). Possible remedies to combat internal eutrophication will also be discussed.

2. How it works

2.1 *Redox equilibria and organic-matter breakdown*

Organic-matter breakdown and the phosphorus-binding capacity of soil complexes are strongly influenced by microbial processes affecting the redox state. Redox reactions can be regarded as reactions in which transfer of electrons takes place and are generally mediated by microbes that derive energy from electron transfer [9]. As free electrons cannot exist in aqueous solutions, redox reactions always consist of a sub-reaction in which electrons are mobilized, and a sub-reaction in which electrons are consumed by an electron acceptor (oxidant).

In well-oxygenated systems, oxygen serves as the primary electron acceptor:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O.$$

As oxygen is thermodynamically the most favourable electron acceptor, this reaction will prevail, and as long as oxygen is present it serves as the primary oxidant in the decay of organic matter:

$$C_{\text{organic}} + 2H_2O \longrightarrow CO_2 + 4H^+ + 4e^-.$$

In most wetlands, however, oxygen penetration into the sediment is limited and is generally restricted to the upper 10 mm [9, 10]. Only in lakes with very low organic matter contents can oxygen penetrate deeper. Once all oxygen has been consumed or if oxygen is absent from the start, the decay of organic matter continues by a series of reactions that represent successively lower redox potentials (Eh).

Once oxygen levels have become sufficiently depleted, nitrate is used as the terminal electron acceptor by bacteria, if it is available:

$$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O$$
$$NO_3^- + 9H^+ + 8e^- \longrightarrow NH_4^+ + 2H_2O + OH^-.$$

This reduction of nitrate to dinitrogen gas (denitrification) or ammonium (ammonification or dissimilatory nitrate reduction to ammonium, DNRA) involves a multitude of electron transfer steps [9, 11].

Alternatively, iron(hydr)oxides and sulphate can become involved at successively lower redox potentials (Eh) [9, 10, 12]:

$$FeOOH + 3H^+ + e^- \longrightarrow Fe^{2+} + 2H_2O$$
$$SO_4^{2-} + 10H^+ + 8e^- \longrightarrow H_2S + 4H_2O.$$

The reduction of Fe and SO_4^{2-} leads to the formation of FeS_x and may result in a strong decrease in the P-binding capacity of the sediment, as FeS_x has fewer sorption sites for P than iron(hydr)oxides (FeOOH) [5, 7, 13, 14]. This is discussed in more detail below.

Under anaerobic conditions, the availability of these alternative electron acceptors strongly affects the breakdown of organic matter. It should be realized that although the consumption sequence of oxidants depends largely on their relative oxidative strengths, the anaerobic respiration pathways are not entirely mutually exclusive, and the different pathways normally show considerable overlap. In general, anaerobic decomposition is complex and mediated by a consortium of physiologically different micro-organisms [9, 10, 12]. Fermenting bacteria bring about extracellular hydrolysis of high-molecular-weight polymers (polysaccharides, proteins, etc.) and ferment the products (monomers such as sugars, amino acids, etc.) to CO_2, H_2, alcohols, acetate, and other organic acids. Acetogenic bacteria are involved in the cleavage of alcohols and organic acids into acetate, CO_2, and H_2. Associated with the fermentative organisms are organisms that derive energy from the products of these reactions. Consumption of acetate, H_2, and CO_2 generally occurs by sulphate-reducing bacteria (SRB) and methanogenic bacteria, the latter converting CO_2 and acetate into methane gas. The presence of the SRB and methanogenic bacteria is therefore essential to ensure that the end-products are consumed and that the anaerobic decay process keeps going [10, 12]. In addition to the availability of electron acceptors, (anaerobic) decomposition is obviously strongly regulated by the availability of degradable organic matter [15].

2.2 *Role of alkalinity*

Apart from the lack of alternative electron acceptors, acid or very poorly buffered conditions favour the accumulation of peat. It is well known that decomposition of organic matter is inhibited in acid waters compared with alkaline waters [5, 16–25]. Roelofs [5] showed that the alkalinization of surface waters in the Dutch peaty lowlands, due to the practice of letting in alkaline river water, was responsible for an increased mineralization of the peaty substrates. The decomposition rate of organic matter appears to be strongly correlated with the internal pH of the detritus, while bicarbonate neutralizes the decay-inhibiting acids [20, 26]. As a result, the decay rate of detritus appears to be a function of the buffer capacity of the surrounding water, rather than of pH [5, 20].

Support for this hypothesis was found in a study of 600 freshwater ecosystems in the Netherlands by Van Katwijk and Roelofs [27]. They found that the ortho-phosphate (PO_4^{3-}, in this review) concentrations and the bicarbonate alkalinity in surface water and sediment pore water solutions changed in the same direction in ordination diagrams. Smolders [28] also found a correlation between bicarbonate alkalinity and the PO_4^{3-} and NH_4^+ concentrations in sediment pore water obtained from organic freshwater sediments in the Netherlands (see also [29]).

The effect of alkalinity on PO_4^{3-} availability has been confirmed by an experiment in which the alkalinity of the water layer above an undisturbed weakly buffered peat layer was increased stepwise (figure 1). The PO_4^{3-} levels in the water layer gradually increased as alkalinity rose. This increase might be attributed to an increased decay rate due to the more alkaline conditions. Apart from enhancing organic matter breakdown, however, bicarbonate can also mobilize PO_4^{3-} because of the competition between HCO_3^- and PO_4^{3-} for anion adsorption sites. Although no distinction could be made between these two mechanisms, this experiment does confirm that increased bicarbonate alkalinity can greatly increase the availability of nutrients in surface waters with organic sediments.

