

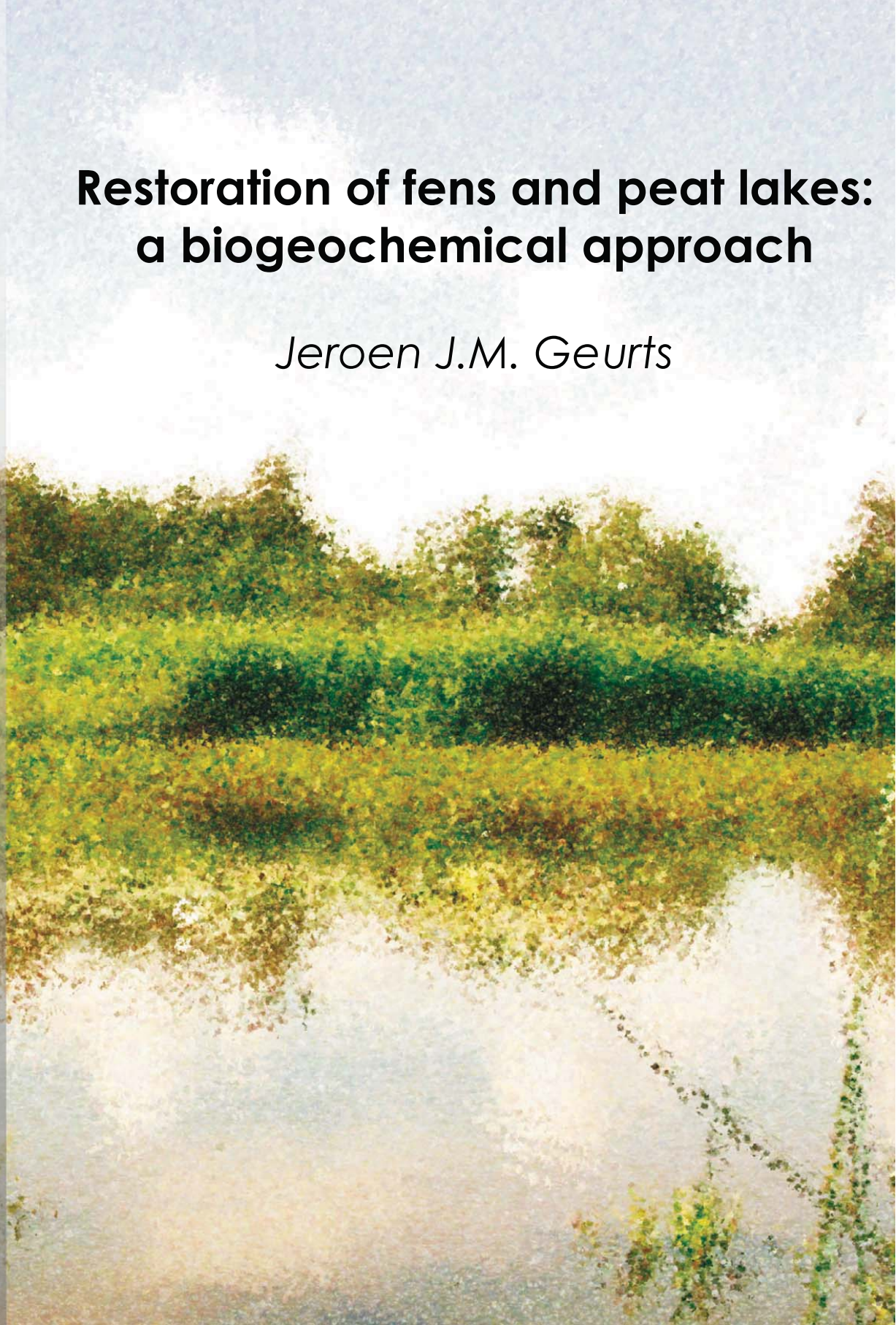
Restoration of fens and peat lakes: a biogeochemical approach

Jeroen J.M. Geurts

Restoration of fens and peat lakes:

a biogeochemical approach

Jeroen J.M. Geurts 2010



Restoration of fens and peat lakes: a biogeochemical approach

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Deze uitgave werd mede mogelijk gemaakt door



*Nobody said it was easy
No one ever said it would be this hard
Oh take me back to the start*

*I was just guessing at numbers and figures
Pulling the puzzles apart.
Questions of science, science and progress
Could not speak as loud as my heart.*

Uit: The Scientist (Coldplay)

Voor Susan en Ivan

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Chapter 1

General introduction



*Jezioro Łuckie, a peat lake full of Stratiotes aloides plants
in Poleski National Park (Lubelskie, Poland)*

Freshwater wetlands, fens and peat lakes

Freshwater wetlands are areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with fresh water that is static or flowing (Ramsar Convention; Mitsch & Gosselink, 1986). Among these freshwater wetland types are minerotrophic fens ("laagvenen" in Dutch), which are peat-forming, aquatic or semi-terrestrial wetlands usually fed by surface and/or groundwater, having a water chemistry that is generally base-rich (Wheeler & Proctor, 2000). In this thesis, fens basically cover all phases in the natural succession from open peat lakes and turf ponds with submerged and floating-leaved plants (Fig. 1), through floating rafts, to helophyte-dominated fens and carr forests (Verhoeven & Bobbink, 2001). There will also be paid attention to soft-water peat lakes and former agricultural soils, including peat soils.



Figure 1. Biodiverse vegetation of submerged and floating-leaved plants in a ditch in Wapserveen.

Decline of fens and peat lakes

Worldwide, freshwater wetlands are being threatened by anthropogenic disturbance, causing huge biodiversity losses (Lake *et al.*, 2000; Dudgeon *et al.*, 2005). Fens and peat lakes that used to be peat forming systems (Kivinen & Pakarinen, 1981) have become a significant source of C, N and P due to

increased peat decomposition (Lamers *et al.*, 2002b; Laiho, 2006; Bragazza *et al.*, 2007). This increase is caused by multiple environmental problems, such as desiccation, eutrophication, pollution and global warming (Gorham, 1995; Smolders *et al.*, 2006). High sulphate loads in polluted rivers and groundwater have led to increased sulphur fluxes and concentrations in fens and marshes, e.g. in the Netherlands (Roelofs, 1991), Germany (Zak & Gelbrecht, 2007), the Everglades (Bates *et al.*, 2002), New York (Boomer & Bedford, 2008b) and the Louisiana delta plain (Swarzenski *et al.*, 2008). The toxicity related to this eutrophication and pollution can play a very important role in the ecological functioning of peatlands. Increased agricultural fertilization and the use of polluted river water to compensate for water shortage have both, directly or indirectly, led to a higher availability of nutrients and potentially toxic compounds such as sulphide and ammonium.

Eutrophication and sulphate pollution have seriously affected biodiversity, vegetation development and terrestrialization in fens (Roelofs, 1991; Koerselman *et al.*, 1995; Wassen & Olde Venterink, 2006). Several characteristic aquatic macrophytes, such as *Stratiotes aloides* L., *Potamogeton compressus* L. and *P. acutifolius* Link have disappeared from lakes, ditches and turf ponds (Roelofs, 1991; Lamers *et al.*, 2002a; Smolders *et al.*, 2003a). These species have been outcompeted by a few fast-growing species (e.g. *Ceratophyllum demersum* L., *Elodea nuttallii* (Planch.) St.John, or green algae and cyanobacteria), leading to a considerable decrease in biodiversity (Kubin & Melzer, 1996; Lamers *et al.*, 1998a; Van der Welle *et al.*, 2006). Besides that, the characteristic plant species that disappeared often served as ecosystem engineers (Jones *et al.*, 1994): key species that can colonize the water layer, form floating mats and initiate terrestrialization processes in fens (Van Diggelen *et al.*, 1996; Grootjans *et al.*, 2006). Without these species, there will be no peat formation, but net peat degradation instead, especially because eutrophication will increase nutrient concentrations in the organic matter (Aerts & Chapin, 2000).

National and European legislation that aims to connect existing nature conservation areas has strongly increased the area of former agricultural land that is available for ecological restoration (National Ecological Network EHS, 1990; Natura 2000; Smolders *et al.*, 2008). Many of these former agricultural lands are converted into wetlands, which often also serve as water storage areas. However, a major problem that has to be overcome in these areas is that these areas have been heavily fertilized in recent decades, resulting in the accumulation of huge amounts of P and N in the soil (Barberis *et al.*, 1996). It is especially P, being less mobile, which accumulates in the top layer of the soil

(Schärer *et al.*, 2007), whereas N can easily leach to deeper layers (Johnston 1994). These exceptionally high nutrient concentrations form the most important constraint on the development and maintenance of biodiverse plant communities at these sites. Inundation of these sites can cause serious PO_4 mobilization to the water layer, depending on the biogeochemical properties of the soil and the water quality (Pant & Ready 2003; Lamers *et al.*, 2005). *Juncus effusus* (soft rush) is one of the notorious eutrophic species that tends to dominate strongly on soils with a high P availability (Smolders *et al.*, 2008; Fig. 2). This easily dispersing species can germinate and grow very fast and outcompete other plant species by shading them (Ervin & Wetzel 2001, 2002). In densely populated regions it is not to be expected that N will be the growth limiting factor for *J. effusus*, because N depositions are generally high (Bobbink *et al.*, 1998). This is supported by studies showing that the most biodiverse nature areas in these regions are found on P-limited soils (Janssens *et al.*, 1998; Wassen *et al.*, 2005).



Figure 2. Domination of *Juncus effusus* on peat baulks in De Deelen.

Important biogeochemical processes

In many surface waters, the primary production of submerged vegetation is P-limited, as N-availability is relatively high (Schindler, 1977; Richardson, 1985; Reddy *et al.*, 1999; Blomqvist *et al.*, 2004), often indicated by N:P ratios in plant

tissue $> 16 \text{ g g}^{-1}$ (Koerselman & Meuleman, 1996; Verhoeven *et al.*, 1996; Wassen *et al.*, 2005). A strong increase in PO_4 concentrations will then irrevocably cause a shift from a clear water state with submerged macrophytes to a hypertrophic state with turbid water dominated by algae and cyanobacteria (Scheffer *et al.*, 1993; Correll, 1998; Rip *et al.*, 2005), especially when there is a continuous supply of PO_4 from external sources or from the sediment (Jeppesen *et al.*, 2005). Resuspension caused by wind, shipping and benthivorous fishes further maintains the turbid state of the water (Ter Heerdt & Hootsmans, 2007). Because of the small water volume per unit of sediment surface and the lack of a thermocline, the sediment plays a key role in determining water quality in shallow fen waters. Therefore, biogeochemical processes in the sediment, wind-induced resuspension and bioturbation have a great impact on water quality and on the growth of algae and submerged macrophytes in these systems (Barko *et al.*, 1991; Søndergaard *et al.*, 2003). Besides that, aquatic macrophytes are also known to be capable of regulating both water quality and sediment characteristics by reducing sediment resuspension, erosion and turbidity (Madsen *et al.*, 2001; Nöges *et al.*, 2003), and by influencing P-availability both positively and negatively (Wigand *et al.*, 1997).

Decomposition rates are mainly determined by the availability of oxygen or alternative electron acceptors, temperature, pH, moisture content, organic matter content and quality, and nutrient levels (Clymo, 1983; Enríquez *et al.*, 1993; Aerts, 2006). Decomposition increases the concentration of particulate and dissolved organic matter in surface waters, leading to increased turbidity and strongly coloured water (Stern *et al.*, 2007). This will negatively affect the growth of submerged macrophytes and lead to a less biodiverse system with only floating or emergent macrophytes, and without terrestrialization and peat formation. It is generally assumed that decomposition of peat soils and sediments also automatically increases nutrient concentrations in sediments and surface waters (McLatchey & Reddy, 1998; Bayley *et al.*, 2005). In aquatic peatland systems, however, decomposition does not always lead to net PO_4 mineralization and increased PO_4 availability in soils and sediments (Bridgham *et al.*, 1998), because PO_4 can be bound immediately after mineralization, for example in Fe-rich (Smolders *et al.*, 2006) or Ca-rich sediments (Reddy *et al.*, 1993). This implies that the actual release of PO_4 is not coupled to high decomposition rates *per se*.

In wet ecosystems, the mobilization and immobilization of PO_4 in surface water and sediment is redox-dependent and to largely determined by its sequestration into different kinds of Fe- PO_4 complexes (Lijklema 1980; Boström *et al.*, 1982; Golterman 1995). In the oxygenated boundary layer between sediment and

water layer, dissolved Fe becomes oxidized and PO_4 is effectively bound by iron oxides and hydroxides (Mortimer, 1941, 1942). This process is especially sensitive to sulphate pollution via surface water or groundwater, which originates from prolonged high atmospheric deposition, sulphate-containing fertilizers, and, probably the most important cause at many locations, oxidation of pyrite deposits in the topsoil or in the deeper subsoil (Lamers *et al.*, 1998b; Bates *et al.*, 2002; Takashima *et al.*, 2002; Lucassen *et al.*, 2004b). This oxidation can be the result of desiccation (aerobic oxidation) or NO_3 leaching (anaerobic denitrification coupled to sulphide oxidation; Haaijer *et al.*, 2006).

Subsequently, reduction of SO_4 and Fe in anaerobic, organic sediments will lead to FeS_x formation, sulphide accumulation and toxicity, and mobilization of Fe-bound PO_4 (Smolders & Roelofs, 1993; Golterman, 1995; Roden & Edmonds, 1997; Wetzel, 2001; Lamers *et al.*, 2002a; Boomer & Bedford, 2008a). In addition, there will be competition between SO_4 and PO_4 for anion binding sites (Caraco *et al.*, 1989; Beltman *et al.*, 2000), and SO_4 could also stimulate organic matter decomposition and alkalization (Drever, 1997). All of these processes result in PO_4 mobilization from the sediment to the water layer (Brouwer *et al.*, 1999; Lucassen *et al.*, 2004a; Zak *et al.*, 2006). This mobilization is generally much higher in peat sediments than in sand or clay sediments, due to the higher availability of organic matter and higher oxygen consumption (Holmer & Storkholm 2001; Lamers *et al.*, 2001b; Loeb *et al.*, 2007). Flooding of a terrestrial system also results in anaerobic soil conditions and the reduction of Fe compounds, which decreases the binding capacity of Fe for P and subsequently leads to the release of Fe-bound P (Patrick & Khalid 1974; Ponnampereuma 1984). This P release during flooding has been shown to depend on the availability of organic matter and the P saturation of Fe binding sites (Loeb *et al.*, 2008).

Many wet ecosystems are more or less 'protected' against PO_4 eutrophication by sufficient supply of anaerobic Fe-rich groundwater. These high Fe concentrations can also immobilize sulphide and prevent toxicity (Smolders *et al.*, 1995; Van der Welle *et al.*, 2006). However, the anthropogenic drawdown of groundwater tables at a landscape scale as well as on a local scale has stopped this discharge of Fe-rich groundwater in many regions. Alkaline surface water hardly contains any Fe, since Fe precipitates under non-acidic aerobic circumstances.

Although much is known about sulphide toxicity in marine environments (Havill *et al.*, 1985; Portnoy & Giblin, 1997; Erskine & Koch, 2000; Azzoni *et al.*, 2001), only few studies have investigated this issue in freshwater wetlands. In these systems, it

may lead to suppressed growth and development, Fe chlorosis, leaf necrosis, suppressed flowering, black and flaccid roots, root decay and even the death of the whole plant (Allam & Hollis, 1972; Armstrong *et al.*, 1996; Smolders & Roelofs, 1996; Van der Welle *et al.*, 2007b). How different plant species deal with sulphide toxicity mainly depends on their ability to oxidize the root zone by radial oxygen loss (Lamers *et al.*, 1998a; Adema *et al.*, 2003; Van der Welle *et al.*, 2007a).

It seems likely, however, that these specific toxicity effects of sulphide interact with the level of eutrophication. On the one hand, eutrophication enhances toxicity, either directly by ammonium accumulation (Roelofs, 1991; Smolders *et al.*, 1996; Lamers *et al.*, 1998a; Britto & Kronzucker, 2002) or indirectly by stimulating decomposition and reduction processes (Rejmankova & Houdkova, 2006). On the other hand, eutrophication may lead to higher biomass production, which may dilute the toxic compounds in plant tissue (Timmer & Stone, 1978; Jarrell & Beverly, 1981; Outridge, 1992). Increased plant growth may also lead to increased root development, and thus to more radial oxygen loss and a less reductive sediment (Jaynes & Carpenter, 1986). To either avoid these toxicity effects or compete with other fen species in a nutrient-rich situation, plants may adopt different growth strategies, such as lateral growth of rhizomes and elevation of the leaf canopy (Grime, 1974).

Diagnostic and prognostic tools

Many studies have shown that growth of aquatic macrophytes is related to water quality (Onaindia *et al.*, 1996; Loughheed *et al.*, 2001; James *et al.*, 2005). This means that species composition is indicative of water quality and, conversely, water quality data can be used to predict the restoration of aquatic vegetation in shallow lakes (Bloemendaal & Roelofs, 1988; Grasmück *et al.*, 1995; Goslee *et al.*, 1997; Van den Berg *et al.*, 2003). Water quality, however, is subject to large temporal fluctuations (e.g. due to seasonal influences, or plant and algal growth), so that frequent sampling is needed for good prediction of vegetation responses, with the exception of alkalinity which seems quite conservative (Vestergaard & Sand-Jensen, 2000). By contrast, the predictive power of certain sediment characteristics may be greater than water chemistry because they are more stable over time and indicative of several important sediment processes, such as nutrient availability in the sediment and nutrient fluxes from the sediment to the overlaying water. Hence, sediment characteristics might be more appropriate and less expensive than water quality data for estimating the chances of reestablishment of aquatic vegetation.

General mechanisms of P binding, and more specifically PO₄ binding, by Fe, Al and Ca compounds in sediment and pore water have been investigated to determine thresholds for PO₄ mobilization to the surface water (Jensen *et al.*, 1992; Golterman, 1998). The pore water Fe:PO₄ ratio, rather than the actual concentration of PO₄ in the pore water, is known to be an important factor determining the potential PO₄ mobilization from peaty sediments to the overlying water. Different studies demonstrated this by finding thresholds for increased P release to the water layer at certain pore water Fe:PO₄ ratios (Smolders *et al.*, 2001; Lofgren & Boström, 1989; Zak *et al.*, 2004). Others determined thresholds for total sediment Fe:P ratios or Al:P ratios to estimate the risk of PO₄ mobilization (Jensen *et al.*, 1992; Ramm & Scheps, 1997; Maassen *et al.*, 2005). In (semi-)terrestrial systems, a good indication of the bioavailable P fraction in the soil is given by the Olsen-P concentration (Olsen *et al.*, 1954), which determines the chance of domination of fast growing species like *J. effusus* (Smolders *et al.*, 2008).

Restoration measures

In the past, various methods have been used to reduce P concentrations in surface water, sediments and soils.

Dredging is often used as a restoration measure in eutrophic peat lakes and fens with high concentrations and mobilization rates of nutrients. Dredging of the nutrient-rich and less reactive upper sediment layer can, however, expose a new, more intact and more reactive peat layer that will decompose faster, particularly in alkaline, S-rich areas that are poor in Fe (Roelofs, 1991; Brouwer *et al.*, 1999). In the Dutch peat lake Geerplas for example, dredging and P-stripping of all inflowing water have led to an even higher nutrient mobilization rate from the sediment to the water layer than before these expensive measures had started (Michielsen *et al.*, 2007). Organic soft-water lakes, which are generally more isolated than minerotrophic lakes can, however, be recovered very successfully by removing the eutrophic, organic sludge layer in order to restore the limitation of biomass production by C, N and P (Roelofs, 1996; Brouwer & Roelofs, 2001; Smolders *et al.*, 2002).

Earlier experiments have demonstrated that the addition of Fe salts may lead to a spectacular improvement of the water quality (Cooke *et al.*, 1993; Boers *et al.*, 1994; Smolders *et al.*, 1995; Smolders *et al.*, 2001; Hansen *et al.*, 2003). After Fe

addition, PO_4 concentrations remained low, algal growth was inhibited and the water became clear, while control treatments without Fe addition became turbid due to persistent high PO_4 mobilization from the sediment. Unfortunately, these effects only lasted for a few months, because Fe is redox-sensitive and doses were too low to compensate for the high Fe consumption by PO_4 or by sulphide originating from SO_4 reduction in the anaerobic sediment. In addition, these systems received high fluxes of Fe-consuming components through the influx of surface water rich in PO_4 and SO_4 .

Ca has been used in different forms to control eutrophication in both lakes and terrestrial systems (Beltman *et al.*, 2001; Brouwer *et al.*, 2002; Varjo *et al.*, 2003; Anderson, 2004). Co-precipitation of PO_4 with calcite (CaCO_3) is important in reducing PO_4 mobilization to the surface water (Boström *et al.*, 1988; Danen-Louwerse *et al.*, 1995; Dittrich & Koschel, 2002). Liming with CaCO_3 has turned out to be an effective additional measure to reduce P availability after top soil removal (Smolders *et al.*, 2008). However, liming leads to an increase in pH and alkalinity (HCO_3^-) and could therefore stimulate decomposition in organic soils and sediments, which will result in additional nutrient mobilization (Smolders *et al.*, 2006).

Al addition is a widely used method to immobilize P in lakes (Rydin & Welch, 1998; Reitzel *et al.*, 2003). Although Al is insensitive to changes in redox potential and therefore able to bind PO_4 to $\text{Al}(\text{OH})_3$ under anoxic conditions (Cooke *et al.*, 1993), it is sensitive to pH changes (Driscoll & Schecher, 1990). This method is most effective between pH 6 and 8 and can cause serious toxicity problems at lower pH (Rydin & Welch, 1998). Moreover, Al addition itself can lead to decreased pH values in soil and surface water (Malecki-Brown *et al.*, 2007). Studies have also shown that the Al will crystallize over time and form gibbsite, leading to a lower binding capacity for P (Berkowitz *et al.*, 2005).

In terrestrial systems, top soil removal seems to be the most efficient measure to create a nutrient-poor situation within a relatively limited time span (Wetzel & Howe 1999; Lamers *et al.*, 2005; Smolders *et al.*, 2008), although it is an expensive measure in many cases. Sometimes it is not even possible to remove enough soil to create P limitation, because deeper soil layers still contain high P concentrations, and additional measures have to be taken. Removing the topsoil also results in the disappearance of the diaspore bank, although in agricultural soils this mainly contains seeds from eutrophic species rather than rare target species (Smolders *et al.*, 2008).

In addition, water treatment residuals (WTRs) are widely used in agricultural soils to increase the P sorption capacity of the soil and reduce off-site P leaching (Novak & Watts, 2004; Agyin-Birikorang *et al.*, 2009). WTRs contain either Fe, Al or Ca as potential P immobilizers (Elliott *et al.*, 2002), with Al-WTRs having the highest ability to immobilize P. Ann *et al.* (2000) compared the effectiveness of several chemical amendments in immobilizing P in soils from a constructed wetland and found that addition of FeCl_3 was clearly most effective, followed by Al and Ca compounds.

Lanthanum-modified clay (LMC), e.g. Phoslock®, proved to be very successful in immobilizing P and reducing algal blooms in many lakes and rivers (Robb *et al.*, 2003; Akhurst *et al.*, 2004; Yang *et al.*, 2004) by trapping all P in the water layer and by forming an active layer on top of the sediment, which immobilizes P at the sediment-water interface. The advantage of LMC is that lanthanum has strong ionic binding characteristics (Stumm & Morgan, 1996) and forms highly stable minerals with a low solubility in the presence of phosphates (Firsching, 1992; Douglas *et al.*, 2000), which are relatively insensitive to changes in pH, redox potential and oxygen concentrations (Ross *et al.*, 2008).

Restoration of fens and peat lakes in the Netherlands: national research programme OBN

The research presented in this thesis was embedded in a larger programme. To investigate the decline of fens and peat lakes in the Netherlands, including the role of important biogeochemical processes and restoration possibilities, fens and peat lakes were integrated in the national OBN research programme ("Overlevingsplan Bos en Natuur / Ontwikkeling en Beheer Natuurkwaliteit; Lamers *et al.*, 2001a) of the Ministry of Agriculture, Nature and Food Quality. The aim of this research program was to use an ecosystem-orientated approach in order to fill gaps in the existing knowledge and to search for highly effective restoration measures. The emphasis was on the definition of key processes and key factors that caused the decline of fens and could lead to their restoration, on the characterization of different types of fens and peat lakes, and on the evaluation of existing restoration measures. This was achieved by comparative field research, field experiments (Fig. 3), mesocosm experiments and laboratory experiments. The results of this applied research should provide simple measurements (prognostic and diagnostic tools), which can immediately be used by conservation area managers to choose between several restoration measures. Ultimately, this should lead to decreased eutrophication and pollution,

to the restoration of specific target vegetation types (Higler, 2000), and to increased biodiversity in fens and peat lakes.



Figure 3. Enclosure experiment in the peat lake Tienhovense Plassen.

This ecosystem-orientated, interdisciplinary approach was only possible by the participation of several research institutes, covering the following topics:

- water and sediment quality in relation to vegetation (B-WARE Research Centre; Radboud University Nijmegen);
- terrestrialization and peat formation (Utrecht University);
- food web interactions (NIOO, Nieuwersluis);
- fauna (Bargerveen Foundation, Nijmegen);
- hydrology (Friesland Water Authority, Leeuwarden; Witteveen+Bos, Deventer);
- fish management and biomanipulation (Witteveen+Bos, Deventer);
- desmids (Koeman en Bijkerk, Haren).

Objectives and outline of the thesis

The research started with an extensive comparative field survey in 145 fens, peat lakes, ditches and turf ponds in the Netherlands, Ireland and Poland (**Chapter 2**). The distribution of aquatic and semi-aquatic macrophytes was investigated in relation to surface water quality, pore water quality and other sediment characteristics, and focused on the occurrence of endangered species.

Considering the importance of biogeochemical interactions for the functioning of macrophytes in fens and peat lakes (Bloemendaal & Roelofs, 1988; Barko *et al.*, 1991; Søndergaard *et al.*, 2003), it was assumed that sediment and sediment pore water characteristics may be important not only for the proper understanding of sediment biogeochemical processes determining water quality in shallow peat lakes, but also for the prediction of the response of plant species composition to restoration measures. More specifically, the use of sediment parameters as diagnostic and prognostic tools for wetland management was evaluated in relation to ecological rehabilitation and the development of new nature reserves.

In **Chapter 3** the interactions among rates of decomposition, net nutrient mineralization and nutrient mobilization to the water layer were studied in peat sediments and floating fen soils from the Netherlands and Ireland. Firstly, 28 non-calcareous peat sediments and floating fen soils were incubated under aerobic and anaerobic conditions to simulate low and high water tables. It was hypothesized that mineralization rates of N and P may be uncoupled from decomposition rates (Bridgham *et al.*, 1998), depending on the nutrient concentrations in the sediment, because anthropogenically disturbed fens may show sediments that have been largely decomposed, but still show high nutrient concentrations. Secondly, mobilization rates of PO_4 and N ($\text{NO}_x + \text{NH}_y$) were investigated in relation to sediment and pore water characteristics in 44 Dutch non-calcareous peat lakes and ditches to find easily measurable indicators to estimate the potential nutrient mobilization from peat sediments to the water layer, and the contribution of internal nutrient mobilization to the overall eutrophication (Roelofs, 1991; Smolders *et al.*, 2006; Janse *et al.*, 2008). It was expected that the actual PO_4 mobilization to the water layer was not determined by high sediment PO_4 concentrations per se, because PO_4 can be immobilized in the sediment (Reddy *et al.*, 1993; Smolders *et al.*, 2006).

Chapter 4 describes a full-factorial mesocosm experiment to test possible interactions between eutrophication, SO_4 pollution and sulphide toxicity in fens at the levels of plant species and plant communities. In the course of three growing seasons, the effects of NP fertilization of the peat, SO_4 enrichment of the water, or a combination were tested in 16 outdoor, semi-controlled mesocosms, each containing four aquatic and seven semi-aquatic macrophyte species with different growth strategies. It was hypothesized that sulphide toxicity would not only differ between species, but also depend on the level of eutrophication. Eutrophication can either enhance toxicity (Roelofs, 1991; Lamers *et al.*, 1998a; Britto & Kronzucker, 2002) or lead to increased biomass production and root

development (Timmer & Stone, 1978; Jarrell & Beverly, 1981; Jaynes & Carpenter, 1986). This could have important implications for water management and for restoration measures in fens, because toxicity effects can be masked in eutrophic areas and may show up when nutrient availability is reduced, even leading to a vegetation collapse.

In **Chapter 5** it is discussed whether Fe application would be a suitable alternative measure to restore water quality in eutrophied, soft-water peat lakes where dredging is not an option. Although PO_4 fixation by Fe salts often turned out to be a short-lived measure in alkaline lakes (Boers *et al.*, 1994; Smolders *et al.*, 1995) due to high Fe consumption rates (Holmer & Storkholm, 2001; Lamers *et al.*, 2001b), it was expected that Fe addition may be much more successful in these relatively isolated soft-water lakes. The effectiveness of PO_4 immobilization by Fe was tested in an enclosure experiment in the rainwater-fed, relatively isolated soft-water lake Uddelermeer (the Netherlands), which is a deep pingo remnant filled with peat. The high PO_4 concentrations and concomitant blooms of algae and cyanobacteria in this turbid lake are a constraint to its restoration (Grontmij, 1996). Four different amounts of iron chloride (FeCl_x) were tested, either added to the anaerobic sediment or to the aerobic surface water. The implications of the findings are discussed in relation to water management in soft-water lakes.

In **Chapter 6**, a new method was tested to immobilize P in former agricultural soils that have become available for ecological restoration and will be converted into wetlands. Because current methods may not always be possible or sufficient, or may have some serious drawbacks, it was investigated whether the addition of Phoslock®, a lanthanum-modified bentonite clay (LMC; Douglas, 2002), would decrease bioavailable P concentrations in the soil and PO_4 mobilization to the water layer in former agricultural soils. The results were compared with those of lime addition (Dolokal). A container experiment was performed using different soil types and different doses of LMC and lime. The soils were exposed to different water levels (moist and flooded) and *J. effusus* plants were used as phytometers (Clements & Goldsmith 1924; Wheeler *et al.*, 1992). If LMC should prove to be effective in decreasing Olsen-P concentrations in former agricultural soils, chances for the development of a more biodiverse vegetation could be improved. LMC addition was expected to be especially effective in flooded soils, because it forms an active layer on top of the soil that reduces PO_4 mobilization to the water layer and prevents algal blooms (Robb *et al.* 2003; Akhurst *et al.* 2004; Yang *et al.* 2004).

The thesis is completed in **Chapter 7**, in which the conclusions of the preceding chapters have been integrated and discussed in the light of other findings within the OBN research programme. Finally, the implications of the results for nature management and fen restoration are presented.

Chapter 2

Sediment Fe:PO₄ ratio as a diagnostic and prognostic tool for the restoration of macrophyte biodiversity in fen waters



*The OBN research team working together in National Park De Weerribben
(photo by Leon Lamers)*

**Jeroen J.M. Geurts, Alfons J.P. Smolders, Jos T.A. Verhoeven,
Jan G.M. Roelofs & Leon P.M. Lamers**
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Summary

1. Globally, freshwater wetlands, including fen waters, are suffering from biodiversity loss due to eutrophication, water shortage and toxic substances, and to mitigate these pressures numerous restoration projects have been launched. Water quality data are generally used to evaluate the chances of reestablishment of aquatic vegetation in fen waters and shallow peat lakes. Here we investigated whether sediment characteristics, which are less prone to fluctuate in time, would result in more reliable predictions.
2. To test if sediment characteristics can indeed be used not only for an easy and early diagnosis of nutrient availability and water quality changes in fen waters, but also for the prognosis of biodiversity response, we recorded the aquatic vegetation and collected surface water, sediment pore water and sediment samples in 145 fen waters in the Netherlands, Ireland and Poland.
3. Endangered macrophyte species were more closely related to surface water chemistry than common species in terms of occurrence and abundance. Sites featuring endangered species appeared to have significantly lower turbidity and pH, and lower concentrations of SO_4 , PO_4 , TP and NH_4 than other sites.
4. PO_4 and TP concentrations in the water layer increased markedly at PO_4 concentrations above 5 - 10 $\mu\text{mol L}^{-1}$ in the sediment pore water. High surface water PO_4 and TP concentrations appeared to be SO_4 -induced and only occurred below certain threshold values for pore water Fe: PO_4 (3.5 mol mol^{-1}) and total sediment Fe:P (10 mol mol^{-1}).
5. Interestingly, the occurrence of endangered species also correlated strongly with sediment and sediment pore water ratios; the number of endangered species increased markedly at pore water Fe: PO_4 ratios above 1 mol mol^{-1} , whereas their actual abundance had the greatest increase at ratios above 10 mol mol^{-1} . Additionally, endangered species seemed to be more sensitive to accumulation of potentially toxic substances such as sulphide and ammonium than non-endangered species.
6. As an indicator of both biogeochemical processes and biodiversity, pore water Fe: PO_4 ratios could be a valuable diagnostic and prognostic tool for the restoration of water quality and biodiversity in fen waters, e.g. for selecting the most promising sites for restoration and for optimisation of restoration measures.

Introduction

Worldwide, freshwater wetlands are being threatened by anthropogenic disturbance, causing huge biodiversity losses (Lake *et al.*, 2000; Dudgeon *et al.*, 2006). In recent decades, many fen waters in the Netherlands have deteriorated, mainly due to eutrophication and pollution (Smolders & Roelofs, 1995; Lamers *et al.*, 2001b, 2002a). Several characteristic aquatic macrophytes, such as *Stratiotes aloides* L., *Potamogeton compressus* L. and *P. acutifolius* Link have declined in lakes, ditches and turf ponds (Roelofs, 1991; Lamers *et al.*, 2002b; Smolders *et al.*, 2003a). For rooting macrophyte species sediment is very important with respect to nutrient availability and toxicity. Moreover, in these shallow, mostly phosphorus-limited fen waters (N:P in plant tissue > 16; Koerselman & Meuleman, 1996; Verhoeven *et al.*, 1996; Wassen *et al.*, 2005), sediment plays a key role in determining water quality, due to the small water volume per unit of sediment surface and the lack of a thermocline. Therefore, biogeochemical processes in the sediment, wind-induced resuspension and bioturbation have a great impact on water quality and growth of algae and submerged macrophytes in these systems (Barko *et al.*, 1991; Søndergaard *et al.*, 2003). Moreover, luxuriant growth of algae and certain fast-growing aquatic macrophyte species will outcompete rooting macrophytes for light, even if the sediment is P-rich.

Many studies have shown that growth of aquatic macrophytes is related to water quality (Onaandia *et al.*, 1996; Loughheed *et al.*, 2001; James *et al.*, 2005). Species composition is thus indicative of water quality and, conversely, water quality data can be used to predict the restoration of aquatic vegetation in shallow lakes (Bloemendaal & Roelofs, 1988; Grasmück *et al.*, 1995; Goslee *et al.*, 1997; Van den Berg *et al.*, 2003). Water quality, however, is subject to large temporal fluctuations (e.g. due to seasonal influences or plant and algal growth), so that frequent sampling is needed for good prediction of vegetation responses, although alkalinity seems quite conservative (Vestergaard & Sand-Jensen, 2000). By contrast, the predictive power of certain sediment characteristics may be greater than water chemistry because they are more stable over time and indicative of several important sediment processes, such as nutrient availability in the sediment and nutrient fluxes from the sediment to the overlaying water. Hence, sediment characteristics might be more appropriate and less expensive than water quality data for estimating the chances of reestablishment of aquatic vegetation. Aquatic macrophytes are known to be capable of regulating both water quality and sediment characteristics by reducing sediment resuspension, erosion and turbidity (Madsen *et al.*, 2001; Nöges *et al.*, 2003), and by influencing the phosphorus availability both positively and negatively (Wigand *et al.*, 1997;

Søndergaard *et al.*, 2003). It is thus obvious that sediment properties are both a product and a limiter of aquatic macrophyte growth (Barko *et al.*, 1991).

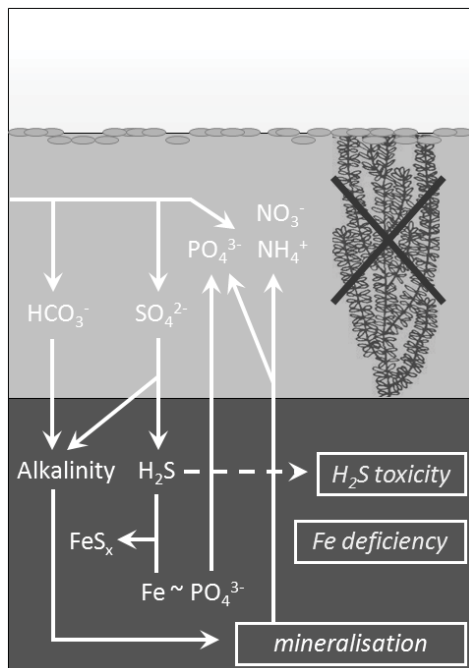


Figure 1. Schematic diagram showing relevant biogeochemical interactions in surface water and sediment of fen waters. Arrows indicate net fluxes of chemical variables. Input of polluted surface water or groundwater leads to SO_4 reduction, FeS_x formation, alkalisation and mineralisation in anaerobic sediments. This may result in H_2S toxicity, Fe deficiency and a net PO_4 mobilisation to the water layer, which eventually leads to a decline in aquatic macrophyte biodiversity.

General mechanisms of phosphorus binding, and more specifically phosphate (PO_4) binding, by iron (Fe), aluminium (Al) and calcium (Ca) compounds in sediment and pore water have been investigated to determine thresholds for PO_4 mobilisation to the surface water (e.g. Jensen *et al.*, 1992; Golterman, 1998; Smolders *et al.*, 2001; Zak *et al.*, 2004; Maassen *et al.*, 2005). PO_4 immobilisation by Fe , Fe oxides or Fe hydroxides is redox-dependent and especially sensitive to sulphate (SO_4) input via surface water or groundwater. Under anaerobic circumstances, SO_4 and Fe reduction lead to sulphide production, FeS_x formation and mobilisation of Fe -bound PO_4 (Fig. 1; Smolders & Roelofs, 1993; Roden & Edmonds, 1997; Wetzel, 2001; Lamers *et al.*, 2002a). In addition, there will be competition between SO_4 and PO_4 for anion binding sites (Caraco *et al.*, 1989; Beltman *et al.*, 2000), and SO_4 could also stimulate organic matter decomposition and alkalisation (Drever, 1997). All of these processes result in PO_4 being released from the sediment (Brouwer *et al.*, 1999; Lucassen *et al.*, 2004a; Zak *et al.*, 2006). In contrast to Fe , Al is insensitive to changes in redox potential and therefore able to bind PO_4 as $\text{Al}(\text{OH})_3$ under anoxic conditions (Cooke *et al.*, 1993). However, the optimum PO_4 binding capacity of Al is limited

to a pH range between 6 and 8 (Rydin & Welch, 1998). For Ca, co-precipitation of PO₄ with calcite (CaCO₃) is important in reducing PO₄ mobilisation to the surface water (Boström *et al.*, 1988; Danen-Louwerse *et al.*, 1995; Dittrich & Koschel, 2002). In peatlands, however, increased alkalinity (HCO₃⁻) is known to be able to stimulate decomposition and therefore mobilise nutrients, including PO₄, from the sediment (Smolders *et al.*, 2006).



Figure 2. Characteristic biodiverse fen water that shows initial terrestrialisation (Het Hol, The Netherlands; 52°13'N, 5°05'E).

Considering the importance of these biogeochemical interactions for the functioning of macrophytes in fen waters, we assume that sediment and sediment pore water characteristics may be important not only for an understanding of sediment biogeochemical processes determining water quality in shallow peat lakes, but also for the prediction of the response of plant species composition to restoration measures. Therefore, we investigated the distribution of aquatic and semi-aquatic macrophytes in 145 fen waters in the Netherlands (Fig. 2), Ireland and Poland in relation to surface water, pore water and other sediment characteristics, focusing on the occurrence of endangered species. Specifically, we evaluate the use of sediment parameters as a diagnostic and prognostic tool for wetland management in relation to ecological rehabilitation and the development of new nature reserves.

Table 1. Characteristics of the 15 areas in The Netherlands and two reference sites in Ireland and Poland where the 145 investigated fen waters were located. n = number of study sites per area.

Name	Coordinates	n	Macrophyte cover %	
			Mean	SE
Alde Feanen	53°07'N, 5°55'E	17	54.9	11.9
De Deelen	53°01'N, 5°55'E	5	35.6	19.4
De Weerribben	52°46'N, 5°56'E	13	84.3	16.0
De Wieden	52°40'N, 6°06'E	23	92.5	13.9
Het Hol	52°13'N, 5°05'E	14	76.6	14.4
Ilperveld	52°27'N, 4°56'E	8	113.9	25.0
Molenpolder	52°09'N, 5°05'E	5	106.9	9.2
Reeuwijkse Plassen	52°02'N, 4°45'E	2	20.5	20.5
Terra Nova	52°13'N, 5°02'E	10	71.3	14.6
Uddelermeer	52°14'N, 5°45'E	1	85.0	
Wormer-Jisperveld	52°30'N, 4°50'E	2	12.8	5.3
Wapserveen	52°50'N, 6°11'E	7	116.8	24.4
Waterland	52°28'N, 5°01'E	2	60.5	24.5
Westbroekse Zodden	52°10'N, 5°07'E	13	37.4	10.9
Zijdelmeer	52°14'N, 4°49'E	1	90.0	
Connemara (IRL)	53°25'N, 10°07'W	11	44.2	10.7
Lubelskie (PL)	51°26'N, 23°06'E	11	87.0	23.3

Methods

FIELD SAMPLING

Between 2002 and 2006, surface water and pore water samples were taken from 145 different fen waters from 15 areas in the Netherlands and two reference sites in Ireland and Poland (Table 1). Both species-rich and species-poor study sites were included, covering shallow peat lakes, turf ponds, peat ditches and terrestrialsing fen waters in different geographical regions. At each site, vegetation relevés were made by estimating the percentage cover of emerged and submerged macrophyte species in a representative 25 m² square, including semi-aquatic macrophytes that colonise the water and potentially induce terrestrialsation. Endangered species (Dutch Red List species) were defined according to Van der Meijden *et al.* (2000). Aquatic macrophytes were divided into trophic groups according to Bloemendaal & Roelofs (1988).

Surface water samples from 10 cm below the water surface were collected in iodated 500 mL polyethylene bottles. Soil pore water was collected anaerobically using 60 mL vacuum syringes connected to ceramic soil moisture samplers (Eijkelkamp Agrisearch Equipment, Giesbeek, the Netherlands), which were installed in the upper 10 cm of the sediment. The first 10 mL was discarded to enable anaerobic sampling. Samples of the upper sediment layer were taken from 79 fen waters using a metal sediment corer. Samples were transported in airtight bags and kept in the dark at 4°C until further analysis.

