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# Internal eutrophication in peat soils through competition between chloride and sulphate with phosphate for binding sites

B. BELTMAN, T.G. ROUWENHORST, M.B. VAN KERKHOVEN,
T. VAN DER KRIFT & J.T.A. VERHOEVEN
*Landscape Ecology, Utrecht University, PO Box 800.84, NL-3508TB Utrecht, The Netherlands, e-mail: B.Beltman@bio.uu.nl*

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**Abstract.** Inputs of surface waters high in chloride and sulphate increased the availability of nutrients in fen peatlands. This 'internal eutrophication' was demonstrated with test plants ('phytometers') and through water and soil analysis. Three experiments are presented in which the level of chloride and/or sulphate was increased to 3 $\text{mmol}_c\ l^{-1}$. In experiment 1 chloride levels were increased from 0.5 to 3 $\text{mmol}_c\ l^{-1}$ as $CaCl_2$ or NaCl. In experiment 2 and 3 similar increased levels for chloride and sulphate (3 $\text{mmol}_c\ l^{-1}$; as NaCl and $Na_2SO_4$) were used. The following results were found:

(i) No differences in soil total-N and total-P were found before and after the treatments in any of the three experiments.
(ii) Experiment 1 showed a significant increase in Bio-Available P (BAP) in pots planted with *Anthoxanthum odoratum* as well as in bare pots for the NaCl and $CaCl_2$ treatments. The plants in these treatments had taken up much more P.
(iii) Experiment 2 showed an increase in soil BAP after treatment with chloride and sulphate in pots planted with *Anthoxanthum odoratum*. The chloride treatment had no effect on plant biomass, whereas the sulphate treatment resulted in a reduction in root biomass and root N and P content. The shoots showed an increase in P content in the sulphate and chloride treatments, while N content remained the same.
(iv) In experiment 3, treatments with chloride and sulphate led to significantly increased biomass and P uptake of *Anthoxanthum odoratum*. Again, no effects on N uptake were found.

These experiments provide evidence for distinctly increased availability of phosphate in peat soils when these come into contact with water with even moderately increased sulphate or chloride levels. Surface water originating from the Rhine river, which is enriched in chloride and sulphate, is often supplied to fen reserves in The Netherlands, to compensate for water losses due to agricultural drainage in the region. The results of this study show that phosphate availability to the vegetation may rise drastically, with detrimental effects on the species density and the occurrence of rare species in the vegetation. Hence, supply of this water should be avoided.

## Introduction

Water levels and water quality are strictly regulated in the reclaimed parts of The Netherlands. Most polders discharge the water surplus into an adjacent one, which in turn discharges into the next, etc. Finally the surplus water is discharged into the main rivers Rhine and Meuse and into the sea. A water surplus exists due to an annual precipitation of 800 mm exceeding evapotranspiration of 400–500 mm. In summer, however, a water shortage usually exists due to a high evapotranspiration. The water losses due to evapotranspiration are replenished by Rhine water, which will affect the water composition. Polders mainly consist of agricultural land, but small (semi-)natural areas are often present. Most of these wet nature reserves are highly valued because of their unique vegetation (Heathwaite 1995; Verhoeven 1992; Wheeler 1980). These species-rich and rare plant communities require a low nutrient availability (Richardson & Marshall 1986). High nutrient levels in Rhine water may be directly detrimental for these plant communities. In a number of cases, nutrients can be stripped off by supplying the water via natural or constructed wetlands (Beltman 1990; Koerselman et al. 1994).

Surprisingly, eutrophication does occur in reserves with a supply of surface water, even if the nutrients were removed prior to the inflow into the reserve (Koerselman 1989; Piek 1996; Roelofs 1991; Verhoeven et al. 1988). Several processes may be involved in the eutrophication of these systems which may vary for the elements N and/or P. As the eutrophication in these cases occurs without an external source of nutrients, it is referred to as ‘internal eutrophication’. Some of the processes involved could be:

- enhanced mineralisation due to bicarbonate enrichment by the supply water (e.g. Curtis 1989; Roelofs 1991)
- competition of Cl and $SO_4$ ions with $PO_4$ for binding places on the soil adsorption complex (e.g. Caraco et al. 1989; Smolders & Roelofs 1995, Koerselman et al. 1994);
- forming of reduced sulphur ($S^{2-}$) after the input of $SO_4$-rich water and precipitation of FeS, which releases $PO_4$ adsorbed to iron to the water column (e.g. Caraco et al. 1989; Smolders & Roelofs 1995).