Alkalinity may increase in response to a change in hydrology, such as letting in alkaline surface water, or due to increased alkalinity of the groundwater [3, 5, 24, 30]. However, alkalinity may also be generated within the system by the reduction of oxidants such as nitrate, iron(hydr)oxides or SO_4^{2-}. The reactions under the heading ‘redox equilibria’ show that all reduction reactions result in a net generation of alkalinity. This process is called internal alkalinization [5]. Internal alkalinization can be observed, for instance, at ‘De Venkoelen’,

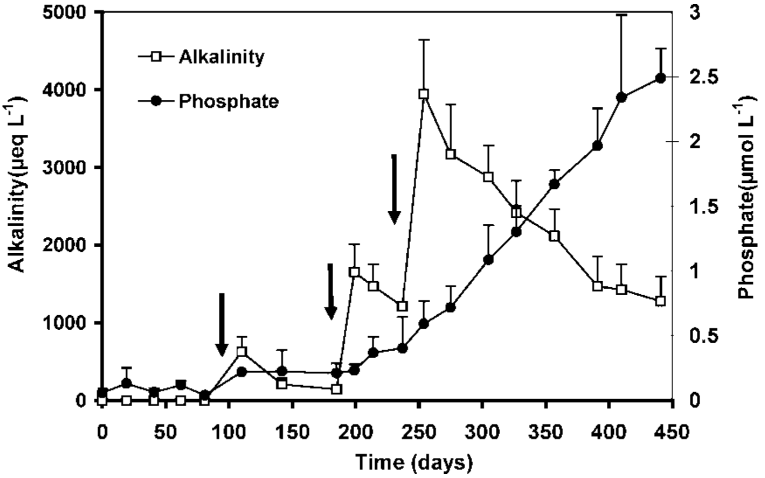

Figure 1. Increased phosphate concentrations in the water layer as a reaction to artificially increased alkalinity above a weakly buffered fen peat sediment derived from the 'Venkoelen' nature reserve (see also figure 2). Alkalinity was increased stepwise on the days marked with an arrow. The experiment was carried out in glass containers (30 × 30 × 30 cm), with a peat layer of 10 cm and a water layer of 18 cm. The containers were placed in a water bath at a constant temperature of 17 °C.

a minerotrophic fen in the south of the Netherlands (figure 2), where this process occurs due to high sulphate reduction rates in summer, resulting in increased alkalinity and decreased SO_4^{2-} concentration in the water layer. In winter, microbial reduction processes are greatly impaired by low temperatures, while the system is supplied with moderately buffered, sulphate-rich groundwater, resulting in increased SO_4^{2-} concentrations and decreased alkalinity of the water layer (figure 2).

2.3 *Increased sulphate loads*

The increased availability of sulphate in ecosystems due to anthropogenic changes has received much attention. The SO_4^{2-} concentrations in the River Rhine are nowadays twice those measured in 1900 [31]. In the Netherlands, water from the River Rhine is let into large areas of the peaty lowlands to prevent desiccation in summer [1, 5, 29, 30]. This is necessary because water levels are kept artificially stable. In the past, or in more natural situations, water levels fluctuated throughout the year, being generally high in winter and low in summer. Current water level regimes in the Netherlands tend to be the opposite: they are kept low in winter to enable rapid runoff of excess water from agricultural lands and relatively high and stable in summer to provide water for growth and evapotranspiration [29]. The water of the river Rhine is alkaline and has relatively high SO_4^{2-} concentrations [5, 7, 30].

In addition, SO_4^{2-} concentrations in groundwater have greatly increased over the last decades, as a consequence of increased atmospheric sulphur (S) deposition and leaching of SO_4^{2-} from agricultural land. Falling water tables and infiltration of nitrate (NO_3^-) from agricultural land and forest soils into the groundwater also increase groundwater SO_4^{2-} concentrations by favouring the oxidation of FeS_x in the subsoil [32, 33].

The potential role of nitrate as a SO_4^{2-} mobilizing agent has so far been largely overlooked. Under natural conditions, nitrate (NO_3^-) concentrations in groundwater are low ($<32\ \mu mol\ l^{-1}$). During the last 60 yr, however, groundwater NO_3^- concentrations have greatly increased in many parts of Europe, due to increased pollution. Excessive use of manure and synthetic fertilizers has resulted in leaching of NO_3^- from agricultural lands. In Europe, the

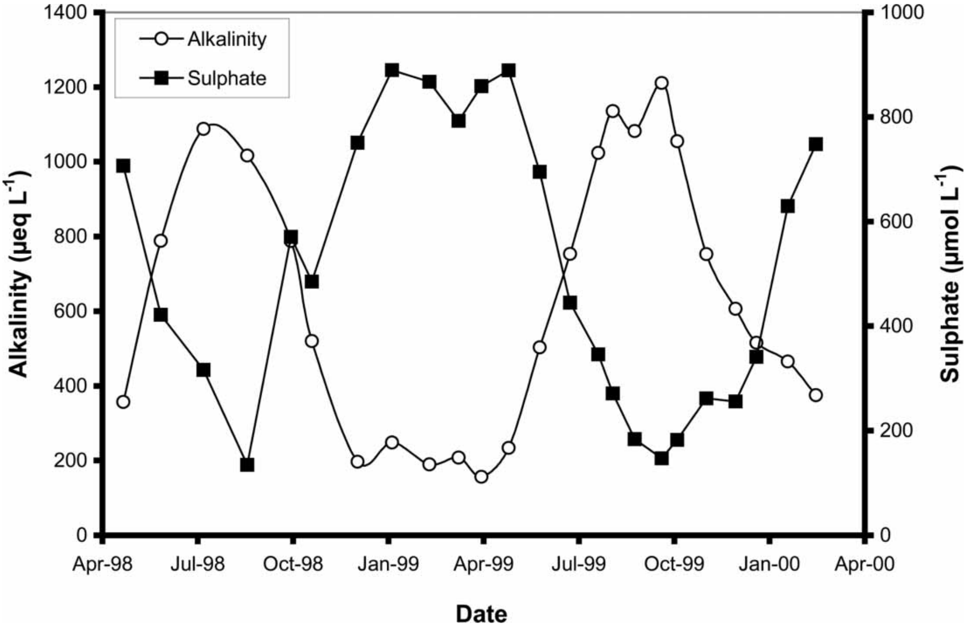

Figure 2. Variation over time of alkalinity and sulphate concentrations in the surface water of the 'Venkoelen', a minerotrophic fen lake near the city of Venlo, the Netherlands. Seasonal variation can be explained by different groundwater discharge rates and biological sulphate reduction in summer.

largest net applications of nitrogen (N) on agricultural land occur in the Netherlands and Belgium, with surpluses of 200 and 125 kg N ha^{-1} yr^{-1}, respectively [34]. In addition, leakage of NO_3^- from forest soils to the groundwater has increased as gaseous ammonia and ammonium sulphate aerosols are effectively filtered by tree crowns. This causes high ammonium (NH_4^+) deposition rates, especially in pine forests, and increased NO_3^- concentrations in the groundwater, as NH_4^+ is rapidly nitrified in forest soils, even under acid conditions [35–37]. Once it has accumulated in groundwater, NO_3^- causes chemolithotrophic oxidation of pyrite in the subsoil [38–41]. Van Steenwijk [42], for instance, observed the presence of a pyrite containing layer which coincided with the disappearance of infiltrating NO_3^- and an increase in SO_4^{2-} concentrations in the groundwater. Hence, it can be concluded that increased leaching of nitrate from agricultural lands and forests can result in greatly increased SO_4^{2-} concentrations in groundwater and, after discharge, in surface water.