CHEMICAL ANALYSIS

Immediately after sampling, 10.5 mL of pore water sample was fixed with 10.5 mL of sulphide antioxidant buffer containing NaOH, Na-EDTA and ascorbic acid (Van Gemerden, 1984). On the same day, sulphide concentrations were measured using a sulphide ion-specific Ag electrode (Orion Research, Beverly, CA, USA) and a double junction calomel reference electrode (Roelofs, 1991). The pH of the water samples was measured using a combined pH electrode with an Ag/AgCl internal reference (Orion Research, Beverly, CA, USA), and a TIM800 pH meter. Alkalinity was determined by titration to pH 4.2 with 0.01 M HCl using an ABU901 Autoburette (Radiometer, Copenhagen, Denmark). Turbidity was determined using an FN-5 Turbidimeter (Toho-Dentan, Tokyo, Japan). Subsequently, surface water samples were filtered through glass microfiber filters (type GF/C, Whatman, Brentford, UK). Citric acid (0.6 mmol L⁻¹) was added to prevent metal precipitation. Extinction at 450 nm was measured (Shimadzu spectrophotometer UV-120-01, Kyoto, Japan) for colorimetric background correction and as an estimate of humic substance concentrations (Smolders *et al.*, 2003b). The samples were stored in iodated polyethylene bottles at -20 °C until further analysis.

Concentrations of PO₄, NO₃, NH₄ and Cl were measured colorimetrically with an Auto Analyzer 3 system (Bran+Luebbe, Norderstedt, Germany), using ammonium molybdate (Henriksen, 1965), hydrazine sulphate (Kamphake *et al.*, 1967), salicylate (Grasshoff & Johannsen, 1972) and ferriammonium sulphate (O'Brien, 1962), respectively. Ca, Fe, Al, S and P were measured using an ICP Spectrometer (IRIS Intrepid II, Thermo Electron Corporation, Franklin, MA). Total S concentrations provided a good estimate of SO₄ concentrations, because only a small percentage of S was present in organic form. This was verified by parallel analysis of various pore water and surface water samples using capillary ion analysis (Waters Corporation, Milford, MA, USA).

A homogenised portion of 200 mg dry sediment (dried 24 h at 105 °C) was digested with 4 mL HNO₃ (65%) and 1 mL H₂O₂ (30%), using a microwave oven (mls 1200 Mega, Milestone Inc., Sorisole, Italy). Digestates were diluted and analysed by ICP as described above.

STATISTICAL ANALYSIS

All statistical analyses were carried out using SPSS for Windows (version 14.0, 2005, SPSS, Chicago, IL, USA). Differences in chemical characteristics between sites with or without Red List species were tested with a Mann-Whitney U-test. Correlations between variables were analysed using Spearman's correlation coefficients (*r*). An unconstrained detrended correspondence analysis (DCA; CANOCO; Ter Braak & Šmilauer, 1998) of the species data was used to show the variation of the environmental variables. Sediment samples were excluded, because of the smaller sample size. Rare species were downweighted and detrending was applied by segments.

Results

AQUATIC VEGETATION

We recorded 108 different species in the investigated fen waters, 20 of them being Dutch Red List species (Table 2). These species could be divided in 64 semi-aquatic macrophytes (including three woody species and three mosses) and 44 aquatic macrophytes (including five charophytes, two algae and one moss). *Nymphaea alba* (39%) and *Nuphar lutea* (33%) were the most common aquatic macrophytes in the investigated fen waters, whereas *Elodea nuttallii* (32%) and *Ceratophyllum demersum* (31%) were the most prevalent submerged species. *Phragmites australis* (16%) was the most common semi-aquatic macrophyte. Endangered species occurred in 53% of the sites, and *Stratiotes aloides* was present in half of these sites, with a mean cover of 39%.

Table 2. Species recorded in the vegetation relevés. Aquatic macrophytes (including two algae) are divided into trophic groups (TG) according to Bloemendaal & Roelofs (1988). O = oligotrophic, M = mesotrophic, E = eutrophic, H = hypertrophic. Dutch Red List species appear in bold. Species are ordered alphabetically within groups.

Aquatic macrophytes	TG	Semi-aquatic macrophytes
<i>Chara globularis</i> Thuillier	O	<i>Acorus calamus</i> L.
<i>Chara hispida</i> L.	O	<i>Agrostis stolonifera</i> L.
<i>Chara vulgaris</i> L.	O	<i>Alisma plantago-aquatica</i> L.
<i>Eleogiton fluitans</i> (L.) Link	O	<i>Alnus glutinosa</i> (L.) Gaertn.
<i>Littorella uniflora</i> (L.) Asch.	O	<i>Berula erecta</i> (Huds.) Coville
<i>Myriophyllum alterniflorum</i> DC.	O	<i>Butomus umbellatus</i> L.
<i>Myriophyllum verticillatum</i> L.	O	<i>Calla palustris</i> L.
<i>Nitella flexilis</i> (L.) J. Agardh	O	<i>Calliergonella cuspidata</i> (Hedw.) Loeske
<i>Potamogeton acutifolius</i> Link	O	<i>Cardamine pratensis</i> L.
<i>Potamogeton polygonifolius</i> Pourr.	O	<i>Carex acuta</i> L.
<i>Sparganium natans</i> L.	O	<i>Carex hirta</i> L.
<i>Utricularia australis</i> R.Br.	O	<i>Carex lasiocarpa</i> Ehrh.
<i>Utricularia intermedia</i> Hayne	O	<i>Carex limosa</i> L.
<i>Utricularia minor</i> L.	O	<i>Carex panicea</i> L.
<i>Elodea canadensis</i> Michaux	M	<i>Carex pseudocyperus</i> L.
<i>Fontinalis antipyretica</i> Hedw.	M	<i>Carex riparia</i> Curtis
<i>Hottonia palustris</i> L.	M	<i>Carex rostrata</i> Stokes
<i>Nitella mucronata</i> (A. Braun) Miquel	M	<i>Cicuta virosa</i> L.
<i>Nymphaea alba</i> L.	M	<i>Cladium mariscus</i> (L.) Pohl
<i>Potamogeton alpinus</i> Balbis	M	<i>Epilobium hirsutum</i> L.
<i>Potamogeton natans</i> L.	M	<i>Equisetum fluviatile</i> L.
<i>Potamogeton obtusifolius</i> Mert. & Koch	M	<i>Equisetum palustre</i> L.
<i>Elodea nuttallii</i> (Planch.) St. John	E	<i>Galium palustre</i> L.
<i>Hydrocharis morsus-ranae</i> L.	E	<i>Glyceria fluitans</i> (L.) R.Br.
<i>Lemna minor</i> L.	E	<i>Glyceria maxima</i> (Hartm.) Holmb.
<i>Lemna trisulca</i> L.	E	<i>Hydrocotyle vulgaris</i> L.
<i>Nuphar lutea</i> (L.) Sm.	E	<i>Hypericum elodes</i> L.
<i>Potamogeton compressus</i> L.	E	<i>Iris pseudacorus</i> L.
<i>Potamogeton crispus</i> L.	E	<i>Juncus acutiflorus</i> Hoffm.
<i>Potamogeton lucens</i> L.	E	<i>Juncus effusus</i> L.
<i>Potamogeton pusillus</i> L.	E	<i>Juncus subnodulosus</i> Schrank
<i>Potamogeton trichoides</i> Cham. & Schltdl.	E	<i>Lycopus europaeus</i> L.
<i>Ranunculus circinatus</i> Sibth.	E	<i>Lysimachia thyrsiflora</i> L.
<i>Stratiotes aloides</i> L.	E	<i>Lythrum salicaria</i> L.
<i>Zannichellia palustris</i> L.	E	<i>Mentha aquatica</i> L.
<i>Ceratophyllum demersum</i> L.	H	<i>Menyanthes trifoliata</i> L.
<i>Ceratophyllum submersum</i> L.	H	<i>Myosotis scorpioides</i> L.
<i>Cladophora</i> spec.	H	<i>Myrica gale</i> L.
<i>Microcystis</i> spec.	H	<i>Oenanthe aquatica</i> (L.) Poir.
<i>Myriophyllum spicatum</i> L.	H	<i>Persicaria amphibia</i> (L.) Gray
<i>Potamogeton mucronatus</i> Sond.	H	<i>Peucedanum palustre</i> (L.) Moench
<i>Potamogeton pectinatus</i> L.	H	<i>Phalaris arundinacea</i> L.

Aquatic macrophytes	TG	Semi-aquatic macrophytes
<i>Spirodela polyrhiza</i> (L.) Schleid.	H	<i>Phragmites australis</i> (Cav.) Steud.
<i>Utricularia vulgaris</i> L.	H	<i>Potentilla palustris</i> (L.) Scop.
		<i>Ranunculus lingua</i> L.
		<i>Rorippa amphibia</i> (L.) Besser
		<i>Rorippa microphylla</i> (Boenn.) Rchb.
		<i>Rorippa palustris</i> (L.) Besser
		<i>Rumex hydrolapathum</i> Huds.
		<i>Sagittaria sagittifolia</i> L.
		<i>Salix cinerea</i> L.
		<i>Schoenoplectus lacustris</i> (L.) Palla
		<i>Schoenoplectus tabernaemontani</i> (C.C.Gmel.) Palla
		<i>Schoenus nigricans</i> L.
		<i>Scorpidium scorpioides</i> (Hedw.) Limpr.
		<i>Sium latifolium</i> L.
		<i>Solanum dulcamara</i> L.
		<i>Sparganium erectum</i> L.
		<i>Sphagnum cuspidatum</i> Hoffm.
		<i>Stachys palustris</i> L.
		<i>Thelypteris palustris</i> Schott
		<i>Typha angustifolia</i> L.
		<i>Typha latifolia</i> L.
		<i>Veronica catenata</i> Pennell

SURFACE WATER QUALITY AND AQUATIC VEGETATION

The investigated fen waters showed a broad range of surface water PO_4 and total phosphorus (TP) concentrations (both ranged from 0.1 to 29 $\mu\text{mol L}^{-1}$). Species from oligotrophic environments never occurred in waters with PO_4 concentrations above 2 $\mu\text{mol L}^{-1}$ (Fig. 3a,b). At PO_4 concentrations above 6 $\mu\text{mol L}^{-1}$, macrophyte cover and number of species decreased, and Red List species were absent (Fig. 3c,d). Endangered semi-aquatic macrophytes were even absent at concentrations above 2 $\mu\text{mol L}^{-1}$. Aquatic macrophyte cover and number of species were highest below 0.5 $\mu\text{mol PO}_4 \text{ L}^{-1}$ (four species and 68% cover, on average) and lowest above 6 $\mu\text{mol PO}_4 \text{ L}^{-1}$ (1.6 species and 31% cover, on average). Eutrophic and hypertrophic species, however, appeared to be rather indifferent and occurred throughout the PO_4 classes.

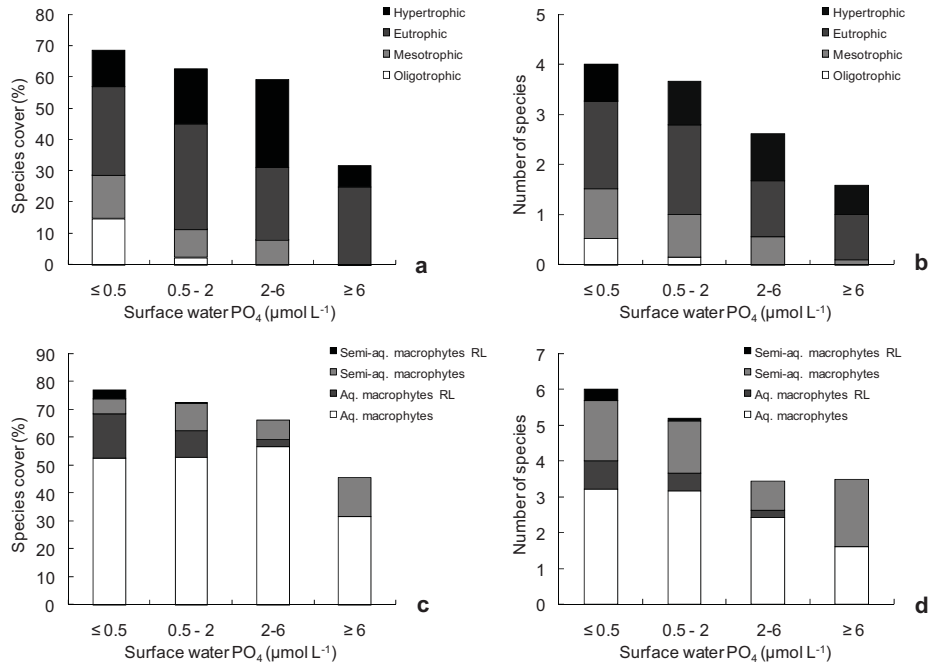


Figure 3. Percentage cover (**a,c**) and number (**b,d**) of aquatic and semi-aquatic macrophyte species at different surface water PO₄ concentrations. (**a,b**) Aquatic macrophytes divided into four different trophic classes according to Bloemendaal & Roelofs (1988). (**c,d**) Aquatic and semi-aquatic macrophytes divided into Red List (RL) and other, non-Red List species.

Red List species correlated more strongly with surface water chemistry variables than other macrophyte species (Fig. 4). The number and abundance of Red List species at a specific site were highly negatively correlated with surface water PO₄, TP and turbidity ($r \geq 0.31$, $P < 0.001$). Red List species were almost absent at sites with PO₄ and TP concentrations $> 1 \mu\text{mol L}^{-1}$ and turbidity levels $> 12 \text{ ppm Pt}$. The number and abundance of other macrophyte species only showed a significant, but weak, negative correlation with turbidity ($r \geq 0.18$, $P < 0.05$). Moreover, sites with Red List species had lower turbidity, pH and surface water concentrations of SO₄, PO₄, TP and NH₄ than sites without Red List species (Mann-Whitney U-test, $P < 0.01$) (Table 3). Surface water alkalinity and Ca, NO₃ and Fe concentrations did not differ significantly between sites with or without Red List species.

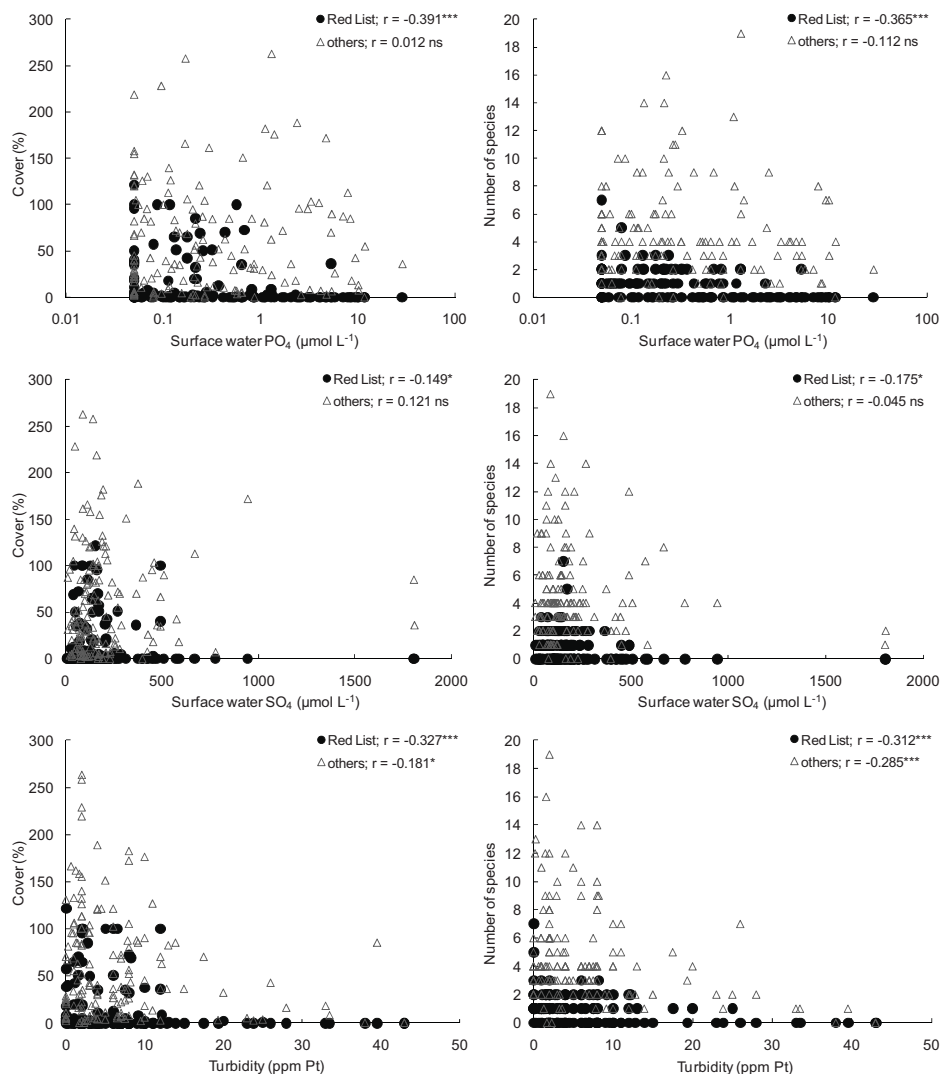


Figure 4. Correlations between surface water characteristics and the percentage cover and number of macrophytes, divided into Red List species and others. Spearman's correlation coefficients are given. ns $P > 0.05$, * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$. Note the logarithmic x-axes for surface water PO_4 .

Table 3. Comparison between the chemical properties of 77 fen waters with Red List species and 68 fen waters without Red List species (including all macrophyte species from Table 2). Means ($\pm$ standard error of the mean), Mann-Whitney U and *P*-values are given (bold values indicate $P \leq 0.05$). Chemical properties are ordered by ascending *P*-value within the different sample types.

	Red List species				U	P
	Not present		Present			
	Mean	SE	Mean	SE		
Surface water	(n = 68)		(n = 77)			
P (μmol L ⁻¹)	5.3	0.7	1.3	0.2	1170	0.000
PO ₄ (μmol L ⁻¹)	2.7	0.6	0.3	0.1	1381	0.000
Turbidity (ppm Pt)	9.8	1.3	4.3	0.5	1584	0.000
pH	7.5	0.1	7.2	0.1	1827	0.001
NH ₄ (μmol L ⁻¹)	30.3	7.2	9.0	1.5	1915	0.002
SO ₄ (μmol L ⁻¹)	266.6	39.9	140.9	11.3	1946	0.004
Al (μmol L ⁻¹)	1.9	0.4	1.2	0.1	2157	0.031
Fe (μmol L ⁻¹)	6.2	1.1	6.9	1.7	2375	0.165
NO ₃ (μmol L ⁻¹)	12.3	4.3	40.5	22.6	2390	0.181
Ca (μmol L ⁻¹)	891.6	46.4	881.4	44.7	2526	0.352
Alkalinity (meq L ⁻¹)	1.9	0.1	1.8	0.1	2586	0.448
Pore water	(n = 68)		(n = 77)			
PO ₄ (μmol L ⁻¹)	20.1	2.9	5.4	1.0	1408	0.000
Fe:PO ₄ (mol mol ⁻¹)	138.9	75.7	1349.2	523.2	1619	0.000
Sulphide (μmol L ⁻¹)	92.9	39.8	9.6	3.7	1658	0.000
P (μmol L ⁻¹)	30.5	4.2	16.6	3.5	1689	0.000
SO ₄ (μmol L ⁻¹)	164.3	23.4	86.5	12.3	1701	0.000
Fe:S (mol mol ⁻¹)	2.3	0.6	5.5	1.2	2012	0.007
pH	6.6	0.0	6.5	0.0	2017	0.008
NO ₃ (μmol L ⁻¹)	3.4	0.6	7.0	1.3	2142	0.030
Fe (μmol L ⁻¹)	90.7	18.8	204.5	42.2	2295	0.097
NH ₄ (μmol L ⁻¹)	288.3	44.9	230.2	35.6	2363	0.154
Ca (μmol L ⁻¹)	1504.2	79.9	1583.3	87.3	2509	0.333
Alkalinity (meq L ⁻¹)	4.5	0.3	4.5	0.2	2528	0.358
Al (μmol L ⁻¹)	3.2	0.5	4.2	1.1	2547	0.387
Sediment	(n = 33)		(n = 46)			
P (μmol g ⁻¹ dry wt)	27.8	2.7	18.0	1.5	477	0.002
Ca (μmol g ⁻¹ dry wt)	523.2	67.6	313.7	30.9	354	0.003
Fe:P (μmol g ⁻¹ dry wt)	10.9	1.0	15.1	1.2	315	0.006
Fe (μmol g ⁻¹ dry wt)	234.9	28.9	262.0	29.7	482	0.354
Al (μmol g ⁻¹ dry wt)	223.4	37.4	201.2	21.9	570	0.379

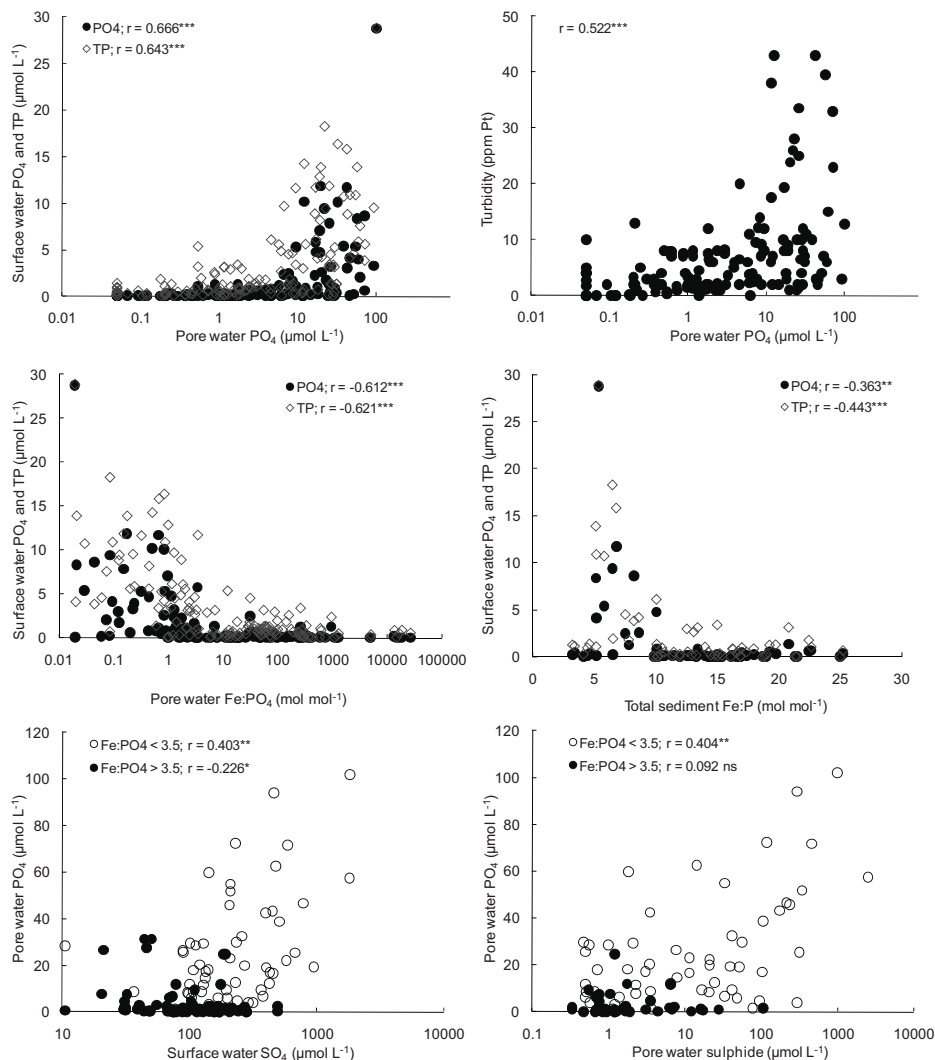


Figure 5. Relations between phosphate concentrations and other characteristics of pore water, surface water and sediment. Spearman's correlation coefficients are given. ns $P > 0.05$, * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$. Note the logarithmic x-axes, except for total sediment Fe:P.

SEDIMENT PORE WATER AND SURFACE WATER QUALITY

Surface water PO_4 and TP concentrations and turbidity increased with increasing pore water PO_4 concentrations ($r \geq 0.52$, $P < 0.001$), and in all cases the greatest increase was observed between 5 and 10 $\mu\text{mol L}^{-1}$ (Fig. 5). The pore water Fe: PO_4 ratio also showed a close correlation with surface water PO_4 and TP

concentrations ($r \geq 0.61$, $P < 0.001$). Above an Fe:PO₄ ratio of 3.5 mol mol⁻¹, which seems to be a threshold value, 99% of the surface water PO₄ concentrations were below 2 µmol L⁻¹ and 89% were below 0.5 µmol L⁻¹. Below this threshold value, however, only 57% of the PO₄ concentrations were below 2 µmol L⁻¹ and 31% were below 0.5 µmol L⁻¹. Total sediment P was positively correlated with pore water PO₄ ($r = 0.268$, $P < 0.01$) and surface water TP ($r = 0.347$, $P < 0.001$), but not with surface water PO₄ (data not shown). In contrast, the total sediment Fe:PO₄ ratio was only negatively correlated with surface water PO₄ and TP ($r \geq -0.363$, $P < 0.01$; Fig. 5). High concentrations of PO₄ and TP in the water layer only occurred below total sediment Fe:P ratios of 10 mol mol⁻¹.

Furthermore, fen waters with high surface water SO₄ concentrations (> 100 µmol L⁻¹) had higher pore water PO₄ concentrations ($r = 0.274$, $P < 0.001$), lower Fe:PO₄ ratios ($r = -0.487$, $P < 0.001$) and higher sulphide concentrations ($r = -0.544$, $P < 0.001$) (Fig. 5). Sulphide concentrations in the anaerobic sediment also correlated well with lower Fe:PO₄ ratios ($r = -0.646$, $P < 0.001$) and higher PO₄ concentrations in the pore water ($r = 0.504$, $P < 0.001$). Pore water alkalinity was positively correlated with pore water concentrations of both NH₄ ($r = 0.397$, $P < 0.001$) and PO₄ ($r = 0.239$, $P < 0.01$).

SEDIMENT QUALITY IN RELATION TO AQUATIC VEGETATION

Concentrations of PO₄, SO₄ and sulphide in the pore water were significantly lower at sites with Red List species than at sites without Red List species (Mann-Whitney U-test, $P < 0.001$; Table 3). The average pore water Fe:PO₄ ratio was nearly 10 times higher at sites with Red List species: 1349 mol mol⁻¹ compared to 139 mol mol⁻¹ ($P < 0.001$). Fe, Ca, Al and NH₄ concentrations in the pore water did not differ significantly between sites with and without Red List species.

Pore water chemistry variables correlated more strongly with the number and abundance of Red List species than with the occurrence of non-Red List species (Fig. 6). The number and abundance of Red List species was negatively correlated with PO₄, SO₄ and sulphide concentrations in the pore water ($r \geq 0.28$, $P < 0.001$; data not shown). There was also a positive correlation between Red List species and the pore water Fe:PO₄ ratio ($r > 0.3$, $P < 0.001$; Fig. 6). Interestingly, the number of non-Red List species showed a much weaker positive correlation with the Fe:PO₄ ratio ($r \leq 0.15$, $P < 0.05$). The greatest increase in number of Red List species was observed at Fe:PO₄ ratios of about 1 mol mol⁻¹, whereas the greatest increase in percentage cover of Red List species was observed at ratios of about 10 mol mol⁻¹. The number of non-Red List species was negatively

correlated with pore water PO_4 and NH_4 concentrations ($r \geq 0.21$, $P < 0.01$; data not shown).

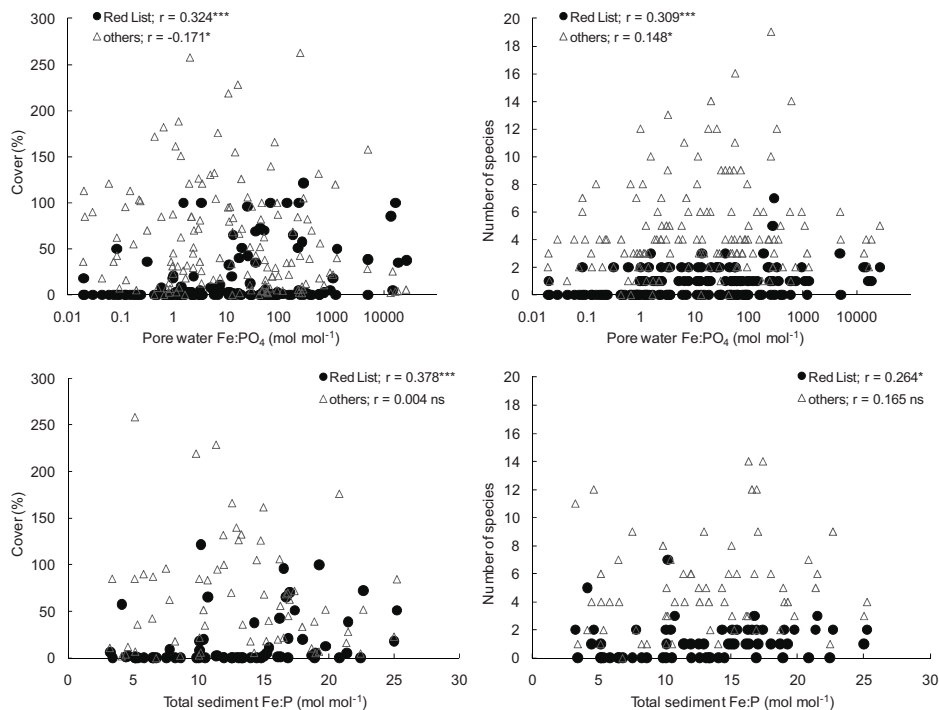


Figure 6. Percentage cover and number of macrophytes, divided into Red List species and others, plotted against pore water Fe:PO₄ and sediment Fe:P ratios. Spearman's correlation coefficients are given. ns $P > 0.05$, * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$. Note the logarithmic x-axes for pore water Fe:PO₄.

The number of Red List species was negatively correlated with total sediment P ($r = -0.303$, $P < 0.01$), whereas the abundance of Red List species had a strong positive correlation with the total sediment Fe:P ratio ($r = 0.378$, $P < 0.001$) (Fig. 6). Non-Red List species were not significantly correlated with either of these variables.

Indirect ordination (DCA) showed a gradient in aquatic macrophyte species composition from turbid, alkaline, P- and S-rich sites with only eutrophic and hypertrophic species to sites with a high pore water Fe:PO₄ ratio and more mesotrophic, oligotrophic and Red List species (Fig. 7). Most semi-aquatic macrophytes were found either at S-rich sites (especially former brackish areas),

Al-rich sites or sites with a high pore water Fe:PO₄ ratio and low PO₄ concentrations.

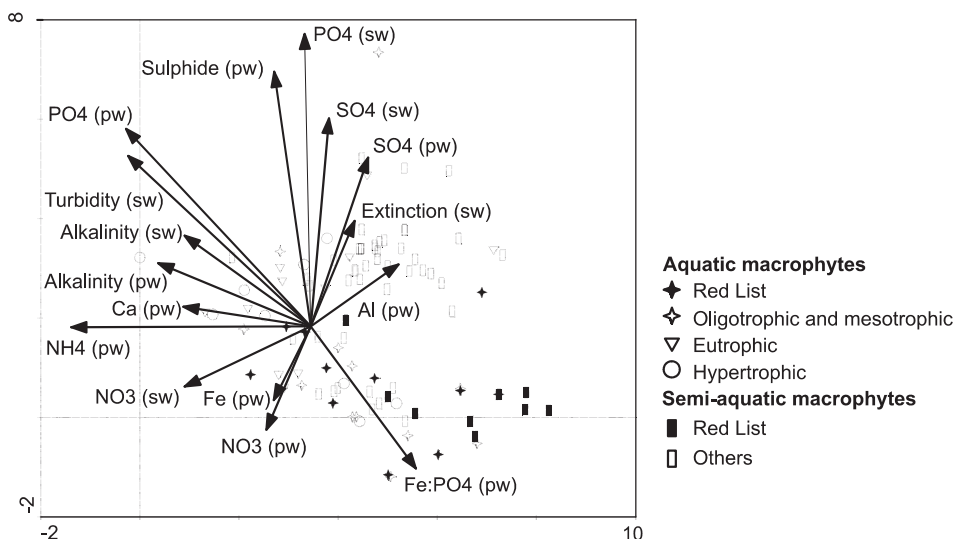


Figure 7. Indirect ordination diagram (DCA) of macrophyte species showing the first two axes (different dots for each category) with environmental variables included (arrows). pw = pore water, sw = surface water.

Discussion

Our study supports the hypothesis that sediment characteristics in shallow fen waters provide valuable information not only for the understanding of biogeochemical key processes, but also for the prediction of biodiversity response after restoration measures. We were able to define threshold values relating to eutrophication, including SO₄-induced nutrient mobilisation.

The number of macrophyte species in fen waters, especially rare species, tended to decrease with higher surface water PO₄ and TP concentrations. This finding was anticipated, since P limitation controls biomass production in fen waters and prevents the dominance of fast growing species, including algae (Grime, 1974; Wheeler & Proctor, 2000). In contrast to James *et al.* (2005), we did not find a relationship between biodiversity and surface water NO₃ concentrations, probably because our study sites had relatively low NO₃ concentrations compared to the wide range in their study. A similar greater dependence on low P availability for rare and endangered species compared to common species

has been found by other authors (Olde Venterink *et al.*, 2003; Wassen *et al.*, 2005). However, in shallow fen waters, the interaction between sediment and surface water (which may be predicted by sediment characteristics), rather than actual concentrations in the water layer, reflect nutrient availability and determine biodiversity. In addition, many aquatic macrophytes take up nutrients directly from the sediment through their roots (e.g. *E. nuttallii*; Nagasaka, 2004), whilst luxuriant growth of other species and algae may withdraw such large amounts of nutrients from the water column that the water becomes poor in P (e.g. *C. demersum*; Lombardo & Cooke, 2003). Fast-growing aquatic macrophytes and algae can, therefore, still dominate an apparently P-poor water layer and outcompete less competitive species, including semi-aquatic macrophytes that colonise the water and induce terrestrialisation, thereby decreasing total biodiversity. Combined, these findings suggest sediment characteristics to be more suitable for ecosystem diagnosis.

The increase in surface water PO_4 and TP concentrations at sites where pore water PO_4 concentrations are greater than 5 to 10 $\mu\text{mol L}^{-1}$ is probably the result of interacting processes in the sediment, which can best be described by the relative concentrations of Fe and PO_4 in the pore water. The reduction of SO_4 and Fe in anaerobic sediments leads to the formation of sulphide and FeS_x (Fig. 1; Smolders & Roelofs, 1993; Roden & Edmonds, 1997; Wetzel, 2001; Lamers *et al.*, 2002a), and stimulates organic matter decomposition and alkalisation (Drever, 1997). Subsequently, Fe-bound PO_4 is mobilised and Fe: PO_4 ratios decrease. SO_4 and HCO_3^- also compete with PO_4 for anion binding sites in the sediment (Caraco *et al.*, 1989; Beltman *et al.*, 2000), leading to an additional release of PO_4 from the sediment. We found that fen waters with high SO_4 concentrations (and most probably a high sulphate load) indeed show increased P mobilisation and decreased pore water Fe: PO_4 ratios. Being a relatively stable process variable, this Fe: PO_4 ratio would be a suitable indicator of present and future P concentrations in surface water and pore water. Below the threshold value of 3.5 mol mol^{-1} there is a greater risk of internal eutrophication. Other studies have found comparable results, demonstrating increased P release to the water layer at pore water Fe: PO_4 ratios below 1 mol mol^{-1} (Smolders *et al.*, 2001), 2 mol mol^{-1} (Lofgren & Boström, 1989) and 3 mol mol^{-1} (Zak *et al.*, 2004). In our study, total sediment Fe:P ratios below 10 mol mol^{-1} were found to indicate P mobilisation to the surface water. Jensen *et al.* (1992) and Ramm & Scheps (1997) concluded that P mobilisation occurred below total sediment Fe:P ratios of 8.3 mol mol^{-1} and 12 mol mol^{-1} , respectively. Maassen *et al.* (2005) determined thresholds for both total sediment Fe:P ratios ($< 6 \text{ mol mol}^{-1}$) and Al:P ratios ($< 12 \text{ mol mol}^{-1}$). For

practical reasons, total sediment ratios may even be preferred over pore water ratios, because they do not require anaerobic sampling.

Interestingly, the pore water Fe:PO₄ ratio described above did not only turn out to be a valuable indicator of P release, but even more importantly, correlated significantly with the number and abundance of Red List species. This correlation is at least equal to or better than the correlations between these vegetation characteristics and single pore water and surface water concentrations. Furthermore, the number of Red List species increased at a lower threshold value than the actual species abundance. The pore water Fe:PO₄ ratio may therefore provide a good prognosis of both potential P concentrations and biodiversity response after restoration measures, owing to the interference with the sulphur cycle and the redox potential of the sediment. The sediment Fe:P ratio has a similar strong correlation with the abundance of Red List species. Favourable ratios could, however, still involve high pore water PO₄ concentrations, which may lead to luxuriant growth of eutrophic species. Relationships between aquatic macrophyte distribution and sediment composition have also been described previously, but without using pore water or sediment ratios (Bloemendaal & Roelofs, 1988; Van Wijck *et al.*, 1992; Baattrup-Pedersen & Riis, 1999).

Endangered species appear to be more sensitive to eutrophication than the other macrophyte species we investigated. The main causes of this phenomenon are probably PO₄ and SO₄ pollution (Lamers *et al.*, 2002a). Consequently, surface water turbidity and sulphide toxicity in the sediment play important roles, as reported earlier (Van den Berg *et al.*, 2003; Smolders *et al.*, 2003a; Van der Welle *et al.*, 2006). In addition, aquatic macrophytes can also be sensitive to NH₄ toxicity (Roelofs, 1991; Smolders *et al.*, 2003a). In the present study, NH₄ concentrations in the surface water did indeed have a negative influence on the occurrence of Red List species. Surprisingly, NH₄ concentrations in the pore water only influenced the total number of species. Both sulphide and NH₄ had a more profound effect on the species abundance than on the number of species. Our data did not indicate possible Fe toxicity (Smolders & Roelofs, 1996; Van der Welle *et al.*, 2006).

MANAGEMENT IMPLICATIONS

As indicators of both biogeochemical processes and biodiversity, the described sediment and sediment pore water ratios provide valuable diagnostic and prognostic tools for the restoration of water quality and rehabilitation of biodiversity in fen waters. They are not only useful for risk assessment, but also for

selecting the most promising measures. The significant linkage to eutrophication-related sediment–water interactions indicates that it is very important to decrease both external and internal eutrophication in fen waters by reducing the influx of P- and SO_4 -rich water. It is especially the supply of SO_4 -rich water to compensate for water shortage in nature reserves and agricultural areas which can cause an overwhelming release of sediment-bound P from the sediment (Phillips *et al.*, 1994; Lamers *et al.*, 1998a; Smolders *et al.*, 2006). Isolating fen waters from allochthonous surface water with a poor quality can be a useful measure to reduce both external and internal nutrient loading, although possible constraints on plant and animal dispersal are not yet known. Concomitant water table fluctuations and temporary desiccation of the sediment may be beneficial as it stimulates the germination of seeds and oxidises the reduced sediment (Lucassen *et al.*, 2005).

The pore water Fe:PO₄ ratio not only turned out to be the most valuable prognostic tool for the restoration of water quality and biodiversity in fen waters, it can also be used as a diagnostic tool in selecting fen waters where ecological restoration and the transformation of former arable land into nature reserves may be successful. Suitable sites should preferably have pore water Fe:PO₄ ratios higher than 10 mol mol⁻¹. In addition, the Fe:PO₄ ratio is also a valuable tool in optimising restoration measures. For example, dredging to reduce eutrophication will only be a suitable option when the Fe:PO₄ ratio of the newly exposed sediment layer is sufficiently high (> 3.5 mol mol⁻¹). In situations where PO₄ sequestration in the sediment (as indicated by the pore water ratios described above) is found to be too low, various Fe, Al and Ca compounds have often been added to raise the pore water ratios to the desired levels (Smolders *et al.*, 1995; Naselli *et al.*, 2003; Reitzel *et al.*, 2005). However, Fe addition is not a useful measure in fen waters with highly reductive sediment and a high load of PO₄ and/or SO_4 , because of the high Fe consumption rate (Boers *et al.*, 1994, Smolders *et al.*, 1995; Roden & Edmonds, 1997). The application of CaCO_3 in fen waters is also doubtful, as HCO_3^- may stimulate decomposition and mobilise nutrients from the sediment (Smolders *et al.*, 2006). It may be better to use redox-insensitive Al compounds in these systems, provided that pH and buffer capacity are high enough to prevent toxic effects (Cooke *et al.*, 1993; Lewandowski *et al.*, 2003). However, amorphous $\text{Al}(\text{OH})_3$ will crystallise (e.g. to gibbsite), decreasing its effectiveness on the long term (Berkowitz *et al.*, 2005). It is therefore very important to focus on both the external and internal sources of eutrophication and toxicity, in order to conserve and restore biodiversity in fen waters.

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Chapter 3

The interaction between decomposition, net N and P mineralization and their mobilization to the surface water in fens



Field work in Lake Emlagharan (Connemara, Ireland; photo by Leon Lamers)

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Abstract

Worldwide, fens and peat lakes that used to be peat-forming systems have become a significant source of C, N and P due to increased peat decomposition. To test the hypothesis that net nutrient mineralization rates may be uncoupled from decomposition rates, we investigated decomposition and net mineralization rates of nutrients in relation to sediment and pore water characteristics. We incubated 28 non-calcareous peat sediments and floating fen soils under aerobic and anaerobic conditions. We also tried to find a simple indicator to estimate the potential nutrient mobilization rates from peat sediments to the water layer by studying their relation with sediment and pore water characteristics in 44 Dutch non-calcareous peat lakes and ditches.

Decomposition rates were primarily determined by the organic matter content, and were higher under aerobic conditions. However, highly decomposed peat sediments with low C:P and C:N ratios still showed high net nutrient mineralization rates. At Fe:PO₄ ratios below 1 mol mol⁻¹, PO₄ mobilization from the sediment to the water layer was considerable and linearly related to the pore water PO₄ concentration. At higher ratios, there was a strong linear correlation between the Fe:PO₄ ratio and PO₄ mobilization. Hence, measuring Fe and PO₄ in anaerobic sediment pore water provides a powerful tool for a quick assessment of internal PO₄ fluxes. Mobilization of mineral N was largely determined by diffusion. Total sediment Fe:S ratios gave an important indication of the amount of Fe that is available to immobilize PO₄. Pore water Fe concentrations decreased at ratios < 1 mol mol⁻¹, whereas pore water PO₄ concentrations and PO₄ mobilization to the water layer increased.

As PO₄ mobilization rates from the sediment to the water layer contribute to almost half of the total P load in Dutch peat lakes and fens, it is of pivotal importance to examine the magnitude of internal fluxes. Dredging of the nutrient-rich upper sediment layer will only be a useful restoration measure if both the influx of P-rich water and its internal mobilization from the newly exposed, potentially more reactive peat layer are sufficiently low.

Introduction

Worldwide, fens and peat lakes that used to be peat-forming systems (Kivinen & Pakarinen, 1981) have become a significant source of C, N and P due to increased peat decomposition (Lamers *et al.*, 2002b; Laiho, 2006; Bragazza *et al.*,

2007). This increase is caused by multiple environmental problems, such as desiccation, eutrophication, pollution and global warming (Gorham, 1995; Smolders *et al.*, 2006). Decomposition rates mainly depend on the availability of oxygen or alternative electron acceptors, temperature, pH, moisture content, organic matter content, organic matter quality and nutrient levels (Clymo, 1983; Enríquez *et al.*, 1993; Aerts, 2006).