This study deals with the impact of a change in ion composition in the surface water on the release of nutrients in fen peat soils. More specifically, we focused on the effects of supply of water enriched in chloride and sulphate on the availability of nitrogen and phosphorus to the vegetation. We used phytometers (test plants, see Wheeler et al. 1992) in pots with fen peat soil which we brought into contact with water with enriched chloride and/or sulphate levels. We tested whether enrichment with chloride or sulphate increased the availability of nitrogen or phosphorus, and whether the plants responded with higher biomass production.

## Experimental design

Three greenhouse experiments were carried out, in which pots filled with fen peat were treated with water with different chemical composition. The fen peat (60–95% organic matter, Table 1) was collected from floating fens and unfertilized peat grasslands in the Vechtplassen area, The Netherlands (Verhoeven et al. 1988). In part of the pots, *Anthoxanthum odoratum* or *Epilobium hirsutum* were planted as phytometers (Wheeler et al. 1992). Five seedlings of four weeks old were planted per pot. At the start of the experiment, the plants received one application of nutrient solution without N and P (Hoagland).

The pots were percolated with water with different concentrations of chloride and sulphate, or with distilled water (control treatment). The percolation volume was three times the soil volume, meaning that soil pore water was exchanged at least 9 times during the treatment. The experiments lasted for 12 to 15 weeks. All treatments were carried out with 10 replicates. Measurements of solution electric conductivity were carried out before and after percolation. The concentrations of the chloride and sulphate were equal to those in Rhine water: 3 $\mathrm{mmol_c\ l^{-1}}$. Natural background concentrations are 0.5 $\mathrm{mmol_c\ l^{-1}\ Cl^-}$ and 0.1 $\mathrm{mmol_c\ l^{-1}\ SO_4^{2-}}$.

Chemical analyses were carried out according to Houba et al. (1995). Total soil N and P were determined by acid digestion with a sulphuric acid – salicylic acid mixture with selenium oxide. Extractable soil N was determined with 0.2 M potassium chloride and extractable soil P with ammonium lactate (Biological Available Phosphorus, BAP, Koerselman et al. 1994). Free available nitrate, ammonium and phosphate were determined after extraction with distilled water. pH was measured in the water and in the KCl-extracts; organic material by Loss On Ignition (LOI). Plant biomass was determined after drying (70 °C, 48 h) and weighing. Plant N and P concentrations were measured after by acid digestion with a mixture of sulfuric acid and salicylic acid with selenium. Chemical analyses were carried out with a SKALAR continuous flow analyzer using standard colorimetric and flame-photometric methods.

Experiment 1 used two 3 $\mathrm{mmol_c\ l^{-1}}$ chloride solutions (as NaCl and Ca $\mathrm{Cl_2}$) which were percolated in pots filled with bare soil or soil planted with *Anthoxanthum odoratum* or *Epilobium hirsutum*. The bare soil pots were kept bare during the experimental period. The soil originated from a floating fen and had 90% LOI. Experiment 2 had the same setup and soil type as

*Table 1.* Nutrient analyses of the peat soil used in the experiments before rinsing (‘0’) and at the start of the experiments (‘1’). Values are means of 10 replicates (±SD) and were tested for significant differences, which were not found (ANOVA, Tukey, $p < 0.05$).