2.4 *Sulphate-mediated eutrophication*

The increased input of SO_4^{2-} in aquatic ecosystems can lead to great changes in anaerobic sediments. As we have seen, SO_4^{2-} serves as an alternative electron acceptor in reductive sediments and stimulates the decomposition of organic matter. Sulphate reduction also results in internal alkalinization, which further enhances decomposition. Large amounts of SO_4^{2-} may also cause PO_4^{3-} release due to the competition between SO_4^{2-} and PO_4^{3-} for anion adsorption sites [13, 43].

Apart from this, sulphide (produced by SO_4^{2-} reduction) also interferes with the iron-phosphorus cycle, by reducing iron(III)(hydr)oxides and iron(III) phosphates [10, 44–48]. Subsequently, highly insoluble FeS_x is formed, reducing the availability of Fe to bind PO_4^{3-} and increasing PO_4^{3-} mobility [12, 14, 46–48].

This phenomenon occurs especially in soils in which a large part of the P content is bound to Fe. Fe-rich sediments tend to retain P that becomes available from decomposition processes and/or external P loading (figure 3). Such sediments can become loaded with P, which in itself should not necessarily cause any problem as long as the SO_4^{2-} loads remain low. However, increased SO_4^{2-} loads can easily mobilize Fe-bound P through sulphide-induced Fe binding, which may lead to eutrophication of such systems [7, 29, 45, 49]. Prolonged high SO_4^{2-} loads to such sediments will ultimately result in sediments in which most of the Fe is bound to reduced sulphur (FeS_x). As a consequence, the capacity of the sediment to retain P will greatly decrease (FeS_x has far fewer sorption sites for P), which may result in decreased total P concentrations but also in a high mobility of P in the sediments. If SO_4^{2-} reduction continues, toxic concentrations of free sulphide may accumulate in the sediment pore water and cause serious problems for rooted aquatic macrophytes by inducing sulphide toxicity and iron deficiency [7, 14, 29, 45, 49–51].

Normally, the classic iron cycle [52, 53] can very well explain the actual release of P from the sediment. In the oxygenated boundary layer between sediment and water layer, dissolved Fe becomes oxidized and PO_4^{3-} is effectively bound by iron(hydr)oxides. This mechanism probably explains the positive relation between the P-release to the water layer and the dissolved-P:dissolved-Fe ratios in sediment pore water described by Smolders *et al.* [47]. Under sulphur-rich reducing conditions, however, most Fe is present as FeS_x, so this mechanism may no longer function [7, 13, 47]. Furthermore, dissolved sulphide (and other reduced compounds) consumes oxygen in the top sediment layer, thus decreasing the thickness of the oxidized boundary layer. This may greatly boost the release of dissolved PO_4^{3-} from the sediment. Increased methane production rates under highly reductive conditions may further stimulate P-release by ebullition, especially in organic sediments [5, 10]. Once the sediment becomes weak and less structured, bottom-feeding fish species such as bream (*Abramis brama*) become more abundant and may further enhance the exchange of nutrients between the sediment and the water layer [54]. Increased activity of benthivorous fish may make the sediments more susceptible to wind- and wave-induced disturbance [55], further increasing turbidity and the release of nutrients from the sediment.

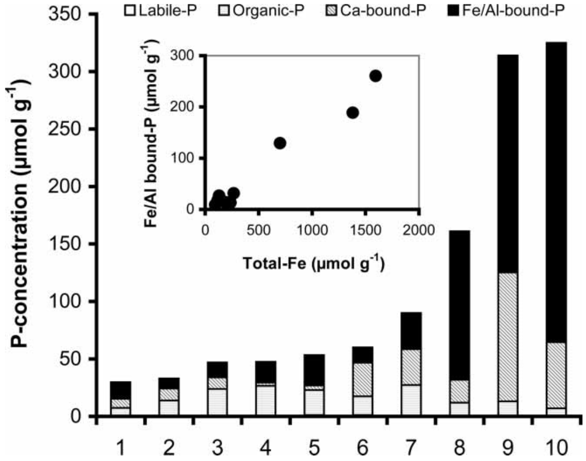

Figure 3. Relationship between total-iron content and iron-bound P concentrations in sediments derived from different lakes in the province of Zuid-Holland (the Netherlands). P fractionation of the sediment was carried out according to Golterman [108] and allowed a distinction between unstable (loosely bound) P, Ca-bound P, organic P, and Fe/Al-bound P. The numbers 1–10 represent different locations.

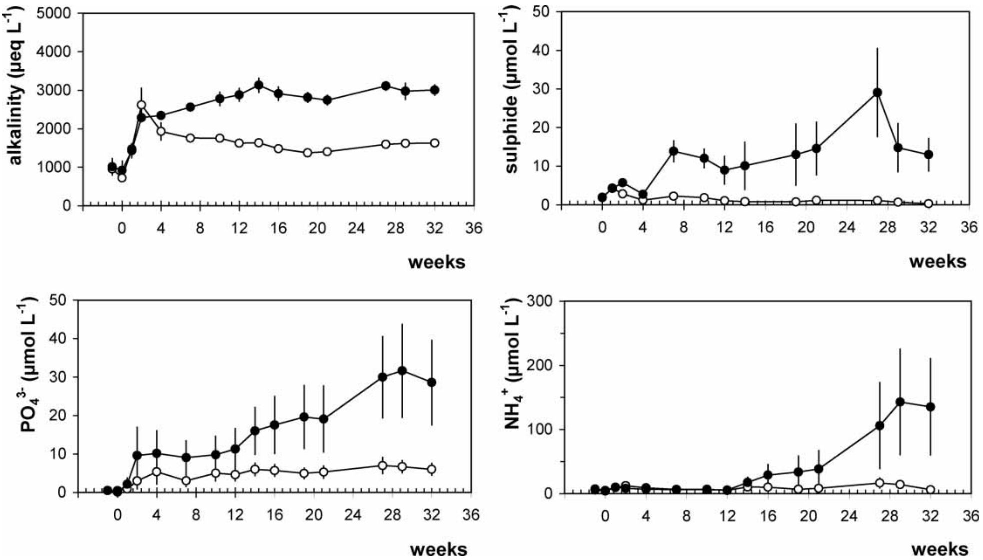

Figure 4. Soil pore water characteristics of monoliths from a minerotrophic fen meadow ('De Bruuk', a nature reserve near the village of Groesbeek, the Netherlands) during 32 weeks of waterlogging with either 0 or 2 mmol l^{-1} sulphate (white and black marks, respectively). The figure shows means with standard errors ($n = 6$). See also [14].