It is generally assumed that decomposition of peat soils and sediments automatically increases nutrient concentrations in sediments and surface waters (McLatchey & Reddy, 1998; Bayley *et al.*, 2005), causing a shift from a clear water state with submerged macrophytes to a hypertrophic state with turbid water dominated by algae and cyanobacteria (Scheffer *et al.*, 1993; Correll, 1998). Decomposition also increases the concentration of particulate and dissolved organic matter in surface waters, leading to increased turbidity and highly colored water (Stern *et al.*, 2007). Resuspension caused by wind, shipping and benthivorous fishes further maintains the turbid state of the water (Ter Heerdt & Hootsmans, 2007). All of this reduces the growth of submerged macrophytes and leads to a less biodiverse system with only floating or emergent macrophytes, and without terrestrialization or peat formation.

In aquatic peatland systems, however, where P is generally the growth-limiting nutrient (Schindler, 1977; Richardson, 1985; Reddy *et al.*, 1999), decomposition does not always lead to net PO_4 mineralization and increased PO_4 availability in soils and sediments (Bridgham *et al.*, 1998), because PO_4 can be bound immediately after mineralization, for example in Fe-rich (Smolders *et al.*, 2006) or Ca-rich sediments (Reddy *et al.*, 1993). Subsequent PO_4 mobilization to the water layer is often related to sediment characteristics that describe the interactions between Fe, PO_4 and S in pore water and sediments (Smolders & Roelofs, 1993; Golterman, 1995), because PO_4 can be mobilized from Fe-P complexes by formation of Fe-S minerals in S-rich anaerobic conditions (Caraco *et al.*, 1989; Roden & Edmonds, 1997; Lamers *et al.*, 1998a). Various studies have found thresholds for pore water Fe: PO_4 ratios and sediment Fe:P ratios below which the risk of PO_4 mobilization is much higher (Jensen *et al.*, 1992; Ramm & Scheps, 1997; Smolders *et al.*, 2001; Geurts *et al.*, 2008). This implies that the actual PO_4 mobilization to the water layer is not automatically coupled to high decomposition rates.

Our study comprised two parts. Firstly, we were interested in the relation between decomposition and net mineralization of P and N, which implies their actual mobilization in the pore water, because anthropogenically disturbed fens may

show sediments that have been largely decomposed but still show high nutrient concentrations. Our hypothesis was that net nutrient mineralization rates could be uncoupled from decomposition rates, depending on the nutrient concentrations in the sediment. Secondly, we wanted to investigate which factors control the actual mobilization of PO_4 and N ($\text{NO}_x + \text{NH}_y$) from the sediment to the water layer in fens and peat lakes, leading to unfavorable effects on aquatic communities. This could also provide simple parameters to estimate the contribution of the internal flux of PO_4 and N to the overall eutrophication (so-called internal eutrophication; Roelofs, 1991; Lamers *et al.*, 2002b; Smolders *et al.*, 2006), which is important for water management.

In the first experiment, we therefore investigated decomposition and net mineralization rates of PO_4 and mineral N in relation to organic matter content, total nutrient ratios and pore water characteristics, in incubation experiments with non-calcareous peat sediments and floating fen soils from 28 different locations in the Netherlands and Ireland, under aerobic and anaerobic conditions (simulating low and high water tables). Floating fen soils were included because they are important for the terrestrialization of fens and because they show higher oxygen infiltration and a higher organic matter content than the peat sediments. In the second experiment, we studied mobilization rates of PO_4 and mineral N in relation to sediment and pore water characteristics in 44 Dutch non-calcareous peat lakes and ditches to find a simple indicator for estimating the potential nutrient mobilization from peat sediments to the water layer. The article discusses findings from both experiments in relation to sediment and water chemistry, as well as their implications for water management and nature management.

Methods

INCUBATION EXPERIMENT

In October 2003, samples of the upper sediment layer (10 cm) were collected in 10 Dutch peat lakes, using a metal sediment corer. The lakes were located in the following areas: De Deelen (53°01'N, 5°55'E; n=2), Het Hol (52°13'N, 5°05'E), Ilperveld (52°27'N, 4°56'E; n=2), Terra Nova (52°13'N, 5°02'E), Westbroek (52°10'N, 5°07'E; n=3) and Zijdelmeer (52°14'N, 4°49'E). In October 2004, sediment samples from 4 peat lakes and samples of the upper soil layer of 14 floating fens soils were collected in Connemara (Ireland; 53°25'N, 10°07'W). Samples were transported in airtight plastic bags and kept in the dark at 4°C until further analysis.

In the laboratory, potential decomposition rates were measured by incubating 50 g of fresh sediment or soil in 250 mL infusion flasks sealed with airtight rubber stoppers. The flasks were placed in the dark on a rotary shaker (100 rpm) at 20 °C. For the anaerobic incubations, the flasks were evacuated and flushed with pure nitrogen gas three times. For the aerobic incubations, the flasks were flushed with ambient air. All incubations were carried out in triplicate. The concentrations of CO₂ and CH₄ were frequently measured over a period of two months using an Infrared Gas Analyzer (IRGA, ABB Advance Optima). CH₄ and CO₂ production rates were calculated by linear regression based on the phase in which concentrations showed a linear increase. We also calculated O₂ consumption rates in this phase to ensure that there was no O₂ depletion in the aerobic incubations. CH₄ and CO₂ production rates were expressed on a dry weight basis and added up to obtain C-production rates, which were used as potential decomposition rates.

Before and after the incubation, pore water samples were collected anaerobically with vacuum syringes (60 mL) connected to soil moisture samplers (Rhizon SMS, Eijkelkamp Agrisearch Equipment, Giesbeek, the Netherlands). The pore water samples were stored in iodated polyethylene bottles (50 mL) at -20 °C until further analysis. The concentrations of PO₄ (soluble reactive phosphorus), NO₃ (including NO₂) and NH₄ were measured colorimetrically with an Auto Analyzer 3 system (Bran+Luebbe, Norderstedt, Germany) according to Geurts *et al.* (2008). Fe, S and P were measured using an ICP Spectrometer (IRIS Intrepid II, Thermo Electron Corporation, Franklin, MA). The mobilization rates of mineral N and PO₄ in the pore water, which will be referred to as net mineralization rates, were calculated in $\mu\text{mol kg}^{-1} \text{ d}^{-1}$ by taking the difference between N (NO_x + NH_y) and PO₄ concentrations in pore water before and after the incubation.

Sediment and soil samples were dried for 24 h at 105 °C to determine the moisture content. The organic matter content was determined after heating dry sediment and soil samples at 550 °C for 4 h. Homogenized portions of 200 mg dry sediment and soil were digested with 4 mL HNO₃ (65%) and 1 mL H₂O₂ (30%), using an Ethos D microwave labstation (Milestone srl, Sorisole, Italy). Digestates were diluted and concentrations of Fe, P and S were determined by ICP as described above. A homogenized portion of 6 mg dry sediment was used to determine C and N content, using a Carlo Erba NA1500 elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA).

POTENTIAL NUTRIENT MOBILIZATION TO THE WATER LAYER

Between 2005 and 2008, sediment samples were collected in 44 Dutch peat lakes and ditches, using a metal sediment corer. The sampling sites were located in the following areas: Amstelveense poel (52°18'N, 4°50'E; n=3), Langeraarsche plassen (52°11'N, 4°43'E; n=9), Nieuwkoopsche plassen (52°08'N, 4°47'E; n=6), Vlietpolder (52°09'N, 4°35'E; n=5), De Wieden (52°39'N, 6°05'E; n=8) and Schutsloterwijde (52°40'N, 6°05'E; n=13). Immediately after sampling, pore water samples were collected anaerobically with vacuum syringes (60 mL) connected to soil moisture samplers (Rhizon SMS, Eijkelkamp Agrisearch Equipment, Giesbeek, the Netherlands). The pH of the pore water samples was measured using a combined pH electrode with an Ag/AgCl internal reference (Orion Research, Beverly, CA, USA), and a TIM800 pH meter. Alkalinity was determined by titration to pH 4.2 with 0.01 M HCl using an ABU901 Autoburette (Radiometer, Copenhagen, Denmark). The pore water samples were further processed and analyzed as described for the incubation experiment. The sediment samples were transported in airtight plastic bags and kept in the dark at 4°C until further analysis. Moisture content, organic matter content and concentrations of Fe, P and S in the sediment were determined as described for the incubation experiment.

To determine potential mobilization rates of PO_4 and mineral N ($\text{NO}_x + \text{NH}_y$) from the sediment to the water layer, glass cylinders ($\varnothing$ 12 cm; 30 cm high) were filled with 10 cm of sediment (1.1 L) and placed in the dark at 20 °C. An 18 cm (2.0 L) layer of demineralized water was carefully added on top of the sediment, preventing resuspension. After 2, 16, 31, and 62 days, samples of the surface water and sediment pore water were taken and analyzed as described for the incubation experiment. The potential mobilization rates of PO_4 and mineral N were calculated in $\text{mmol m}^{-2} \text{ y}^{-1}$ by linear regression of surface water concentrations between $t=2$ and $t=62$ days.

STATISTICAL ANALYSIS

The effects of organic matter content on C production rates were analyzed using linear mixed effect models with organic matter as a fixed factor and site as a random factor. This analysis was performed using the nlme package (ver. 3.1) in the R statistical and programming environment (ver. 2.8.0; R Development Core Team, 2005). Other statistical analyses were carried out using SPSS for Windows (ver. 15.0, 2006, SPSS, Chicago, IL, USA). Correlations between variables were determined by regression analyses.

Results

INCUBATION EXPERIMENT

Potential C production (decomposition) rates under aerobic conditions were almost two times higher than under anaerobic conditions (Fig. 1). The highest C production rates were observed in the Irish floating fen soils, which had a higher organic matter content (70-95%) than the sediments we investigated, but also showed a relatively large variation in C production rates. The sediments showed a significant positive linear correlation between organic matter content and C production in both anaerobic and aerobic decomposition ($R^2 = 0.4 - 0.5$; $P < 0.05$; mixed effect models). The floating fen soils were excluded from this analysis, because mixed effect models indicated that the site effect was much larger than that of organic matter content, and that this was caused by the floating fen soils.

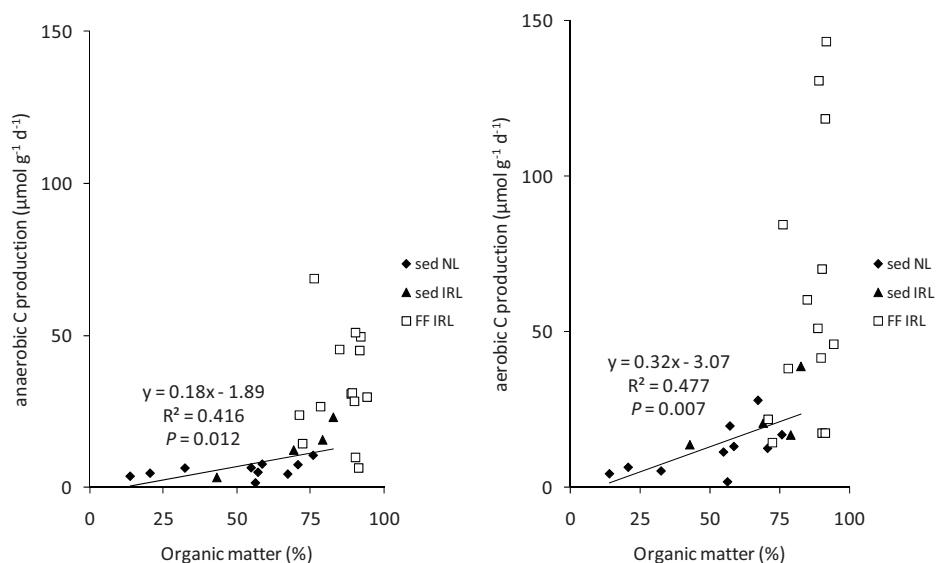


Figure 1. Relationship between organic matter content and C production rates during anaerobic (left) and aerobic (right) incubation in peat sediments (sed) and floating fen soils (FF) from different locations in the Netherlands (NL) and Ireland (IRL). Relations for the peat sediments were described using linear mixed effect models.

The net mineralization rates of mineral N correlated positively with the C production rates for all peat sediments and floating fen soils, but the net N mineralization rates in the Dutch sediments were relatively high compared to

their C production rates (Fig. 2). Unexpectedly, the net anaerobic N mineralization rates in the Irish floating fen soils were, on average, twice as high as under aerobic conditions. Strikingly, the net N mineralization rates correlated negatively with the C:N ratios in the Dutch sediments ($R^2 = 0.2$; $P > 0.05$), but positively with the C:N ratios in the Irish floating fen soils ($R^2 = 0.2 - 0.4$; $P < 0.05$), which generally had the highest C:N ratios (data not shown).

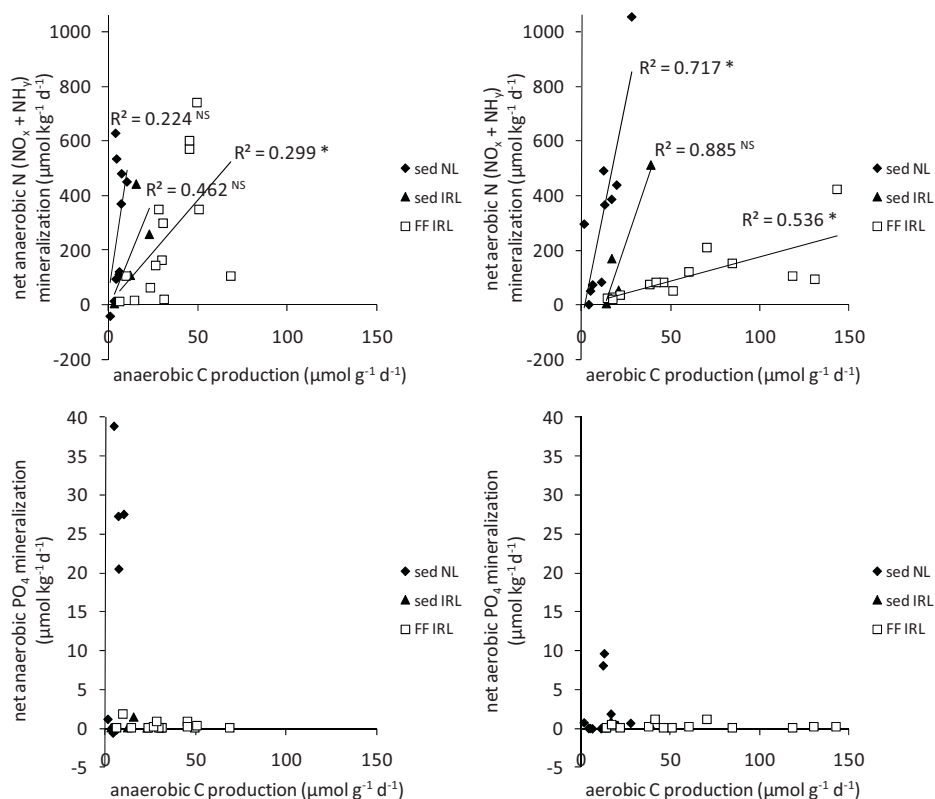


Figure 2. Relationship between C production rates and net mineralization rates of N (NO_x and NH_4) and PO_4 during anaerobic (left) and aerobic (right) incubation in peat sediments (sed) and floating fen soils (FF) from different locations in the Netherlands (NL) and Ireland (IRL). The relations between C production and net N mineralization rates were described by linear regression analysis (* $P < 0.05$, ^{NS} $P > 0.05$).

By contrast, the net PO_4 mineralization rates did not correlate positively with the C production rates and were only high in some of the Dutch sediments with low C production rates (Fig. 2). The highest net PO_4 mineralization rates were measured under anaerobic conditions. The Irish floating fen soils with high C

production rates mostly had higher C:P ratios (537 ± 264 SD g g^{-1}) than the Dutch and Irish sediments and showed very low net PO_4 mineralization rates ($< 1 \mu\text{mol kg}^{-1} \text{d}^{-1}$; Fig. 2). The Dutch sediments with a high net PO_4 mineralization rate had relatively low C:P ratios (265 ± 119 SD g g^{-1}).

Fig. 3 shows that there was a negative correlation between the net PO_4 mineralization rate and both the pore water Fe: PO_4 ratio and the sediment Fe:S ratio. Substantial PO_4 mineralization only occurred below pore water Fe: PO_4 ratios of $12.5 \text{ mol mol}^{-1}$, sediment Fe:P ratios of 7.5 mol mol^{-1} (data not shown) and sediment Fe:S ratios of 0.6 mol mol^{-1} . We did not find any effects of Al and Mn on mineralization rates.

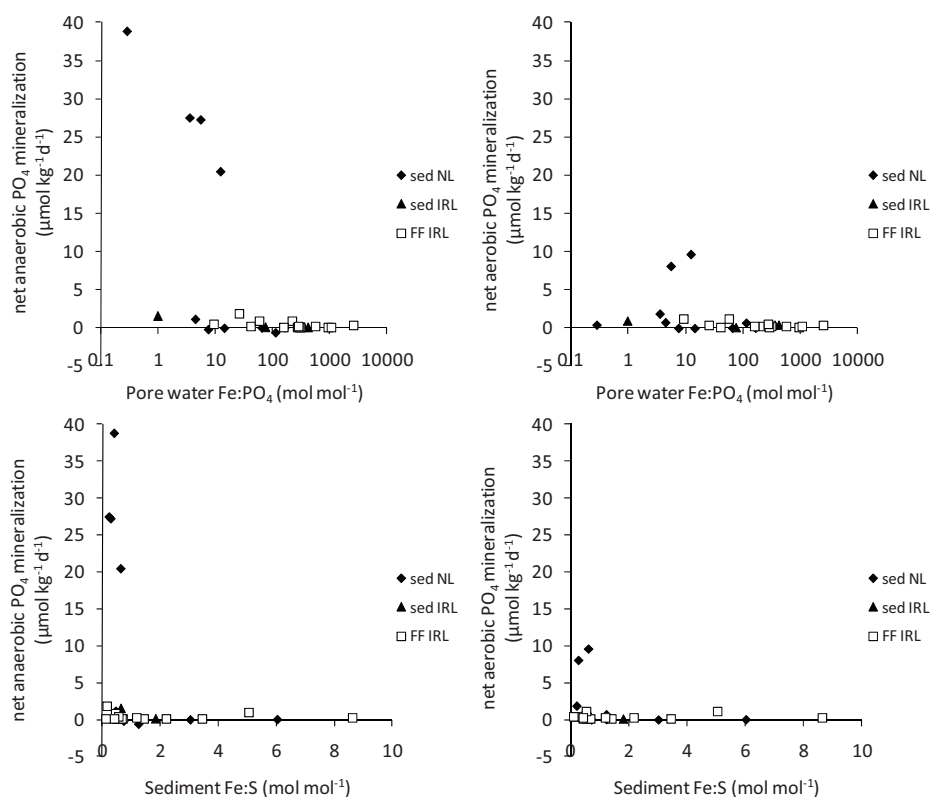


Figure 3. Relationship between pore water Fe: PO_4 ratios, sediment Fe:S ratios and net PO_4 mineralization rates during anaerobic (left) and aerobic (right) incubation in peat sediments (sed) and floating fen soils (FF) from different locations in the Netherlands (NL) and Ireland (IRL). Note the logarithmic x-axes for pore water Fe: PO_4 .

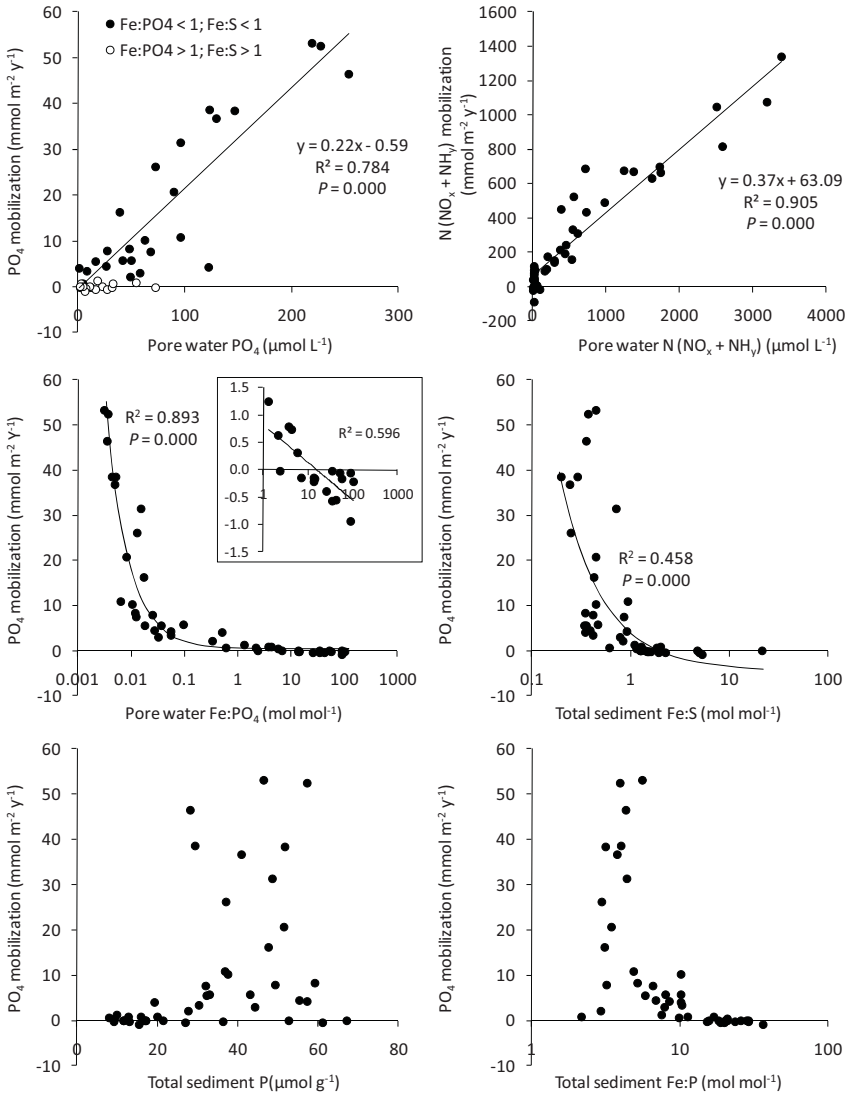


Figure 4. Relationship between sediment and pore water characteristics and mobilization rates of PO_4 and N (NO_x and NH_y) from peat sediments to the water layer.

POTENTIAL NUTRIENT MOBILIZATION TO THE WATER LAYER

There was a huge variation in PO_4 mobilization from the peat sediments to the water layer (-1.0 to $53.2 \text{ mmol m}^{-2} \text{y}^{-1}$; -0.03 to $1.65 \text{ g PO}_4\text{-P m}^{-2} \text{y}^{-1}$; Fig. 4). The PO_4 mobilization rate correlated best with the pore water PO_4 concentration (Fig. 4). This was only true, however, if the pore water Fe:PO4 ratio and the sediment Fe:S ratio were lower than 1 mol mol^{-1} ($R^2 = 0.78$; $P = 0.000$). At these low ratios, PO_4

mobilization rates strongly increased. At higher pore water Fe:PO₄ ratios and sediment Fe:S ratios, PO₄ mobilization rates were very low, but in this range they correlated well with the pore water Fe:PO₄ ratio ($R^2 = 0.60$; $P = 0.000$). Sediments with high PO₄ mobilization rates always had relatively high total sediment P concentrations ($> 28 \mu\text{mol g}^{-1}$), low pore water Fe concentrations ($< 1.5 \mu\text{mol L}^{-1}$) and low sediment Fe:P ratios ($< 10 \text{ mol mol}^{-1}$) (Fig. 4). However, total P concentrations were not a good indicator of PO₄ mobilization to the water layer. N mobilization from the peat sediments to the water layer varied between -93 and 1339 mmol m⁻² y⁻¹ (-1.3 to $18.8 \text{ g m}^{-2} \text{ y}^{-1}$) and correlated very well with the pore water N concentration ($R^2 = 0.91$; $P = 0.000$) (Fig. 4).

Discussion

As expected, the soils and sediments in the incubation experiment showed a higher decomposition (C production) rate under aerobic conditions as a result of higher availability of oxygen, acting as an optimal terminal electron acceptor for decomposition (Freeman *et al.*, 2004; Laiho, 2006). Decomposition rates were also determined by the organic matter content, which provides simple organic compounds acting as electron donors. Above 75% organic matter, however, aerobic decomposition was no longer limited by electron donor availability. Increased decomposition rates lead to the release of dissolved and particulate organic matter in surface water, which decreases light availability under water (Stern *et al.*, 2007). Decomposition rates were lowest in the Dutch sediments, which had already been decomposed to a larger extent as shown by the lower organic matter content at the start of the experiment, and were therefore less reactive than the more intact Irish floating fen soils. As decomposition rates did not correlate with variables related to chemical and physical soil characteristics, e.g. lignin and cellulose concentrations, lignin:nutrient ratios, and size fractions (results not shown), they could not be used as reliable indicators of decomposition (Tomassen *et al.*, 2004; Prescott, 2005).

The general assumption that decomposition of peat soils and sediments automatically leads to increased nutrient concentrations (McLatchey & Reddy, 1998; Bayley *et al.*, 2005) was found to be true for N (NO_x and NH_y), but not for PO₄. Moreover, the net mineralization rates of mineral N and PO₄ were relatively high in the Dutch sediments compared to their C production rates. This means that highly decomposed peat sediments may still show high net nutrient mineralization rates, caused by their lower C:N and C:P ratios (higher nutrient concentrations), by a lower capacity of these sediments to chemically retain

nutrients, especially PO_4 , or by lower microbial consumption of nutrients. These sediments can therefore be an unexpectedly large source of nutrients.

Much more than NO_x and NH_y , PO_4 can be bound in the sediment immediately after mineralization, for example in sediments that are rich in Fe, Al or Ca (Bridgham *et al.*, 1998; Kopacek *et al.*, 2001; Smolders *et al.*, 2006). Fe in particular is considered to be important in binding PO_4 in peat sediments and soils. This is consistent with our results, which showed that net PO_4 mineralization rates were lower at high pore water Fe: PO_4 ratios. Under anaerobic conditions, net PO_4 mineralization rates were higher, because Fe is reduced and ferrous Fe is formed, which is less able to bind PO_4 (Patrick & Khalid, 1974; Ponnampерuma, 1984).

Our nutrient mobilization measurements also showed that PO_4 mobilization from the sediment to the water layer becomes much higher below Fe: PO_4 ratios of 1 mol mol^{-1} . This is consistent with other studies, which found that the risk of PO_4 mobilization increases below pore water Fe: PO_4 ratios of 1-3.5 mol mol^{-1} (Lofgren & Boström, 1989; Smolders *et al.*, 2001; Zak *et al.*, 2004; Geurts *et al.*, 2008). Total sediment P concentrations were only indicative at low values ($< 28 \mu\text{mol g}^{-1}$), but were not reliable at higher values. The actual mobilization of PO_4 from the sediment to the water layer is of pivotal importance for the biodiversity of aquatic systems, due to the induction of blooms of algae and cyanobacteria and the dominance of floating-leaved macrophytes (Correll, 1998). At a high internal PO_4 flux it is also more difficult to return from a hypertrophic turbid water state to a clear water state with submerged macrophytes (Scheffer *et al.*, 1993). This indicates that PO_4 mobilization to the water layer is more important than the actual PO_4 mineralization inside the sediment.

The classic iron cycle (Mortimer, 1941, 1942) can very well explain the actual release of PO_4 from the sediment. In the oxygenated boundary layer between sediment and water layer, dissolved Fe becomes oxidized and PO_4 is effectively bound by iron(hydr)oxides. This mechanism probably explains the negative relation between the PO_4 mobilization to the water layer and the pore water Fe: PO_4 ratios. Where there is insufficient Fe in the pore water to bind PO_4 (Fe: PO_4 ratio $< 1 \text{ mol mol}^{-1}$), PO_4 mobilization from the sediment to the water layer will be mainly determined by diffusion of pore water PO_4 (Reddy *et al.*, 1996). This is comparable with mobilization of mineral N from the sediment to the water layer, which is largely determined by diffusion.

The capacity of the sediment to bind PO_4 also depends on the total S concentration in the sediment, because SO_4 is reduced to sulphide under

anaerobic conditions and may accumulate in the sediment, depending on its actual sequestration by Fe and other metals. Because Fe has a higher binding affinity for sulphide than for PO_4 , this will lead to a lower sediment binding capacity for PO_4 and subsequently to the release of PO_4 (Caraco *et al.*, 1989; Smolders & Roelofs, 1993; Lamers *et al.*, 1998a). The sediment Fe:S ratio can therefore give an important indication of the amount of Fe that is still available to immobilize PO_4 . In our study, the critical Fe:S ratio for PO_4 mobilization to the water layer turned out to be 1 mol mol^{-1} . Fe:S ratios below 1 mol mol^{-1} decrease the availability of Fe oxides and hydroxides, which are able to adsorb P, leading to decreased pore water Fe concentrations and increased pore water PO_4 concentrations (Fig. 5). Systems with high SO_4 loads show decreasing sediment Fe:S ratios, causing a state shift towards a situation with low Fe availability and high PO_4 mobilization rates. Returning to the initial state of high Fe availability will, however, be more difficult because this requires either the oxidation of reduced S compounds in the sediment, in combination with transport of excess S out of the system, or artificial Fe addition.

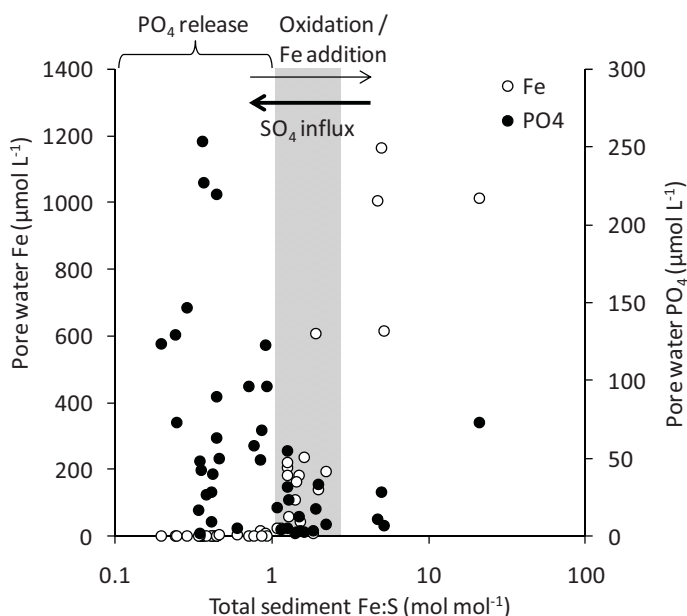


Figure 5. Relationship between total sediment Fe:S ratios and pore water concentrations of Fe and PO_4 . Possible state shifts between states with low and high Fe availability are indicated by arrows (see text for additional explanation).

PO₄ mobilization rates from the sediment to the water layer were relatively low compared to those found in other studies, which reported maximal mobilization rates of 4.4-10.2 g PO₄-P m² y⁻¹ (Lofgren & Boström, 1989; Jensen *et al.*, 1992; Kozerski *et al.*, 1999; Martynova, 2008). Nevertheless, the PO₄ mobilization rates we measured contribute to almost half of the total P load in Dutch peat lakes and fens (0.03 – 3.7 g PO₄-P m⁻² y⁻¹; Janse *et al.*, 2008). In the field, however, biological and physical factors can also be very important in further increasing PO₄ mobilization to the water layer. Such factors include resuspension by wind (Thomas & Schallenberg, 2008), benthic feeding by fish (Persson, 1997), and PO₄ uptake by algae and subsequent release (Correll, 1998).

In situations where PO₄ concentrations in the sediment pore water and PO₄ mobilization to the water layer are too high, it is possible to add Fe, Al or Ca compounds to immobilize PO₄, but these additions all have serious drawbacks (Geurts *et al.*, 2008). Dredging is also often used as a restoration measure in eutrophic peat lakes and fens with high nutrient mobilization rates. In alkaline, S-rich areas that are poor in Fe, however, dredging of the less reactive, but nutrient-rich upper sediment layer will expose a new, more intact and more reactive peat layer, which will decompose faster (Roelofs, 1991; Brouwer *et al.*, 1999). In the Dutch peat lake Geerplas, dredging and P-stripping of all inflowing water have led to an even higher nutrient mobilization rate from the sediment to the water layer than before these expensive measures had started (Michielsen *et al.*, 2007). In such a case, it is not only necessary to decrease the influx of P-rich water, but particularly also the influx of alkaline, S-rich water, because this will slow down decomposition processes in the sediment and subsequent nutrient mobilization to the water layer.

Conclusions

(1) Decomposition rates were primarily determined by the organic matter content, and were higher under aerobic conditions. However, peat sediments that were already highly decomposed still showed high net nutrient mineralization rates, because of lower C:P and C:N ratios in the sediment and a lower PO₄ binding capacity.

(2) Low pore water Fe:PO₄ ratios and low sediment Fe:S ratios led to net PO₄ mineralization in non-calcareous peat sediments and PO₄ mobilization from the sediment to the water layer.

(3) Below Fe:PO₄ ratios of 1 mol mol⁻¹, PO₄ mobilization from the sediment to the water layer was considerable and linearly related to the pore water PO₄ concentration, leading to undesirable effects on aquatic communities. At higher ratios, there appeared to be a strong linear correlation between the Fe:PO₄ ratio and PO₄ mobilization. This means that measuring Fe and PO₄ in the anaerobic sediment pore water provides a powerful tool for a quick scan of the internal PO₄ fluxes. N mobilization from the sediment to the water layer was largely determined by diffusion.

(4) In addition, the sediment Fe:S ratio gave an important indication of the amount of Fe that is available to immobilize PO₄. The availability of iron(hydr)oxides decreased when the Fe:S ratio became lower than 1 mol mol⁻¹, leading to decreased pore water Fe concentrations, increased pore water PO₄ concentrations and increased PO₄ mobilization to the water layer. Either oxidation of the sediment or Fe addition is needed to return to a state with higher relative Fe availability.

(5) As PO₄ mobilization rates from the sediment to the water layer contribute to almost half of the total P load known for Dutch peat lakes and fens, it is of pivotal importance to examine the magnitude of internal fluxes. Dredging of the nutrient-rich upper sediment layer will only be a useful restoration measure if both the influx of P-rich water and its internal mobilization from the newly exposed, potentially more reactive peat layer are sufficiently low.

Acknowledgements

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Chapter 4

Interacting effects of sulphate pollution, sulphide toxicity and eutrophication on vegetation development in fens: A mesocosm experiment



*Overview of the mesocosm experiment, located at the Botanical Gardens
of the Radboud University Nijmegen*

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Abstract

Both eutrophication and SO_4 pollution can lead to higher availability of nutrients and potentially toxic compounds in wetlands. To unravel the interaction between the level of eutrophication and toxicity at species and community level, effects of SO_4 were tested in nutrient-poor and nutrient-rich fen mesocosms. Biomass production of aquatic and semi-aquatic macrophytes and colonization of the water layer increased after fertilization, leading to dominance of highly competitive species. SO_4 addition increased alkalinity and sulphide concentrations, leading to decomposition and additional eutrophication. SO_4 pollution and concomitant sulphide production considerably reduced biomass production and colonization, but macrophytes were less vulnerable in fertilized conditions. The experiment shows that competition between species, vegetation succession and terrestrialization are not only influenced by nutrient availability, but also by toxicity, which strongly interacts with the level of eutrophication. This implies that previously neutralized toxicity effects in eutrophied fens may appear after nutrient reduction measures have been taken.

Introduction

Increased eutrophication has seriously affected biodiversity, vegetation development and terrestrialization in fens (Roelofs, 1991; Koerselman *et al.*, 1995; Wassen and Olde Venterink, 2006). In addition, the toxicity related to this eutrophication can play a very important role. Increased agricultural fertilization and the use of polluted river water to compensate for water shortages have both, directly or indirectly, led to a higher availability of nutrients and potentially toxic compounds such as sulphide and ammonium. As a result, many characteristic plant species have disappeared and have been outcompeted by a few fast-growing species (e.g. *Glyceria maxima* (Hartm.) Holmb., *Juncus effusus* L., *Ceratophyllum demersum* L., *Elodea nuttallii* (Planch.) St. John, or green algae and cyanobacteria), leading to a considerable decrease in biodiversity (Kubin and Melzer, 1996; Lamers *et al.*, 1998a; Van der Welle *et al.*, 2006). Besides that, the characteristic plant species that disappeared often served as ecosystem engineers (Jones *et al.*, 1994): key species that can colonize the water layer, form floating mats and initiate terrestrialization processes in fens (Grootjans *et al.*, 2006). Without these species, there will be no peat formation, but net peat degradation, especially because eutrophication will increase nutrient concentrations in the organic matter (Aerts & Chapin, 2000).

High sulphate loads in polluted rivers and groundwater have led to increased sulphur fluxes and concentrations in fens and marshes, e.g. in the Netherlands (Roelofs, 1991), the Everglades (Bates *et al.*, 2002), New York (Boomer & Bedford, 2008b) and the Louisiana delta plain (Swarzenski *et al.*, 2008). This sulphate pollution can be the result of prolonged high atmospheric deposition, sulphate-containing fertilizers, and, probably the most important cause at many locations, oxidation of pyrite deposits in the deeper subsoil (Lamers *et al.*, 1998b; Bates *et al.*, 2002; Takashima *et al.*, 2002; Lucassen *et al.*, 2004b). This oxidation can be the result of desiccation (aerobic oxidation) or NO₃ leaching (anaerobic denitrification coupled to sulphide oxidation; Haaijer *et al.*, 2006). Accelerated sulphate reduction in anaerobic sediments may lead to increased decomposition of organic matter, increased phosphate mobilization and accumulation of dissolved sulphide (Caraco *et al.*, 1989; Lamers *et al.*, 2002a; Boomer & Bedford, 2008b). Groundwater discharge may supply high concentrations of iron, which can immobilize sulphide and prevent toxicity (Smolders *et al.*, 1995; Van der Welle *et al.*, 2006).

Although much is known about sulphide toxicity in marine environments (Havill *et al.*, 1985; Portnoy & Giblin, 1997; Erskine & Koch, 2000; Azzoni *et al.*, 2001), quite a few studies have investigated this in freshwater wetlands. In these systems, it may lead to suppressed growth and development, iron chlorosis, leaf necrosis, suppressed flowering, black and flaccid roots, root decay and even the death of the whole plant (Allam & Hollis, 1972; Armstrong *et al.*, 1996; Smolders & Roelofs, 1996; Van der Welle *et al.*, 2007b). How different plant species deal with sulphide toxicity mainly depends on their ability to oxidize the root zone by radial oxygen loss (Lamers *et al.*, 1998a; Adema *et al.*, 2003; Van der Welle *et al.*, 2007a).

It seems likely, however, that these specific toxicity effects of sulphide interact with the level of eutrophication. On the one hand, eutrophication enhances toxicity, either directly by ammonium accumulation (Roelofs, 1991; Smolders *et al.*, 1996; Lamers *et al.*, 1998a; Britto & Kronzucker, 2002) or indirectly by stimulating decomposition and reduction processes (Rejmankova & Houdkova, 2006). On the other hand, eutrophication may lead to higher biomass production, which may dilute the toxic compounds in plant tissue (Timmer & Stone, 1978; Jarrell & Beverly, 1981; Outridge, 1992). Increased plant growth may also lead to increased root development, and thus to more radial oxygen loss and a less reductive sediment (Jaynes & Carpenter, 1986). As a consequence, toxicity effects in plants can be masked in eutrophic areas, but may show up when nutrient availability is reduced. Therefore, restoration measures aimed at reducing eutrophication may even lead to a vegetation collapse. To either

avoid these toxicity effects or compete with other fen species in a nutrient-rich situation, plants may adopt different growth strategies, such as lateral growth of rhizomes and elevation of the leaf canopy (Grime, 1974).

Although field surveys may be used to study interacting effects of sulphate pollution and eutrophication in fens, it is difficult to distinguish between these two effects for different plant species, and to find causal relationships in such a complex field situation. On the other hand, ecophysiological laboratory experiments can be used to study these interacting effects more accurately for certain species, but it may be hard to extrapolate these results to the field situation.

The objective of this study was to investigate the interacting effects of nutrient availability and toxicity. More specifically, we wanted to test the effects of sulphate pollution in outdoor, semi-controlled fen mesocosms under nutrient-poor and nutrient-rich conditions. In the course of three growing seasons, we tested the effects of NP fertilization of the peat, sulphate enrichment of the water, or a combination, in 16 mesocosms, each containing four aquatic and seven semi-aquatic macrophyte species with different growth strategies. It was hypothesized that sulphide toxicity would not only differ between species, but also depend on the level of eutrophication, which could have important implications for water management and restoration measures in fens.

Material and methods

EXPERIMENTAL SET-UP

In March 2005, 16 shallow polyethylene mesocosms ($w \times d \times h = 1.0 \times 1.0 \times 0.3$ m) were placed at the Radboud University Nijmegen Botanical Gardens. Each mesocosm was divided into a 'terrestrial' compartment and an 'aquatic' compartment. The terrestrial compartment (40% of the surface area), which was filled with unfertilized Baltic peat (Holland Potgrond, Poeldijk, The Netherlands), was separated from the aquatic part by a plywood board covered with anti-rooting cloth to create a gradually sloping peat bank (Fig. 1). The aquatic compartment had a thin sediment layer of peat on the bottom. Each mesocosm was then filled with 150 L demineralized water (to a depth of about 25 cm in the aquatic compartment). Water level fluctuations of ± 5 cm over time were allowed. Because initial pH was low (between 4 and 5), the peat in each mesocosm was limed with 175 g "Dolokal" (75% CaCO_3 , 10% MgCO_3 , and 5% MgO) before starting the experiment to achieve a pH between 5 and 6, and 20

g NaHCO_3 was added to the surface water to increase the alkalinity to 1.5 meq L^{-1} , which is a common value in Dutch fens. The NaHCO_3 addition was repeated in May and August 2005.

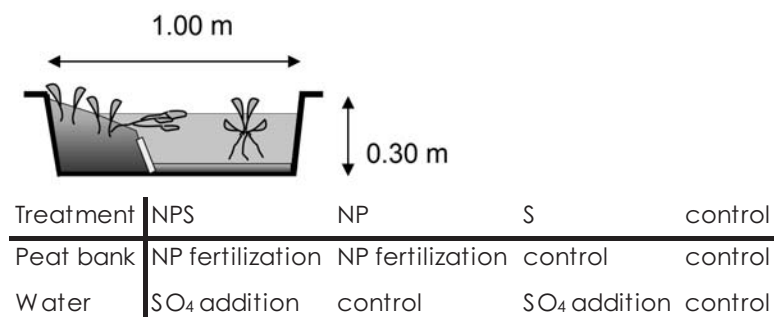


Figure 1. Experimental set-up and configuration of the treatments used in the mesocosm experiment ($n=4$), including aquatic and semi-aquatic plants. Baltic peat was used to create both the bank and the sediment layer.