| | Total-N | Total-P | N($H_2O$) | P($H_2O$) | N(KCl) | BAP |
|---|---|---|---|---|---|---|
| *Experiment 1* | | | | | | |
| 0 | 15.0 ± 1.0 | 0.97 ± 0.10 | – | – | – | – |
| 1 ctrl | 12.7* | 0.93* | 2.62 ± 1.86 | 1.71 ± 1.70 | 1.41 ± 1.23 | 54 ± 16 |
| 1 $CaCl_2$ | 13.2* | 1.02* | 1.74 ± 2.36 | 1.87 ± 1.23 | 1.11 ± 1.49 | 51 ± 15 |
| 1 NaCl | 13.2* | 0.82* | 2.69 ± 2.62 | 1.80 ± 1.43 | 2.75 ± 2.61 | 56 ± 12 |
| *Experiment 2* | | | | | | |
| 0 | – | – | 6.1 ± 7.5 | 1.6 ± 0.8 | 14.7 ± 12.2 | 87 ± 34 |
| 1 ctrl | 13.5 ± 0.4 | 0.82 ± 0.03 | 2.1 ± 3.2 | 0.3 ± 0.4 | 32.4 ± 7.7 | 52 ± 10 |
| 1 NaCl | 15.7 ± 0.6 | 0.96 ± 0.04 | 9.5 ± 9.8 | 0.6 ± 0.5 | 21.4 ± 11.3 | 65 ± 10 |
| 1 $NaSO_4$ | 14.6 ± 0.9 | 0.93 ± 0.12 | 4.0 ± 3.4 | 0.4 ± 0.3 | 20.3 ± 12.5 | 58 ± 34 |
| *Experiment 3* | | | | | | |
| 0 | 22.6 ± 1.9 | 0.55 ± 0.13 | BD | BD | – | 51 ± 11 |
| 1 ctrl | 23.5 ± 0.6 | 0.53 ± 0.04 | BD | BD | – | 57 ± 9 |
| 1 NaCl | 23.2 ± 1.3 | 0.55 ± 0.07 | BD | BD | – | 53 ± 6 |
| 1 $NaSO_4$ | 23.5 ± 1.4 | 0.58 ± 0.06 | BD | BD | – | 64 ± 23 |

Total N and Total P as mg $g^{-1}$. N($H_2O$), P($H_2O$): water-extractable N and P; N(KCl): KCl-extractable N; BAP: Bio-Available P, all as mg $kg^{-1}$; Experiments 1 and 2 were carried out with a floating fen soil with 90% organic matter and $pH_{water}$ 6.1, experiment 3 with peat soil with 60% organic matter and $pH_{water}$ 5.4. ctrl, control treatment, – not determined; * replicates lost. BD, below detection limit of the SKALAR continuous flow analyzer of 0.015 mg $l^{-1}$ $PO_4$, 0.12 mg $l^{-1}$ $NH_4$ or 0.25 mg $l^{-1}$ $NO_3$.

experiment 1, but NaCl and $Na_2SO_4$ solutions (3 $mmol_c$ $l^{-1}$) were used and only *Anthoxanthum odoratum* was used as a phytometer. Experiment 3 was identical to experiment 2, but a more solid peat soil (60% LOI, c. 40% sand) was used.

## Results

### Experiment 1

Dry weight at the end of the experiment for *Epilobium* showed no differences for the various treatments (Table 2). *Anthoxanthum* showed a reduced growth for the $CaCl_2$ treatment compared with the NaCl treatment, while both did

*Table 2.* Experiment 1. Biomass dry weight (g) and total N and P content (mg) of *Epilobium hirsutum* and *Anthoxanthum odoratum* shoots (S) and roots (R) at the end of the experiment. Values are means of 10 samples ± SD. Significant differences are denoted by different letters.

| Treatment | Biomass S | Biomass R | Ncont S | Ncont R | Pcont S | Pcont R |
|---|---|---|---|---|---|---|
| *Epilobium hirsutum* | | | | | | |
| $CaCl_2$ | $0.1781 \pm 0.1232^a$ | $0.0399 \pm 0.0275^a$ | 0.816 | 0.259 | 1.063 | 0.095 |
| NaCl | $0.1573 \pm 0.1057^a$ | $0.0633 \pm 0.0644^a$ | 0.654 | 0.477 | 1.484 | 0.148 |
| Control | $0.1288 \pm 0.1239^a$ | $0.0388 \pm 0.0271^a$ | 0.480 | 0.302 | 0.249 | 0.088 |
| *Anthoxanthum odoratum* | | | | | | |
| $CaCl_2$ | $0.0091 \pm 0.0035^b$ | $0.0107 \pm 0.0073^b$ | 0.085 | 0.067 | 0.042 | 0.017 |
| NaCl | $0.0202 \pm 0.0108^a$ | $0.0305 \pm 0.0201^a$ | 0.207 | 0.187 | 0.157 | 0.041 |
| Control | $0.0113 \pm 0.0089^{ab}$ | $0.0165 \pm 0.0093^{ab}$ | 0.103 | 0.098 | 0.032 | 0.026 |

Note: Due to small amounts of biomass, samples had to be pooled for N and P analysis; in these cases the average concentration of 5 pooled samples has been used. No statistical test has been applied on these data.

not differ from the control (Table 2).The P content of *Epilobium* shoots was much higher in both chloride treatments than in the control (no statistical test possible, see note Table 2). The values for *Anthoxanthum* did not show clear patterns.