Many experiments have confirmed that increased SO_4^{2-} loads indeed lead to increased nutrient availability [5, 14, 15, 25, 47–49, 56–58]. Figure 4, for instance, shows the results of an experiment in which the SO_4^{2-} loads of monoliths obtained from a minerotrophic fen meadow were experimentally increased (see also [14]). A SO_4^{2-} load of 2 mmol l^{-1} led to a clear increase in alkalinity as well as in the PO_4^{3-}, S^{2-}, and NH_4^+ concentrations of the soil pore water (figure 4). At the end of the experiment, biomass regrowth after harvesting was significantly smaller on SO_4^{2-}-treated soils, especially for *Carex* species [59], though *Juncus* species appeared to be more resistant to the changes. Additional experiments confirmed that sulphide toxicity was the main cause of the decline of *Carex* species in the SO_4^{2-} treatments [59].

The decline of vegetation dominated by species such as *Stratiotes aloides* and *Potamogeton compressus* in the Netherlands can be attributed to increased SO_4^{2-} loads and the resulting increase in PO_4^{3-} and NH_4^+ levels in the water layer, as well as increased concentrations of S^{2-} in sediment pore water [28, 60, 61]. Sulphide and ammonium toxicity, iron deficiency, and increased competition by free floating macrophyte species may occur separately but frequently also occur simultaneously (multiple stress), resulting in a considerable decrease in vitality and finally in the complete decline of mesotrophic vegetation types (figure 5).

Vegetation shifts in aquatic systems have also been revealed by an analysis of the extensive database collected by De Lyon and Roelofs [62]. This database includes the weighted means of many physico-chemical variables for most of the aquatic and semi-aquatic macrophyte species in the Netherlands. In an analysis of this database, Smolders *et al.* [61] tried to establish a relationship between the weighted means of the SO_4^{2-} and PO_4^{3-} concentrations in the water layer for aquatic plants in the Netherlands. For species from very reductive sediments ($Eh < -150$ mV), a very clear relationship was found between these weighted means [61]. As SO_4^{2-} is reduced in these sediments, SO_4^{2-}-induced eutrophication by the mechanisms described above can occur, and higher surface water SO_4^{2-} levels may correspondingly result in higher PO_4^{3-} levels.

Among the species of reductive sediments, one can distinguish a group of species of waters with SO_4^{2-} concentrations <0.5 mmol l^{-1} and PO_4^{3-} concentrations <5 µmol l^{-1} (figure 6).

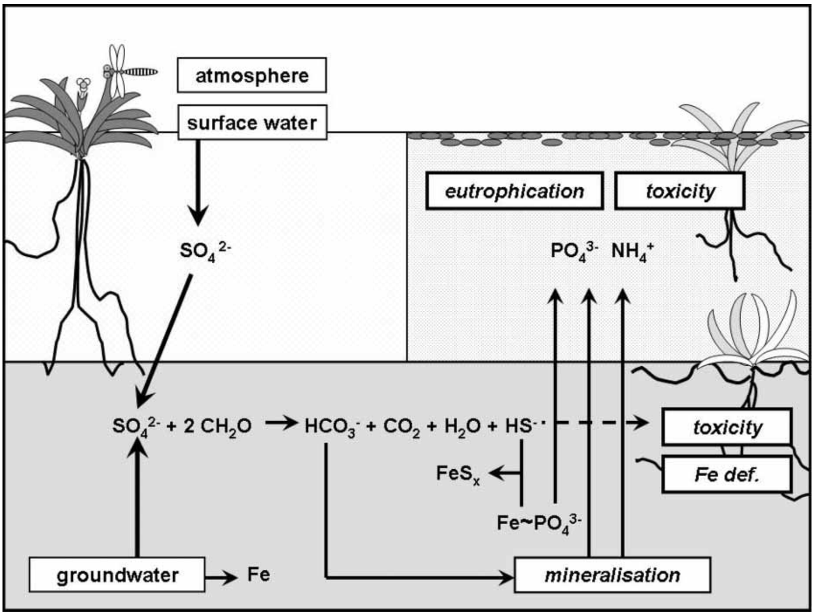

Figure 5. Multiple environmental stress hypothesis explaining the decline of *Stratiotes aloides* in the Netherlands. Sulphate enters via surface water, groundwater, or atmospheric deposition. The reduction of sulphate to sulphide causes eutrophication as the sulphide interacts with P binding, and mineralization is stimulated by alkalinity generation. As a result, the water layer becomes eutrophied, leading to the dominance of floating species and algae. Simultaneously, sulphide and ammonium toxicity and iron deficiency may occur.

These are species such as *S. aloides*, *Potamogeton compressus*, *Potamogeton acutifolius*, and *Utricularia vulgaris*, which were once highly characteristic of the shallow surface waters in the minerotrophic regions of the Netherlands, and are typical species of mesotrophic waters. Two further groups that can be distinguished (II and III in figure 6) are characteristic of waters with higher SO_4^{2-} (weighted average between 0.7 and 1.2 mmol l^{-1}) and PO_4^{3-} concentrations (weighted average between 5 and 10 μmol l^{-1}). These groups include species such as *Spirodela polyrhiza*, *Lemna trisulca*, and *Ceratophyllum demersum*, which tend to replace *S. aloides* or become co-dominant in *Stratiotes* vegetation that has gradually become eutrophied [30].

Species of brackish waters with reductive sediment also appear to fit very well into the scheme shown in figure 6. These species occur in waters with naturally high SO_4^{2-} concentrations and hence also high PO_4^{3-} concentrations. It is important to realize that species adapted to brackish water conditions have a competitive advantage over species that are not adapted to high salinity, and therefore probably do not suffer from competition by non-rooting freshwater species. Compared with pristine conditions, waters with *Ceratophyllum submersum*, *Lemna gibba*, and *Azolla filiculoides* also have increased SO_4^{2-} concentrations, but the weighted average of the PO_4^{3-} concentrations in the water layer is very high. We suggest that these species become dominant in waters in which, owing to sediment characteristics [48], increased SO_4^{2-} reduction leads to very strong PO_4^{3-} mobilization, or in waters where external PO_4^{3-} loads play an important role.