In April 2005, five semi-aquatic macrophyte species, which are characteristic of fens and key species for terrestrialization ("ecosystem engineers"), were planted in each mesocosm on the lower peat bank. We used *Menyanthes trifoliata* L. (total fresh weight (FW) per mesocosm $28.0 \pm 5.3 \text{ g}$), *Thelypteris palustris* Schott ($15.7 \pm 4.1 \text{ g}$), *Ranunculus lingua* L. ($23.0 \pm 11.7 \text{ g}$), *Calla palustris* L. ($50.6 \pm 8.4 \text{ g}$) and *Equisetum fluviatile* L. ($11.1 \pm 2.1 \text{ g}$). In addition, two semi-aquatic macrophyte species characteristic of nutrient-rich locations were planted higher on the peat bank ("eutrophic helophytes"): *G. maxima* (total FW per mesocosm $14.0 \pm 4.1 \text{ g}$) and *J. effusus* ($15.8 \pm 1.6 \text{ g}$). Four aquatic macrophytes were placed in the aquatic compartment: *E. nuttallii* (total FW per mesocosm $4.0 \pm 0.2 \text{ g}$), *C. demersum* ($21.9 \pm 1.1 \text{ g}$), *Stratiotes aloides* L. ($55.1 \pm 9.9 \text{ g}$) and *Potamogeton compressus* L. ($2.7 \pm 0.9 \text{ g}$), which was planted in the thin peat layer (sediment) at the bottom of the aquatic compartment. *C. demersum* was the only "non-rooting aquatic macrophyte", whereas the other aquatic species were classified as "rooting aquatic macrophytes". All macrophytes species were collected in representative Dutch fens.

Mesocosms were then allocated to four different treatments (NPS, NP, S and control), each with four replicates (Fig. 1). The peat banks of the NPS and NP treatments peat banks were fertilized with CaPO_4 (70 kg P ha^{-1}) and NH_4NO_3 (600 kg N ha^{-1} ; half as slow release granules) at the beginning of May 2005. This fertilization is representative of that in agricultural areas (Schils & Snijders, 2004)

and was repeated in June 2006 and May 2007. The S and control treatments received a background dose of CaPO_4 only once, in May 2006 (6.7 kg P ha^{-1}), to avoid P-deficiency after one year. In the NPS and S treatments Na_2SO_4 was added to the water layer at the beginning of May 2005, up to a final concentration of 2 mmol L^{-1} , which is a common value in S-polluted fens in the Netherlands. The addition was repeated every two months to create a flux of about $1000 \text{ kg S ha}^{-1} \text{ yr}^{-1}$.

SAMPLING

Four to five times per year, between April 2005 and September 2007, surface water samples were collected in iodated polyethylene bottles (100 mL). Three to four times per year, soil moisture samplers (Eijkelpamp Agrisearch Equipment, Giesbeek, the Netherlands) and vacuum glass infusion bottles (30 mL) were used to anaerobically sample pore water in the sediment and in the upper 10 cm of the peat bank (10, 20 and 30 cm on the slope). In June 2005, June 2006 and September 2006, samples from the peat bank were taken to determine bio-available phosphorus concentrations (Olsen *et al.*, 1954). In September 2007, at the end of the third growing season, all the aboveground biomass of the macrophytes was harvested, dried for 24 h at 70°C , and weighed to determine total dry weight. At the end of the first two growing seasons, total dry weight of semi-aquatic macrophytes was determined from non-destructive estimates of macrophyte cover, followed by a conversion to dry weight, based on macrophyte cover and total dry weight biomass in September 2007, which correlated very well ($r^2 = 0.92$). A distinction was made between plants that grew on the peat bank and in the water. For the aquatic macrophytes, total dry weight in the first 2 years was determined by measuring the total fresh weight biomass and the dry weight of a subsample, followed by a conversion to total dry weight biomass.

CHEMICAL ANALYSIS

Immediately after sampling, 10.5 mL of pore water sample was fixed with 10.5 mL of sulphide antioxidant buffer containing NaOH, Na-EDTA and ascorbic acid (Van Gernerden, 1984). Sulphide concentrations were measured on the same day, using a sulphide ion-specific Ag electrode (Orion Research, Beverly, CA, USA) and a double junction calomel reference electrode (Roelofs, 1991). The pH of the surface water and pore water samples was measured using a combined pH electrode with an Ag/AgCl internal reference (Orion Research, Beverly, CA, USA), and a TIM800 pH meter. Alkalinity ($\text{meq H}^+ \text{ L}^{-1}$) was determined by titration to pH 4.2 with 0.01 M HCl using an ABU901 Autoburette (Radiometer, Copenhagen, Denmark). Surface water turbidity was determined using a Turb550

turbidity meter (WTW, Weilheim, Germany). Subsequently, surface water samples were filtered through glass microfibre filters (type GF/C, Whatman, Brentford, UK). Extinction at 450 nm was measured (Shimadzu spectrophotometer UV-120-01, Kyoto, Japan) for colorimetric background correction and as an estimate of humic acid concentrations (Smolders *et al.*, 2003b). Citric acid (0.6 mmol L^{-1}) was added to prevent metal precipitation. The samples were stored in iodated polyethylene bottles (50 mL) at -20°C until further analysis.

The concentrations of PO_4 , NO_3 and NH_4 were measured colorimetrically with an Auto Analyzer 3 system (Bran+Luebbe, Norderstedt, Germany), using ammonium molybdate (Henriksen, 1965), hydrazine sulphate (Kamphake *et al.*, 1967) and salicylate (Grasshoff & Johannsen, 1972), respectively. Fe, S and P were measured using an ICP Spectrometer (IRIS Intrepid II, Thermo Electron Corporation, Franklin, MA). Total S concentrations provided a good estimate of SO_4 concentrations, because only a small percentage of S was present in organic form. This was verified by parallel analysis of various pore water and surface water samples using capillary ion analysis (Waters Corporation, Milford, MA, USA).

A homogenized portion of 200 mg dry plant material was digested with 4 mL HNO_3 (65%) and 1 mL H_2O_2 (30%), using an Ethos D microwave labstation (Milestone srl, Sorisole, Italy). Digestates were diluted and concentrations of phosphorus and sulphur were determined by ICP as described above. A homogenized portion of 2 mg dry plant material was used to determine carbon and nitrogen content using a Carlo Erba NA1500 elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA). Weighted average N:P, C:N, N:P and C:S ratios of the vegetation were then calculated on total dry weight basis for aquatic and semi-aquatic macrophytes that grew in the water layer and semi-aquatic macrophytes that grew on the peat bank. Free amino acids were extracted from fresh shoot material according to Van Dijk & Roelofs (1988), using 70% ethanol containing 10 mL thiodiglycol and citric acid (700 mg L^{-1}), and concentrations were measured by High Performance Liquid Chromatography (Varian Liquid Chromatograph 5000) using a cation exchange column (LKB UP8).

STATISTICAL ANALYSIS

All statistical analyses were carried out using SPSS for Windows (version 15.0, 2006, SPSS, Chicago, IL, USA). Pore water concentrations from different positions on the slope of the peat bank were averaged. Data were $\log(+1)$ transformed to make variances less dependent on sample means, and to obtain a normal distribution. Time effects were tested with GLM repeated measures. Differences between

treatments in terms of biogeochemical variables, plant biomass, vegetation element ratios and free amino acid concentrations were determined by univariate ANOVA, with a Bonferroni post-hoc test. A Games-Howell post-hoc test was used if variances were not equal in Levene's test of equality of error variances.

Table 1. *P* values of the time effects (time), NP fertilization effects (fert), SO₄ addition effects (SO₄) and interaction effects for the pore water and surface water concentrations of PO₄, NO₃, NH₄, SO₄, sulphide and humic acids, as tested by GLM repeated measures. Bold values indicate $P \leq 0.05$.

	compartment	time	fert	SO ₄	time*fert	time*SO ₄	fert*SO ₄	time*fert*SO ₄
PO ₄	sediment	0.000	0.000	0.002	0.000	0.000	0.524	0.000
	peat bank	0.000	0.000	0.022	0.000	0.021	0.939	0.303
	water	0.000	0.000	0.134	0.000	0.394	0.300	0.490
NO ₃	sediment	0.000	0.006	0.016	0.027	0.785	0.452	0.837
	peat bank	0.000	0.000	0.002	0.000	0.025	0.257	0.038
	water	0.000	0.273	0.166	0.000	0.435	0.461	0.185
NH ₄	sediment	0.000	0.171	0.000	0.000	0.000	0.000	0.000
	peat bank	0.000	0.000	0.000	0.000	0.000	0.979	0.050
	water	0.000	0.032	0.020	0.000	0.129	0.953	0.580
SO ₄	sediment	0.000	0.456	0.000	0.180	0.000	0.116	0.096
	peat bank	0.000	0.030	0.000	0.000	0.000	0.582	0.001
	water	0.000	0.595	0.000	0.135	0.000	0.466	0.159
sulphide	sediment	0.000	0.048	0.000	0.129	0.003	0.261	0.047
	peat bank	0.000	0.041	0.000	0.297	0.037	0.173	0.193
humic acids	sediment	0.000	0.516	0.000	0.002	0.000	0.266	0.340
	peat bank	0.000	0.630	0.000	0.176	0.000	0.607	0.524
	water	0.000	0.435	0.000	0.000	0.000	0.986	0.008

Results

EFFECTS ON BIOGEOCHEMISTRY

PO₄, NO₃ and NH₄ concentrations in pore water and surface water changed over time in all compartments, and these changes were different for the fertilized and unfertilized treatments (Table 1). PO₄ concentrations in the peat bank, the sediment pore water and the surface water were much higher in the NP fertilization treatments than in the other treatments (Figs. 2 and 3). Bio-available phosphorus concentrations in the fertilized peat, as determined by Olsen extraction, varied between 10 and 26 $\mu\text{mol g}^{-1}$ dry wt in the first year, which was

20 to 50 times higher than in the unfertilized peat (data not shown). Total phosphorus concentrations increased only threefold in the fertilized peat, up to $37 \mu\text{mol g}^{-1}$ dry wt (data not shown).

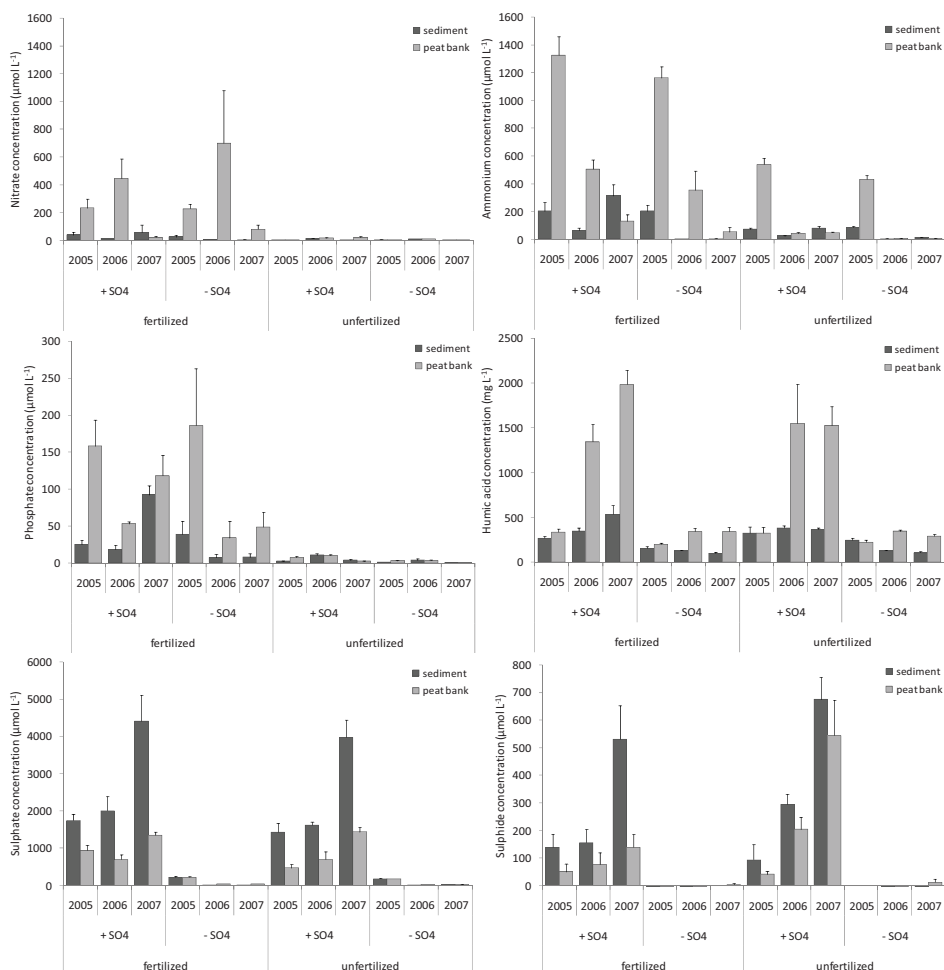


Figure 2. Effects of the various treatments on the pore water biogeochemistry of the peat bank and the sediment. Average concentrations (±SEM) are given for each year.

NO₃ concentrations in the fertilized peat banks increased to 450-700 $\mu\text{mol L}^{-1}$ in the second year, which was 40 to 60 times higher than in the unfertilized peat banks (Fig. 2). In the first year, NH₄ concentrations in the peat bank and sediment pore water of both NP fertilization treatments were 2.5 times higher than in the other treatments. In the following years, however, NH₄ concentrations decreased

(Fig. 2). Fertilization only slightly increased total nitrogen concentrations in the peat, up to $750 \mu\text{mol g}^{-1}$ dry wt. Surface water NO_3 and NH_4 concentrations were only higher in the first year after NP fertilization (Fig. 3).

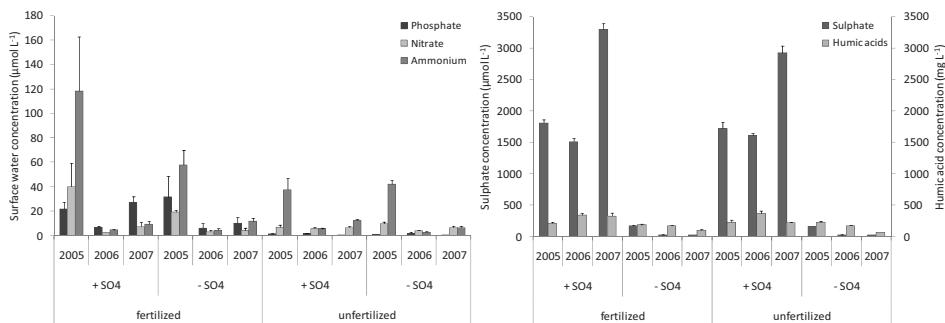


Figure 3. Effects of the various treatments on the surface water biogeochemistry. Average concentrations ($\pm\text{SEM}$) are given for each year.

After SO_4 addition, average SO_4 concentrations in the surface water increased in time to $1500 \mu\text{mol L}^{-1}$ in the first year and $3000 \mu\text{mol L}^{-1}$ in the third year (Table 1; Fig. 3), which was 20–40 times higher than average SO_4 concentrations in the other treatments ($20\text{--}175 \mu\text{mol L}^{-1}$). This addition also led to comparable differences in SO_4 concentrations in the pore water of the sediment and the peat bank (Fig. 2). In addition, sulphide concentrations in the SO_4 treatments already increased in the first growing season (Fig. 2), not only in the sediment but also in the peat bank (115 and $45 \mu\text{mol L}^{-1}$ respectively). These sulphide concentrations further increased in the second and third year, up to $675 \mu\text{mol L}^{-1}$ (Table 1; Fig. 2). In the final 2 years, SO_4 addition led to a higher alkalinity in all compartments (data not shown). Pore water concentrations became 4 meq L^{-1} in the peat bank and 6 meq L^{-1} in the sediment, which was almost four times higher than in the treatments without SO_4 addition. Surface water alkalinity increased to 2.4 meq L^{-1} in the SO_4 treatments, against 1.4 meq L^{-1} in the other treatments. Humic acid concentrations also increased after SO_4 addition (Table 1) and finally became three to four times higher in the surface water and four to six times higher in the pore water (Figs. 2 and 3).

The changes in pore water PO_4 and NH_4 concentrations over time were different for the treatments with and without SO_4 addition (Table 1). During the experiment, pore water PO_4 concentrations decreased over time in the NP treatment without SO_4 addition (Fig. 2). In the NP treatment with SO_4 addition, however, PO_4 concentrations increased again in the third year, resulting in 2.5

times higher concentrations in the peat bank ($P > 0.05$) and 11 times higher concentrations in the sediment ($P < 0.001$) compared to the NP treatment. While pore water NH_4 concentrations decreased over time, higher NH_4 concentrations were measured in the SO_4 treatments than in the treatments without SO_4 addition in the third year (only significant for sediment pore water; Fig. 2).

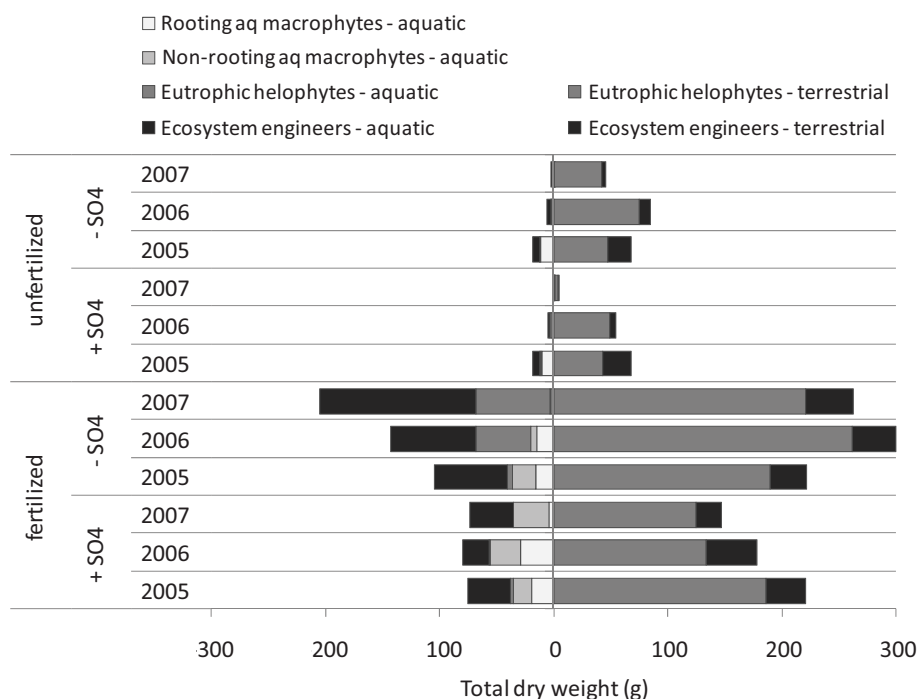


Figure 4. Effects of the various treatments on the biomass of rooting and non-rooting aquatic macrophytes, ecosystem engineers and eutrophic helophytes in the aquatic (left) and terrestrial (right) parts of the mesocosms. Starting biomasses for these plant groups were 5.2, 2.5, 17.5 and 4.4 g dry weight per mesocosm, respectively. Species are grouped as shown in Table 2.

EFFECTS ON MACROPHYTE GROWTH

In general, macrophyte growth changed considerably over time, and these changes were different for the different treatments (Table 2). Both aquatic and semi-aquatic macrophytes increased in biomass after NP fertilization of the peat bank ($P < 0.05$; Table 2; Fig. 4). The total biomass of semi-aquatic macrophytes colonizing the aquatic compartment was also much higher in the fertilized treatments, finally resulting in 100 times more biomass than in the unfertilized treatments. *Menyanthes trifoliata* and *G. maxima* colonized the aquatic

compartment most in the fertilized treatments, whereas *J. effusus* and *G. maxima* were the dominant species on the peat bank in these treatments (Fig. 5).

Table 2. *P* values of the time effects (time), NP fertilization effects (fert), SO₄ addition effects (SO₄) and interaction effects for all aquatic and semi-aquatic macrophytes, as tested by GLM repeated measures. Bold values indicate $P \leq 0.05$. EE = ecosystem engineer, EH = eutrophic helophyte, RAM = rooting aquatic macrophyte, NAM = non-rooting aquatic macrophyte.

	compartment	time	fert	SO ₄	time*fert	time*SO ₄	fert*SO ₄	time*fert*SO ₄
All semi-aquatic macrophytes	aquatic	0.037	0.000	0.015	0.000	0.015	0.128	0.235
	terrestrial	0.000	0.000	0.000	0.000	0.000	0.021	0.004
	total	0.000	0.000	0.000	0.000	0.000	0.112	0.006
<i>R. lingua</i> (EE)	aquatic	0.556	0.454	0.185	0.386	0.072	0.731	0.248
	terrestrial	0.011	0.036	0.364	0.503	0.073	0.701	0.648
	total	0.075	0.062	0.152	0.302	0.030	0.721	0.336
<i>E. fluviatile</i> (EE)	aquatic	0.700	0.001	0.008	0.745	0.240	0.010	0.264
	terrestrial	0.002	0.000	0.001	0.209	0.000	0.234	0.000
	total	0.002	0.000	0.001	0.181	0.000	0.134	0.000
<i>G. maxima</i> (EH)	aquatic	0.015	0.000	0.001	0.050	0.000	0.000	0.001
	terrestrial	0.000	0.000	0.000	0.511	0.001	0.313	0.200
	total	0.000	0.000	0.000	0.126	0.000	0.027	0.034
<i>T. palustris</i> (EE)	aquatic	0.354	0.337	0.337	0.354	0.354	0.337	0.354
	terrestrial	0.127	0.403	0.026	0.070	0.354	0.518	0.304
	total	0.131	0.352	0.028	0.107	0.329	0.511	0.326
<i>J. effusus</i> (EH)	terrestrial	0.000	0.000	0.001	0.000	0.000	0.016	0.000
<i>C. palustris</i> (EE)	aquatic	0.000	0.043	0.073	0.078	0.030	0.294	0.434
	terrestrial	0.000	0.039	0.206	0.213	0.323	0.618	0.403
	total	0.000	0.004	0.020	0.211	0.000	0.373	0.546
<i>M. trifoliata</i> (EE)	aquatic	0.180	0.000	0.085	0.007	0.192	0.232	0.528
	terrestrial	0.000	0.000	0.197	0.000	0.109	0.188	0.316
	total	0.000	0.000	0.008	0.000	0.014	0.918	0.316
All aq. macrophytes	aquatic	0.000	0.000	0.062	0.003	0.018	0.022	0.016
<i>P. compressus</i> (RAM)	aquatic	0.000	0.553	0.039	0.023	0.047	0.905	0.313
<i>S. aloides</i> (RAM)	aquatic	0.000	0.032	0.868	0.000	0.649	0.470	0.108
<i>C. demersum</i> (NAM)	aquatic	0.017	0.001	0.108	0.257	0.030	0.256	0.007
<i>E. nuttallii</i> (RAM)	aquatic	0.001	0.016	0.787	0.002	0.637	0.763	0.673

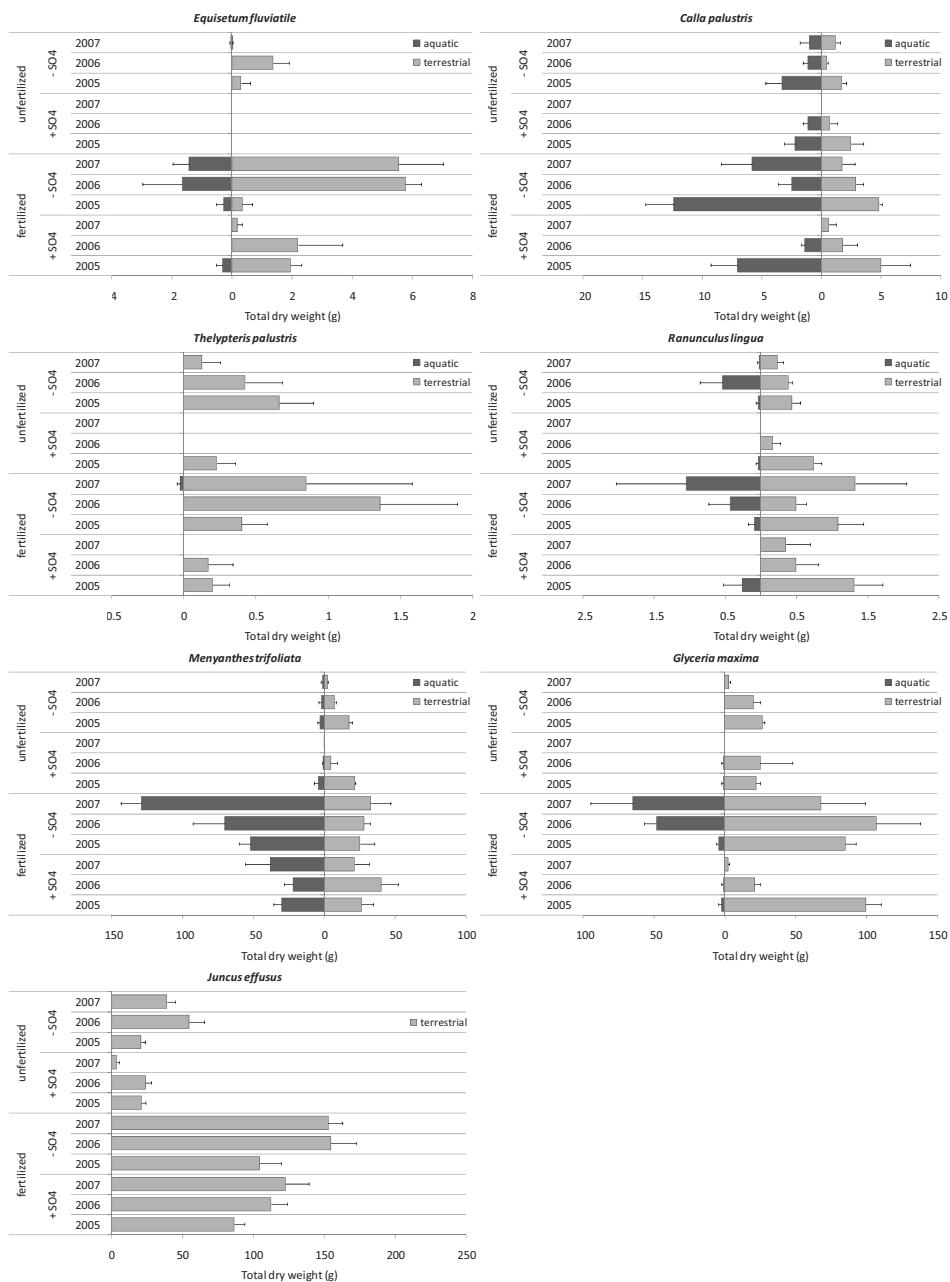


Figure 5. Effects of the various treatments on the biomass of semi-aquatic macrophytes in the aquatic (left) and terrestrial (right) parts of the mesocosms (±SEM).

In the third year, SO_4 addition had led to much lower semi-aquatic macrophyte biomass than without SO_4 addition (Fig. 4): 60% lower in the fertilized SO_4 treatments and 92% lower in the unfertilized SO_4 treatments. *Juncus effusus* and *M. trifoliata* appeared to be least sensitive to SO_4 addition (Fig. 5). At the end of the experiment, all macrophytes except *J. effusus* had died or almost completely disappeared in the unfertilized SO_4 treatment, whereas only *T. palustris* and *P. compressus* had died in the fertilized SO_4 treatment and only *E. nuttallii* had died in the control treatment (Figs. 5 and 6). *Menyanthes trifoliata* was the only semi-aquatic macrophyte that persisted in the aquatic compartment of the NPS treatment after 3 years. Colonization of the water layer by semi-aquatic macrophytes only increased over time in the NP treatment without SO_4 addition (Fig. 5; Table 2; $P < 0.05$). In contrast, most aquatic macrophytes decreased in this treatment and grew best in the NPS treatment (Fig. 6; Table 2; $P < 0.05$). This was especially true for *C. demersum*, a non-rooting species, which increased its biomass in this treatment over the course of the experiment.

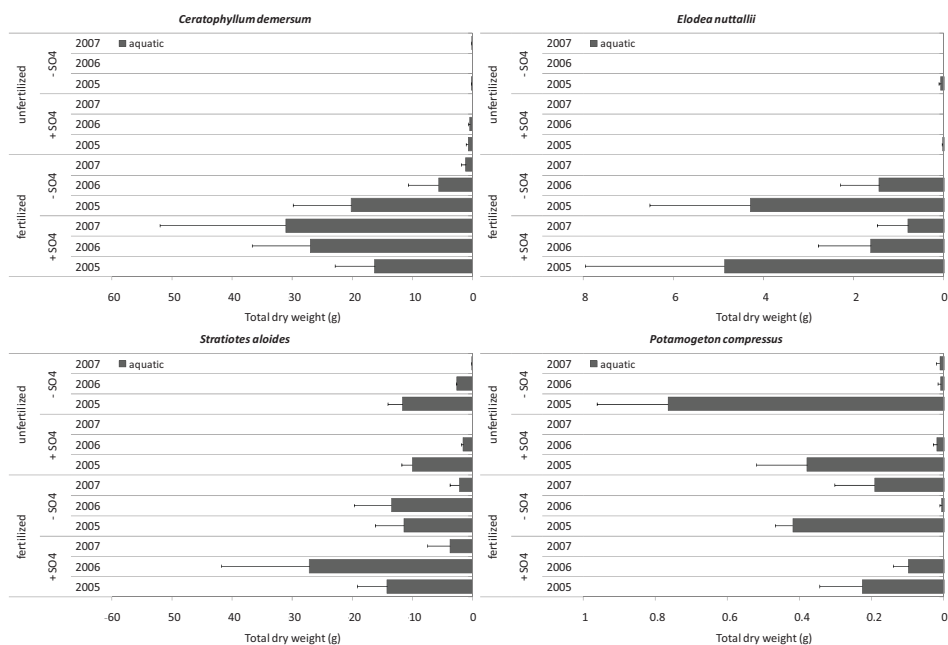


Figure 6. Effects of the various treatments on the biomass of aquatic macrophytes in the aquatic part of the mesocosms ($\pm$ SEM).

At the end of the experiment, vegetation N:P ratios were higher in the control treatment ($13\text{--}19 \text{ g g}^{-1}$) than in the fertilized treatments ($2\text{--}5 \text{ g g}^{-1}$; $P < 0.05$; Fig. 7).

N:P ratios also decreased in the unfertilized SO₄ treatment (7-16 g g⁻¹; Fig. 7). In addition, fertilization decreased the C:N ratios of the terrestrial vegetation and the C:P ratios of the aquatic and terrestrial vegetation ($P < 0.05$; data not shown). Vegetation C:S ratios in the SO₄ treatments were 2-6 times lower than those in treatments without SO₄ addition ($P < 0.05$; data not shown).

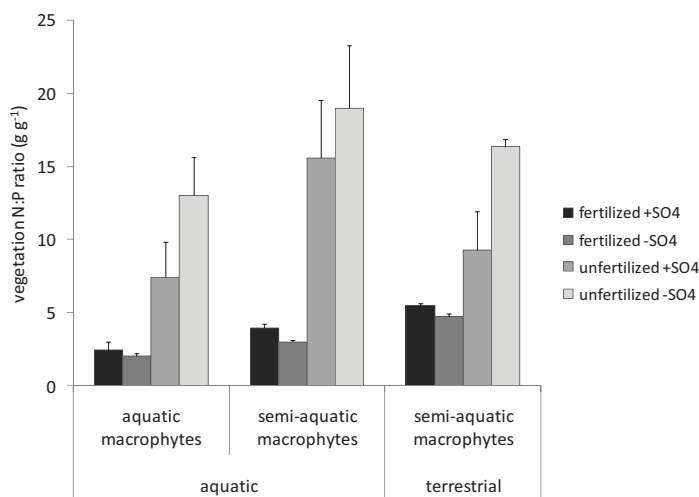


Figure 7. N:P ratios of the aboveground biomass of the vegetation in the various treatments after 3 years ($\pm$ SEM). The vegetation is divided into aquatic and semi-aquatic macrophytes in the water layer (aquatic compartment), and semi-aquatic macrophytes on the peat bank (terrestrial compartment).

Discussion

This mesocosm experiment has yielded clear evidence of interacting effects of SO₄ pollution (including sulphide toxicity) and eutrophication on biogeochemistry and vegetation development in fens.

In the fertilized treatments, nutrient concentrations not only increased rapidly in the peat bank, but they also leached to the surface water and the sediment, especially in the first year. Although this was not specifically intended, it will also happen in small, natural water bodies. As expected, fertilization led to the dominance of fast-growing eutrophic species, whose growth strategy outcompeted most ecosystem engineers (key species for terrestrialization). In the unfertilized treatments, however, ecosystem engineers did not profit from their relatively better competitive position under low nutrient conditions. Nutrient

concentrations in these treatments may have been somewhat lower than under mesotrophic conditions in the field. The nutrient availability also appeared to be too low to induce colonization of the water layer by semi-aquatic macrophytes in these treatments over a three-year period. Colonization of the water layer only occurred in the fertilized treatments, where ecosystem engineers were able to use the abundance of nutrients to grow into the water and avoid competition with dominating eutrophic species on the peat bank. Furthermore, fertilization led to a considerable decrease in the N:P ratio of the vegetation, which may indicate a shift from P-limitation to N-limitation (N:P ratio < 14; Koerselman & Meuleman, 1996; Whigham *et al.*, 2002). In addition, fertilization decreased C:P ratios of the vegetation to values below 200 g g⁻¹, suggesting that decomposition was no longer limited by P (Brinson, 1977). C:N ratios of the terrestrial vegetation in the fertilized treatments dropped to values below 20-25 g g⁻¹, suggesting that decomposition was no longer limited by N either (Swift *et al.*, 1979). This means that eutrophication may lead to higher nutrient concentrations in plants, which can lead to increased decomposition rates of the litter (Aerts & Chapin, 2000) and, therefore, hamper terrestrialization.

It was remarkable that already in the first year, SO₄ addition to the water layer led to increased SO₄ and sulphide concentrations in both the sediment and the peat bank. This means that anaerobic conditions in the peat were rapidly established. These are favorable conditions for the reduction of SO₄, leading to sulphide production, decomposition of organic matter and alkalization (Smolders & Roelofs, 1993; Lamers *et al.*, 1998a; Swarzenski *et al.*, 2008). Higher rates of decomposition and bicarbonate production can explain the increasing humic acid concentrations (Mitchell & McDonald, 1992) and alkalinity in all compartments of the SO₄ treatments in the course of the experiment. In addition, high alkalinity enhances decomposition even further, provided that the peat is easily decomposable (Roelofs, 1991; Brouwer *et al.*, 1999). The higher PO₄ and NH₄ concentrations in the sediment and the peat bank of the SO₄ treatments at the end of the experiment cannot be explained only by sulphide-induced inhibition of nutrient uptake (Koch *et al.*, 1990), but probably also by increased decomposition rates and PO₄ mobilization from iron binding sites as a result of sulphide production (Smolders & Roelofs, 1993; Roden & Edmonds, 1997; Wetzel, 2001). This PO₄ mobilization could easily occur, because SO₄ addition led to pore water Fe:PO₄ ratios decreasing well below threshold values of 1-5 mol mol⁻¹ for PO₄ mobilization (results not shown; Lofgren & Boström, 1989; Zak *et al.*, 2004; Geurts *et al.*, 2008). Furthermore, just like direct fertilization, SO₄ addition decreased the N:P ratio of the vegetation, possibly indicating a shift from P-limitation to N-limitation (Koerselman & Meuleman, 1996). These results confirm

that SO_4 pollution leads to extra internal mobilization of nutrients (termed internal eutrophication) in fens (Roelofs, 1991; Lamers *et al.*, 2002a; Smolders *et al.*, 2006).

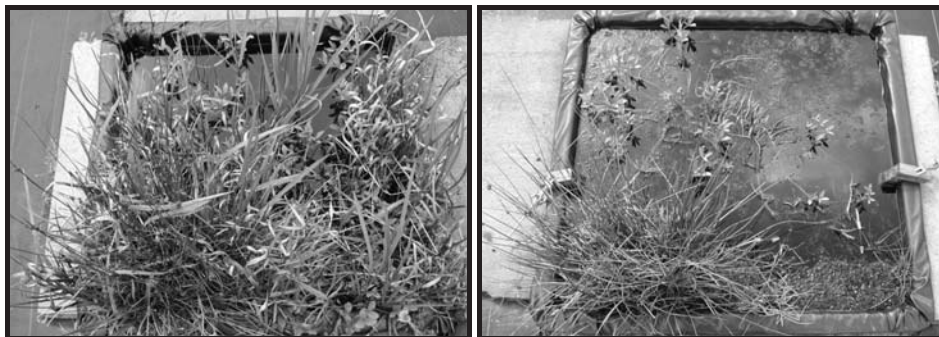


Figure 8. Photographs of two fertilized mesocosms at the end of the third growing season (September 2007) without (left) and with SO_4 addition (right).

Vegetation development was greatly influenced by the effects of SO_4 addition. The accumulation of sulphide led to highly toxic levels (Roelofs, 1991; Smolders *et al.*, 1995), comparable to field concentrations (Hotes *et al.*, 2005; Geurts *et al.*, 2008), which most probably resulted in the disappearance of several sensitive species and a much lower total biomass (Fig. 8). This toxicity effect was, however, more disastrous under nutrient-poor conditions, where almost all species disappeared completely. Macrophytes in the fertilized treatments were less vulnerable to sulphide toxicity, probably because of a combination of dilution due to higher biomass production and greater oxidation of the sediment and the peat bank by radial oxygen loss due to higher root biomass (Jaynes & Carpenter, 1986; Adema *et al.*, 2003). The latter may also explain the slightly lower sulphide concentrations in the fertilized SO_4 treatment compared to the unfertilized SO_4 treatment (Lamers *et al.*, 1998a; Van der Welle *et al.*, 2007a). In addition, SO_4 addition and concomitant sulphide production hampered the colonization of the water layer by ecosystem engineers, such as *C. palustris* and *R. lingua*, in most cases, which has important implications for terrestrialization and succession in fens. Only *M. trifoliata* was able to use such a growth strategy with rhizomes that colonize the surface water in the fertilized SO_4 treatment and could thus avoid both sulphide toxicity and competition with eutrophic species on the peat bank. Although all macrophytes incorporated relatively more sulphur in their tissue in the SO_4 treatments than in the other treatments, we did not find indications of sulphur accumulation in S-rich amino acids as an adaptation to high sulphide concentrations (results not shown; Ruiz *et al.*, 2003; Droux, 2004).

Remarkably, aquatic macrophytes seemed to profit from the sulphide toxicity in the fertilized treatments. There were probably two reasons for this. On the one hand, semi-aquatic macrophytes completely colonized the water layer in the fertilized treatment without SO_4 , which left little space, light and nutrients for any of the aquatic macrophytes to grow. On the other hand, aquatic macrophytes can take up nutrients directly from the surface water with their shoots (Eugelink, 1998; Lombardo & Cooke, 2003), making them less dependent on their roots and less susceptible to sulphide in the sediment. This was especially an advantage for the rootless species *C. demersum*, which grew best in the fertilized SO_4 treatment.

In addition to sulphide toxicity, increased NH_4 concentrations in the SO_4 treatments may have led to toxic effects. Although NH_4 toxicity is much more likely at low pH (De Graaf *et al.*, 1998; Lucassen *et al.*, 2002; Van den Berg *et al.*, 2005), there are indications that NH_4 concentrations of $100 \mu\text{mol L}^{-1}$ or higher may also lead to toxic effects at circumneutral pH (Roelofs, 1991; Lucassen *et al.*, 2006). We did, however, not find an increase in N-rich amino acids, indicative of N-stress (results not shown; Marschner, 1986; Smolders *et al.*, 1996), which makes NH_4 toxicity less plausible.

Conclusions

This mesocosm experiment has shown that interspecific competition, vegetation succession and terrestrialization are not only influenced by nutrient availability, but also by SO_4 pollution. Aquatic and semi-aquatic macrophytes developed different growth strategies to cope with competition, sulphide toxicity, or both. It is important to note that the effects of SO_4 pollution itself are influenced by the degree of eutrophication, which means that toxicity effects in plants can be masked in eutrophic areas. Restoration measures that only focus on nutrient reduction in that case can lead to a vegetation collapse in fens that receive SO_4 -polluted water. This means that measures are needed that also take into account the flux of SO_4 -rich water coming into these ecosystems.

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Chapter 5

Iron addition to surface water or sediment as a measure to restore water quality in organic soft-water lakes



Injection of iron chloride solution into the sediment of enclosures in Lake Uddelermeer (The Netherlands; photo by Leon Lamers)

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Abstract

PO₄ eutrophication has led to the ecological deterioration of many surface waters, including Atlantic soft-water lakes. If dredging of the organic sludge layer is not an option, alternative strategies are needed to combat eutrophication. Although PO₄ fixation by Fe salts often turned out to be a short-lived measure in alkaline lakes, due to high Fe consumption rates, Fe addition may be much more successful in relatively isolated organic soft-water lakes. We therefore tested the immobilization of PO₄ by iron chloride (FeCl_x) in 15 enclosures in the anthropogenically eutrophied soft-water pingo Lake Uddelermeer (the Netherlands), by adding FeCl_x either to the anaerobic sediment or to the aerobic surface water.

All Fe-treated sediments had much higher Fe:PO₄ ratios in the pore water (> 10 mol mol⁻¹) than untreated sediments. PO₄ concentrations in sediment pore water and surface water, as well as turbidity and chlorophyll-a concentrations of the water layer, were lowest after sediment injection of 100 g Fe m⁻². Fe addition to the surface water was much less effective than injection into the sediment. Despite reduced turbidity, submerged soft-water macrophytes were absent because the sediment remained too anaerobic to allow germination.

Considering the isolated position of Lake Uddelermeer, it is expected that Fe addition will remain effective for much longer than in alkaline fens. This makes it a successful and durable measure to restore water quality in organic soft-water lakes where dredging is not possible, provided that the influx of SO₄-rich and PO₄-rich water is restricted.

Introduction

In many surface waters, the primary production of submerged vegetation is (co-) limited by phosphate (PO₄), as nitrogen availability is relatively high (Schindler 1977; Blomqvist *et al.*, 2004). A strong increase in PO₄ concentration will irrevocably lead to a hypertrophic state with turbid water, luxurious growth of algae and cyanobacteria, and the absence of submerged plant species, especially when there is a continuous supply of PO₄ from external sources or from the sediment (Scheffer *et al.*, 1993; Jeppesen *et al.*, 2005). The PO₄ cycle is very closely linked to the iron (Fe) cycle in wet ecosystems. In lakes and other surface waters, the mobilization and immobilization of PO₄ in surface water and sediment is to a large extent determined by its sequestration into different kinds of Fe-PO₄

complexes (Lijklema 1980; Boström *et al.*, 1982; Golterman 1995). Many wet ecosystems are more or less 'protected' against PO_4 eutrophication by a sufficient supply of anaerobic Fe-rich groundwater. However, desiccation at landscape scale as well as local scale has stopped this discharge of Fe-rich groundwater in many places. Alkaline surface water hardly contains any Fe, since Fe precipitates under non-acidic aerobic circumstances. The pore water Fe: PO_4 ratio, rather than the actual concentration of PO_4 in the pore water, is known to be an important factor determining the potential PO_4 flux between peaty sediments and the overlying water (Smolders *et al.*, 2001; Geurts *et al.*, 2008).

Earlier experiments have demonstrated that the addition of Fe salts may lead to a spectacular improvement of the water quality (Cooke *et al.*, 1993; Boers *et al.*, 1994; Smolders *et al.*, 1995; Smolders *et al.*, 2001; Hansen *et al.*, 2003). After Fe addition, PO_4 concentrations remained low, algal growth was inhibited and the water became clear, while control treatments without Fe addition became turbid due to persistent high PO_4 mobilization from the sediment. Unfortunately, these effects only lasted for a few months, because Fe doses were too low to compensate for the high Fe consumption by PO_4 or by sulphide originating from sulphate (SO_4) reduction. In addition, these systems received high fluxes of Fe-consuming components through the influx of surface water, which contains a lot of PO_4 and SO_4 . This is a significant problem for the restoration of minerotrophic fens (Lamers *et al.*, 2002b; Swarzenski *et al.*, 2008). In organic lakes, Fe and SO_4 reduction rates and the concomitant release of phosphate from sediments are generally much higher than in lakes with sandy or clay sediments, due to the higher availability of organic matter and higher oxygen consumption (Holmer & Storkholm 2001; Lamers *et al.*, 2001b; Loeb *et al.*, 2007).