2.5 *Role of nitrate*

On agricultural lands in particular, large amounts of NO_3^- may be leached from the top layer to the deeper soil layers. In situations where agricultural lands are located on top of anaerobic

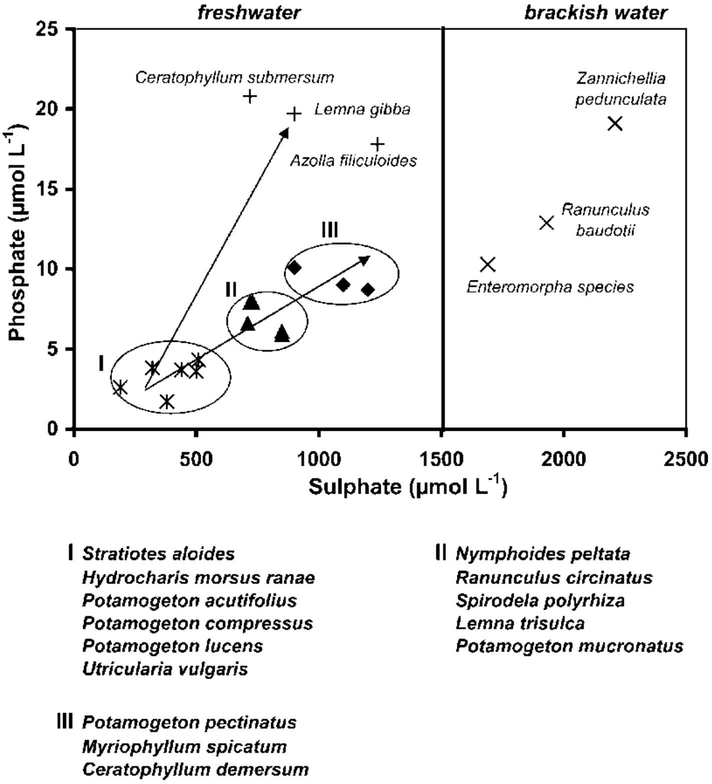

Figure 6. Relationship between the weighted average of the phosphate and sulphate concentrations in the water layer for aquatic plants preferring sediments with different reductive states (Eh). The positions of species characteristic of reductive sediments (Eh < -150 mV) are indicated in the figure by squares (I), triangles (II), diamonds (III), and crosses. All data are derived from [62].

peaty soils, this might lead to increased decomposition of the peat, as NO_3^- functions as an alternative electron acceptor (oxidant). Drainage ditches in such polder areas in the Netherlands are characterized by the presence of large amounts of organic mud which cannot be explained by the external input via surface water inlet. The mud is very probably produced within the systems, from the decomposition of the local peat layers. Apart from aerobic decomposition due to falling water tables and anaerobic SO_4^{2-}-mediated breakdown, nitrate-mediated decomposition probably plays an important role in these agricultural systems. This will be a subject of further research in the near future.

However, NO_3^- does not necessarily enhance internal eutrophication. As NO_3^- is an energetically more favourable electron acceptor in anaerobic sediments than Fe and SO_4^{2-}, high NO_3^- loads may function as a redox buffer, limiting the reduction of Fe and SO_4^{2-} [9, 63]. In addition, NO_3^- reducing bacteria have the capacity to grow anaerobically, with Fe(II) as an electron donor, resulting in the production of Fe(III) [64–66]. It is indeed known that NO_3^- reduction can lead to the oxidation of Fe(II) [39–41, 67, 68] and metal sulphides [69–72], and so may increase the PO_4^{3-}-binding capacity of sediments under anaerobic conditions.

The hypothesis that NO_3^- may actually prevent internal eutrophication was confirmed by recent research in Dutch alder carr fens [33, 73]. During the last decades, alder carrs in the Netherlands have become highly eutrophied [73, 74]. Enclosure experiments have shown that high SO_4^{2-} reduction rates lead to PO_4^{3-} mobilization and subsequent eutrophication [58]. However, field observations also revealed that no eutrophication occurs if there is a constant input of groundwater that contains not only SO_4^{2-} but also high concentrations of NO_3^- [33]. The alder carrs that were fed by groundwater with high NO_3^- concentrations were characterized by the lowest PO_4^{3-} concentrations and the development of aquatic plants characteristic of clear waters [33].

This role of NO_3^- as a redox buffer was confirmed by subsequent laboratory experiments [33], in which a continuous flow of NO_3^--rich medium led to a higher redox potential and much lower methane concentrations in the alder carr sediment than the same medium without NO_3^-. In addition, the release of Fe and S^{2-}, resulting from the oxidation of FeS_x, Fe^{2+}, and S^{2-} was much lower in sediments receiving NO_3^--rich medium than in those receiving medium without NO_3^-, while the release of SO_4^{2-} was higher as a result of nitrate-induced oxidation of FeS_x.

Based on these observations, we propose the following mechanism for the current situation in the Netherlands. NO_3^- leaching from agricultural lands and forest soils leads to increased NO_3^- concentrations in the groundwater. When NO_3^- reaches FeS_x-containing subsoil layers, it may oxidize FeS_x, leading to the mobilization of SO_4^{2-} and a decrease in the NO_3^- concentration. The resulting NO_3^-:SO_4^{2-} ratio strongly affects the quality of groundwater-fed fens. If SO_4^{2-} concentrations are high, and NO_3^- concentrations are low, eutrophication may occur as a result of SO_4^{2-} reduction-related processes such as PO_4^{3-} mobilization and Fe immobilization (FeS_x accumulation). However, if NO_3^- concentrations are also high, SO_4^{2-} and Fe reduction are impaired, and mobilization of PO_4^{3-} from iron-phosphate complexes is prevented. In addition, NO_3^- may oxidize reduced Fe compounds, increasing the amount of Fe^{3+} capable of binding PO_4^{3-}. Hence, NO_3^- leaching into the groundwater increases the risk of eutrophication of the discharge areas by mobilizing SO_4^{2-} in FeS_x containing aquifers. However, if NO_3^- reaches a discharge area in sufficiently high concentrations, it may prevent actual eutrophication (at least of the directly fed parts) by functioning as a redox buffer [33].

2.6 *Effects of temporary oxidation*

It is well known that some aquatic macrophytes, such as isoetid species, release large amounts of oxygen from their roots and so maintain an oxidized state in the sediments [51, 75–77]. As a consequence, PO_4^{3-} is bound to iron(hydr)oxide and remains highly immobile [78]. Taking away the oxygen source by experimental removal of the vegetation results in an increase in iron and PO_4^{3-} availability due to a large decrease in redox potential [76]. These aquatic macrophytes may therefore lower the PO_4^{3-} availability by maintaining Fe in an oxidized state. They can also decrease the nitrogen (N) availability by stimulating coupled nitrification–denitrification processes [51, 79]. In the root zones and the water layer, NH_4^+ is nitrified to highly mobile NO_3^-, while NO_3^- diffuses to the deeper anoxic sediment where it is denitrified. In this way, oligotrophic conditions can persist for as long as 10 000 yr, *e.g.* in soft-water lakes.

Temporary desiccation of sediments can mimic these effects and lead to lower nutrient concentrations, while permanent high water levels may have the opposite effect. During desiccation, pore-water PO_4^{3-} concentrations tend to decrease as PO_4^{3-} binds to oxidized Fe(III) compounds, such as iron phosphate, iron(hydr)oxide-phosphate, and humic-iron-phosphate complexes [59, 78, 80, 81]. Nitrification is stimulated after desiccation, while subsequent waterlogging suppresses nitrification and stimulates denitrification [14, 33]. During desiccation, bicarbonate is also consumed by the oxidation of FeS_x and the absence of alkalinity-generating processes like denitrification. This can result in more poorly buffered conditions after rewetting and hence in a decreased decomposition of organic matter.

However, Lucassen *et al.* [82] found that desiccation may lead to severe acidification and mobilization of heavy metals when the sediment S/(Ca + Mg) ratio is high (>0.7 in alder carr forest). Total Ca + Mg should be regarded as a measure of the buffer capacity due to carbonate dissolution and cation exchange. The solubility of PO_4^{3-} complexes, including apatite ($Ca_5(PO_4)_3(OH,F,Cl)$), strengite ($FePO_4$), and variscite ($AlPO_4$), is also strongly influenced by pH. With decreasing pH, apatite is the first to dissolve, followed by variscite and strengite [83]. Hence, the present sulphur pollution in many freshwater wetlands forms a threat not only by inducing SO_4^{2-}-mediated internal eutrophication, but also by increasing the sensitivity of wetlands to desiccation [59, 82]. The combination of increased sulphur loading and a growing risk of the occurrence of desiccation is therefore a major cause for concern. Furthermore, the high SO_4^{2-} concentrations generated by desiccation and the subsequent runoff following rehydration inevitably cause internal eutrophication in reduced peaty soils and sediments where the water is discharged.

At the same time, however, temporary desiccation of the top layer of the sediment appears to be important in preventing undesirable vegetation development in well-buffered systems such as alder carr forests [73, 84, 85]. Oxidation of insoluble FeS_x leads to mobilization of SO_4^{2-} and precipitation of Fe as $FePO_4$ and Fe(III) hydroxides. After reflooding, the mobile SO_4^{2-} is removed from the system via the flowing water layer, while oxidized Fe is gradually reduced again, also resulting in the release of immobilized P. Hence, one would expect only a minor effect of temporary desiccation. However, in the presence of significant amounts of insoluble reduced Fe, such as iron sulphides (FeS_x) or siderite ($FeCO_3$), oxidation of the sediment results in a net production of Fe(III), which greatly increases the amount of reducible oxidized Fe in the sediment capable of binding o-PO_4^{3-} and may thus produce a more lasting beneficial effect of desiccation [84].

This effect is illustrated by the results of an experiment in which the effect of two water regimes (with and without a 6 week desiccation period) were tested on two sediment types [84]. One sediment originated from a zone that is fed by SO_4^{2-}- and Fe-rich seepage during a large part of the year and that temporarily dries out during the summer (T-sediment). This sediment had a relatively high reduced Fe (FeS_x) content. The other sediment was derived from a formerly dry zone without reduced Fe (D-sediment) (figure 7) and had a low reduced Fe content. The results showed that P release from the sediment and the concomitant development of algae and lemnids in the water layer depend on the sediment type and the interaction between sediment type and water-table fluctuations. In the T-sediment, total P concentrations in the water layer differed greatly between the temporary desiccation treatment and the control treatment. Desiccation of T-sediment greatly diminished the accumulation of total P in the water layer and the concomitant biomass production of lemnids and algae in the water layer (figure 7).

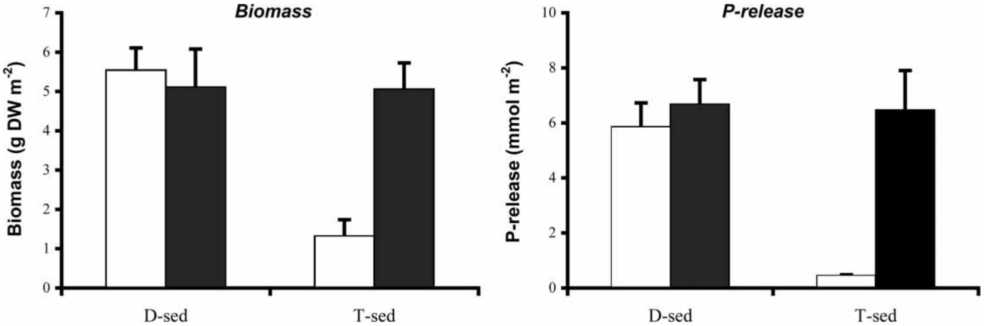

Figure 7. Total P release and development of algae + *Lemna* spec. biomass above two different sediments (T and D sediment, see text) from alder carr forests in the Netherlands. Values are for a 3 month period after a 6 week desiccation period (removal of the water layer; white bars) or a control treatment with constant flooded conditions (black bars). The water layer of the control treatment was replaced when the sediment of the desiccation treatment was reflooded [84].

In sediments with a high reduced iron concentration, release of P to the water layer apparently remained low for a considerable time after desiccation and subsequent re-flooding. This can be explained by the effect that, after desiccation and re-flooding, the same amount of P is now immobilized by a much larger pool of oxidized iron, and it thus takes a longer time before all iron is reduced again, and the same amount of P is mobilized.

In the D-sediment, however, temporary desiccation did not lead to significant differences in pore water P or in (total) P concentrations in the water layer after re-flooding (figure 7). In both treatments, the water layer was extremely eutrophied, with a very high production of filamentous algae and lemnids. Formerly dry sediments such as the D-sediment have not been influenced by groundwater for a long time and do not possess a reduced Fe pool, which is why desiccation did not result in an additional increase in the reducible Fe pool [84].