Many Atlantic soft-water lakes that were originally characterized by Isoetid vegetation (e.g. *Littorella uniflora* (L.) Asch. and *Lobelia dortmanna* L.) have also deteriorated as a result of eutrophication. Because these lakes are generally more isolated than minerotrophic lakes, their oligotrophic vegetation can be recovered very successfully by removing the eutrophic, organic sludge layer in order to restore the limitation of biomass production by carbon, nitrogen and phosphorus (Roelofs 1996; Brouwer & Roelofs 2001; Smolders *et al.*, 2002). In the soft-water lake we investigated, however, dredging was not allowed, because this was expected to frustrate the conservation of important paleontological values in the peat sediment.

Hence, we wanted to test whether Fe application would be a suitable alternative measure to restore water quality in eutrophied, organic soft-water lakes where dredging is not an option. We used enclosures to test the effectiveness of PO_4 immobilization in a rainwater-fed, relatively isolated soft-water lake in the Netherlands, Lake Uddelermeer, which is a deep pingo remnant filled with peat. The high PO_4 concentrations and concomitant blooms of algae and cyanobacteria in this turbid lake are a constraint to its restoration and have even led to swimming bans. Four different amounts of iron chloride (FeCl_x) were tested, either added to the anaerobic sediment as Fe(II)Cl_2 or to the aerobic surface water as Fe(III)Cl_3 . The implications of the findings are discussed in relation to water management in soft-water lakes.

Methods

EXPERIMENTAL DESIGN AND SAMPLING

Lake Uddelermeer (52°15' N; 5°46' E) is a 6-hectare pingo lake, formed approximately 12,000 years ago during the last ice age (Polak 1959). The lake, originally 17 m deep, is now filled with 15 m of peat, which has a top layer of highly decomposed sludge, and a 1-2.5 m water layer. It used to comprise a nutrient-poor Isoetid vegetation a century ago, with species such as *Isoetes lacustris* L. and *Lobelia dortmanna* (Van Eeden 1886), but anthropogenic influences have gradually enriched the lake with nutrients. Nowadays it is an extremely eutrophic system, with excessive growth of cyanobacteria in summer, turbid water, a thick nutrient-rich sludge layer on top of the more structured peat, and increased resuspension by benthivorous fish species, including *Abramis brama* L. (bream; Grontmij 1996).

To test various potential methods of FeCl_x addition, an enclosure experiment was set up in the northwestern part of the lake in March 2002, using 15 bottomless polycarbonate cylinders ($\varnothing$ 1 m; 1.5 m high; Smolders *et al.*, 1995; Lamers *et al.*, 2002a; Lucassen *et al.*, 2004a). The bottom of each cylinder was pushed 30 cm into the organic sediment and the top protruded approximately 20 cm above the water surface, creating an isolated water column of 800-900 dm³. All cylinders were anchored using lines and poles.

In May 2002, a large plant sprayer with nebulizer was used to inject different FeCl_x solutions either into the top 10 cm of the sediment or into the water column. In six enclosures, Fe(II)Cl_2 was carefully injected into the sediment, because this is the most common form of Fe in anaerobic sediments. The final doses were 100 g Fe

m^{-2} ($n=3$) and 50 g Fe m^{-2} ($n=3$). In six other enclosures, Fe(III)Cl_3 was added to the surface water, corresponding to final doses of 10 g Fe m^{-2} ($n=3$) and 5 g Fe m^{-2} ($n=3$). We used lower doses in the surface water to reduce direct acidification effects. A NaCl solution was injected into the sediment of the remaining enclosures to equal the molar amount of chloride in the highest FeCl_x treatment ($n=3$).

Each month, surface water and pore water samples were taken from the enclosures (March 2002 until February 2003). Surface water samples were collected in iodated 500 mL polyethylene bottles. Sediment pore water was collected anaerobically using 60 mL vacuum syringes connected to ceramic soil moisture samplers (Eijkelpamp Agrisearch Equipment, Giesbeek, the Netherlands), which were installed in the upper 10 cm of the sediment. Immediately after sampling, 10.5 mL of each pore water sample was fixed with 10.5 mL of sulphide antioxidant buffer containing NaOH, Na-EDTA and ascorbic acid (Van Gernerden 1984). Sulphide concentrations were measured on the same day, using an ion-specific Ag electrode and a double junction calomel reference electrode (Roelofs 1991). Sediment samples (upper 10 cm) were collected at six locations outside the enclosures, using a metal sediment corer. They were transported in airtight bags and were stored in the dark at 4°C until P fractionation analyses.

CHEMICAL ANALYSIS

The pH and alkalinity of the water samples were measured using a standard Ag/AgCl electrode (Orion Research, Beverly, CA, USA) combined with a TIM800 pH meter and an ABU901 Autoburette (Radiometer, Copenhagen, Denmark). Surface water turbidity was determined using an FN-5 Turbidimeter (Toho-Dentan, Tokyo, Japan). Subsequently, the surface water samples were filtered over glass microfiber filters (type GF/C, Whatman, Brentford, UK). The filters were packed in aluminum foil and frozen (-20°C) until chlorophyll-a determination. In September 2002, filters were also used to determine total P concentrations in algal biomass. Citric acid was added to the water samples to a final concentration of 0.6 mmol L^{-1} to prevent metal precipitation. Extinction at 450 nm was measured for colorimetric background correction using a spectrophotometer (Shimadzu UV-120-01, Kyoto, Japan). The samples were stored in iodated polyethylene bottles at -20°C until further analysis.

The sediment samples were used for a sequential P fractionation analysis according to Psenner *et al.* (1988). The buffered dithionite and hydroxide fractions were pooled and presented as Fe/Al fraction. A homogenized portion

of 200 mg dry sediment (dried 24 h at 105°C) was digested with 4 mL HNO₃ (65%) and 1 mL H₂O₂ (30%), using a microwave oven (type mls 1200 Mega, Milestone Inc., Sorisole, Italy). Loss on ignition was determined after heating dry sediment samples at 550°C for 4 h.

The concentration of PO₄ was measured colorimetrically with a Technicon Auto Analyzer II system (Technicon Instruments Corp., Tarrytown, NY, USA), using ammonium molybdate (Henriksen 1965). Nitrate and ammonium were measured colorimetrically with a Traacs 800+ auto-analyzer (Technicon Instruments Corp., Tarrytown, NY, USA), using hydrazine sulphate (Kamphake *et al.*, 1967) and salicylate (Grasshoff & Johannsen 1972), respectively. Na and K were measured by flame photometry (FLM3 Flame Photometer, Radiometer, Copenhagen, Denmark) and Cl was measured colorimetrically with ferriammonium sulphate (O'Brien 1962). Ca, Mg, Mn, Fe, Al, S, P and Zn were measured using an inductively coupled plasma emission spectrophotometer (Spectroflame, Spectro Analytical Instruments, Kleve, Germany). Total S concentrations provided a good estimate of SO₄ concentrations, because only a small percentage of S was present in organic form. This was verified by parallel analysis of various pore water and surface water samples using capillary ion analysis (Waters Corporation, Milford, MA, USA).

Chlorophyll-a was extracted with 80% ethanol for 5 min at 70°C in the dark. The extinction of the extracted solution was measured at 665 nm and 750 nm using a spectrophotometer (Shimadzu UV-120-01, Kyoto, Japan), and chlorophyll-a concentrations were calculated according to Roijackers (1981).

STATISTICAL ANALYSIS

All statistical analyses were carried out using SPSS for Windows (version 15.0, 2006, SPSS, Chicago, IL, USA). Data were log(+1) transformed to make variances less dependent on sample means, and to obtain a normal distribution. Time effects were tested with GLM repeated measures. Differences between treatments in terms of biogeochemical variables were determined with a Tukey post-hoc test.

Results

The surface water of Lake Uddelermeer had very high phosphorus (6 µmol P L⁻¹) and nitrogen (220 µmol N L⁻¹) concentrations (data from Veluwe Water Board). In addition, most sediment samples from the lake had relatively high total P concentrations (15-50 µmol g⁻¹ dry wt), except for the sandy sediment of the

north-eastern part of the lake ($1.8 \mu\text{mol g}^{-1}$ dry wt; data not shown). Total P concentrations were highest in the middle of the lake, where the thickest sludge layer was present. Most of the P turned out to be easily exchangeable, because the largest fractions were labile P (20%) and Fe/Al-bound P (75%). The Ca-bound P fraction in the sediment was relatively low ($< 5\%$), as could be expected in a soft-water lake. Total Al concentrations were 1.5-3.5 times higher than total Fe concentrations. Total sediment Fe:P ratios ranged between 1 and 6 mol mol^{-1} , while the Al:P ratio ranged between 3 and 13 mol mol^{-1} . Fe:PO₄ ratios in the sediment pore water varied from 1.5 to 3.0 mol mol^{-1} and Al:PO₄ ratios varied from 0.2 to 0.4 mol mol^{-1} at the start of the experiment.

PO₄ concentrations in the sediment pore water decreased in all enclosures with Fe-treated sediments (treatment effect; Fig. 1; Table 1) and there was a significant time x treatment effect from July to December. The effect was largest after injection of the highest dose of 100 g Fe m^{-2} into the sediment. Moreover, only in this treatment did PO₄ concentrations in the pore water remain low for more than ten months ($< 3.6 \mu\text{mol L}^{-1}$). PO₄ concentrations in the water layer were relatively low in this treatment during the entire year ($< 3 \mu\text{mol L}^{-1}$; Fig. 2), whereas concentrations were much higher in all other treatments in late summer and autumn ($5\text{-}20 \mu\text{mol L}^{-1}$; time x treatment effect; Table 1). Compared to the other treatments and the control, Fe concentrations in the sediment pore water became 10-20 times higher after injection of 50 g Fe m^{-2} and 400-600 times higher after injection of 100 g Fe m^{-2} (Table 1). In addition, all Fe-treated sediments had much higher Fe:PO₄ ratios in the pore water, which remained above 10-100 mol mol^{-1} for nine months (Fig. 3). In all Fe treatments, Fe concentrations in the water layer became 2-100 times higher for at least four months during the growing season.

Table 1. *P*-values of the time effects (time), Fe addition effects (treat) and interaction effects (time x treat) for several chemical variables, as tested by GLM for repeated measures. Bold values indicate $P \leq 0.05$. Tukey = treatments (in g Fe m⁻²) that are significantly different from the control in the Tukey post-hoc test.

	time	time*treat	treat	Tukey
Surface water				
PO ₄ (μmol L ⁻¹)	0.000	0.046	0.117	
Fe (μmol L ⁻¹)	0.000	0.000	0.000	100, 50, 10, 5
Turbidity (ppm Pt)	0.000	0.113	0.066	
Chlorophyll-a (μg L ⁻¹)	0.000	0.139	0.036	100
pH	0.000	0.000	0.000	100
NH ₄ (μmol L ⁻¹)	0.000	0.330	0.123	
Ca (μmol L ⁻¹)	0.000	0.001	0.001	100, 50
Pore water				
PO ₄ (μmol L ⁻¹)	0.103	0.134	0.014	100
Fe (μmol L ⁻¹)	0.000	0.000	0.000	100, 50
Fe:PO ₄ (mol mol ⁻¹)	0.000	0.000	0.000	100, 50
pH	0.000	0.000	0.002	100
NH ₄ (μmol L ⁻¹)	0.000	0.029	0.575	
Ca (μmol L ⁻¹)	0.000	0.000	0.000	100, 50

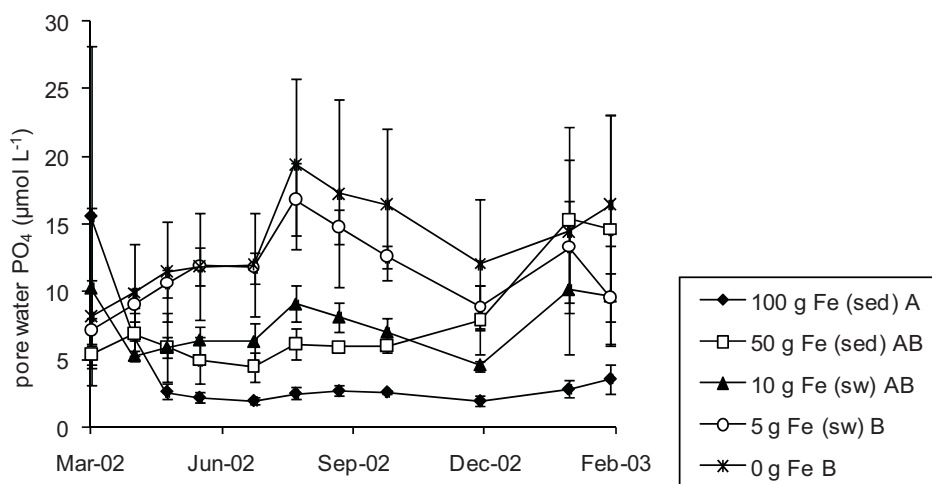


Figure 1. Effects of the various treatments on the phosphate concentrations in the sediment pore water ($\pm$ SEM). Treatments started after the second sampling date. Letters indicate differences between treatments ($P < 0.05$). sw = surface water treatment, sed = sediment treatment.

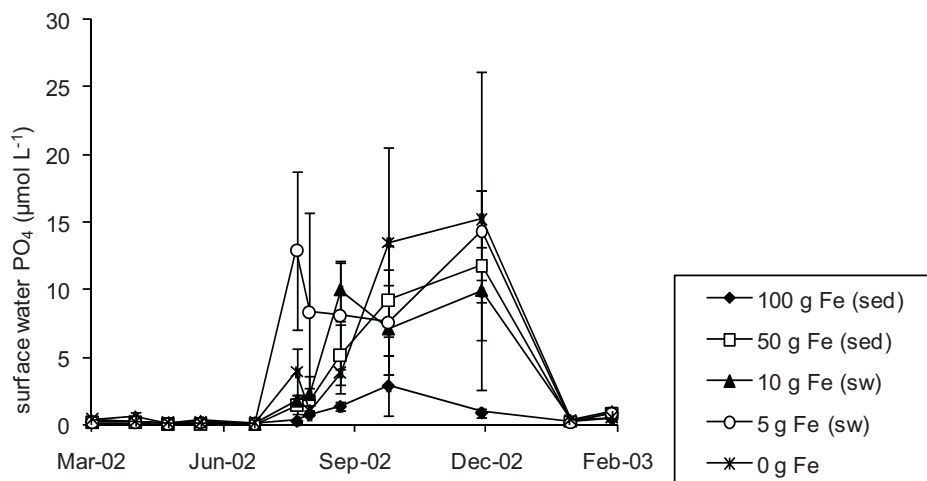


Figure 2. Effects of the various treatments on the PO_4 concentrations in the surface water ($\pm\text{SEM}$). Treatments started after the second sampling date. Letters indicate differences between treatments ($P < 0.05$). sw = surface water treatment, sed = sediment treatment.

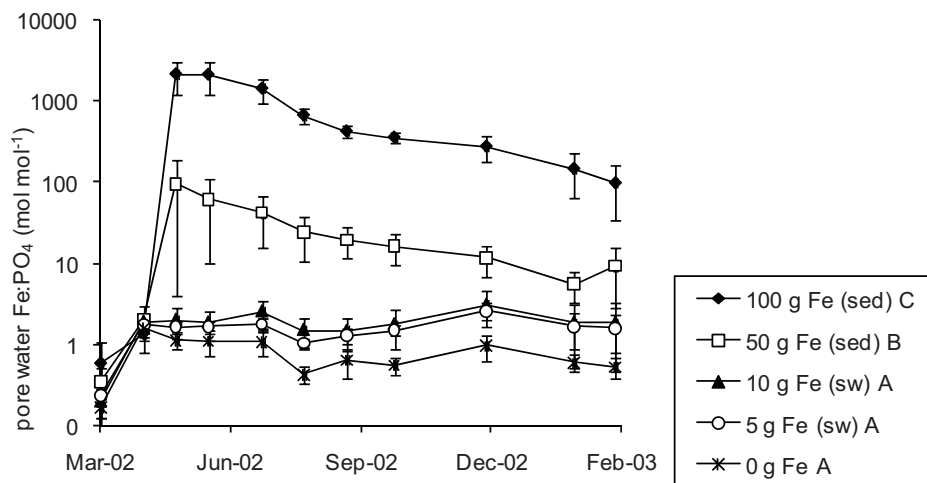


Figure 3. Effects of the various treatments on the Fe: PO_4 ratio in the sediment pore water ($\pm\text{SEM}$). Treatments started after the second sampling date. Letters indicate differences between treatments ($P < 0.05$). sw = surface water treatment, sed = sediment treatment. Note the logarithmic y-axis.

Only after injection of 100 g Fe m^{-2} into the sediment did surface water turbidity remain low (2-8 ppm Pt) for at least three months, whereas turbidity in the other enclosures increased to 17-48 ppm Pt due to the growth of algae, the presence of detritus or both (Fig. 4&5). Turbidity in summer was highest in the enclosures without Fe addition (control), with maximum values of more than 50 ppm Pt. However, no submerged aquatic macrophytes developed in the enclosures that were clear all year round. Chlorophyll-a concentrations showed comparable results, reaching maximum values of $60\text{--}70 \mu\text{g L}^{-1}$ in the highest Fe treatment, whereas concentrations in the other treatments increased to $100\text{--}250 \mu\text{g L}^{-1}$ (Fig. 6). P concentrations in algal biomass (sampled in September 2002) were also lowest in the highest Fe treatment ($7.5 \mu\text{mol L}^{-1}$ versus $10\text{--}17 \mu\text{mol L}^{-1}$), but no significant differences were found between the various treatments (data not shown).

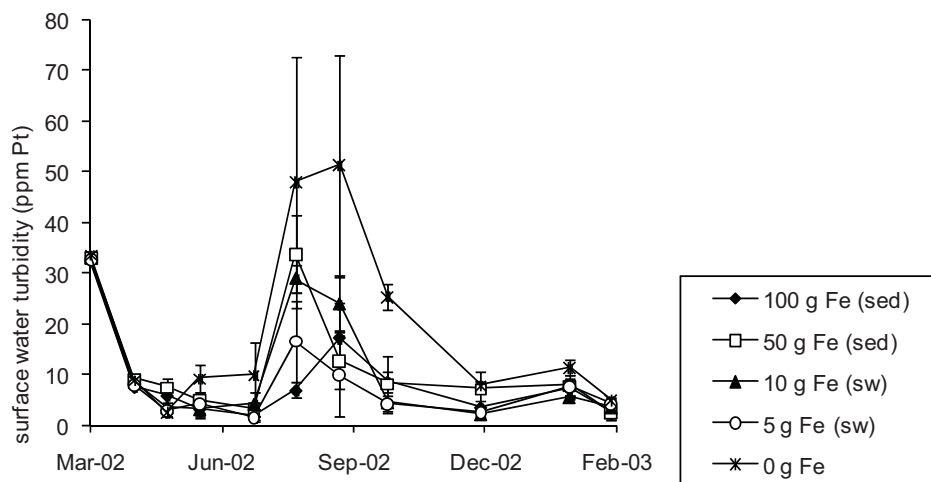


Figure 4. Effects of the various treatments on the turbidity of the surface water ($\pm$ SEM). Treatments started after the second sampling date. Letters indicate differences between treatments ($P < 0.05$). sw = surface water treatment, sed = sediment treatment.

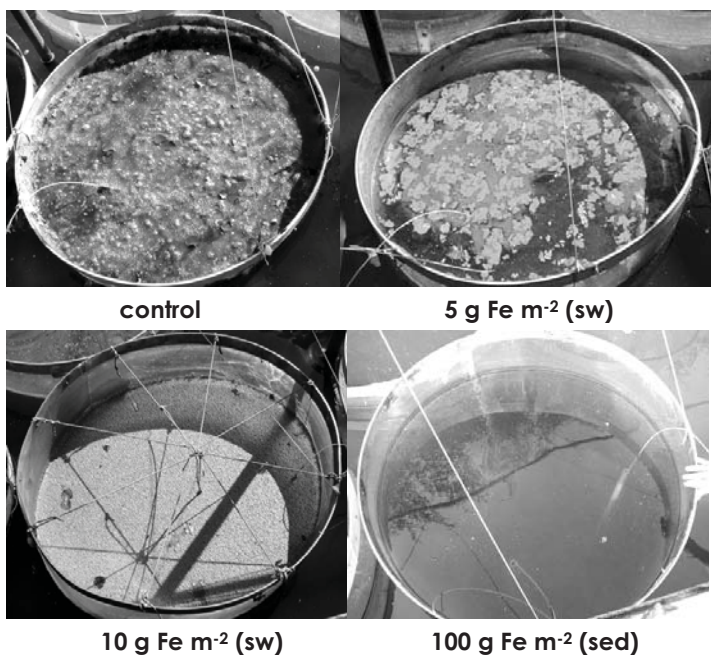


Figure 5. Photographs of different treatments after three months. sw = surface water treatment, sed = sediment treatment.

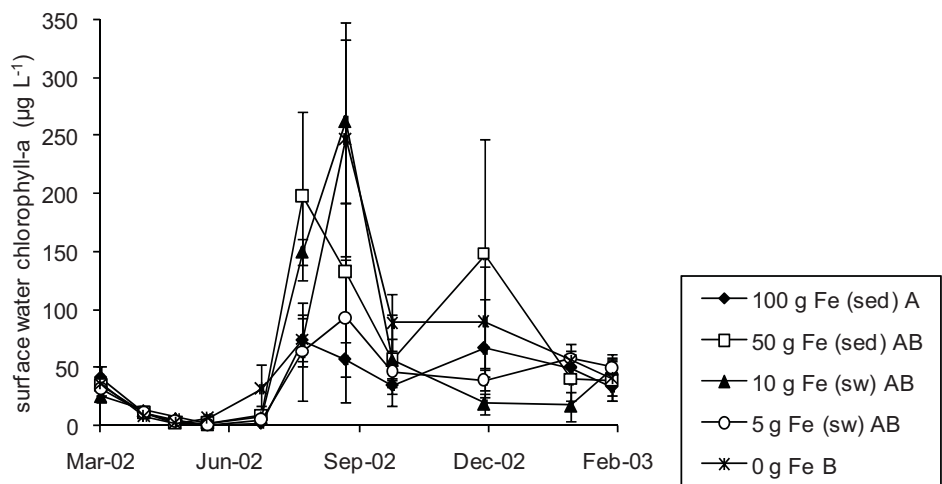


Figure 6. Effects of the various treatments on the chlorophyll-a concentration in the surface water ($\pm$ SEM). Treatments started after the second sampling date. Letters indicate differences between treatments ($P < 0.05$). sw = surface water treatment, sed = sediment treatment.

There was a transient decrease in surface water pH to 3 after the injection of 100 g Fe m⁻² (Fig. 7), and alkalinity was totally depleted. The decrease in pH was much lower in the other treatments (4.5-6.0). In the sediment pore water, pH only decreased to 5.5 in the highest Fe treatment (data not shown). After four months, pH and alkalinity of the surface water had recovered, although the time to recovery was a few months longer in the sediment. In the highest Fe treatment, Al concentrations in the surface water and sediment pore water increased temporarily after Fe injection, but values remained very low (maximum 7.6 µmol L⁻¹; data not shown).

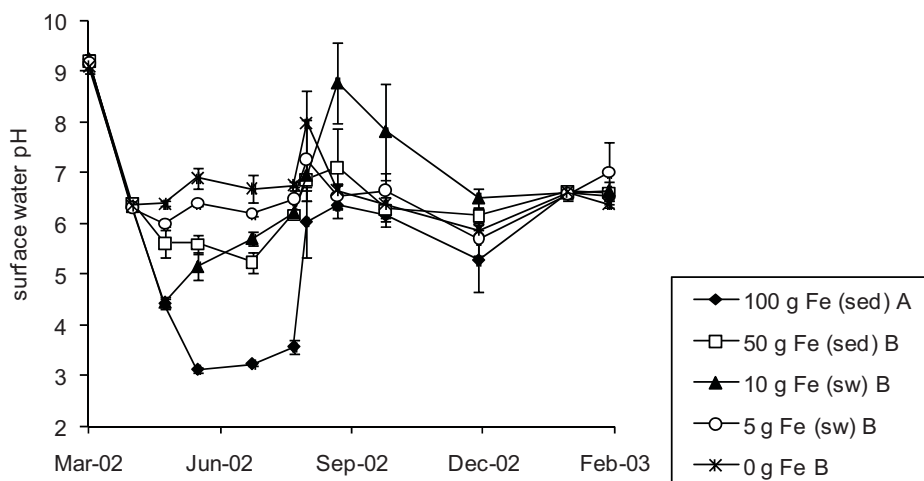


Figure 7. Effects of the various treatments on the pH of the surface water ($\pm$ SEM). Treatments started after the second sampling date. Letters indicate differences between treatments ($P < 0.05$). sw = surface water treatment, sed = sediment treatment.

SO₄ (70-100 µmol L⁻¹) and sulphide (20-50 µmol L⁻¹) concentrations were relatively low and hardly decreased after Fe addition. Although NH₄ concentrations in the surface water increased to values of up to 250 µmol L⁻¹ after Fe addition, there was no significant difference between the treatments (Fig. 8). Pore water NH₄ concentrations varied between the different Fe treatments (time x treatment effect; Table 1), but did not differ from the control treatment. After injection of 100 g Fe m⁻², Ca concentrations in the sediment pore water increased by a factor of 12-16 (Fig. 9), whereas Ca concentrations in pore water increased by a factor of five after injection of 50 g Fe m⁻². The same effect was found for Mg and Mn (results not shown). However, Ca concentrations in the surface water only

increased by a factor of 2-4. Although Cl concentrations in the surface water increased, values remained relatively low (maximum 2 mmol L⁻¹).

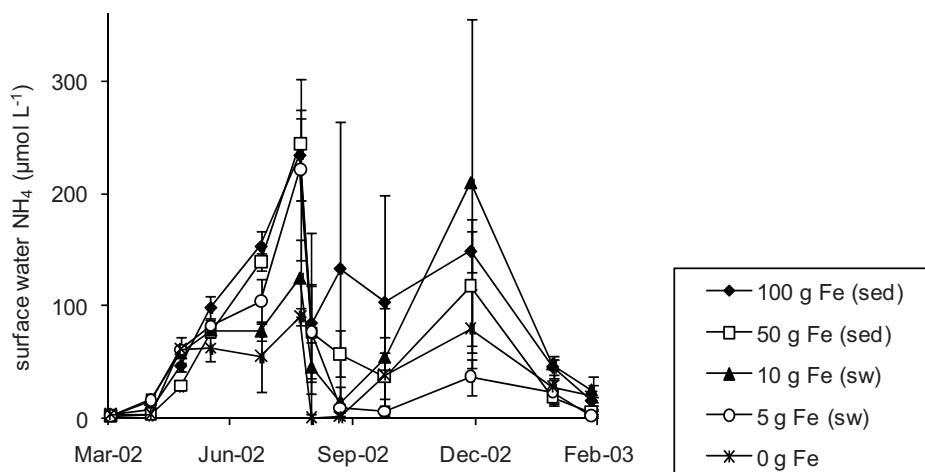


Figure 8. Effects of the various treatments on the NH₄ concentrations in the surface water ($\pm$ SEM). Treatments started after the second sampling date. Letters indicate differences between treatments ($P < 0.05$). sw = surface water treatment, sed = sediment treatment.

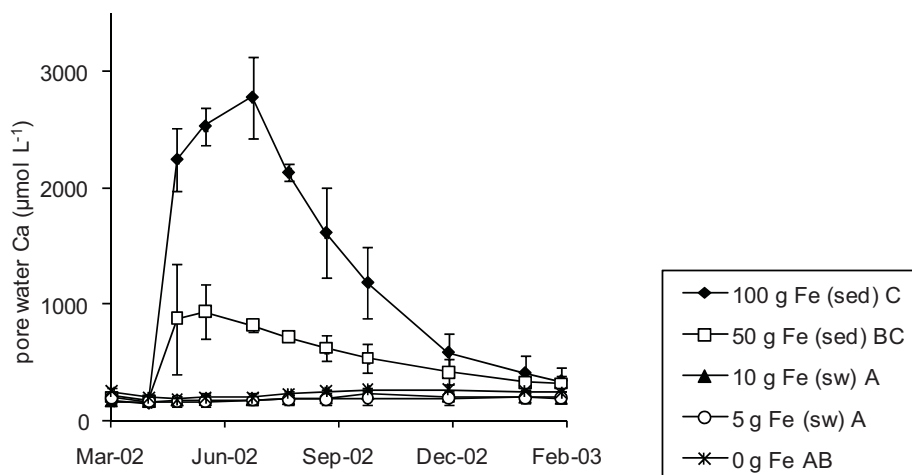


Figure 9. Effects of the various treatments on the Ca concentrations in the sediment pore water ($\pm$ SEM). Treatments started after the second sampling date. Letters indicate differences between treatments ($P < 0.05$). sw = surface water treatment, sed = sediment treatment.

Discussion

Fe addition to the sediment was more effective than addition to the water layer, because it precipitated with PO_4 in the sediment and increased Fe: PO_4 ratios in the pore water to target levels above 1-3.5 mol mol⁻¹ (Smolders *et al.*, 2001; Geurts *et al.*, 2008), preventing PO_4 mobilization to the water layer. Diffused Fe²⁺ from the sediment is converted to Fe³⁺(hydr)oxides in the oxygenated boundary layer between the sediment and the water layer. In this layer, PO_4 precipitates with Fe³⁺(hydr)oxides, which inhibits diffusion of PO_4 from the sediment to the water layer (Mortimer 1942). Another advantage of sediment addition is that dissolved sulphide can be bound, which prevents sulphide toxicity (Smolders *et al.*, 1995; Van der Welle *et al.*, 2007b). Addition of Fe to the surface water was much less effective in binding PO_4 , because lower doses of Fe had to be used to prevent strong acidification of the water layer. Surface water addition is therefore not recommended as a restoration measure.

Addition of 100 g Fe m⁻² to the sediment led to the most efficient PO_4 binding of all the treatments, and the water remained clear for longer than in the other treatments. The same amount of Fe was used by Boers *et al.* (1994) and Smolders *et al.* (1995) in alkaline fen waters. Fe: PO_4 ratios in the sediment pore water were maintained at a very high level and pore water PO_4 concentrations remained low during the experiment. On average, injection of the highest Fe dose into the sediment also led to the lowest P concentrations in both the surface water and the algal biomass. In summer, however, there were large differences in turbidities and in PO_4 concentrations between enclosures with the same treatment. This was probably caused by variations in the densities of algae, *Lemna* spp., detritus and zooplankton.

The absence of submerged macrophytes, even in the clear enclosures, suggests that the sediment was too anaerobic for typical soft-water species to germinate. However, diaspores of these species, including *Littorella uniflora*, *Lobelia dortmanna* and *Isoetes* spp., are known to remain viable for more than 30 years (Arts & Van der Heijden 1990; Bellemakers *et al.*, 1996; J. Roelofs 2008, Radboud University, Nijmegen, The Netherlands, personal communication) and have the ability to rapidly colonize lakes from an intact diaspore bank by clonal growth (Brouwer *et al.*, 2002). Temporary desiccation of the littoral zone by lowering the water level may therefore be a good measure to trigger the germination of soft-water species (Brouwer & Roelofs 2001). Besides that, if Fe addition is extended to include the whole lake, the sediment will be better oxygenated than in the

enclosures, thanks to greater wave action, although this will also lead to more resuspension of sediment particles.

Dredging of the organic sludge layer would still be the best measure to restore pingo lakes, such as that in the Weerterbos area (the Netherlands; E. Lucassen & J. Roelofs 2008, Radboud University, Nijmegen, The Netherlands, personal communication). However, if this is not possible and the sludge layer remains anaerobic, colonization by soft-water macrophytes will only be possible from lake banks where the organic layer has been removed by sod cutting. This is, therefore, a prerequisite to the restoration of soft-water communities in Lake Uddelermeer.

The experiments by Boers *et al.* (1994) and Smolders *et al.* (1995) showed that Fe addition to sediments only remained effective for one year. However, these alkaline fen waters were not hydrologically isolated, implying a large influx of water with high PO_4 and/or SO_4 concentrations and consequently a high Fe consumption rate by both PO_4 and sulphide produced from SO_4 . Considering the much more isolated position of Lake Uddelermeer and the low SO_4 and sulphide concentrations, it is expected that in this case, addition of 100 g Fe m^{-2} to the sediment will remain effective much longer. An example of such a successful Fe addition in a soft-water lake is that at Lake Beuven-Zuid (the Netherlands), where only 25 g Fe m^{-2} was applied to the sediment and where the water remained clear for more than 25 years (J. Roelofs 2008, Radboud University, Nijmegen, The Netherlands, personal communication), although the sediment of this lake is less organic than that of Lake Uddelermeer.

The temporary decrease in pH and alkalinity was caused by the oxidation of Fe^{2+} in the water layer. Although this may have a negative impact on the growth of many aquatic macrophytes, seed viability and germination of soft-water species is normally not affected by low pH (Arts & Van der Heijden 1990; Bellemakers *et al.*, 1996), and certainly not by the transient decrease in pH in our experiment. Additionally, the capacity of Fe to bind PO_4 is reduced at a pH below 4 (Stumm & Morgan 1996), which may even lead to PO_4 mobilization. This effect could be reduced by adding NaOH to the FeCl_2 solution prior to injection, to increase the pH. It should only be increased to a maximum of 4.5, however, because above a pH of 5 Fe will be oxidized and precipitated, which reduces its effectiveness (Stumm & Morgan 1996).

Since much of the P in the sediment of Lake Uddelermeer was bound to Fe, it can be mobilized from the sediment when SO_4 concentrations increase and iron

sulphides (FeS_x) are formed (Lamers *et al.*, 2001b; Roden & Edmonds 1997). However, the 2-3 times higher total Al concentrations in the sediment indicate that a significant part of the metal-bound P may have been bound to Al. P mobilization from this source is unlikely, as Al does not precipitate with sulphide. In addition, the sulphide concentrations we measured were relatively low and SO_4 reduction rates were probably low as well, considering the low SO_4 concentrations in the lake and the low alkalinity (Roelofs 1991). The increased NH_4 , Ca, Mg and Mn concentrations were most probably caused by cation exchange from the sediment adsorption complex by Fe (Ponnamperuma 1972). This may even be beneficial, because the released Ca may bind PO_4 by (co)precipitation at higher pH values (Stumm & Morgan 1996). The NH_4 that is released will be nitrified to NO_3 in the oxidized water layer, and denitrification will finally result in the loss of N from the system, which is beneficial to soft-water plant communities (Brouwer *et al.*, 2002; Smolders *et al.*, 2002).

It can be concluded that Fe addition to the sediment, rather than to the surface water, can be a successful measure to restore water quality in organic soft-water lakes where dredging of the sludge layer is not an option. The replenishment of Fe for the purpose of PO_4 binding in the sediment and at the sediment-water interface will only be useful when the influx of SO_4 -rich and PO_4 -rich water is restricted and SO_4 and sulphide levels in the sediment are low. In any case, if the sediment does not have important paleontological values, dredging of the nutrient-rich organic top layer of the sediment remains preferable as a measure to restore water and sediment quality in organic soft-water lakes (Brouwer & Roelofs 2001).

Implications for Practice

- Dredging of the sludge layer is the best restoration measure in eutrophied organic soft-water lakes. However, if this is not possible, iron addition can be a successful alternative measure to restore water and sediment quality.
- Injection of iron into the sediment is more efficient than addition of iron to the surface water, also because higher iron dosages can be used. Based on our study, an iron dose of 100 g m^{-2} is proposed, which improved both water quality and sediment quality considerably.
- Iron addition is only recommended in rather isolated soft-water lakes where the influx of phosphate-rich and sulphate-rich water is restricted and the iron consumption rate is low. Iron addition will remain effective for much longer and needs to be repeated less frequently.

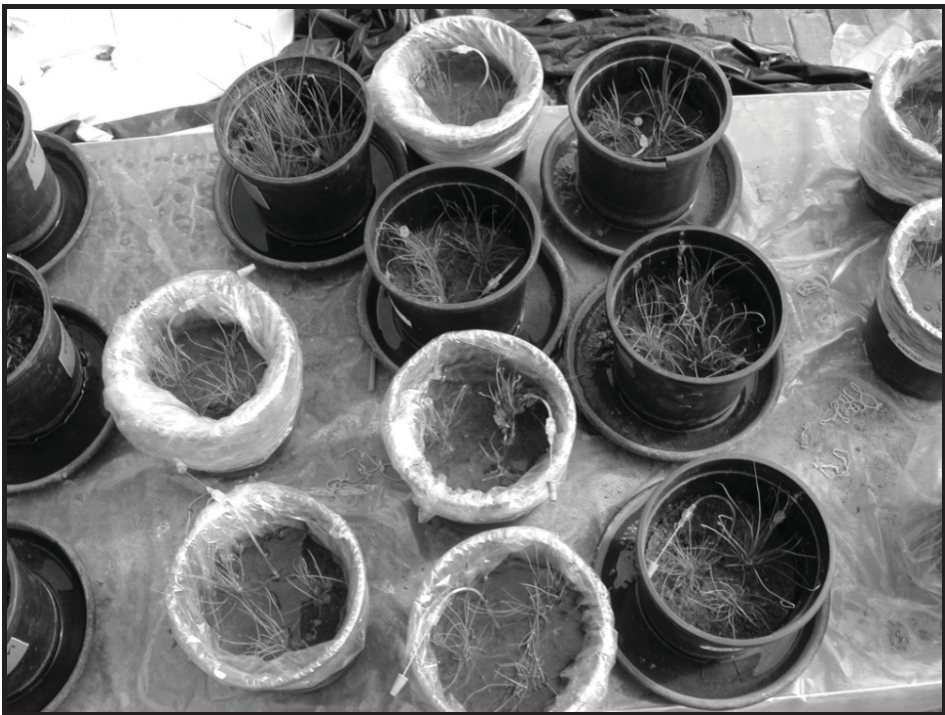
- Sod cutting and temporary desiccation of the littoral zone may be an additional measure, which will lead to oxidation of the anaerobic sediment and will enhance germination of typical soft-water species. These species then have the opportunity to vegetatively colonize the lake.

Acknowledgments

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Chapter 6

Ecological restoration on former agricultural soils; applying lanthanum-modified clay and lime to bind phosphate and decrease *Juncus effusus* growth



Experimental set-up of the container experiment with Juncus effusus plants

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Jan G.M. Roelofs & Leon P.M. Lamers**
Submitted to Ecological Engineering

Abstract

In Europe, high phosphorus (P) concentrations form the most important constraint on the ecological restoration of biodiverse vegetation on former agricultural soils, because they lead to dominance of highly competitive species like *Juncus effusus* or to algal blooms in flooded situations. If top soil removal is not sufficient or not possible, alternative methods have to be found. We therefore investigated whether modified bentonite clay to which 5% lanthanum had been added (LMC) and lime could effectively decrease bioavailable P and phosphate mobilization to the water layer in different soil types.

A container experiment was performed using peaty and sandy soils with different Olsen-P concentrations, mixed with different doses of LMC and lime. The soils were exposed to two different common water regimes (moist and flooded). *J. effusus* seedlings were used as phytometers.

LMC and lime only decreased extractable P concentrations in some of the P-rich sandy soils. The highest LMC dose was able to decrease phosphate mobilization to the water layer in the sandy soils, indicating that this treatment may be most effective in preventing growth of algae and cyanobacteria in flooded situations. However, neither LMC nor lime was sufficiently effective in reducing Olsen-P concentrations and *J. effusus* growth. Lime addition eventually even led to additional nutrient mobilization by alkalization and increased mineralization of the soil.

Our experiments show that LMC, rather than lime, may be used for successful restoration of wetlands on former agricultural sandy soils, as an alternative or additional measure for top soil removal, to allow biodiverse vegetation to develop in flooded situations, whereas it is inefficient in preventing *J. effusus* dominance under moist conditions.

Introduction

Several national and European legislations that aim to connect existing nature conservation areas have strongly increased the area of former agricultural land that is available for ecological restoration (Natura 2000; Smolders *et al.*, 2008). However, a major problem that has to be overcome in these areas is that they have been heavily fertilized in recent decades, resulting in the accumulation of huge amounts of phosphorus (P) and nitrogen (N) in the soil (Barberis *et al.*, 1996).

It is especially P, being less mobile, which accumulates in the top layer of the soil (Schärer *et al.*, 2007), whereas N can easily leach out to deeper layers (Johnston 1994). These exceptionally high nutrient concentrations form the most important constraint on the development and maintenance of biodiverse plant communities at these sites.

Juncus effusus (soft rush or common rush) is one of the notorious eutrophic species that tends to dominate strongly on soils with a high P availability (Smolders *et al.*, 2008). This easily dispersing species can germinate and grow very fast and outcompete other plant species by shading them (Ervin & Wetzel 2001, 2002). In densely populated regions it is not expected that N will be the growth limiting factor for *J. effusus*, because N depositions are generally high (Bobbink *et al.*, 1998). This is supported by studies showing that the most biodiverse nature areas are found on P-limited soils (Janssens *et al.*, 1998; Wassen *et al.*, 2005). A good indication of the bioavailable P fraction in the soil is given by the Olsen-P concentration (Olsen *et al.*, 1954), which should not exceed 200-300 $\mu\text{mol kg}^{-1}$ soil if domination of *J. effusus* is to be prevented (Smolders *et al.*, 2008).

An additional problem may arise if former agricultural lands are converted into wetlands, which often also serve as water storage areas. This can cause serious phosphate mobilization to the water layer, depending on the biogeochemical properties of the soil and the quality of the water that is used for rewetting (Pant & Reddy 2003; Lamers *et al.*, 2005). Flooding of a site results in anaerobic soil conditions and the reduction of iron compounds, which decreases the binding capacity of iron for P and may subsequently lead to the release of iron-bound P (Patrick & Khalid 1974; Ponnamperna 1984). This P release during flooding has been shown to depend on the availability of organic matter and the P saturation of iron binding sites (Loeb *et al.*, 2008).

In the past, different methods have been used to reduce P concentrations in surface water, pore water, sediments and soils. In terrestrial systems, top soil removal seems to be the most efficient measure to create a nutrient-poor situation within a relatively limited time span (Wetzel & Howe 1999; Lamers *et al.*, 2005; Smolders *et al.*, 2008), although it is an expensive measure in many cases. Sometimes it is not even possible to remove enough soil to create P limitation, because deeper soil layers still contain high P concentrations, and additional measures have to be taken. Removing the topsoil also results in the disappearance of the diaspore bank, although in agricultural soils this mainly contains seeds from eutrophic species and not from rare target species (Smolders *et al.*, 2008). In addition to or instead of topsoil removal, different

compounds have been used to immobilize P *in situ*. Water treatment residuals (WTRs) are widely used in agricultural soils to increase the P sorption capacity of the soil and reduce off-site P leaching (Novak & Watts 2004; Agyin-Birikorang *et al.*, 2009). WTRs contain either iron, aluminum or calcium as potential P immobilizers (Elliott *et al.*, 2002), with aluminum-WTRs having the highest ability to immobilize P. Ann *et al.* (2000) compared the effectiveness of specific compounds containing aluminum, iron and calcium in immobilizing P in soils from a constructed wetland and found that addition of FeCl₃ was clearly most effective, followed by aluminum and calcium compounds.

Calcium has been used in different forms to control eutrophication in both lakes and terrestrial systems (Beltman *et al.*, 2001; Brouwer *et al.*, 2002; Varjo *et al.*, 2003; Anderson 2004). Liming with CaCO₃ has turned out to be an effective additional measure to reduce P availability after top soil removal (Smolders *et al.*, 2008). However, liming leads to an increase in pH and alkalinity and could therefore increase decomposition rates in organic soils, which will also result in additional nutrient mobilization (Smolders *et al.*, 2006). Iron compounds have also been used to bind P both in terrestrial systems (Schärer *et al.*, 2007) and, especially, in aquatic systems (Boers *et al.*, 1994; Smolders *et al.*, 2001; Hansen *et al.*, 2003), but iron has the disadvantage of being redox-sensitive (Ann *et al.*, 2000). Aluminum addition is a widely used method to immobilize P in lakes (Rydin & Welch 1998; Reitzel *et al.*, 2003). Although aluminum is not redox-sensitive, it is sensitive to pH changes (Driscoll & Schecher 1990; Cooke *et al.*, 1993). This method is most effective between pH 6 and 8 and can cause serious toxicity problems at lower pH. Moreover, aluminum addition itself can lead to decreased pH values in soil and surface water (Malecki-Brown *et al.*, 2007). Studies have also shown that the aluminum will crystallize over time and form gibbsite, leading to a lower binding capacity for P (Berkowitz *et al.*, 2005).

Because all the above-mentioned compounds may show some serious drawbacks, we investigated whether the addition of lanthanum-modified clay (LMC), a bentonite clay to which 5% lanthanum has been added (Douglas 2002), would be an effective alternative method to immobilize P in former agricultural soils. To our knowledge, LMC addition is a novel method in terrestrial systems. The results were compared with those of lime addition. The advantage of LMC is that it forms highly stable minerals in the presence of phosphates (Douglas *et al.*, 2000), which are relatively insensitive to changes in pH, redox potential and oxygen concentrations (Ross *et al.*, 2008). LMC already proved to be very successful in immobilizing P and reducing algal blooms in many lakes and rivers (Robb *et al.*, 2003; Akhurst *et al.*, 2004; Yang *et al.*, 2004) by trapping all P in the

water layer and by forming an active layer on top of the sediment, which immobilizes P at the sediment-water interface. If LMC should prove to be effective in decreasing Olsen-P concentrations in former agricultural soils to below the threshold of 200-300 $\mu\text{mol kg}^{-1}$ soil (260-390 $\mu\text{mol L}^{-1}$ fresh soil; Smolders *et al.*, 2008), domination of fast growing species like *J. effusus* could be prevented, and chances for the development of a more biodiverse vegetation could be improved. LMC addition is expected to be especially effective in flooded soils, because it forms an active layer on top of the soil that reduces phosphate mobilization to the water layer. This might avert blooms of algae and cyanobacteria in the overlying water layer.

To test the effectiveness of LMC and lime in decreasing bioavailable P and phosphate mobilization to the water layer in different types of former agricultural soils, a container experiment was performed using three sandy soils with different Olsen-P concentrations and one peaty soil. We used these very different soil types because of the differential impacts LMC and lime may have upon soils with variable organic matter contents and buffering capacities. The soils were mixed with two different doses of LMC and one lime dose, and exposed to two different water regimes (moist and flooded) that frequently occur after restoration measures have been taken. To investigate whether the possible decrease in P concentrations would indeed decrease the growth of eutrophic plant species, *J. effusus* seedlings were planted in the containers and monitored as phytometers (Clements & Goldsmith 1924; Wheeler *et al.*, 1992) for three months. This enabled us to investigate whether LMC could be used as an effective alternative to the expensive removal of nutrient-rich top soil or as an additional measure after top soil removal.

Methods

EXPERIMENTAL SET-UP

In January 2008, three soil types were collected from different locations in the Netherlands. Nutrient-rich sandy soil was collected from a fertilized meadow on De Kieftskamp estate near Vorden (52°05'N, 6°20'E). Nutrient-poor sandy soil was collected from a fallow site on Staverden estate near Uddel (52°16'N, 5°44'E). Peaty soil was collected from a former pasture in the Vossenbroek nature reserve near Epe (52°19'N, 6°00'E).

After the soils had been homogenized in a concrete mixer, samples of each soil type were dried for 24h at 70°C and Olsen-P concentrations were determined by

extraction according to Olsen *et al.* (1954) and Smolders *et al.* (2008). Subsequently, the nutrient-rich sandy soil was mixed with the nutrient-poor sandy soil in such proportions that soils were created with Olsen-P concentrations of about 500, 1000 and 2000 $\mu\text{mol kg}^{-1}$ soil (Table 1). We will refer to these soils as S500, S1000 and S2000.

Table 1. Initial Olsen-P and total-P concentrations, bulk density and organic matter content of the peat soil and the three sandy soil types ($\pm$ SD; $n=8$) and the derived concentrations of lanthanum-modified clay (LMC) and lime that were added in the different treatments.

Soil	Olsen-P ($\mu\text{mol kg}^{-1}$)	Total-P (mmol kg^{-1})	Bulk density(kg L^{-1})	Organic matter %	LMC1x (g L^{-1} soil)	LMC5x (g L^{-1} soil)	lime (g L^{-1} soil)
Peat	3973 (213)	53.1 (4.3)	0.35 (0.01)	38 (0.4)	4.4	21.8	3.5
S500	451 (68)	6.8 (1.3)	1.30 (0.04)	0.8 (0.1)	1.8	9.1	13.3
S1000	802 (158)	8.3 (1.8)	1.28 (0.05)	1.1 (0.1)	3.2	15.9	13.1
S2000	1917 (294)	11.1 (2.6)	1.22 (0.03)	1.8 (0.1)	7.2	36.2	12.5

In a greenhouse at the Botanical Gardens of the Radboud University Nijmegen, 128 plastic containers with a diameter of 15 cm were filled with 10 cm (1.77 L) of soil. Four different treatments were applied to each soil type ($n=8$):

- control treatment
- single lanthanum-modified clay dose using 100 g Phoslock® per g Olsen-P (LMC1x; Table 1)
- 5-fold lanthanum-modified clay dose using 500 g Phoslock® per g Olsen-P (LMC5x; Table 1)
- a lime dose of 10 g kg^{-1} fresh soil using Dolokal (75% CaCO_3 , 10% MgCO_3 and 5% MgO ; Smolders *et al.*, 2008; Table 1);

LMC and lime were thoroughly mixed with the different soil types. Half of the containers were placed on a dish filled with demineralized water to keep the soils moist. The other half of the containers were flooded with 5 cm of demineralized water on top of the soil. To compensate for evaporation, demineralized water was added to maintain constant water levels. All containers were covered with two layers of white, nontransparent plastic to prevent plant growth and high soil temperatures. Etiolated seedlings were carefully removed.

A permanent soil moisture sampler of 10 cm (Rhizon SMS, Eijkelkamp Agrisearch Equipment, Giesbeek, the Netherlands) was inserted diagonally into the soil of each container. Vacuum glass infusion bottles (30 mL) were attached to the soil moisture samplers to anaerobically sample soil pore water on days 1, 8, 47, 104, and 176. Water samples were taken from the water layer of the flooded soils on

days 19, 40, 103, and 145. Small samples of the vertical profile of the soils were taken on days 1, 8, 41, 110, and 176. These soil samples were dried for 24h at 70°C and used for Olsen-P extractions (Olsen *et al.*, 1954; Smolders *et al.*, 2008).

After 145 days, the plastic cover was removed and three tufts of *J. effusus* seedlings with a shoot length of 5 mm and a dry weight of 7 mg were planted in each container. The water on the flooded soils was temporarily removed until plants were tall enough to reach the water surface. Plant growth was monitored by regularly measuring the length of the longest shoots. After 243 days, three months after planting, the aboveground plant biomass was harvested, dried for 48h at 70°C and weighed.

CHEMICAL ANALYSIS

The pH of the surface water and pore water samples was measured using a combined pH electrode with an Ag/AgCl internal reference (Orion Research, Beverly, CA, USA), and a TIM800 pH meter. Alkalinity was determined by titration to pH 4.2 with 0.01 M HCl using an ABU901 Autoburette (Radiometer, Copenhagen, Denmark). The samples were stored in iodated polyethylene bottles at -20 °C until further analysis.

The concentrations of PO₄, NO₃, and NH₄ were measured colorimetrically with an Auto Analyzer 3 system (Bran+Luebbe, Norderstedt, Germany) according to Geurts *et al.* (2008). The concentrations of Ca, Fe, La, P, and Olsen-P were measured using an ICP Spectrometer (IRIS Intrepid II, Thermo Electron Corporation, Franklin, USA).

Homogenized portions of 200 mg dry plant material were digested with 4 mL HNO₃ (65%) and 1 mL H₂O₂ (30%), using an Ethos D microwave labstation (Milestone srl, Sorisole, Italy). Digestates were diluted and concentrations of P were determined by ICP as described above. Digestion analyses on 200 mg LMC showed that it contained 5% La, 1% Ca, 0.8% Al, 0.5% Fe, 0.3% Na, 0.3% Mg, and 0.1% K. Homogenized portions of 3 mg dry plant material were used to determine carbon and nitrogen content, using a Carlo Erba NA1500 elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA). Weighted average N:P ratios in plant tissue were then calculated on a total dry weight basis.

STATISTICAL ANALYSIS

All statistical analyses were carried out using SPSS for Windows (version 15.0, 2006, SPSS, Chicago, IL, USA). Data were log(+1) transformed to make variances less dependent on sample means, and to obtain a normal distribution. Time effects

and time x treatment effects for chemical variables and *J. effusus* shoot length in the different moist and flooded soil types of the different treatments were tested with GLM repeated measures combined with a Tukey post-hoc test. Differences between treatments in terms of chemical variables, plant biomass, shoot length and plant element ratios at the end of the experiment were determined by a univariate ANOVA combined with a Tukey post-hoc test.

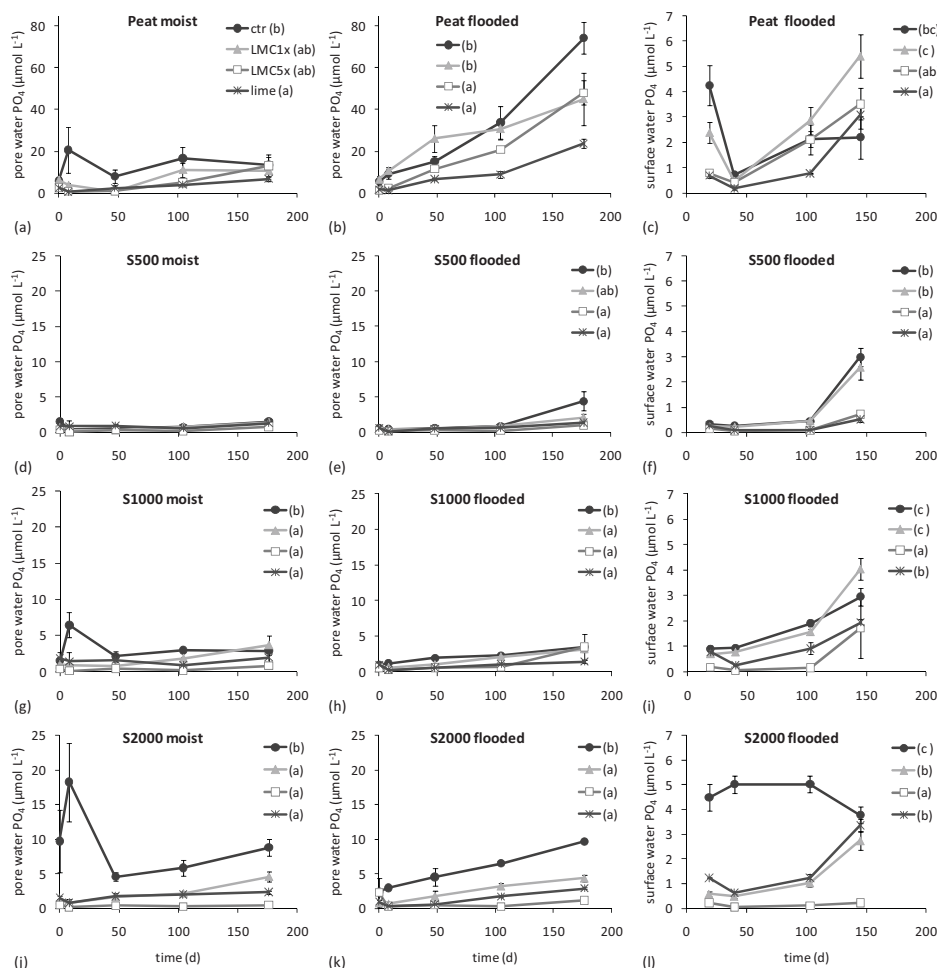


Figure 1. Phosphate concentrations in pore water and surface water for the peat soil and the three sandy soil types under moist and flooded conditions. Significant differences between treatments, as tested by GLM repeated measures ($P \leq 0.05$), are indicated by different letters. Note that different scales are used for the peaty soil and surface water graphs.

Table 2. Mean values ($\pm$ SD) of chemical variables in **pore water and soil** for the different treatments of the **moist** peat soil and the three sandy soil types after 176 days. Significant differences between treatments are indicated by different letters (univariate ANOVA, $P \leq 0.05$).

	Fe ($\mu\text{mol L}^{-1}$)	NH ₄ ($\mu\text{mol L}^{-1}$)	NO ₃ ($\mu\text{mol L}^{-1}$)	PO ₄ ($\mu\text{mol L}^{-1}$)	Olsen-P ($\mu\text{mol kg}^{-1}$ DW)	pH	Alkalinity (meq L^{-1})
Peat							
ctr	151 (98)	167 ^{ab} (82)	36.1 (40.0)	13.5 (7.6)	6714 (518)	6.1 ^{ab} (0.0)	0.9 ^a (0.1)
LMC1x	285 (223)	120 ^a (49)	35.0 (17.6)	10.6 (7.4)	6867 (598)	6.0 ^a (0.0)	1.0 ^a (0.4)
LMC5x	435 (383)	340 ^{ab} (193)	13.4 (10.7)	13.1 (10.4)	6022 (436)	6.2 ^b (0.1)	1.6 ^a (0.9)
lime	273 (133)	406 ^b (172)	34.3 (18.3)	6.7 (1.9)	6275 (836)	6.9 ^c (0.1)	3.7 ^b (0.2)
S500							
ctr	108 ^b (20)	36 ^a (8)	4.4 (2.6)	1.5 (0.3)	454 (154)	5.9 ^a (0.1)	0.5 ^a (0.1)
LMC1x	110 ^b (12)	43 ^a (2)	2.4 (1.1)	1.4 (0.3)	488 (78)	6.0 ^{ab} (0.1)	0.5 ^a (0.0)
LMC5x	97 ^{ab} (14)	37 ^a (15)	6.2 (4.2)	0.8 (0.8)	371 (77)	6.2 ^b (0.2)	0.6 ^a (0.1)
lime	76 ^a (11)	80 ^b (15)	4.0 (3.4)	1.3 (0.9)	404 (87)	7.0 ^c (0.0)	4.0 ^b (0.3)
S1000							
ctr	89 (22)	63 ^a (19)	3.0 ^{ab} (2.2)	2.9 (0.4)	660 (145)	5.9 ^a (0.1)	0.6 ^a (0.0)
LMC1x	132 (25)	93 ^{ab} (36)	15.6 ^b (19.7)	3.7 (2.6)	594 (76)	6.1 ^a (0.3)	0.9 ^a (0.3)
LMC5x	116 (41)	73 ^{ab} (24)	1.7 ^a (0.2)	0.8 (0.2)	809 (252)	6.2 ^a (0.1)	0.8 ^a (0.2)
lime	76 (16)	144 ^b (33)	3.5 ^{ab} (3.6)	2.0 (2.0)	772 (113)	7.0 ^b (0.1)	3.8 ^b (0.4)
S2000							
ctr	166 (63)	170 (98)	1.6 (0.7)	8.8 ^c (2.3)	2151 ^b (463)	5.7 ^a (0.1)	0.5 ^a (0.2)
LMC1x	153 (59)	182 (73)	1.2 (0.5)	4.6 ^b (1.5)	2149 ^b (268)	5.8 ^a (0.1)	0.7 ^a (0.1)
LMC5x	156 (51)	175 (72)	1.9 (0.4)	0.4 ^a (0.6)	1193 ^a (226)	5.9 ^b (0.0)	0.7 ^a (0.1)
lime	97 (21)	284 (64)	1.3 (0.3)	2.3 ^b (0.5)	3775 ^c (170)	6.9 ^c (0.1)	4.0 ^b (0.4)

Results

EFFECTS ON BIOGEOCHEMISTRY

Pore water phosphate concentrations during the experiment were highest in the peaty soil and S2000 (Fig. 1). Only in the peaty soil were phosphate concentrations higher in the flooded soils than in the moist soils. In almost all cases, phosphate concentrations were highest in the control treatments, and lower in all other treatments. Phosphate concentrations in the peaty soil decreased 2-3 times in the lime treatments, whereas phosphate concentrations in the sandy soils decreased most (2-10 times) in the treatment with a 5-fold dose of lanthanum-modified clay (LMC5x). In the long term, phosphate significantly decreased in all treatments of S2000 (Tables 2 & 3). Phosphate concentrations in the surface water of the flooded peaty soils only decreased in the lime treatment (Fig. 1c). Surface water phosphate concentrations on the sandy soils also significantly decreased in the LMC5x treatment. In the long term, however,

surface water phosphate concentrations were only lower than the control treatment in the LMC5x and lime treatments of S500 and in the LMC5x treatment of S2000 (Table 4).

Olsen-P concentrations in the soil remained quite stable over time in all control treatments, but there was a significant time x treatment effect in the moist sandy soils, the flooded peaty soil and the flooded S1000 and S2000 soils ($P < 0.05$). In the moist soils, Olsen-P concentrations only decreased in the LMC5x treatment of S2000, whereas concentrations actually increased in the lime treatment of this soil (Table 2). In the flooded soils, Olsen-P concentrations decreased 2-4 times compared to the control in all treatments of S1000 and S2000, with the largest decrease in the LMC5x treatments (Table 3). After 176 days, Olsen-P concentrations in the LMC5x treatments were even lower than those in the control treatment of S500.

Table 3. Mean values ($\pm$ SD) of chemical variables in **pore water and soil** for the different treatments of the **flooded** peat soil and the three sandy soil types after 176 days. Significant differences between treatments are indicated by different letters (univariate ANOVA, $P \leq 0.05$).

	Fe ($\mu\text{mol L}^{-1}$)	NH ₄ ($\mu\text{mol L}^{-1}$)	NO ₃ ($\mu\text{mol L}^{-1}$)	PO ₄ ($\mu\text{mol L}^{-1}$)	Olsen-P ($\mu\text{mol kg}^{-1}$ DW)	pH	Alkalinity (meq L^{-1})
Peat							
ctr	454 (213)	571 ^a (57)	2.8 (2.6)	74.3 ^b (15.2)	9110 ^{ab} (1730)	5.7 ^a (0.4)	1.7 ^a (0.1)
LMC1x	398 (267)	704 ^{ab} (52)	2.2 (1.2)	45.0 ^{ab} (25.3)	7285 ^a (912)	6.1 ^{ab} (0.3)	2.0 ^b (0.1)
LMC5x	472 (141)	870 ^b (158)	1.5 (0.1)	48.1 ^{ab} (11.7)	6812 ^a (573)	6.1 ^{ab} (0.1)	2.2 ^b (0.2)
lime	570 (12)	817 ^b (100)	1.2 (0.2)	23.8 ^a (4.3)	16865 ^b (9599)	6.3 ^b (0.1)	3.6 ^c (0.3)
S500							
ctr	69 (12)	36 (4.6)	1.0 ^a (0.5)	4.4 ^b (2.7)	400 (155)	5.9 ^a (0.2)	0.4 ^a (0.1)
LMC1x	68 (10)	37 (6.2)	2.2 ^a (2.1)	2.1 ^{ab} (1.1)	329 (71)	6.1 ^a (0.1)	0.4 ^a (0.1)
LMC5x	26 (19)	28 (15)	12.9 ^b (6.5)	1.0 ^a (0.1)	427 (121)	6.4 ^b (0.1)	0.5 ^a (0.1)
lime	30 (23)	45 (19)	2.6 ^a (1.5)	1.4 ^{ab} (1.0)	434 (129)	7.2 ^c (0.1)	3.5 ^b (0.3)
S1000							
ctr	72 (40)	55 ^a (25)	0.9 (0.5)	3.5 (0.8)	873 ^c (199)	5.9 ^a (0.1)	0.4 ^a (0.0)
LMC1x	81 (21)	84 ^{ab} (4.2)	1.2 (1.6)	3.2 (0.8)	379 ^{ab} (34)	6.4 ^b (0.1)	0.9 ^b (0.0)
LMC5x	78 (23)	102 ^{ab} (24)	3.2 (4.3)	3.5 (3.7)	260 ^a (106)	6.4 ^b (0.1)	0.8 ^b (0.0)
lime	60 (18)	139 ^b (33)	1.0 (1.0)	1.4 (0.5)	411 ^b (56)	7.1 ^c (0.1)	3.7 ^c (0.3)
S2000							
ctr	115 (10)	71 (34)	1.1 (1.0)	9.6 ^c (0.3)	1012 ^c (63)	5.8 ^a (0.1)	0.4 ^a (0.0)
LMC1x	92 (68)	89 (52)	1.9 (0.8)	4.4 ^b (1.0)	637 ^b (96)	6.2 ^b (0.2)	0.8 ^{ab} (0.3)
LMC5x	44 (42)	60 (92)	9.8 (12.2)	1.1 ^a (0.6)	383 ^a (18)	6.4 ^b (0.3)	0.9 ^b (0.3)
lime	44 (26)	135 (27)	7.7 (13.4)	2.9 ^b (0.3)	590 ^b (147)	6.9 ^c (0.1)	3.7 ^c (0.4)

Table 4. Mean values ($\pm$ SD) of chemical variables in the **surface water** for the different treatments of the **flooded** peat soil and the three sandy soil types after 145 days. Significant differences between treatments are indicated by different letters (univariate ANOVA, $P \leq 0.05$).

	Fe ($\mu\text{mol L}^{-1}$)	NH ₄ ($\mu\text{mol L}^{-1}$)	NO ₃ ($\mu\text{mol L}^{-1}$)	PO ₄ ($\mu\text{mol L}^{-1}$)	pH	Alkalinity (meq L^{-1})
Peat						
ctr	68.7 (36.7)	14.8 (6.2)	7.4 ^a (8.4)	2.2 ^a (1.7)	5.7 ^a (0.1)	0.5 ^a (0.1)
LMC1x	111.2 (26.8)	14.5 (4.6)	36.2 ^b (12.9)	5.4 ^b (1.7)	5.7 ^a (0.1)	0.6 ^a (0.2)
LMC5x	70.5 (20.7)	9.5 (1.8)	27.4 ^{ab} (18.2)	3.5 ^{ab} (1.2)	5.9 ^a (0.1)	0.5 ^a (0.1)
lime	58.4 (28.2)	8.7 (0.7)	45.0 ^b (15.9)	3.1 ^{ab} (1.1)	6.7 ^b (0.1)	2.2 ^b (0.4)
S500						
ctr	8.9 ^c (2.4)	6.6 (1.8)	22.0 ^{ab} (5.6)	3.0 ^b (0.7)	5.8 ^a (0.0)	0.2 ^a (0.0)
LMC1x	8.6 ^c (4.0)	5.2 (2.1)	12.3 ^a (12.1)	2.6 ^b (1.0)	5.9 ^a (0.1)	0.2 ^a (0.0)
LMC5x	2.9 ^b (1.1)	7.1 (2.2)	76.5 ^b (13.7)	0.7 ^a (0.2)	6.4 ^b (0.1)	0.3 ^b (0.1)
lime	0.2 ^a (0.2)	4.6 (2.0)	21.9 ^{ab} (7.6)	0.5 ^a (0.2)	7.4 ^c (0.3)	2.8 ^c (0.6)
S1000						
ctr	5.8 ^b (1.9)	6.1 (1.7)	35.7 (11.3)	3.0 ^{ab} (0.7)	5.2 ^a (0.2)	0.1 ^a (0.0)
LMC1x	8.4 ^b (1.6)	6.3 (2.4)	34.3 (10.4)	4.0 ^b (0.9)	6.1 ^b (0.1)	0.4 ^b (0.1)
LMC5x	3.9 ^{ab} (5.4)	9.7 (2.0)	39.4 (9.4)	1.7 ^a (2.4)	6.2 ^b (0.1)	0.4 ^b (0.1)
lime	0.7 ^a (0.3)	6.4 (2.2)	29.2 (11.7)	1.9 ^{ab} (0.3)	7.5 ^c (0.1)	3.3 ^c (0.2)
S2000						
ctr	4.3 ^b (1.3)	7.0 (2.6)	31.3 (12.6)	3.8 ^b (0.7)	5.1 ^a (0.2)	0.1 ^a (0.0)
LMC1x	5.3 ^b (0.9)	6.8 (1.8)	25.1 (9.4)	2.7 ^b (0.8)	6.2 ^b (0.1)	0.4 ^b (0.1)
LMC5x	0.6 ^a (0.8)	6.9 (1.3)	56.7 (27.0)	0.2 ^a (0.2)	6.5 ^b (0.1)	0.3 ^b (0.0)
lime	0.7 ^a (0.3)	10.8 (2.0)	30.5 (14.0)	3.4 ^b (0.5)	7.7 ^c (0.1)	3.0 ^c (0.3)

Especially in the short term, pore water ammonium concentrations in the sandy soils increased in all treatments compared to the controls (Fig. 2), with by far the largest increase in the LMC5x treatment (6-90 times higher). Water extractions of LMC revealed that LMC itself released large quantities of ammonium (8 $\mu\text{mol g}^{-1}$ LMC; data not shown), which could result in ammonium concentrations of 75-300 $\mu\text{mol L}^{-1}$ soil in this experiment. In the peaty soils, ammonium concentrations increased in the short term and remained highest in the LMC5x and lime treatments. In the sandy soils, however, ammonium concentrations decreased in the long term. Long-term results showed the highest ammonium concentrations in the lime treatments of all soils, where they were twice as high as in the controls (Tables 2 & 3). The LMC treatments had no significant long-term effect on pore water ammonium concentrations, except for the flooded peaty soil, in which ammonium concentrations were 1.5 times higher than in the control (Table 3). Only transient increases in ammonium concentrations were measured in the surface water, especially in the LMC5x treatments (Fig. 2). Nitrate concentrations in the pore water and the surface water of the LMC treatments increased to as

much as $600 \mu\text{mol L}^{-1}$ in the first weeks, after which nitrate concentrations generally decreased again (Table 4). It was only in the moist sandy soils that pore water N concentrations correlated well with Olsen-P concentrations ($r^2 = 0.64$).

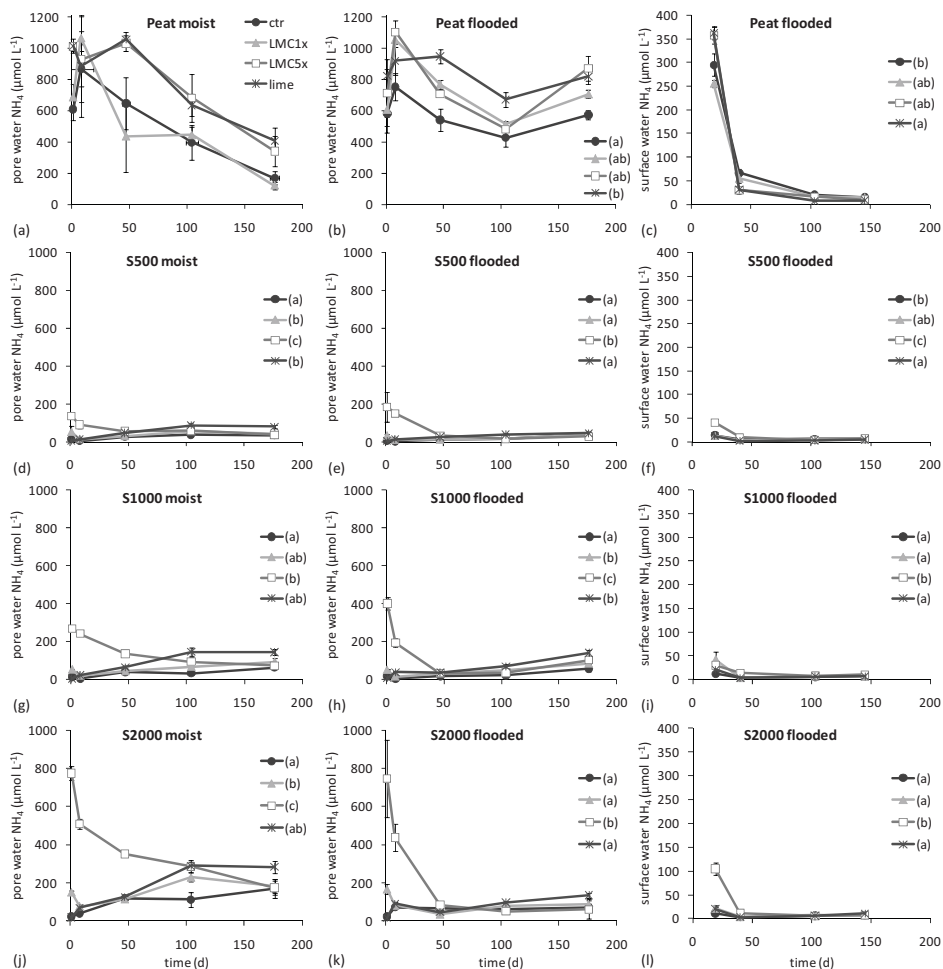


Figure 2. Ammonium concentrations in pore water and surface water for the peat soil and the three sandy soil types under moist and flooded conditions. Significant differences between treatments, as tested by GLM repeated measures ($P \leq 0.05$), are indicated by different letters. Note that different scales are used for the peaty soil and surface water graphs.

From the beginning, alkalinity was higher in the peaty soils than in the sandy soils (Tables 2 & 3). In the lime treatments, alkalinity and pH in the pore water and the surface water strongly increased in all soils (Tables 2-4). Alkalinity in these soils

increased 6-9 times in the pore water and 17-23 times in the surface water, whereas pH values increased by 1-1.5 units. Alkalinity and pH also increased significantly in the LMC treatments of most soils, but this increase was much smaller than in the lime treatments.

Lanthanum concentrations in the pore water and surface water increased in all LMC treatments and were highest in the LMC5x treatments (data not shown). However, lanthanum concentrations only rose to 4-9 $\mu\text{mol L}^{-1}$ in the pore water and 2-5 $\mu\text{mol L}^{-1}$ in the shallow surface water. Iron concentrations were generally highest in the peaty soils, although they increased in all sandy soils during the experiment. Iron concentrations in the moist sandy soils became higher than in the flooded sandy soils, whereas the opposite was observed in the peaty soils (Tables 2 & 3). In the first weeks, iron concentrations in the pore water were significantly lower in the LMC treatments of all sandy soils as well as in the surface water in all treatments of all soils compared to their controls (data not shown). In the long term, iron concentrations were lowest in the lime treatments of the moist S500 soils (Tables 2).

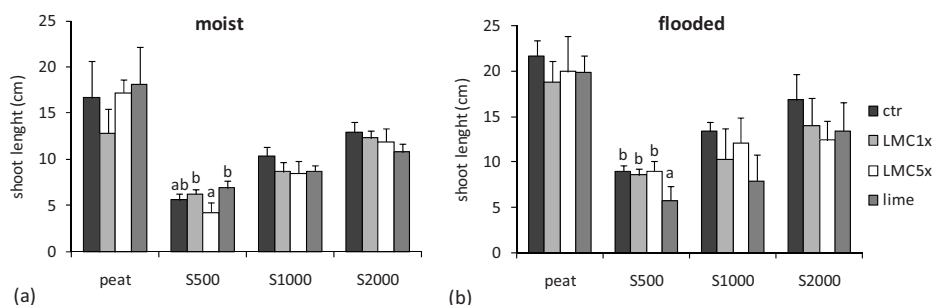


Figure 3. Shoot length of *Juncus effusus* plants on the peat soil and the three sandy soil types under moist and flooded conditions after 243 days ($\pm$ SEM). Significant differences between treatments, as tested by univariate ANOVA ($P \leq 0.05$), are indicated by different letters.

EFFECTS ON PLANT GROWTH

Shoot length and biomass of *J. effusus* were highest on the peaty soil, followed by S2000, S1000 and S500 (Figs. 3 & 4). Shoot length increased over time on all soil types, and this increase differed between treatments on S1000 and S2000 ($P < 0.05$). In the long term (after 243 days), treatments did not significantly decrease shoot length and biomass compared to the controls in most cases, under both moist and flooded conditions (Figs. 3 & 4). Shoot lengths on the flooded S500 were significantly lower in the lime treatment, while biomass was lower in the

LMC5x and lime treatment. On the moist S1000, biomass was only lower in the LMC1x treatment.

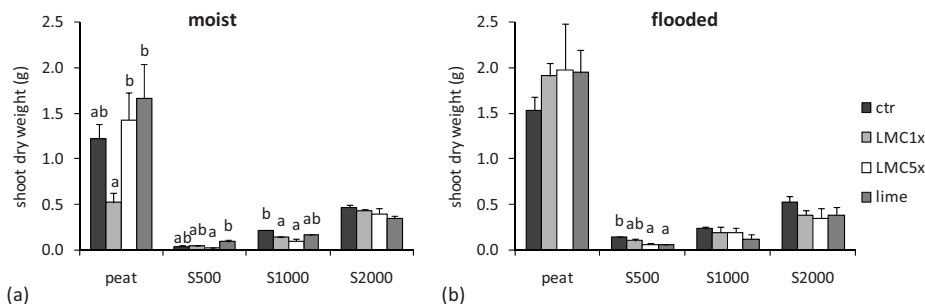


Figure 4. Aboveground biomass of *Juncus effusus* plants on the peat soil and the three sandy soil types under moist and flooded conditions after 243 days ($\pm$ SEM). Significant differences between treatments, as tested by univariate ANOVA ($P \leq 0.05$), are indicated by different letters.

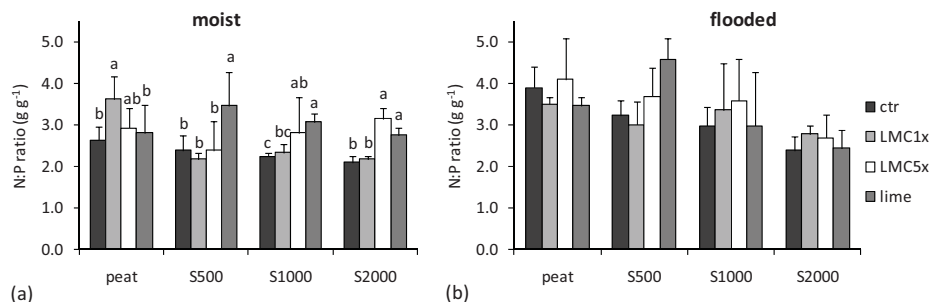


Figure 5. N:P ratios in plant tissue for the peat soil and the three sandy soil types under moist and flooded conditions after 243 days ($\pm$ SEM). Significant differences between treatments, as tested by univariate ANOVA ($P \leq 0.05$), are indicated by different letters.

Shoot length and plant biomass correlated positively with Olsen-P concentrations ($r^2 = 0.4$ - 0.5) and pore water concentrations of phosphate ($r^2 = 0.5$ - 0.6) and nitrogen ($r^2 = 0.5$ - 0.8). The correlation with Olsen-P concentrations, as measured in the middle of the growth period, was highest in the moist sandy soils ($r^2 = 0.7$ - 0.8). N:P ratios in plant biomass were generally low (2 - 4 g g^{-1} ; Fig. 5), with N concentrations ranging between 12 and 27 mg g^{-1} and P concentrations ranging between 4 and 8 mg g^{-1} (data not shown). N:P ratios on the flooded sandy soils decreased with increasing Olsen-P concentrations. On the moist sandy soils, N:P ratios in the lime treatments were significantly higher than in the controls.

Compared to the control treatments, N concentrations in plant tissue increased in all addition treatments on the sandy soils, whereas they decreased on the peaty soil.

Discussion

Additions of lanthanum-modified clay (LMC) and lime decreased pore water phosphate concentrations over time in the P-rich sandy soils. In addition, the highest LMC dose was able to decrease phosphate mobilization to the water layer in the sandy soils, indicating that LMC application may be most effective in a flooded situation. Lower phosphate concentrations in the water layer prevent blooms of algae and cyanobacteria and create better light conditions for the growth of various plant species (Roelofs 1991; Jeppesen *et al.*, 2005). Because LMC was originally developed for application in surface waters, it has only been used in aquatic systems till now (Robb *et al.*, 2003; Akhurst *et al.*, 2004; Yang *et al.*, 2004).

Although LMC decreased Olsen-P concentrations in some of the P-rich sandy soils, they did not fall below the threshold of 200-300 $\mu\text{mol kg}^{-1}$ soil (260-390 $\mu\text{mol L}^{-1}$ fresh soil; Smolders *et al.*, 2008). This means that *J. effusus* would still be able to dominate on these soils during moist or waterlogged conditions or when the water layer covering the soil is thin enough to allow its growth, without opportunities for a biodiverse vegetation to develop (Janssens *et al.*, 1998). LMC and lime were indeed not effective enough in reducing *J. effusus* growth, although shoot length and biomass were decreased in the flooded P-poor sandy soils. This implies that *J. effusus* could have mobilized organically bound P or P bound by Fe, Al or Ca in these soils (Dinkelaker *et al.*, 1989; Shen *et al.*, 2002; Tweel & Bohlen 2008). It is less likely that *J. effusus* can mobilize P that is bound by LMC, because lanthanum has strong ionic binding characteristics (Stumm & Morgan 1996) and forms highly stable minerals with a low solubility in the presence of phosphates (Firsching 1992; Douglas *et al.*, 2000). The soils were relatively rich in Fe and thus presumably also rich in Fe-bound P, suggesting that the effects of LMC and lime may have been lower than they would have been in Fe-poor soils.

The low N:P ratios in plant tissue that we found on all soil types may indicate that *J. effusus* was limited in its growth by N and not by P (N:P ratio $\ll 14$; Koerselman & Meuleman 1996), although N:P ratios of individual plant species cannot be used to predict their growth-limiting nutrient (Bedford *et al.*, 1999; Güsewell &

Koerselman 2002). In addition, plant tissue concentrations of N and P were higher than the threshold concentrations for nutrient limitation ($N < 9.5$ mg/g; $P < 1$ mg/g; Güsewell & Koerselman, 2002). It seems more likely, however, that there was at least co-limitation of N and P, because plants grew better with increasing Olsen-P concentrations in the soil. Unlike Smolders *et al.* (2008) we did find a positive relationship between N concentrations in pore water and plant biomass, which can probably be explained by the positive correlation between the pore water N concentrations and the Olsen-P concentrations. Moreover, LMC and lime decreased pore water phosphate concentrations in the sandy soils and sometimes increased nitrate and ammonium concentrations, whereas they decreased plant biomass and shoot length. This implies that phosphate was the main nutrient limiting the growth of *J. effusus* on the sandy soils, which is why mobilization of nitrate and ammonium in some of the treatments did not increase *J. effusus* growth. However, there was no correlation between the high pore water N concentrations and the high Olsen-P concentrations ($r^2 = 0.1$) in the peaty soils, although there was still a positive relationship between pore water N concentrations and plant biomass ($r^2 = 0.5$), which could indicate N limitation for *J. effusus* on the peaty soils.

This mobilization of nitrate and ammonium did not last very long in the LMC treatments, because it was primarily released from the LMC itself, whereas it lasted much longer in the lime treatments. This was caused by the extreme increase in pH and alkalinity we observed after lime addition, which led to an increase in decomposition rates in the peaty soils and P-rich sandy soils and subsequently to additional nutrient mobilization (Smolders *et al.*, 2006). In the other sandy soils, ammonium was probably dispelled from the soil absorption complex by calcium. The decrease in iron concentrations in the LMC5x and lime treatments was probably caused by the increase in pH in these treatments, which causes iron to become less soluble (Stumm & Morgan 1996). The lanthanum concentrations released in the LMC treatments were rather low, because lanthanum ions are very tightly adsorbed to the bentonite clay (Ross *et al.*, 2008). The measured concentrations are not expected to be toxic to plants, animals or micro-organisms (Greenop & Robb 2001; Persy *et al.*, 2006), although plants and animals may accumulate lanthanum in their tissue (Weltje *et al.*, 2002; Lüring & Tolman, 2010).

A problem that may arise if LMC is mixed with the upper 10 cm of the soil in the field is that *J. effusus* can form deeper roots, to reach untreated P-rich soil layers. Therefore, LMC could only be used if the whole P-saturated soil layer is treated (Smolders *et al.*, 2008). The highest LMC dose turned out to be the most effective

in reducing phosphate concentrations and plant growth in our experiment, which means that it will only be cost-effective in combination with top soil removal or if the top soil is heavily polluted and top soil removal is too expensive. It is difficult to indicate the cost-effectiveness in general, because it strongly depends on the actual depth of the P-rich soil layer and on the pollution status of the soil. If top soil removal is not preferred, the greatest effect of LMC application to restore wetlands on former agricultural sandy soils can be expected for flooded situations, because it significantly decreased phosphate mobilization to the water layer in our experiment and has proved to be very successful in reducing phosphate mobilization and algal growth in surface waters (Robb *et al.*, 2003; Akhurst *et al.*, 2004; Yang *et al.*, 2004). This would avoid the possible adverse effects of liming, which leads to increased decomposition and eutrophication in the long run. The application of LMC in a flooded situation, for example in water storage areas, will create a better initial situation for the development of a more biodiverse aquatic or semi-aquatic vegetation on former agricultural sandy soils than in a waterlogged or moist situation, where domination of eutrophic plant species like *J. effusus* leads to very low biodiversity. Another advantage of using LMC in water storage areas would be that temporarily stored surface water would not become enriched with phosphate.

Implications for Practice

- It is in flooded situations that LMC application may have the greatest effect in terms of successful ecological restoration of former agricultural sandy soils, because LMC, rather than lime, decreased phosphate mobilization to the water layer in sandy soils, which prevents blooms of algae and cyanobacteria.
- In moist or waterlogged conditions or when there is a thin water layer on the soil *J. effusus* will still be able to dominate on former agricultural soils treated with LMC or lime, without opportunities for a biodiverse vegetation to develop. Although LMC can decrease Olsen-P concentrations, they do not fall below the threshold of 200-300 $\mu\text{mol kg}^{-1}$ soil that prevents domination of *J. effusus*.
- Liming is not recommended as a restoration measure for organic soils, because it leads to long-term mobilization of nitrate and ammonium, caused by an extreme increase in pH and alkalinity after lime addition, leading to increased decomposition rates and additional nutrient mobilization. Liming may be used as an additional restoration measure in soils with a low organic content.

- LMC application may only be cost-effective in combination with removal of the most P-rich top soil, or if the top soil is heavily polluted and its removal is too expensive.