Oxidation of the top layer of sediment may also be achieved by increased light levels on the sediment surface. Figure 8 shows the effects of increased light levels on the sediment surface on the oxygen profiles in the sediment top layer and the PO_4^{3-} concentrations in the water layer. The sediment used in this experiment was extremely reduced, with a high FeS_x content and a very low concentration of dissolved iron (figure 8). In this experiment, increased irradiance resulted in the growth of benthic algae on the sediment surface. Oxygen produced by these algae resulted in oxidation of the sediment top layer (figure 8) and hence in the oxidation of iron sulphide compounds. As a result, reducible iron concentrations increased in the top layer, and PO_4^{3-} was bound more effectively in this layer, resulting in a decreased release of PO_4^{3-} to the water layer (figure 8).

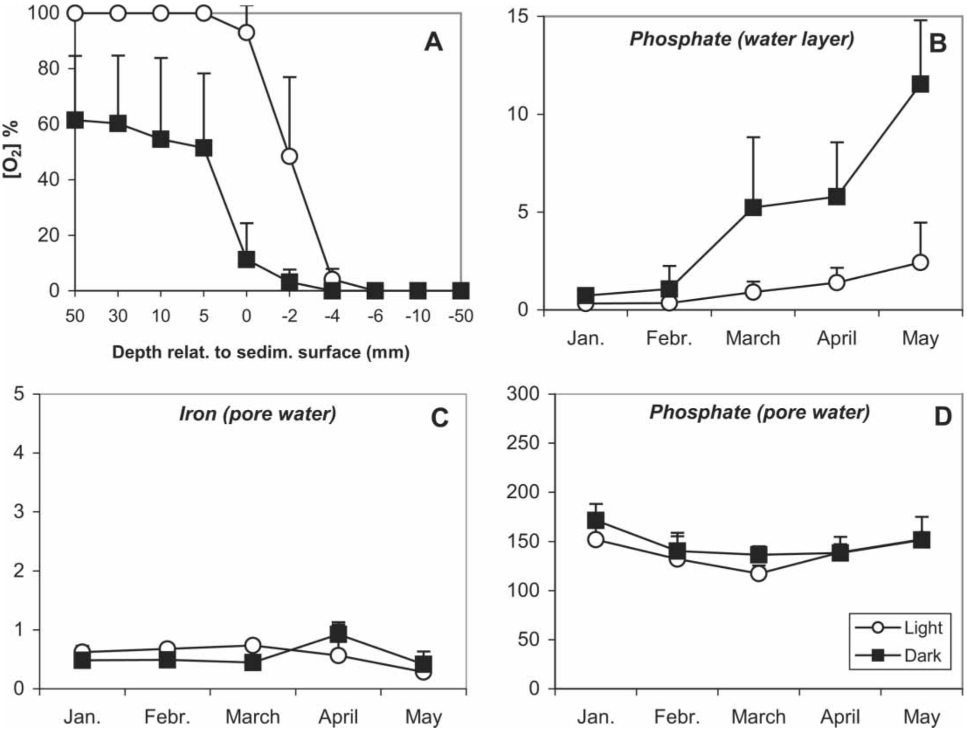

Figure 8. Oxygen profiles at the water/sediment interface (A), phosphate concentrations in the water layer (B), and iron (C) and phosphate (D) concentrations in sediment pore water of a reduced sulphur- rich sediment under dark (black squares) and light conditions (white circles) during a 5 month experimental period. Experiments ($n = 3$) were carried out in glass containers (25 × 25 × 30 cm), with a 10 cm sediment layer and an 18 cm water layer. Under light conditions, benthic algae were growing on the sediment surface.

3. What to do about it

3.1 *How to prevent eutrophication*

The release of PO_4^{3-} from eutrophic sediments strongly depends on the redox state of the top layer. As light may stimulate the growth of water plants and benthic algae, which may subsequently oxidize the top layer of the sediment, turbid water results in internal eutrophication, while internal eutrophication results in turbid waters. Natural water-level fluctuations (temporary desiccation in summer) may be a prerequisite to prevent internal eutrophication of wetlands [73, 84, 85]. This is likely to be especially true for marshes and moorland pools. Another advantage of the oxidation of the top layer of the sediment is the fact that many seeds in the seed beds, which do not geminate in very reductive sediments, germinate and colonize the bottom very quickly after a short drought [28]. Ill-considered measures to prevent desiccation at any cost may have disastrous consequences for such systems [73, 74]. A recent strategy to minimize the use of allochthonous water in drainage ditches involves the application of a more natural water-table management strategy, allowing higher tables in winter and lower tables in summer. In addition, this is expected to decrease PO_4^{3-} concentrations and stimulate germination of aquatic macrophytes. However, this strategy needs further research. Artificial oxygenation of the water layer may also increase the redox state of the sediment top layer and prevent the release of PO_4^{3-} to the water column [86]. It is especially in relatively small, shallow lakes that this might be a plausible method to combat internal eutrophication.

3.2 *Biomanipulation*

Clear water is essential for the development of submerged plant communities, often dominated by Characeae. This condition may be achieved via a bottom-up approach, leading to a significant reduction in the nutrient availability, or by a more top-down approach like biomanipulation [54, 87–90]. Biomanipulation is defined as the deliberate exploitation of the interactions between components of the aquatic ecosystem, in order to reduce the algal biomass [87]. The main aim is to increase zooplankton (mainly *Daphnia*) grazing on phytoplankton, thereby changing from a state of turbid water to one of clear water, even though the nutrient concentrations remain equal [89]. To achieve this, the system has to be ‘pushed’ through the hysteresis effect that prevents an easy transition from one state to the other. Once submerged vegetation has established, it helps to maintain the clear-water equilibrium by providing a habitat and refuge for zooplankton, preventing resuspension of sediment particles, competing with algae for nutrients and depressing algal growth by the excretion of allelopathic substances [89, 91].

In many shallow lakes, the desired change to clear water has been achieved by a drastic reduction of the zooplanktivorous and benthivorous fish stocks [54, 87, 88, 92–94]. This involves a reduction to 10–15 $\mathrm{kg\,ha^{-1}}$ and 15–25 $\mathrm{kg\,ha^{-1}}$ of zooplanktivorous and benthivorous fish, respectively (generally corresponding to a minimum reduction of 75%). In addition, piscivorous fish like *Esox lucius* (Northern pike) and *Stizostedion lucioperca* (Pikeperch) may be introduced or reintroduced. In some fens, such biomanipulation turned out to be very effective in re-establishing underwater light conditions that are favourable to submerged macrophytes. In others, however, the water remained turbid or became turbid again quickly after the measures were taken, and submerged plant communities failed to develop.