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Chapter 7

Synthesis



Many hands make light work (IJperveld, The Netherlands; photo by Artur Banach)

Introduction

Worldwide, fens and peat lakes are being threatened by multiple environmental problems, such as desiccation, eutrophication, pollution and global warming (Gorham, 1995; Smolders *et al.*, 2006). This has led to increased peat decomposition and sludge production, disappearance of macrophyte species, biodiversity losses and hampered terrestrialization (Roelofs, 1991; Koerselman *et al.*, 1995; Lamers *et al.*, 2002b; Laiho, 2006). This thesis therefore discusses important biogeochemical processes involved in the decline of fens and peat lakes, which also provide the key to their restoration. These processes include the mobilization and immobilization of PO_4 , SO_4 reduction and concomitant sulphide toxicity, and peat decomposition, which all have important implications for water and sediment quality, and for vegetation development. In this synthesis, the conclusions of the preceding chapters will be integrated and discussed in the light of other findings within the national OBN research programme. The implications of the results for nature management and fen restoration are presented and simple quality measurements are provided, which can immediately be used by conservation area managers to choose between several restoration measures. This should lead to decreased eutrophication and pollution, to the restoration of specific target vegetation types, and to increased biodiversity in fens and peat lakes.

Mechanisms and threats

MOBILIZATION AND IMMOBILIZATION OF PO_4

PO_4 mobilization rates from the sediment to the water layer (Chapter 3) were relatively low compared to those found in other studies (Lofgren & Boström, 1989; Jensen *et al.*, 1992; Kozerski *et al.*, 1999; Martynova, 2008), but contribute to almost half of the total P load in Dutch peat lakes and fens (Janse *et al.*, 2008). The classic iron cycle (Mortimer, 1941, 1942) can very well explain the actual release of PO_4 from peat sediments. In the oxygenated boundary layer between sediment and water layer, dissolved Fe^{2+} from the sediment becomes oxidized and PO_4 is effectively bound to Fe^{3+} oxides and hydroxides, which inhibits diffusion of PO_4 from the sediment to the water layer. This mechanism explains the negative relation between the PO_4 mobilization from the sediment to the water layer and the pore water Fe: PO_4 ratios. Where there is insufficient Fe in the pore water to bind PO_4 (Fe: PO_4 ratio < 1 to 3.5 mol mol⁻¹), PO_4 mobilization from the sediment to the water layer will be mainly determined by the pore water PO_4 concentration (Chapter 2 & 3). Total sediment P concentrations were found to

be only indicative at low values ($< 28 \mu\text{mol g}^{-1}$), but were not reliable at higher values (Chapter 3). Net PO_4 mineralization rates were higher under anaerobic conditions and at low pore water Fe: PO_4 ratios (Chapter 3), because Fe^{3+} will be reduced to Fe^{2+} under anaerobic conditions, which is less able to bind PO_4 (Patrick & Khalid, 1974; Ponnampерuma, 1984).

The capacity of the sediment to bind PO_4 also depends on the total S concentration in the sediment. The reduction of SO_4 and Fe in anaerobic sediments leads to the formation and accumulation of sulphide and FeS_x (Smolders & Roelofs, 1993; Roden & Edmonds, 1997; Wetzel, 2001; Lamers *et al.*, 2002a), and stimulates organic matter decomposition and alkalinization (Drever, 1997). Because Fe has a higher binding affinity for sulphide than for PO_4 , this will lead to a lower sediment binding capacity for PO_4 . The advantage is that it may prevent sulphide toxicity (Smolders & Roelofs, 1995; Van der Welle *et al.*, 2007b), but it will also lead to the release of Fe-bound PO_4 and the decrease of Fe: PO_4 ratios (Caraco *et al.*, 1989; Smolders & Roelofs, 1993; Lamers *et al.*, 1998a). SO_4 and HCO_3^- may also compete with PO_4 for anion binding sites in the sediment (Caraco *et al.*, 1989; Beltman *et al.*, 2000), leading to an additional release of PO_4 from the sediment. We found that fen waters with high SO_4 concentrations ($> 100 \mu\text{mol L}^{-1}$), and most probably a high sulphate load, indeed show increased P mobilization and decreased pore water Fe: PO_4 ratios (Chapter 2). High total Al concentrations in the sediment may indicate that a significant part of the metal-bound P has been bound to Al instead (Chapter 5). P mobilization from this source is unlikely, as Al does not precipitate with sulphide. The sediment Fe:S ratio can therefore give an important indication of the amount of Fe that is still available to immobilize PO_4 . Fe:S ratios below 1 mol mol^{-1} decrease the availability of Fe oxides and hydroxides, which are able to adsorb P, leading to decreased pore water Fe concentrations, increased pore water PO_4 concentrations and increased PO_4 mobilization to the water layer (Chapter 3).

In the field, however, biological and physical factors can also be very important in further increasing PO_4 mobilization to the water layer. Such factors include resuspension by wind (Thomas & Schallenberg, 2008), benthic feeding by fish (Persson, 1997), and PO_4 uptake by algae and subsequent release (Correll, 1998).

EUTROPHICATION

The actual mobilization rate of PO_4 from the sediment to the water layer is of pivotal importance for the biodiversity of aquatic systems, due to the induction of blooms of algae and cyanobacteria and the dominance of floating-leaved macrophytes (Correll, 1998). At a high internal PO_4 flux it is also more difficult, if

not impossible, to return from a hypertrophic turbid water state to a clear water state with submerged macrophytes (Scheffer *et al.*, 1993). Therefore, the number of macrophyte species in fen waters, especially rare species, tended to decrease with higher surface water PO_4 concentrations (Chapter 2). This finding was anticipated, since P limitation generally controls biomass production in fen waters and prevents the dominance of fast growing species, including algae (Grime, 1974; Wheeler & Proctor, 2000). In contrast to James *et al.* (2005), we did not find a relationship between biodiversity and surface water NO_3 concentrations (Chapter 2). Similar findings, showing greater dependence on low P availability for rare and endangered species compared to common species, have been reported for terrestrial systems (Olde Venterink *et al.*, 2003; Wassen *et al.*, 2005).

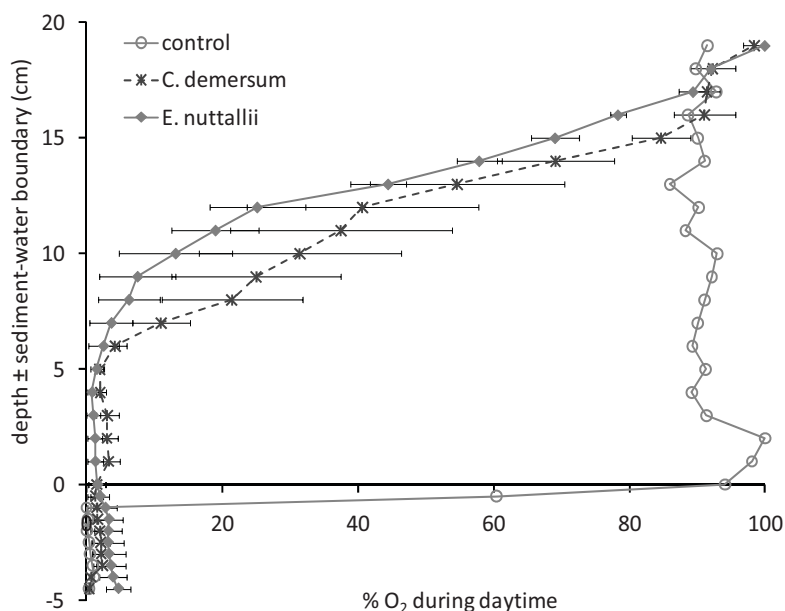


Figure 1a. Oxygen concentrations during daytime ($\pm$ SEM), as measured with microelectrodes (Microscale Measurements, The Hague, the Netherlands), in a vertical profile from surface water to sediment in dense vegetation (height 18 cm) of *Ceratophyllum demersum* and *Elodea nuttallii* ($n=3$; Geurts & Harpenslager, unpublished data). Depths are given relative to the sediment-water boundary.

In shallow fen waters, however, the interaction between sediment and surface water, rather than actual concentrations in the water layer, reflect nutrient availability and determine biodiversity. Many aquatic macrophytes take up

nutrients directly from the sediment through their roots (e.g. *Elodea nuttallii*; Nagasaka, 2004), whilst luxuriant growth of other species and algae may withdraw such large amounts of nutrients from the water column that the water becomes poor in P (e.g. *Ceratophyllum demersum*; Lombardo & Cooke, 2003). There are also indications that dense mats of submerged macrophytes create a vertical oxygen gradient in the water layer and an anoxic zone just above the sediment (Fig. 1a) in order to facilitate the mobilization of PO_4 from the sediment to the water layer (Fig. 1b; Søndergaard *et al.*, 2003; Loeb *et al.*, 2008), which is especially useful for non-rooting species like *C. demersum*. During daytime, submerged macrophytes in a dense vegetation will only photosynthesize in the upper part of the water layer in which insolation is high enough, whereas respiration will dominate in the lower part of the water layer that remains dark (Wetzel, 2001). Fast-growing aquatic macrophytes and benthic algae can, therefore, still dominate an apparently P-poor water layer and outcompete other species, including semi-aquatic macrophytes that colonize the water and induce terrestrialization, thereby decreasing total biodiversity.

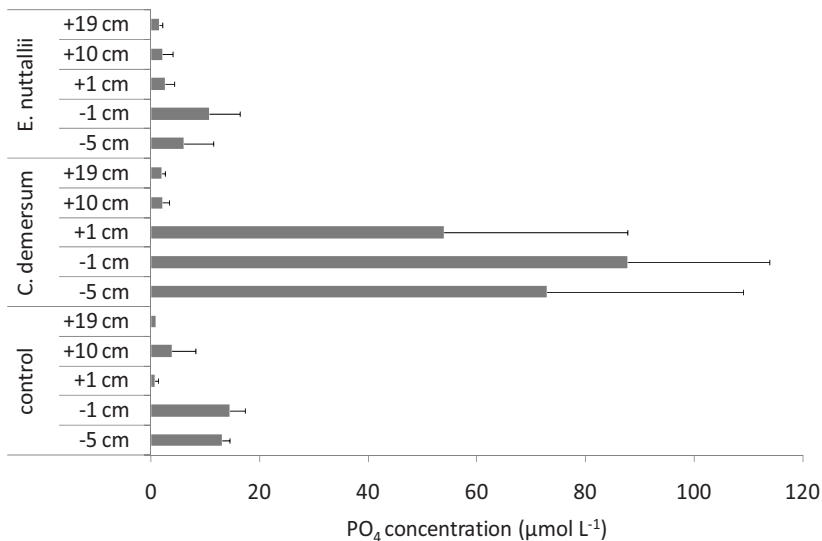


Figure 1b. PO_4 concentrations ($\pm$ SEM) in a gradient from surface water to sediment in dense vegetation of *Ceratophyllum demersum* and *Elodea nuttallii* ($n=3$; Geurts & Harpenslager, unpublished data). Depths are given relative to the sediment-water boundary.

Interestingly, the pore water $\text{Fe}:\text{PO}_4$ ratio described above did not only turn out to be a valuable indicator of P release, but even more importantly, correlated

significantly with the number and abundance of Red List species (Chapter 2). Furthermore, the number of Red List species increased at a lower threshold value than the actual species abundance. The sediment Fe:P ratio has a similar strong correlation with the abundance of Red List species (Chapter 2). Relationships between aquatic macrophyte distribution and sediment composition have also been described previously, but without using ratios in pore water or sediment (Bloemendaal & Roelofs, 1988; Van Wijck *et al.*, 1992; Baattrup-Pedersen & Riis, 1999). Endangered species also appear to be more sensitive to eutrophication than other investigated macrophyte species (Chapter 2). This is probably caused by PO₄ or SO₄ pollution or by both (Lamers *et al.*, 2002a), increasing surface water turbidity and sulphide toxicity in the sediment (Chapter 4; Van den Berg *et al.*, 2003; Smolders *et al.*, 2003a; Van der Welle *et al.*, 2006). Chapter 5 demonstrated that Fe addition to the sediment could lead to efficient PO₄ binding and decreased water turbidity. However, the sediment was apparently too anaerobic for typical submerged soft-water macrophytes to germinate, despite a clear water state all year round in some cases.

As expected, fertilization led to the dominance of fast-growing eutrophic species (Chapter 4), whose growth strategy outcompeted most ecosystem engineers (key species for terrestrialization). Without fertilization, however, ecosystem engineers did not profit from their relatively better competitive strength and did not colonize the water layer, because nutrient availability appeared to be too low in this experimental setting. Colonization of the water layer only occurred in the fertilized treatments, where ecosystem engineers were able to use the abundance of nutrients to grow into the water and avoid competition with dominating eutrophic species on the peat bank. Furthermore, fertilization led to a considerable decrease in the N:P ratio of the vegetation (Chapter 4), which may indicate a shift from P-limitation to N-limitation (N:P ratio < 14; Koerselman & Meuleman, 1996; Whigham *et al.*, 2002).

The low N:P ratios in plant tissue of *Juncus effusus* (Chapter 6), a noxious species in many wetlands, seems to indicate at first sight that this species was also limited in its growth by N and not by P. However, because N:P ratios of individual plant species cannot be used to predict their growth-limiting nutrient (Bedford *et al.*, 1999; Güsewell & Koerselman, 2002), it seems more likely that there was at least co-limitation of N and P, because plants grew better with increasing Olsen-P concentrations in the soil. This implies that PO₄ was the main nutrient limiting the growth of *J. effusus* on sandy soils, which is why mobilization of nitrate and ammonium did not increase *J. effusus* growth (Chapter 6). However, there was still a positive relationship between pore water N concentrations and plant

biomass in the peaty soils ($r^2 = 0.5$), which could indicate N co-limitation for *J. effusus* on peaty soils.

S POLLUTION

SO₄ addition to the water layer of mesocosms led to increased SO₄ and sulphide concentrations in both the sediment and the peat bank already within one year (Chapter 4). This means that anaerobic conditions in the peat were rapidly established, stimulating SO₄ reduction, sulphide production, decomposition of organic matter and alkalization (Smolders & Roelofs, 1993; Lamers *et al.*, 1998a; Swarzenski *et al.*, 2008). Therefore, higher PO₄ and NH₄ concentrations in the sediment and the peat bank after three years of SO₄ addition cannot be explained only by sulphide-induced inhibition of nutrient uptake (Koch *et al.*, 1990), but probably also by increased decomposition rates and PO₄ mobilization from iron binding sites as a result of higher Fe consumption rates by sulphide (Smolders & Roelofs, 1993; Roden & Edmonds, 1997; Wetzel, 2001). This PO₄ mobilization could easily occur, because SO₄ addition led to pore water Fe:PO₄ ratios decreasing well below threshold values of 1 to 3.5 mol mol⁻¹ for PO₄ mobilization (Chapter 2-4; Lofgren & Boström, 1989; Smolders *et al.*, 2001; Zak *et al.*, 2004).

SO₄ pollution will also lead to decreasing sediment Fe:S ratios, causing a state shift towards a situation with low Fe availability and high PO₄ mobilization rates (Chapter 3). It is especially the supply of SO₄-rich water to compensate for water shortage in nature reserves and agricultural areas, in addition to SO₄ production due to desiccation and subsequent FeS_x oxidation, which will cause this overwhelming release of sediment-bound P from the sediment (Phillips *et al.*, 1994; Lamers *et al.*, 1998a; Smolders *et al.*, 2006). Furthermore, just like direct fertilization, SO₄ addition decreased the N:P ratio of the vegetation, possibly indicating a shift from P-limitation to N-limitation (Chapter 4; Koerselman & Meuleman, 1996). These results confirm that SO₄ pollution leads to extra internal mobilization of nutrients (termed internal eutrophication) in fens (Roelofs, 1991; Lamers *et al.*, 2002a; Smolders *et al.*, 2006). It can therefore be concluded that interspecific competition, vegetation succession and terrestrialization are not only influenced by nutrient availability, but also by SO₄ pollution.

TOXICITY

SO₄ pollution leads to the accumulation of highly toxic sulphide concentrations if the availability of dissolved Fe is low (Roelofs, 1991; Smolders & Roelofs, 1995; Hotes *et al.*, 2005), which results in the disappearance of several sensitive species and a much lower total biomass (Chapter 2 & 4). Chapter 4 showed that aquatic

and semi-aquatic macrophytes developed different growth strategies to cope with sulphide toxicity, competition, or both. Moreover, macrophytes were less vulnerable to sulphide toxicity under nutrient-rich conditions, probably because of a combination of dilution due to higher biomass production and greater oxidation of the sediment and the peat bank by radial oxygen loss due to higher root biomass (Jaynes & Carpenter, 1986; Adema *et al.*, 2003). This means that the effects of SO_4 pollution itself are influenced by the degree of eutrophication, which implies that toxicity effects in plants can be masked in eutrophic areas. In addition, SO_4 pollution and concomitant sulphide production hampered the colonization of the water layer by ecosystem engineers in most cases (Chapter 4), which has important implications for terrestrialization and succession in fens. Although macrophytes incorporated relatively more sulphur in their tissue after SO_4 addition, there were no indications of sulphur accumulation in S-rich amino acids as an adaptation to high sulphide concentrations (Chapter 4; Ruiz *et al.*, 2003; Droux, 2004).

Remarkably, aquatic macrophytes seemed to profit indirectly from the sulphide toxicity under nutrient-rich conditions (Chapter 4), because semi-aquatic macrophytes did not completely colonize the water layer. Besides that, aquatic macrophytes were able to take up nutrients directly from the surface water with their shoots (Eugelink, 1998; Lombardo & Cooke, 2003), making them less dependent on their roots and thus less susceptible to sulphide in the sediment. This was especially an advantage for the rootless species *C. demersum*.

SO_4 pollution can increase NH_4 concentrations via stimulated decomposition and, in addition to sulphide toxicity, possibly lead to NH_4 toxicity. Although NH_4 toxicity is much more likely at low pH (De Graaf *et al.*, 1998; Lucassen *et al.*, 2002; Van den Berg *et al.*, 2005), there are indications that NH_4 concentrations of 100 $\mu\text{mol L}^{-1}$ or higher are toxic to aquatic macrophytes at circumneutral pH (Roelofs, 1991; Smolders *et al.*, 2003a; Lucassen *et al.*, 2006). In Chapter 4 no increase in N-rich amino acids, indicative of N-stress (Marschner, 1986; Smolders *et al.*, 1996), was observed, which makes NH_4 toxicity less plausible. However, Chapter 2 showed that NH_4 concentrations in the surface water may have a negative influence on the occurrence of Red List species, whereas NH_4 concentrations in the pore water influenced the total number of species. Both sulphide and NH_4 had a more profound effect on the species abundance than on the number of species.

DECOMPOSITION

As expected, decomposition rates of peat soils and sediments were higher under aerobic conditions (Chapter 3) as a result of the greater availability of oxygen, acting as an optimal terminal electron acceptor for both decomposition and oxidation of phenolic compounds (Freeman *et al.*, 2004; Laiho, 2006). Fig. 2 demonstrates that lowering of the water level increases the oxygen availability in peat soils, leading to increased CO₂ production rates. However, after calculation it turned out that the increased CO₂ production rates in the cores from Kamerik-Kockengen were primarily caused by acidification as a result of oxidation processes and subsequent conversion of HCO₃⁻ to CO₂.

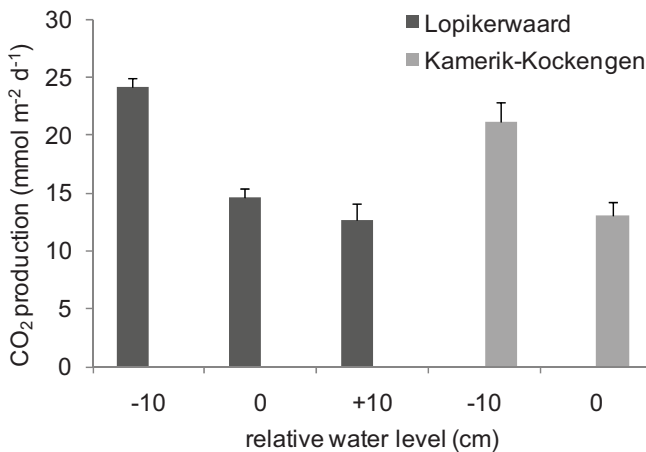


Figure 2. CO₂ production rates ($\pm$ SEM) in peat cores originating from two peaty grasslands in the Netherlands under different hydrological conditions (n=4; Geurts & Van Diggelen, unpublished data). "0" = field water level, i.e. 40-50 cm below soil surface.

Besides that, decomposition rates were primarily determined by the organic matter content. Above 75% organic matter, however, aerobic decomposition was no longer limited by electron donor availability. Decomposition rates were lowest in sediments that had already been decomposed to a larger extent, which were therefore less reactive than more intact peat soils. As decomposition rates did not correlate with variables related to chemical and physical soil characteristics, e.g. lignin and cellulose concentrations, lignin:nutrient ratios, and size fractions (Chapter 3), they could not be used as reliable indicators of potential decomposition rates (Tomassen *et al.*, 2004; Prescott, 2005).

The general assumption that decomposition of peat soils and sediments automatically leads to increased nutrient concentrations (McLatchey & Reddy, 1998; Bayley *et al.*, 2005) was found to be true for N (NO_x and NH_y), but not for PO_4 (Chapter 3). Moreover, net nutrient mineralization rates were relatively high in highly decomposed peat sediments compared to their C production rates. This could be explained by their relatively high nutrient concentrations (lower C:N and C:P ratios), by a lower capacity of these sediments to chemically retain nutrients, especially PO_4 , or by lower microbial consumption of nutrients. Fertilization decreased C:P ratios of the vegetation to values below 200 g g^{-1} , suggesting that decomposition was no longer limited by P (Chapter 4; Brinson, 1977). C:N ratios of the terrestrial vegetation also dropped after fertilization to values below $20\text{--}25 \text{ g g}^{-1}$, suggesting that decomposition was no longer limited by N either (Swift *et al.*, 1979). This means that eutrophication may lead to higher nutrient concentrations in plants, which can lead to increased decomposition rates of the litter (Aerts & Chapin, 2000) and, therefore, hamper peat formation and terrestrialization.

Higher decomposition rates will also lead to a release of dissolved and particulate organic matter in surface water, which will decrease light availability under water and thus decrease growth of submerged macrophytes (Barko *et al.*, 1991; Van Duin *et al.*, 2001; Stern *et al.*, 2007). Increased decomposition and bicarbonate production following SO_4 addition led to higher humic acid concentrations and alkalinity (Chapter 4; Mitchell & McDonald, 1992). High alkalinity enhances decomposition of easily decomposable peat even further (Roelofs, 1991; Brouwer *et al.*, 1999), leading to additional sludge production, which is a great problem for water management.

Management implications: risk assessment and possible solutions

DIAGNOSTIC AND PROGNOSTIC TOOLS

As indicators of both biogeochemical processes and biodiversity, sediment and sediment pore water ratios provide valuable diagnostic and prognostic tools for the restoration of water quality and rehabilitation of biodiversity in fen waters (Chapter 2 & 3). They are not only useful for risk assessment, but also for selecting the most promising measures.

Being a relatively stable process variable, the $\text{Fe}:\text{PO}_4$ ratio turns out to be a suitable indicator of present and future P concentrations in surface water and pore water. Below threshold values of 1 to 3.5 mol mol^{-1} there is a greater risk of

internal eutrophication (Chapter 2 & 3), which may lead to undesirable effects on aquatic communities. In that case PO_4 mobilization from the sediment to the water layer was considerable and linearly related to the pore water PO_4 concentration (Chapter 3). At higher ratios, there appeared to be a strong linear correlation between the Fe: PO_4 ratio and PO_4 mobilization. Other studies have found comparable results, demonstrating increased P release to the water layer at pore water Fe: PO_4 ratios below 1 mol mol⁻¹ (Smolders *et al.*, 2001), 2 mol mol⁻¹ (Lofgren & Boström, 1989) and 3 mol mol⁻¹ (Zak *et al.*, 2004). This means that measuring Fe and PO_4 in the anaerobic sediment pore water provides a powerful tool for a quick scan of the internal PO_4 fluxes.

The pore water Fe: PO_4 ratio is not only the most valuable prognostic tool for potential P concentrations after restoration measures, but also turned out to be indicative of the biodiversity response in fen waters (Chapter 2). Besides that, it can be used as a diagnostic tool in selecting fen waters where ecological restoration and the transformation of former arable land into nature reserves may be most successful. Suitable sites should preferably have pore water Fe: PO_4 ratios higher than 10 mol mol⁻¹ (Chapter 2). Finally, the Fe: PO_4 ratio can be a valuable tool in optimizing restoration measures.

Total sediment Fe:P ratios below 10 mol mol⁻¹ were also found to indicate P mobilization to the water layer (Chapter 2 & 3). This is comparable with Jensen *et al.* (1992) and Ramm & Scheps (1997) who concluded that P mobilization occurred below total sediment Fe:P ratios of 8.3 mol mol⁻¹ and 12 mol mol⁻¹, respectively. Maassen *et al.* (2005) determined thresholds for both total sediment Fe:P ratios (< 6 mol mol⁻¹) and Al:P ratios (< 12 mol mol⁻¹). For practical reasons, total sediment ratios may even be preferred over pore water ratios, because they do not require anaerobic sampling. In addition, the sediment Fe:S ratio gave an important indication of the amount of Fe that is available to immobilize PO_4 . The critical Fe:S ratio for PO_4 mobilization to the water layer turned out to be 1 mol mol⁻¹ (Chapter 3). Returning to a more favourable state of high Fe availability will be difficult in most cases because this requires either oxidation of reduced S compounds in the sediment in combination with transport of excess S out of the system, or artificial Fe addition.

REDUCTION OF INTERNAL AND EXTERNAL EUTROPHICATION

As PO_4 mobilization rates from the sediment to the water layer amount to almost half of the total P load known for Dutch peat lakes and fens (Chapter 3; Janse *et al.*, 2008), it is of pivotal importance to be able to estimate the magnitude of these internal fluxes (Lamers *et al.*, 2002b). This also indicates that it is very

important to decrease both external and internal sources of eutrophication and toxicity in fen waters by reducing the influx of P- and SO_4 -rich water, in order to conserve and restore biodiversity in fen waters. However, restoration measures that only focus on nutrient reduction can lead to a vegetation collapse in fens that receive SO_4 -polluted water (Chapter 4). This means that measures always need to take into account the influx of SO_4 -rich water to these ecosystems.

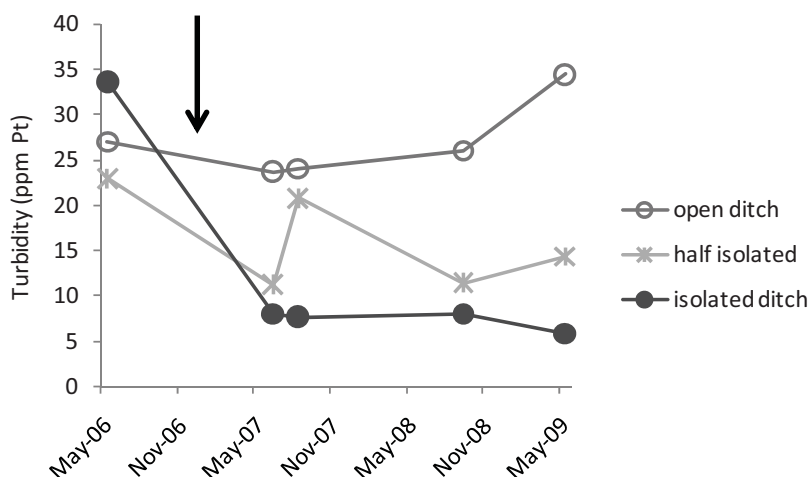


Figure 3. Surface water turbidity in open, half isolated and isolated ditches in Reeuwijk (The Netherlands; $n=1-6$; Geurts, unpublished data). The arrow indicates the start of the isolation.

Isolating fen waters from allochthonous surface water with a poor quality can be a useful measure to reduce both external and internal nutrient loading (e.g. Wieden & Weerribben; Geurts, unpublished data), although plant and animal dispersal may be hampered (Beltman *et al.*, 2005; Boedeltje, 2005). This measure often leads to a less turbid water layer, which improves the chances for submerged macrophytes to develop (Fig. 3 & 4; Chapter 2). In small water bodies (e.g. ditches and turf ponds), however, isolation or partial isolation can lead to the accumulation of PO_4 , NH_4 and sulphide in the anaerobic sludge layer (Geurts, unpublished data), because the water flow has stopped, which hampers the export of nutrients and sludge. Concomitant water table fluctuations and temporary desiccation of the sediment or littoral zone may be beneficial as these measures lead to the oxidation of the reduced sediment and stimulate the germination of seeds (Brouwer & Roelofs, 2001; Lucassen *et al.*, 2005). Aquatic diaspores are known to possibly remain viable for more than 30 years (Arts & Van der Heijden, 1990; Bellemakers *et al.*, 1996) and macrophytes

may therefore have the ability to rapidly colonize lakes from an intact diaspore bank by clonal growth (Brouwer *et al.*, 2002).

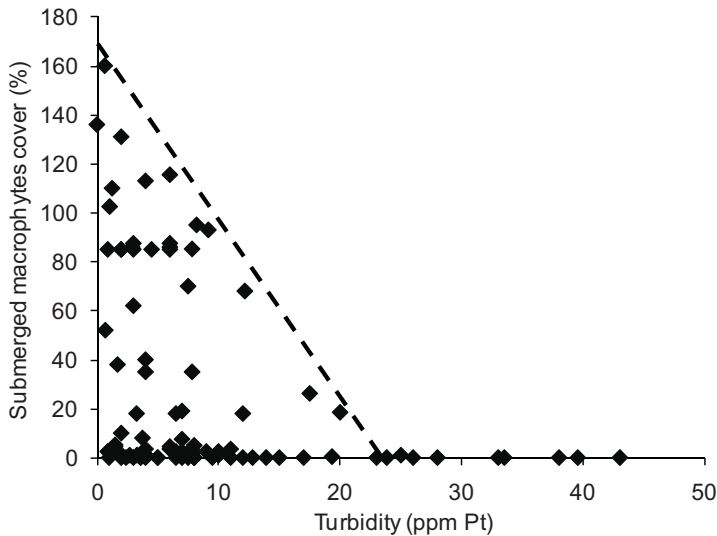


Figure 4. Correlation between surface water turbidity and the cover of submerged macrophytes in 145 fen waters in the Netherlands, Ireland and Poland (Geurts, unpublished data; Chapter 2). The dashed line indicates the maximum cover of submerged macrophytes at a given turbidity value.

DREDGING

Dredging is often used as a restoration measure in eutrophic peat lakes and fens with high nutrient mobilization rates (Ryding, 1982; Van der Does *et al.*, 1992; Verberk *et al.*, 2007). In alkaline, S-rich areas that are poor in Fe, however, dredging of the less reactive, but nutrient-rich upper sediment layer may expose a new, more intact and more reactive peat layer, which will decompose faster (Roelofs, 1991; Brouwer *et al.*, 1999). In the Dutch peat lake Geerplas for example, dredging and P-stripping of all inflowing water have eventually led to even higher nutrient mobilization rates from the P-rich sediment to the water layer than before these expensive measures had started (Michielsen *et al.*, 2007). For dredging to be a useful restoration measure, however, it is not only necessary to decrease the influx of P-rich water, but particularly also the influx of alkaline, S-rich water, because only this will slow down decomposition processes in the newly exposed, potentially more reactive peat layer and decrease subsequent nutrient mobilization to the water layer. Besides that, dredging will only be a

suitable option when the Fe:PO₄ ratio of the newly exposed sediment layer is sufficiently high (> 3.5 mol mol⁻¹; Chapter 2 & 3).

In eutrophied organic soft-water lakes, dredging of the nutrient-rich organic top layer of the sediment would be the best measure to restore water and sediment quality, provided that they are isolated from external eutrophic or alkaline surface water and groundwater (Chapter 5; Brouwer & Roelofs, 2001). However, if dredging is not possible and the top layer of the sediment remains anaerobic, colonization by soft-water macrophytes will only be possible from lake banks where the organic layer has been removed by sod cutting.

P IMMOBILIZATION METHODS

In situations where PO₄ concentrations in the sediment pore water and PO₄ mobilization rates to the water layer are found to be too high, as indicated by the pore water ratios described above, various Fe, Al and Ca compounds have been added to immobilize PO₄ and raise the pore water ratios to the desired levels (Smolders *et al.*, 1995; Naselli *et al.*, 2003; Reitzel *et al.*, 2005). However, these additions all have serious drawbacks.

Fe addition

Iron chloride injection into the sediment appeared to be more effective than addition to the water layer (Chapter 5), because it precipitated with PO₄ in the sediment and increased Fe:PO₄ ratios in the pore water to target levels above 1-3.5 mol mol⁻¹ (Chapter 2 & 3; Smolders *et al.*, 2001), preventing PO₄ mobilization to the water layer. Fe addition to the water layer was also much less effective in binding PO₄, because lower doses of Fe had to be used to prevent too strong acidification of the water layer. Surface water addition is therefore not recommended as a restoration measure in moderately buffered systems.

The addition of 100 g Fe m⁻² to the sediment led to the most efficient PO₄ binding and the lowest water turbidity in organic soft-water lakes (Chapter 5). Besides that, Fe:PO₄ ratios in the sediment pore water were maintained at a very high level and pore water PO₄ concentrations remained low. An equal dosage of Fe was used by Boers *et al.* (1994) and Smolders *et al.* (1995) in alkaline fen waters, but they showed that Fe addition to sediments only remained effective for one year. Therefore, Fe addition is only a useful measure in fen waters with a moderately reductive sediment, a low influx of SO₄-rich and PO₄-rich water, low sulphide concentrations, and therefore low Fe consumption rates (Boers *et al.*, 1994, Smolders *et al.*, 1995; Roden & Edmonds, 1997). In that case, Fe addition will remain effective for much longer periods and the measure needs to be

repeated less frequently. An example of a successful Fe addition is that in the soft-water lake Beuven-Zuid (the Netherlands), where only 25 g Fe m⁻² was applied to the sediment and where the water remained clear for more than 25 years (J.G.M. Roelofs, Radboud University Nijmegen, personal communication).

The hydrolysis and oxidation of Fe in the water layer can, however, lead to a temporary decrease in alkalinity and pH, which may have a negative impact on the growth of many aquatic macrophytes, although seed viability and germination are normally not affected by a transient decrease in pH (Arts & Van der Heijden, 1990; Bellemakers *et al.*, 1996). The increase in NH₄, Ca, Mg and Mn concentrations after Fe addition (Chapter 5) is most probably caused by cation exchange from the sediment adsorption complex by Fe (Ponnamperuma 1972). Ca release may even be beneficial, because Ca may bind PO₄ by (co)precipitation at higher pH values (Stumm & Morgan, 1996). The NH₄ that is released will be nitrified to NO₃ in the oxidized water layer, and denitrification will finally result in the loss of N from the system, which is beneficial to macrophyte communities (Brouwer *et al.*, 2002; Smolders *et al.*, 2002). However, if NH₄ accumulates in the sediment it may become toxic to sensitive macrophyte species (Chapter 2; Roelofs, 1991; Smolders *et al.*, 2003a; Lucassen *et al.*, 2006).

Al addition

Instead of Fe, it may be a better option to use redox-insensitive Al compounds in alkaline fens, provided that pH and buffer capacity are high enough to prevent toxic effects (Cooke *et al.*, 1993; Lewandowski *et al.*, 2003). On the long term, however, amorphous Al(OH)₃ will crystallize (e.g. to gibbsite), which will decrease its effectiveness and even lead to release of formerly bound P (Berkowitz *et al.*, 2005).

Lime addition

The application of CaCO₃ (lime) to bind P in fen waters is doubtful, because a strong increase in alkalinity and pH after lime addition leads to increased decomposition rates in organic soils and subsequently to additional nutrient mobilization from the sediment (Chapter 6; McKinley & Vestal, 1982; Smolders *et al.*, 2006). Besides that, calcium can displace ammonium from the soil absorption complex, which also leads to long-term mobilization of ammonium and nitrate. Therefore, liming is not recommended as a restoration measure for organic soils, but it may be used as an additional restoration measure in soils with a low organic content.

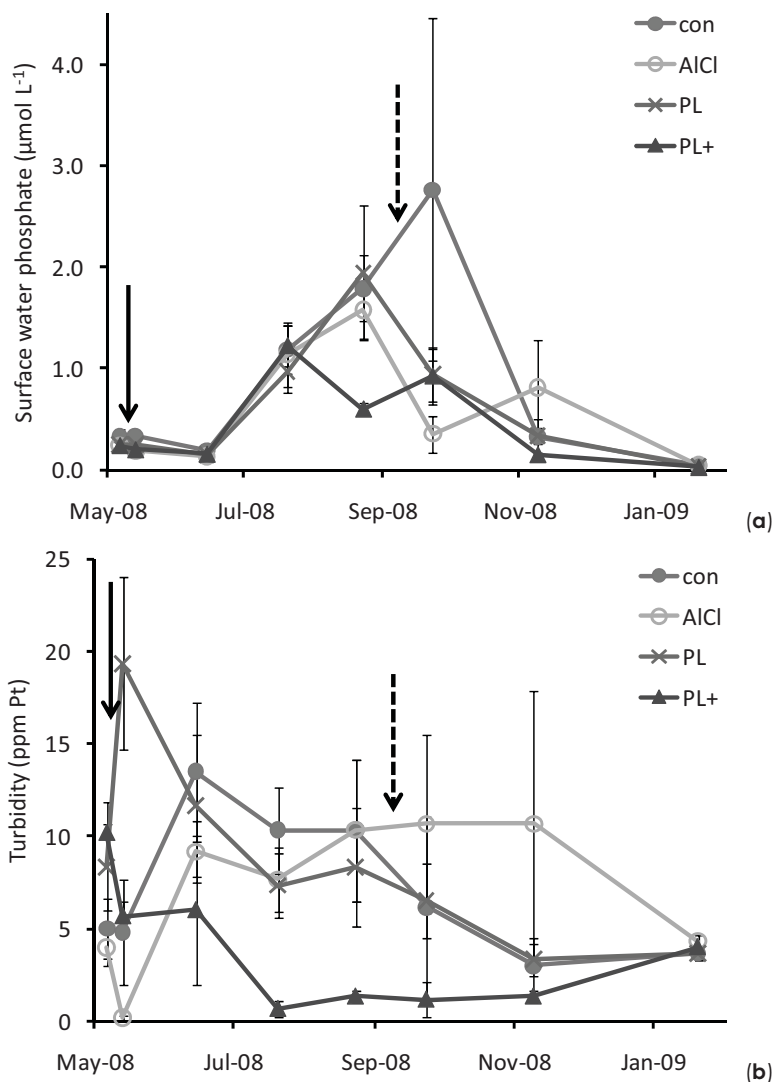


Figure 5. Surface water PO₄ concentrations (a) and turbidity (b) in an enclosure experiment in the Dutch peat lake Tienhovense Plassen (Geurts & Van de Wouw, unpublished data). The following treatments were applied (n=3): con = control, AICI = 40 g m⁻² aluminium chloride, PL = 385 g m⁻² LMC (Phoslock®), PL+ = 425 g m⁻² LMC (Phoslock®) + polyaluminum chloride. The solid arrow indicates the start of the treatments. The dashed arrow indicates PO₄ addition of 10 μmol L⁻¹. PO₄ concentrations in the PL+ treatment differed significantly from the control ($P = 0.020$; GLM repeated measures). For turbidity there was a significant time x treatment effect ($P = 0.000$; GLM repeated measures).

Addition of lanthanum-modified clay

Application of Phoslock®, a lanthanum-modified bentonite clay (LMC; Douglas, 2002), could avoid the possible adverse effects of liming. The highest dose used was able to decrease PO₄ mobilization to the water layer in sandy soils (Chapter 6), indicating that LMC application may be most effective in a flooded situation. This will prevent blooms of algae and cyanobacteria and create better light conditions for the growth of various plant species (Roelofs, 1991; Jeppesen *et al.*, 2005). Fig. 5a shows that the addition of LMC and AlCl decreased surface water PO₄ concentrations in a peat lake during the growing season, but only the combined addition of LMC and poly-AlCl led to significantly decreased PO₄ concentrations and to a long-term clear water state (Fig. 5b).

Because LMC was originally developed for application in surface waters, it has only been used in aquatic systems without peat sediment till now, where it proved to be very successful in reducing PO₄ mobilization and algal growth (Robb *et al.*, 2003; Akhurst *et al.*, 2004; Yang *et al.*, 2004). LMC also decreased pore water PO₄ concentrations, plant biomass and shoot length in sandy soils, but sometimes increased nitrate and ammonium concentrations (Chapter 6). However, the mobilization of nitrate and ammonium did not last very long, because it was primarily released from the LMC itself. The release of lanthanum was rather low, because lanthanum ions are very tightly adsorbed to the bentonite clay (Ross *et al.*, 2008). The measured concentrations are not expected to be toxic to plants, animals or micro-organisms (Greenop & Robb, 2001; Persy *et al.*, 2006), although plants may accumulate lanthanum in their tissue (Weltje *et al.*, 2002).

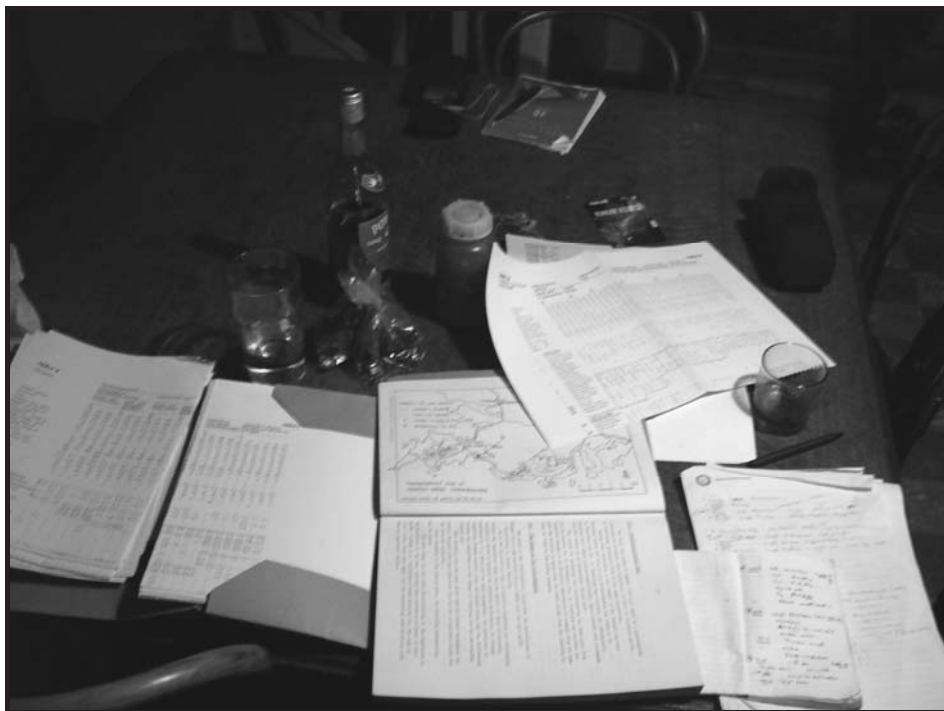
Chapter 6 showed that LMC decreased Olsen-P concentrations in some of the P-rich sandy wetland soils, but not below the threshold of 200-300 µmol kg⁻¹ soil (260-390 µmol L⁻¹ fresh soil; Smolders *et al.*, 2008). This means that *J. effusus* can still dominate on these soils during moist or waterlogged conditions or when the water layer covering the soil is thin enough to allow its growth, without opportunities for a biodiverse vegetation to develop (Janssens *et al.*, 1998). This implies that *J. effusus* may have mobilized organically bound P or P bound by Fe, Al or Ca in these soils (Dinkelaker *et al.*, 1989; Shen *et al.*, 2002; Tweel & Bohlen, 2008). It is less likely that *J. effusus* can mobilize P that is bound by LMC, because lanthanum has strong ionic binding characteristics (Stumm & Morgan, 1996) and forms highly stable minerals with a low solubility in the presence of phosphates (Firsching, 1992; Douglas, 2000).

An additional problem that may arise if LMC is mixed with the upper 10 cm of the soil in the field is that *J. effusus* or other rapidly colonizing species can form deeper roots, to reach untreated P-rich soil layers. Therefore, LMC could only be used if the whole P-saturated soil layer is treated (Smolders *et al.*, 2008). Because high amounts are needed to be effective in reducing PO_4 concentrations and plant growth, it will only be cost-effective in combination with top soil removal or if the top soil is heavily polluted and top soil removal is too expensive. It is difficult to indicate the cost-effectiveness in general, because it strongly depends on the actual depth of the P-rich soil layer and on the pollution status of the soil. If top soil removal is not preferred, the greatest effect of LMC addition in order to restore wetlands on former agricultural sandy soils can be expected for flooded situations, for example in water storage areas. This will create a better initial situation for the development of a more biodiverse aquatic or semi-aquatic vegetation on former agricultural sandy soils than in a waterlogged or moist situation, where domination of eutrophic plant species like *J. effusus* leads to very low biodiversity (Kemmers *et al.*, 2004; Lamers *et al.*, 2005). Another advantage of using LMC in water storage areas would be that temporarily stored surface water would not become enriched with PO_4 .

General conclusion

This thesis emphasizes the essential role of biogeochemical knowledge in the ecological restoration of fens and peat lakes: the regulation of PO_4 mobilization, SO_4 reduction, sulphide toxicity and peat decomposition all have important implications for water and sediment quality, and for vegetation development. As indicators of both biogeochemical processes and potential biodiversity, sediment and sediment pore water ratios provide valuable diagnostic and prognostic tools for the restoration of fens and peat lakes. These ratios are not only useful for risk assessment, but also for selecting the most promising measures. In many cases, however, it turns out to be difficult to tackle the high P concentrations present by P immobilization methods or dredging. Besides decreasing the influx of nutrient-rich water, it is therefore important to prevent the influx of alkaline and S-rich water, because this hydrological measure will slow down decomposition processes and internal mobilization of nutrients. It can be concluded that if the right measures are chosen on the basis of simple measurements, it is certainly possible to restore the biodiversity in declined fens and peat lakes.

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Nederlandse samenvatting

Herstel van laagveenwateren: een biogeochemische kijk op de zaak



Laagveenplas Terra Nova met op de achtergrond de Loenderveense Molen

Speciaal bedoeld voor niet-ecologen

*Ecologen wordt daarom aangeraden om
(ook) de Synthesis (Hoofdstuk 7) te lezen*

Laagveenwateren

Laagvenen zijn van oorsprong veenvormende, waterrijke gebieden die gevoed worden door mineraalrijk grondwater en/of oppervlaktewater vanuit rivieren, meren, kanalen en sloten. In Nederland is door grootschalige vervening (turfwinning; Figuur 1) in deze laagvenen een halfnatuurlijk landschap ontstaan van plassen, petgaten, sloten, legakkers, trilvenen, rietmoerassen, veenweiden en broekbossen (Figuur 2 op blz. 156). Laagveenwateren laten hierbij alle fases zien in de natuurlijke opeenvolging van ondergedoken en drijvende waterplanten via drijvende veenpakketten (kraggen) met moeras- en oeverplanten tot moerasbos. Dit wordt ook wel verlanding genoemd (Figuur 1).



Figuur 1. Links: Turfwinning met baggerbeugels in een laagveengebied in West-Nederland omstreeks 1800. Het veen uit de petgaten wordt op legakkers te drogen gelegd, platgestampt en tot turven gesneden.

Rechts: Verlanding van een laagveenplas door natuurlijke opeenvolging van planten in de tijd en ophoping van veen, dat uit dode planten bestaat (Wandplaat in het Poleski National Park museum, Urszulin, Polen).

Achteruitgang

Wereldwijd worden laagveenwateren bedreigd door verschillende milieuproblemen, zoals verdroging, vermesting ("eutrofiëring"), vervuiling en klimaatverandering. Dit heeft geleid tot meer veenafbraak en baggerproductie, het vrijkomen van voedingsstoffen, het verdwijnen van plant- en diersoorten

(lagere soortenrijkdom) en het uitblijven van verlanding. De grootste problemen worden veroorzaakt door een toename van de voedingsstof **fosfaat** en door vervuiling met **sulfaat** (zwavel). Daarnaast speelt ook de hardheid van het water een rol.

Fosfaat spoelt uit vanaf bemeste landbouwpercelen of komt binnen via rivierwater, maar ook komt fosfaat vaak vrij uit de waterbodem van de laagveenplas zelf ("nalevering"). De hoeveelheid fosfaat die uit de waterbodem vrijkomt, bedraagt maar liefst bijna de helft van de totale aanvoer van fosfaat in laagveenwateren (Hoofdstuk 3). Een toename van fosfaat zorgt er vooral voor dat voedselarm, helder water verandert in voedselrijk, troebel water. Hierdoor zijn verschillende kenmerkende waterplanten (zoals Krabbenscheer, Plat fonteinkruid en Spits fonteinkruid) op grote schaal verdwenen. Ze zijn namelijk weggeconcentreerd door woekerende soorten zoals Grof hoornblad, Smalle waterpest of algen. Het blijkt dat het aantal soorten waterplanten, en vooral het aantal zeldzame soorten, afneemt als er meer fosfaat in het water zit (Hoofdstuk 2). Het is vervolgens heel moeilijk om weer helder water te krijgen door de grote nalevering van fosfaat uit de waterbodem.

Sulfaat komt binnen via grondwater (in gebieden met veel ijzer-zwavelverbindingen zoals pyriet in de ondergrond), rivierwater of neerslag ("zure regen"). Sulfaat wordt in zuurstofloze waterbodems omgezet in de giftige stof **sulfide** ("rotte-eiergas"). Deze omzetting leidt ook tot veenafbraak en het vrijkomen van voedingsstoffen en andere gifstoffen, zoals **ammonium**. Verschillende soorten waterplanten zijn gevoelig voor deze gifstoffen en zullen verdwijnen ten gunste van slechts enkele soorten die er wel tegen kunnen. Hierdoor zal de soortenrijkdom in een laagveenplas dalen. Bovendien wordt het water harder, waardoor de afbraak nog sneller gaat.

Omdat laagveenwateren relatief ondiep zijn, wordt de waterkwaliteit en de groei van waterplanten voor een groot deel bepaald door het opwervelen van bodemdeeltjes door wind of vissen en door processen die plaatsvinden in de waterbodem. Het gaat dan om chemische omzettingen door bacteriën, schimmels en andere levende wezens in de bodem ("biogeochemische processen"). Van de andere kant kunnen waterplanten de processen in de waterbodem juist beïnvloeden door bijvoorbeeld het water boven de bodem zuurstofloos te maken (Hoofdstuk 7), of door het opwervelen van bodemdeeltjes tegen te gaan waardoor de troebelheid van het water vermindert.

Het nationale onderzoeksprogramma OBN Laagveenwateren

Het onderzoek in dit proefschrift maakt deel uit van het nationale onderzoeksprogramma OBN Laagveenwateren van het Ministerie van Landbouw, Natuur en Voedselkwaliteit. De afkorting OBN stond vroeger voor "Overlevingsplan Bos en Natuur" en tegenwoordig voor "Ontwikkeling en Beheer Natuurkwaliteit". Het doel van dit onderzoeksprogramma was om de achteruitgang van laagveenwateren in Nederland te onderzoeken door de processen die hierbij een rol spelen te ontrafelen en door mogelijke herstelmaatregelen uit te proberen. De resultaten van dit toegepaste onderzoek moeten simpele meetmethoden opleveren, die direct gebruikt kunnen worden door water- en natuurbeheerders. Hiermee kunnen zij makkelijker kiezen tussen verschillende herstelmaatregelen die vermessing en vervuiling moeten tegengaan en de soortenrijkdom in laagveenwateren moeten laten toenemen. Dit onderzoeksprogramma was alleen mogelijk door samenwerking tussen verschillende onderzoeksinstituten, zodat naar het hele ecosysteem kon worden gekeken: water- en bodemkwaliteit, algen, planten en dieren (Figuur 3 op blz. 156). Er werd gebruik gemaakt van vergelijkend veldonderzoek in verschillende typen laagveenwateren (Hoofdstuk 2&3), veldexperimenten (Hoofdstuk 5&7), experimenten in proefbakken (Hoofdstuk 4) en in kweekruimtes (Hoofdstuk 3&6), en metingen op het laboratorium.

Belangrijke processen

HET VRIJKOMEN VAN DE VOEDINGSSTOF FOSFAAT

Normaal gesproken wordt fosfaat in het zuurstofrijke, bovenste laagje van de waterbodem aan ijzer gebonden, waardoor fosfaat niet of nauwelijks vrijkomt in het water. De verhouding tussen ijzer en fosfaat in het bodemvocht is daarom belangrijk voor het al dan niet vrijkomen van fosfaat (Hoofdstuk 2&3). Als er onvoldoende ijzer aanwezig is om fosfaat te binden, dan bepaalt de hoeveelheid fosfaat in het bodemvocht hoeveel fosfaat er vrijkomt in het water. De ijzer:fosfaat verhouding in het bodemvocht bleek ook een belangrijke indicatie te geven van het aantal soorten zeldzame waterplanten dat in een laagveenplas voorkomt (Hoofdstuk 2).

Hoe goed fosfaat gebonden wordt in de bodem is ook afhankelijk van de hoeveelheid sulfaat (zwavel). Laagveenwateren hebben vaak een zuurstofloze bodem, waarin sulfaat en ijzer worden omgezet in giftig sulfide en ijzersulfide (Figuur 4 op blz. 157). Hierdoor blijft er minder ijzer over om fosfaat te binden

(lagere ijzer:fosfaat verhouding) en komt fosfaat dus vrij in het water (Hoofdstuk 2). Bovendien leidt deze omzetting tot veenafbraak in de bodem. Om erachter te komen hoeveel ijzer er nog beschikbaar is om fosfaat te binden in de bodem, is daarom de verhouding tussen ijzer en zwavel belangrijk. Als er in de bodem meer zwavel aanwezig is dan ijzer, is er nauwelijks ijzer beschikbaar om fosfaat te binden, waardoor fosfaat vrijkomt in het water (Hoofdstuk 3).

Behalve door deze chemische processen komt fosfaat ook vrij na opwerveling van bodemdeeltjes door wind, door vissen die in de bodem wroeten en door het afsterven van algen en waterplanten.

SULFAATVERVUILING

In Hoofdstuk 4 werd sulfaatvervuiling uitgetest in proefbakken ("mesocosms") van 1 m² met mini-laagvenen. Deze mini-laagvenen bestonden uit een oever, een waterlaag, een waterbodem en verschillende water- en oeverplanten. Kunstmatige sulfaatvervuiling van het water bleek in deze proefbakken al binnen 1 jaar te leiden tot meer sulfaat en giftig sulfide in zowel de waterbodem als de oever. Het ontstaan van sulfide geeft aan dat het veen in de proefbakken al snel zuurstofloos is geworden, waardoor sulfaat omgezet kon worden in sulfide en er meer veenafbraak was. Bij deze veenafbraak kwamen vervolgens humuszuren en extra voedingsstoffen vrij, waaronder fosfaat en ammonium, waardoor de groei van gevoelige water- en oeverplanten negatief beïnvloed werd.

Als er weinig ijzer aanwezig is in de bodem, dan vindt er ophoping plaats van het giftige sulfide. Dit leidde tot het verdwijnen van gevoelige water- en oeverplanten en een afname van minder gevoelige planten in de proefbakken (Hoofdstuk 4). Dit effect bleek ook in verschillende Nederlandse laagveenwateren op te treden (Hoofdstuk 2). Bovendien groeiden er in de proefbakken minder oeverplanten het water in, wat een belangrijke belemmering vormt voor de natuurlijke verlanding van laagveenwateren.

Verrassend genoeg bleek dat de planten in de proefbakken minder gevoelig waren voor sulfaatvervuiling als de oevers bemest werden (Figuur 5 op blz. 157). Dit komt doordat planten harder konden groeien, waardoor het giftige sulfide minder effect had. Daarnaast konden de planten meer wortels vormen, waardoor ze meer zuurstof in de bodem konden pompen. Zuurstof zorgt er namelijk voor dat sulfide in de bodem weer omgezet wordt in sulfaat, dat niet giftig is. Dit betekent dat de negatieve effecten van sulfaatvervuiling beïnvloed kunnen worden door de voedselrijkdom van de bodem. In voedselrijke laagveenwateren worden de giftige effecten van sulfide dus gemaskeerd. Het

gevaar hiervan is dat maatregelen die de voedselrijkdom van een gebied verlagen onbedoeld ervoor kunnen zorgen dat de giftige effecten van sulfide weer toenemen.

Ophoping van ammonium kan ook tot giftige effecten leiden. Normaal gesproken is ammonium vooral giftig voor planten als de bodem zuur is, maar ammonium kan bij waterplanten ook giftig zijn als dit niet zo is. In Hoofdstuk 4 kon dit niet worden aangetoond, maar in Hoofdstuk 2 bleek dat de aanwezigheid van ammonium in het water een negatieve invloed had op het voorkomen van zeldzame plantensoorten.

VEENAFBRAAK

Zoals verwacht, verliep de afbraak van veen en de vorming van kooldioxide (CO_2) sneller onder invloed van zuurstof (Hoofdstuk 3). Er komt bijvoorbeeld meer zuurstof in de bodem als het waterpeil in een veengebied wordt verlaagd, wat in de meeste gevallen dus tot meer veenafbraak zal leiden. In de onderzochte laagvenen bleek de afbraaksnelheid daarnaast voornamelijk bepaald te worden door de hoeveelheid organisch materiaal in de bodem. De kwaliteit van dit organisch materiaal en de grootte van de bodemdeeltjes bleken niet bepalend te zijn. Afbraaksnelheden waren het laagst in waterbodems die al verder afgebroken waren en hoger in intacte veenbodems.

In Hoofdstuk 3 bleek verder dat een snellere veenafbraak niet per se hoeft te leiden tot het vrijkomen van meer voedingsstoffen. Dit komt doordat de onderzochte veenbodems met een hoge afbraaksnelheid juist relatief weinig voedingsstoffen bevatten. Bovendien konden de vrijgekomen voedingsstoffen (vooral fosfaat) goed worden gebonden in de bodem. In deze relatief intacte veenbodems kan een toename van de voedselrijkdom ervoor zorgen dat het veen sneller afgebroken wordt, wat de veenvorming en verlanding in laagveenwateren erg moeilijk maakt. De veenbodems met een lage afbraaksnelheid bevatten juist veel voedingsstoffen en konden de vrijgekomen voedingsstoffen ook slechter binden. De grote hoeveelheid voedingsstoffen leidt vervolgens tot een sterke toename van algen, die van het water een groene soep maken. Bovendien komen bij veenafbraak bodemdeeltjes en humuszuren vrij in het water, waardoor er nog minder licht doordringt onder water en waterplanten dus nog moeilijker onder water kunnen groeien.

Betekenis van mijn onderzoek voor het beheer

EENVOUDIGE METINGEN OM DE JUISTE HERSTELMAATREGELEN TE KIEZEN

De verhoudingen tussen verschillende chemische stoffen in de waterbodem blijken waardevolle informatie te geven voor het herstel van de waterkwaliteit en de soortenrijkdom in laagveenwateren (Hoofdstuk 2&3). Ze kunnen zowel gebruikt worden voor een diagnose van de huidige situatie als voor een prognose van het mogelijke herstel. Er wordt door water- en natuurbeheerders meestal alleen in het water gemeten en niet in de bodem. Dit moet dus veranderen.

De ijzer:fosfaat verhouding in het bodemvocht bleek geschikt om de nalevering van fosfaat uit de waterbodem te bepalen, omdat deze verhouding relatief stabiel is. Als deze verhouding lager is dan 1:1 tot 3,5:1, dan is het risico op het vrijkomen van fosfaat in het water veel groter en zullen er meer algen en minder soorten waterplanten kunnen groeien. Dit betekent dat het meten van ijzer en fosfaat in het bodemvocht een handige methode is om op een snelle manier de nalevering van fosfaat te kunnen bepalen. Om praktische redenen kan het bepalen van de totale ijzer:fosfor verhouding in de waterbodem soms handiger zijn. In het algemeen kan worden gesteld dat laagveenwateren en voormalige landbouwgebieden op veen met een ijzer:fosfaat verhouding boven de 10:1 zeer geschikt zijn om herstelmaatregelen in uit te voeren (Hoofdstuk 2). De ijzer:fosfaat verhouding kan vervolgens ook gebruikt worden om de herstelmaatregelen te optimaliseren.

De ijzer:zwavel verhouding in de waterbodem gaf ook een belangrijke indicatie van de hoeveelheid ijzer die beschikbaar is om fosfaat te binden. Er komt veel meer fosfaat vrij in het water als deze verhouding lager is dan 1:1 (Hoofdstuk 3). Het is vaak moeilijk om een gunstigere verhouding tussen ijzer en zwavel in de bodem te krijgen, omdat zwavelverbindingen hiervoor omgezet moeten worden in sulfaat onder invloed van zuurstof (door verdroging). Dit sulfaat moet vervolgens ook afgevoerd worden. Een andere mogelijkheid is om kunstmatig ijzer toe te dienen aan een laagveenplas (Hoofdstuk 5).

VERMINDERING VAN INTERNE NALEVERING EN EXTERNE AANVOER VAN VOEDINGSSTOFFEN

Omdat voedingsstoffen (fosfaat, nitraat, ammonium) en gifstoffen (sulfide, ammonium) in laagveenwateren voor een groot deel uit de waterbodem vrijkomen, is het erg belangrijk om zowel het vrijkomen van deze stoffen uit de waterbodem (interne nalevering) als de aanvoer van buitenaf te verlagen. Hiervoor is het belangrijk om de inlaat van voedselrijk en sulfaatrijk water te

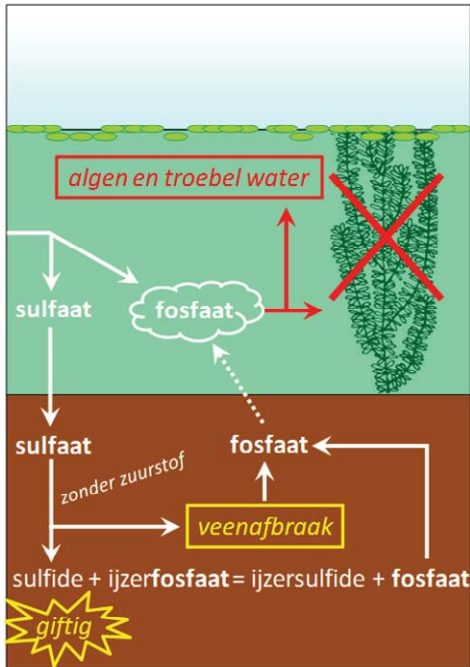
beperken (zie eerder bij "Sulfaatvervuiling"), bijvoorbeeld door een laagveenplas (gedeeltelijk) te isoleren.



Figuur 2. Luchtfoto van laagveengebied Het Hol, omringd door de Loosdrechtse plassen (Foto: Leon Lamers, tijdens een vlucht in mei 2005). Het water in Het Hol is helder en blauw, net als in de zandplas linksboven. Het water in de veenplas onderaan is echter troebel.



Figuur 3. Het onderzoeksteam van OBN Laagveenwateren gezamenlijk aan het werk in een petgat met Krabbenscheer in de Weerribben (Foto: Leon Lamers).



Figuur 4. Schema waarin weergegeven wordt hoe vervuiling door sulfaat kan leiden tot het vrijkomen van fosfaat, algengroei en troebel water zonder ondergedoken waterplanten. In de zuurstofloze bodem wordt sulfaat omgezet in giftig sulfide, waardoor ook veenafbraak plaatsvindt. Sulfide bindt vervolgens aan ijzer, waardoor er fosfaat vrijkomt in het water. Daar zorgt een toename van fosfaat ervoor dat voedselarm, helder water verandert in voedselrijk, troebel water.



Figuur 5. Foto's van 2 proefbakken met een bemeste oever na 3 jaar. **Links:** zonder sulfaat. **Rechts:** met sulfaat. Sulfaatvervuiling heeft dus een duidelijk negatief effect op de plantengroei.

In de Wieden en de Weerribben wordt al zo weinig mogelijk water met een slechte kwaliteit ingelaten, wat heeft geleid tot een betere waterkwaliteit en meer kans op de groei van ondergedoken waterplanten, vooral dieper het gebied in (Hoofdstuk 2&7). Het hiermee gepaard gaande tijdelijk lager worden van het waterpeil en droogval van oevers kan voordelig zijn, doordat dit de waterbodem zuurstofrijker maakt en het kiemen van zaden bevordert. In kleinere

laagveenwateren, zoals sloten en petgaten, kan isolatie echter juist leiden tot het ophopen van zuurstofloze bagger met voedingsstoffen en gifstoffen erin, doordat er geen doorstroming meer is (Hoofdstuk 7). Ook kan de verspreiding van planten en dieren gehinderd worden.

BAGGEREN ALS HERSTELMAATREGEL

Het baggeren van de waterbodem wordt vaak gebruikt als herstelmaatregel in voedselrijke laagveenwateren. In laagveenwateren met hard, sulfaatrijk water en een ijzerarme bodem kan baggeren van de bovenste sliblaag echter een oudere veenlaag blootleggen, die sneller afbreekt dan de weggehaalde sliblaag die al ver afgebroken was. Om baggeren succesvol te laten zijn, is het dus ook daarvoor nodig om zo weinig mogelijk hard en sulfaatrijk water in te laten. Dit om te voorkomen dat er versnelde veenafbraak optreedt en er extra voedingsstoffen vrijkomen. Baggeren is daarom alleen een geschikte maatregel als de ijzer:fosfaat verhouding in de blootgelegde veenlaag hoog genoeg is (Hoofdstuk 2&3).

KUNSTMATIG VASTLEGGEN VAN FOSFAAT ALS HERSTELMAATREGEL

Als er te veel fosfaat uit de waterbodem vrijkomt in het water, dan kunnen verschillende stoffen worden toegediend om fosfaat kunstmatig vast te leggen in de bodem. Deze stoffen bevatten vaak ijzer, aluminium of calcium (kalk), die allemaal hun nadelen hebben. Daarom is er in Hoofdstuk 6 ook een nieuwe stof uitgetest: Phoslock®.

Ijzer toedienen

In een cilinderexperiment in het Uddelermeer, een geïsoleerd, voedselrijk meer met een veenbodem, bleek het injecteren van ijzer in de waterbodem effectiever dan het toedienen van ijzerpoeder aan het water. Dit kwam doordat de ijzer:fosfaat verhouding in het bodemvocht in het eerste geval veel hoger werd en er minder fosfaat vrijkwam in het water. Ook werd er in het water een lagere dosis toegediend om verzuring van het water te voorkomen. De meest effectieve fosfaatbinding werd gerealiseerd met een dosis van 100 gram ijzer per m², waarbij ook het water het helderst werd (Figuur 6 op blz. 160). In laagveenwateren die fosfaat- en sulfaatrijk water ontvangen werkt deze maatregel maar kort, omdat het ijzer al na een jaar opgebruikt is om fosfaat en giftig sulfide te binden. Het nadeel van het toedienen van ijzer is ook dat het verzuring kan veroorzaken, wat een negatief effect heeft op veel waterplanten en -dieren. Dit is afhankelijk van de hardheid van het water. Daarnaast maakt ijzer ammonium vrij uit de bodem, wat bij ophoping giftig kan zijn voor sommige waterplanten (Hoofdstuk 2).

Aluminium toedienen

Het voordeel van aluminium ten opzichte van ijzer is dat de binding met fosfaat niet gevoelig is voor sulfide, omdat aluminium geen sulfide kan binden. Aluminium kan echter wel verzuring van het water veroorzaken. Bovendien blijkt aluminium na verloop van tijd het fosfaat minder effectief te binden, waardoor gebonden fosfaat zelfs weer vrij kan komen in het water.

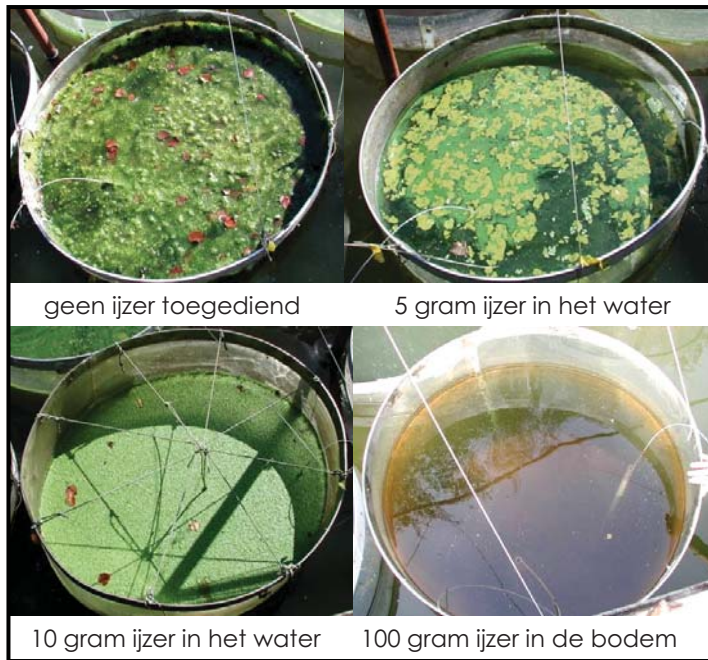
Bekalken

Het nadeel van bekalken is dat de zuurgraad en de hardheid van het water en de bodem toenemen, waardoor veenafbraak gestimuleerd wordt en voedingsstoffen juist vrijkomen (Hoofdstuk 6). Daarnaast kan kalk ammonium vrijmaken uit de bodem. Bekalken wordt daarom niet aangeraden als herstelmaatregel in veenbodems.

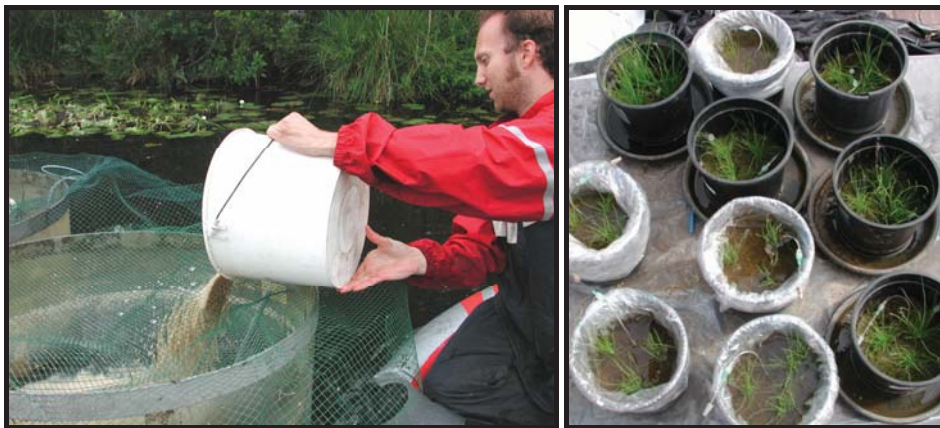
Phoslock® toedienen

Phoslock® bestaat uit kleideeltjes met daarin het metaal lanthaan als fosfaatbindende stof. In een cilinderexperiment in de Tienhovense plassen werd de werking van Phoslock® vergeleken met aluminium (Figuur 7; Hoofdstuk 7). Beide stoffen bleken in staat om fosfaat in het water te verminderen, maar alleen een combinatie van beide stoffen leidde tot minder fosfaat en helder water op de lange termijn.

In veel gebieden in Europa, en zeker in Nederland, worden op voormalige landbouwgronden nieuwe natuurgebieden ontwikkeld. Vaak gaat het hierbij om ontwikkeling van nieuwe moerassen en plassen. Het probleem is echter dat de bodem tjokvol fosfaat zit, met alle gevolgen van dien. In een potexperiment met voormalige landbouwbodems (zand en veen) werd daarom de werking van Phoslock® vergeleken met kalk (Figuur 7; Hoofdstuk 6). Alleen in overstroomde zandbodems bleek de hoogste dosis Phoslock® in staat om het vrijkomen van fosfaat in de waterlaag te verminderen, wat in de praktijk zal leiden tot minder algengroei, helderder water en groei van waterplanten. Zoals gehoopt werd de groei van de ongewenste plant Pitrus (Figuur 8 op blz. 161) geremd, maar niet genoeg om de overheersing van deze soort te verminderen. Dit kwam doordat er in de bodem nog teveel fosfaat beschikbaar was voor Pitrus. Waarschijnlijk kan Pitrus fosfaat vrijmaken dat in de bodem gebonden is aan ijzer, aluminium, calcium of organisch materiaal. Bij gebruik van Phoslock® bleek er ook ammonium vrij te komen, maar dit was slechts tijdelijk en minder veel dan bij gebruik van kalk.



Figuur 6. Foto's van verschillende behandelingen met ijzerpoeder in cilinders in het Uddelermeer na 3 maanden.





Figuur 8. Overheersing van Pitrus op een legakker in De Deelen.



Figuur 9. Verschillende soorten drijvende en ondergedoken waterplanten in een sloot in Wapserveen.

Het nadeel van het gebruik van Phoslock® in voormalige landbouwgronden is dat ongewenste planten als Pitrus dieper kunnen wortelen dan de behandelde bodemlaag van 10 cm om toch aan voldoende fosfaat te komen. Het is echter te duur om ook diepere bodemlagen te behandelen. Daarom zal Phoslock® in

dat geval alleen rendabel zijn in combinatie met het afgraven van de bovenste laag van de bodem, of als de grond vervuild is en afgraven te duur is. Phoslock® zal het beste werken als voormalige landbouwgrond bij natuurontwikkeling diep genoeg wordt overstroomd, zodat er geen planten als Pitus kunnen groeien. Er is dan meer kans op een grotere soortenrijkdom aan waterplanten (Figuur 9). In overloopgebieden heeft het gebruik van Phoslock® daarnaast het voordeel dat tijdelijk opgeslagen water niet verontreinigd wordt met fosfaat.

Algemene conclusies van mijn onderzoek

Dit proefschrift benadrukt hoe belangrijk het is om biogeochemische kennis te hebben bij het ecologisch herstel van laagveenwateren. Het vrijkomen van fosfaat, de omzetting van sulfaat in giftig sulfide en veenafbraak hebben allemaal belangrijke consequenties voor de water- en bodemkwaliteit en de groei van water- en oeverplanten. De verhoudingen tussen verschillende chemische elementen in de waterbodem blijken een goede indicatie te geven van zowel biogeochemische processen als soortenrijkdom. Deze verhoudingen kunnen daarom gebruikt worden om in te schatten hoe het er voor staat met een laagveenplas, en om de kansen op herstel goed te kunnen inschatten. Op die manier kunnen voor elke situatie de meest veelbelovende maatregelen worden gekozen. Het blijkt in veel gevallen echter moeilijk te zijn om de al aanwezige hoge fosfaatconcentraties te verlagen door baggeren of door fosfaat vast te leggen. Naast het verminderen van de aanvoer van voedselrijk water, is het daarom belangrijk om ook de aanvoer van hard, sulfaatrijk water te verminderen. Deze hydrologische maatregel zorgt voor een langzamere veenafbraak (met minder baggervorming) en het verminderd vrijkomen van voedingsstoffen uit de waterbodem.

Er kan gelukkig ook worden geconcludeerd dat het zeker mogelijk is om aangetaste laagveenwateren te herstellen, mits de juiste maatregelen worden gekozen. Dit kan op basis van eenvoudige metingen.

Dankwoord

Omdat het inmiddels al 8 jaar geleden is dat ik met mijn onderzoek ben begonnen en in die tijd 2 verschillende werkgevers en 5 contracten heb gehad, zijn er natuurlijk een heleboel mensen die ik wil bedanken voor hun bijdrage aan dit proefschrift.

Allereerst wil ik Leon bedanken. Jij bent al die jaren mijn directe begeleider geweest en nu logischerwijs ook mijn copromotor. Je was zowel een hulp bij het veldwerk (waarbij je telkens op een ijsje trakteerde na afloop), bij het uitdenken van nieuwe experimenten en bij het schrijven van dit proefschrift. Je bleef altijd positief en motiveerde mij om door te gaan. Zonder jou was het allemaal een stuk moeilijker gegaan. Ook de gezamenlijke reizen naar het buitenland zullen me altijd bij blijven: het veldwerk in Ierland en Polen en de congressen in o.a. Estland en Finland (met de onvergetelijke dropijsjes).

Natuurlijk bedank ik ook Jan, mijn promotor, voor zijn inbreng, deskundigheid en gezelligheid. Ik kende je al voor ik ging studeren, omdat ik op de middelbare school samen met je zoon Gijs onderzoekjes voor Biologie heb gedaan bij jou thuis en op de universiteit. Ook toen ging het al over algen en fosfaat herinner ik me. Achteraf gezien heeft die eerste kennismaking met jouw vakgebied ervoor gezorgd dat ik later op de afdeling Aquatische Ecologie & Milieubiologie terecht kwam, eerst als student en later als junior onderzoeker. Bedankt dat je me de kans hebt gegeven om te promoveren.

Fons, mijn andere copromotor, bedank ik voor zijn bijdrage aan zo'n beetje alle artikelen in dit proefschrift. Je kwam altijd met goede ideeën bij het opzetten en uitvoeren van experimenten en met nuttige suggesties bij het schrijven.

Het grootste deel van mijn onderzoek vond plaats binnen het onderzoeksprogramma OBN Laagveenwateren, gefinancierd door het Ministerie van LNV. Graag wil ik alle onderzoekers binnen het onderzoeksconsortium en het deskundigenteam Laagveenwateren bedanken voor hun praktische hulp en/of begeleiding. In het bijzonder noem ik hier Judith Sarneel (ik vond het leuk om met je samen te werken, vooral bij het gezamenlijke mesocosm experiment), Hein Pijnappel en Babette Bontes (het vele veldwerk in binnen- en buitenland in de 1^e fase van het onderzoek was erg gezellig met jullie), Miguel Dionisio Pires, Marjolijn Christianen, Harry Boonstra, Jos Verhoeven, Jos Schouwenaars, Marcel Klinge,

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Studenten zijn door de jaren heen onmisbaar gebleken bij het doen van experimenten en metingen in het veld en op het lab. Daarom wil ik de volgende MSc en BSc studenten heel erg bedanken voor hun harde werk: Bart, Jan en Paul (alledrie ook mede-auteur van een artikel), José (nu mijn collega en paranimf; succes met het uitzoeken van je jurk!), Bas, Bart-Jan, Erik, Karina, Kim, Pieter, Piet-Jan, Ruud en Sarah Faye.



Ook hebben verschillende collega's mij geholpen in het veld en met analyses op het lab. Martin, jij was een onmisbare kracht bij het vaak zware veldwerk, wat regelmatig beloond werd met kaartjes voor je favoriete club NEC. Bedankt ook dat je mijn paranimf wilt zijn! Roy, bedankt voor je hulp op het lab en in het veld,

maar natuurlijk ook voor de gezelligheid aan de koffietafel (bakkie doen?) en bij het organiseren van de voetbalpoules (dit jaar mogen we weer!). Germa, bedankt voor je praktische hulp op het lab en alle regelingen waarvoor ik bij je terecht kon. Voor de secretariële ondersteuning wil ik de beide José's en Maria hartelijk bedanken.



Bij onderzoekcentrum B-WARE bedank ik Rick, Jeroen, Judith, Moni, Atheer, Kim Phuong en meerdere stagiair(e)s voor de vele analyses die jullie voor mij gedaan hebben en hulp bij veldwerk. Jelle, Rien en Liesbeth, hartstikke bedankt voor jullie hulp bij het meten van vele monsters op de ICP en auto-analyzers van het GI. Gerard, Yvette, Walter en Harry, bedankt voor jullie hulp bij het mesocosm experiment, dat 3 jaar gelopen heeft bij het kassencomplex. Jan Klerkx (Bèta Vertalingen) bedank ik voor het corrigeren van het Engels in de hoofdstukken 2 t/m 6 van dit proefschrift.



Graag wil ik ook mijn andere collega's en oud-collega's van de afdeling Aquatische Ecologie & Milieubiologie, onderzoekcentrum B-WARE, Experimentele Plantenecologie, Dierecologie, Stichting Bargerveen en Milieukunde bedanken

voor de fijne tijd en de goede (werk)sfeer. In het bijzonder noem ik hier Marlies (tegelijk begonnen in het UL, heel lang mijn kamergenoot geweest en samen onderzoek gedaan in het "verre" Waterland), Roos (kamergenoot in het Huygensgebouw, leuk dat ik paranimf mocht zijn bij jouw promotie!), Artur (thanks for your help and for showing me some typical Polish food and drinks), Dries (bedankt voor het verhelpen van mijn computerproblemen), Bert (bedankt dat je in mijn contract bij B-WARE een deadline voor het afronden van mijn proefschrift opnam, want dit was een goede stimulans, ook al heb ik deze deadline niet gehaald!), Casper, Christian, Christina, Leon van den Berg, Maaike de Graaf, Marjolijn en Tjisse (allen tijdelijk kamergenoot geweest, bedankt voor de gezelligheid!), Eelke, Eric, Emiel, Esther, Eva, Ger, Hannie, Hilde, Ivan, Jan van Groenendaal, Joop, José, Maaike Weijters, Mark, Monique, Niels, Peter, Philippine en Roland (en niet te vergeten onze gevleugelde vrienden Rinus, Lori en Pummel). Het groepje mensen waarmee ik op vrijdag tussen de middag volleybal speel, wil ik bedanken voor de gezelligheid en de broodnodige sportieve afleiding.

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Als laatste wil ik Susan bedanken. Jij bent al meer dan 12 jaar mijn grote liefde, mijn belangrijkste steun en toeverlaat. We waren al snel maatjes in het eerste jaar van de opleiding Biologie (gelukkig was je uitgeloot voor Geneeskunde) en we hadden samen veel lol tijdens de practica en colleges. Gelukkig kon je daarna toch Geneeskunde gaan doen en ben je nu huisarts. Mede door deze gezamenlijke achtergrond ben je altijd erg geïnteresseerd geweest in mijn werk. Als ik vastliep met mijn onderzoek (vooral bij het schrijven), dan wist je me altijd op te vrolijken en zorgde je ervoor dat ik thuis het werk van me af kon zetten. Ook vond je het leuk om me een aantal keer te helpen met veldwerk. Door de geboorte van Ivan vormen we sinds januari met z'n drietjes een gezinnetje. Ivan, ik ben heel erg blij dat je er bent, nog voor mijn proefschrift af is. Ik hoop dat je dit boekje ooit zelf zal doorlezen als je later groot bent!

Jeroen

Curriculum vitae

Op 27 december 1978 werd ik geboren in Nijmegen. Ik groeide op in het Brabantse Beers en ging daar naar de Dr. Jan de Quayschool. Van 1991 tot 1997 zat ik op het Merletcollege in Cuijk (VWO). In 1997 begon ik met mijn studie Biologie aan de Katholieke Universiteit Nijmegen (KUN, inmiddels Radboud Universiteit geheten). Na 2 jaar ging ik verder met de bovenbouwstudie Natuurwetenschappelijke Milieukunde. In een milieuspecialistische stage bij de afdeling Aquatische Ecologie & Milieubiologie (KUN) deed ik onder begeleiding van Hilde Tomassen en Fons Smolders onderzoek naar de effecten van vernatten op het herstel van hoogveenvegetaties. Daarna deed ik een milieukundige stage bij TNO-NITG in Delft onder begeleiding van Geert van Wirdum en Rob Leuven (KUN). Hierin schreef ik een stappenplan voor de monitoring van hoogveenherstelprojecten. Na het afronden van mijn studie in 2001 deed ik een half jaar tijdelijk werk bij een uitzendbureau.

Begin 2002 werd ik voor 1 jaar aangesteld als junior onderzoeker op de afdeling Aquatische Ecologie & Milieubiologie aan de KUN, waar ik eerder stage had gelopen, om toegepast onderzoek te gaan doen. Ik deed o.a. onderzoek in het Uddelermeer (zie Hoofdstuk 5 van dit proefschrift) en in boerensloten in Waterland, naast verschillende kleine projecten. Begin 2003 werd mijn contract verlengd, omdat het 3-jarig project OBN Laagveenwateren (1^e fase) van het Ministerie van LNV werd opgestart. Dit was een gezamenlijk project met de Universiteit Utrecht (Landschapsecologie), het NIOO in Nieuwersluis (Centrum voor Limnologie), Stichting Bargerveen, Witteveen+Bos (Integraal Waterbeheer), Wetterskip Fryslân en Alterra (Ecologie & Milieu). Mijn onderwerp binnen dit project was water- en bodemkwaliteit in relatie tot vegetatieherstel. In 2006 werd het project vervolgd met een 2^e fase, die ruim 3 jaar duurde. Hiervoor werd ik aangesteld bij Onderzoekcentrum B-WARE, een spin-off bedrijf van de Radboud Universiteit. Vanaf juli 2009 ben ik weer 2 jaar in dienst bij de afdeling Aquatische Ecologie & Milieubiologie en doe ik onderzoek naar de effecten van ijzersuppletie in de laagveenplas Terra Nova, samen met het NIOO in Nieuwersluis en Waternet.



Vegetatiesuccessie in Het Hol

Onderzoekcentrum B-WARE



Onderzoekcentrum B-WARE B.V. is een spin-off bedrijf van de afdeling Aquatische Ecologie & Milieubiologie, welke deel uitmaakt van het onderzoeksinstituut IWW (Institute for Water and Wetland Research) van de Radboud Universiteit Nijmegen. B-WARE werd in november 2002 opgericht en combineert de expertise van zuiver wetenschappelijk en toegepast universitair onderzoek. Kennisontwikkeling en -uitwisseling tussen de Universiteit en B-WARE is het uitgangspunt en staat borg voor hoogwaardig toegepast onderzoek, noodzakelijk voor het oplossen van praktijkvragen van opdrachtgevers.

Specialisatie

De werkwijze bestaat uit de combinatie van analyses in de veldsituatie en het opzetten en uitvoeren van veldexperimenten en experimenten onder gecontroleerde laboratoriumcondities, naast deskresearch. De verkregen resultaten dragen direct bij aan het ontwikkelen van nieuwe inzichten binnen het natuur- en waterbeheer en worden bijvoorbeeld toegepast bij natuurherstel en -ontwikkeling, en waterberging. Deze werkwijze maakt het mogelijk dat de adviezen bij uitvoering in de praktijk een grote kans van slagen hebben. Er wordt onderzoek verricht aan sturende processen in onder meer hoogvenen, laagvenen, meren, plassen, vennen, beekdalen, heiden, soortenrijke graslanden, polders en broekbossen.

Voor wie?

Onderzoekcentrum B-WARE verricht onderzoek voor ministeries, provincies, provinciale landschappen, gemeenten, particuliere terreinbeheerders en natuur-beschermingsorganisaties, waterschappen en adviesbureaus.

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