In hypertrophic lakes, turbidity is the only possible stable situation. Biomanipulation will only work after PO_4^{3-} concentrations are reduced to a range in which two alternative stable states are possible [89]. The actual threshold value seems to lie below about 7 μmol total $\mathrm{P\,l^{-1}}$, although shallow lakes may be clear at much higher concentrations [88, 95]. This can be attributed to the strong influence of submerged macrophytes on water quality, as explained earlier. Poor results with biomanipulation in fens well within the range of two alternative stable states are often caused by insufficient reduction of the fish stock or by massive fish remigration from small interconnected ditches or through fish exclosures [96]. In most fen waters, the best way of fighting eutrophication seems to lie in a combination of biomanipulation (top-down control) and active reduction of the influx and internal mobilization of PO_4^{3-} (bottom-up).

3.3 *Phosphate inactivation*

Phosphorus can be very effectively bound in the form of calcium phosphates. In south-west Norway, for instance, P concentrations as high as 100 mmol g^{-1} DW are encountered in the sediments, but the lakes can still be characterized as ultra-oligotrophic, since almost all P is present in the form of highly insoluble fluorapatite ($Ca_5F(PO_4)_3$). In hard-water lakes, lime additions have shown some potential for controlling P availability [97, 98]. Lime application may supersaturate the water column with Ca^{2+}, which can result in precipitation of (hydroxy)apatite and also cause precipitation of phytoplankton. Binding P as calcium phosphate precipitation might have great advantages, as Ca-bound P is redox-insensitive. However, compared with Fe and Al additions, liming seems to be less effective [86], and multiple treatments may be necessary for long-term management of phytoplankton biomass [97, 98]. In soft-water lakes with a peaty sediment, the addition of lime to bind PO_4^{3-} will not work, because of the strong stimulation of P mineralization in fen peat (see above), overruling any possible effect of chemical binding of P [5, 28, 29].

The addition of Fe or Al to sediments to bind PO_4^{3-} (PO_4^{3-} inactivation) has a strong de-eutrophying effect in both lakes and fens [47, 49, 86, 98–102]. Burley *et al.* [86] concluded that Fe(III) and Al addition were more effective than liming, although cost-effectiveness considerations may make these methods less desirable [47, 98]. If there is a constant supply of SO_4^{2-} enriched water, the response is only transient, because Fe consumption is extremely high [47, 49, 86]. In such cases, Fe addition has proved to be too laborious and costly to be recommended as a general and large-scale restoration measure against eutrophication [47].

Aluminium addition has the advantage that Al-bound P is redox-insensitive and indeed seems to be able to bind P more effectively than Fe [103]. A special problem related to the addition of aluminium salts, however, is the fact that Al may cause toxicity symptoms, especially in the fauna component of the system. Acidification due to $Al_x(OH)_3$ formation (hydrolization) may lead to high concentrations of highly toxic inorganic monomeric Al (Al^{3+}) [104], while subsequent polymerization reactions (formation of Al hydroxides) can temporarily result in an even greater toxicity [105]. Although, in well-buffered (alkaline) lakes, such highly toxic shock events will be both local and temporary, they may still be considered highly undesirable, especially when valuable fauna components are present.

The presence of dense macrophyte stands may cause problems, especially when Ca, Fe, or Al is applied directly to the water layer [102]. In cases where P is bound to the top layer following the addition of Ca/Fe/Al, sediment P may be taken up directly from below the treated top layer. The nutrients taken up from the sediment by these macrophytes then become available in the water layer due to senescence and decay. Finally, Ca/Fe/Al-treated sediment may become buried if sedimentation rates remain relatively high and so lose their effectiveness [102].

3.4 *Sediment removal*

Dredging of PO_4^{3-}-enriched and/or iron-depleted sediments is another option and can be highly effective [106, 107]. However, if no additional measures are taken, the effect of sediment removal is also temporary. In eutrophied, poorly buffered systems, sediment removal may lead to a strong decrease in nutrient levels in the water layer, but also to a severe decrease in the base saturation of the sediment. As long as water rich in acid and/or ammonium enters the system, acidification or re-acidification of these systems may occur. An adequate additional measure to counteract re-acidification may be a controlled supply of calcareous groundwater [106]. Problems linked with sediment removal, however, are not only the high costs but also the fact that, according to the present environmental standards, the sediment in many cases has to be technically classified as chemical waste because of accumulated toxic compounds.

4. Final comments

It can be concluded that internal eutrophication may play an important role in the deterioration of aquatic ecosystems. Increased breakdown of organic matter under anaerobic conditions due to increased alkalinity and increased availability of oxidants (SO_4^{2-} and possibly nitrate) play key roles in this process. In addition, the interference of SO_4^{2-} with the iron-phosphate cycle is of paramount importance. The restoration of the original, semi-natural hydrology (high water levels in winter and low water levels in summer), both at the landscape level and at the habitat level, may reduce the negative effects or may even be a prerequisite for an acceptable water quality. Such measures will decrease the SO_4^{2-} and alkalinity loads of the systems and might also increase the P-binding capacity of the sediments if temporary desiccation should occur.

Biomanipulation is a costly but potentially effective method by which an alternative stable state can be reached, which permits clear water even while nutrient concentrations in the water layer remain high. Treatments of whole water bodies with lime, iron, or aluminium salts have also proved to be potentially effective. However, such measures are also costly, while the improvement of the water quality is often transient.

More generally, it is important to realize that agriculture on peaty substrates, which is currently being practised on a large scale in the Netherlands, is not sustainable. A complete hydrological isolation of large areas would probably be the best way to prevent internal eutrophication processes. Allowing more rain water to accumulate in the wetlands would reduce not only the alkalinity but also the SO_4^{2-} load. Next, old seepage systems might be restored, which would result locally in a renewed supply of iron via the groundwater. Raising water tables and decreasing nitrate loads from former agricultural lands could further diminish the SO_4^{2-} concentrations in groundwater. This might allow large marshes to start re-developing, and peat could build up again in areas where organic soil is currently broken down rapidly. This would diminish soil subsidence as well as net carbon losses to the atmosphere. Given the agricultural functions involved, such measures would not be a feasible option at present. In the long run, however, these alternative options might become more attractive because agriculture is economically under great pressure, especially in the wet lowland areas.

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