The soil analyses for Total-N, Total-P, P($H_2O$), N($H_2O$), N(KCl) and BAP showed no differences among the treatments at the start of the experiment (Table 1). At the end of the experiment, BAP was significantly higher in the $CaCl_2$ and NaCl treatments than in the control in the *Anthoxanthum* pots and in the bare pots (Table 3). This trend was not found in the *Epilobium* pots. The values for P($H_2O$) and Total P showed no differences.

### *Experiment 2*

Shoot dry weight of *Anthoxanthum* did not differ significantly among the treatments, whereas root dry weight was lower in both treatments compared to the control. The total dry weight showed a significantly lower value for the sulphate treatment than for the control and chloride treatments (Table 4). Shoot N content did not differ, but root N content was lower in the sulphate treatment due to lower dry weight, not to the N concentration. Shoot phosphorus content was significantly higher than the control in both treatments, root P content only in the chloride treatment.

Total as well as extractable soil N and P at the start of the experiment did not show significant differences among the treatments (Table 1). At the end of the experiment, BAP in both treatments was significantly higher compared

*Table 3.* Experiment 1. Soil analyses for extractable N (N(KCl)) and Bio-Available P (BAP) (mg $kg^{-1}$) and Total N and P (mg $g^{-1}$) at the end of the experiment. Values are means of 10 samples ± SD. Significant differences are denoted by different letters.

| Treatment | BAP | N(KCl) | Total P | Total N |
|---|---|---|---|---|
| *Epilobium hirsutum* | | | | |
| $CaCl_2$ | $51 \pm 11^e$ | 1.72 ± 1.83 | 1.05 ± 0.06 | 14.8 ± 0.9 |
| NaCl | $49 \pm 9^e$ | 3.27 ± 2.38 | 1.06 ± 0.19 | 14.9 ± 1.5 |
| Control | $56 \pm 14^e$ | 0.29 ± 0.61 | 1.21 ± 0.19 | 19.5 ± 2.9 |
| *Anthoxanthum odoratum* | | | | |
| $CaCl_2$ | $74 \pm 12^a$ | 4.16 ± 1.87 | 1.07 ± 0.12 | 14.5 ± 1.3 |
| NaCl | $78 \pm 9^a$ | 0.43 ± 0.55 | 1.07 ± 0.23 | 14.4 ± 1.2 |
| Control | $60 \pm 13^b$ | 3.39 ± 3.22 | 0.95 ± 0.06 | 13.4 ± 0.8 |
| Bare (no plants) | | | | |
| $CaCl_2$ | $51 \pm 15^c$ | 0.60 ± 0.77 | 1.00 ± 0.06 | 13.7 ± 1.2 |
| NaCl | $56 \pm 12^c$ | 4.42 ± 5.45 | 1.00 ± 0.05 | 14.4 ± 0.9 |
| Control | $34 \pm 16^d$ | 0.50 ± 0.48 | 1.11 ± 0.31 | 14.6 ± 2.4 |

*Table 4.* Experiment 2. Biomass dry weight (g) and total N and P content (mg) of *Anthoxanthum odoratum* shoots (S) and roots (R) at the end of the experiment. Values are means of 10 samples ± SD. Significant differences are denoted by different letters.

| Treatment | Biomass | Ncont S | Ncont R | Pcont S | Pcont R |
|---|---|---|---|---|---|
| $Na_2SO_4$ | $1.07 \pm 0.12^b$ | $4.05 \pm 0.47^a$ | $1.80 \pm 0.17^b$ | $0.75 \pm 0.13^a$ | $0.28 \pm 0.05^b$ |
| NaCl | $1.18 \pm 0.10^a$ | $4.07 \pm 0.52^a$ | $2.25 \pm 0.25^a$ | $0.82 \pm 0.11^a$ | $0.38 \pm 0.04^a$ |
| Control | $1.35 \pm 0.34^a$ | $4.02 \pm 1.08^a$ | $2.34 \pm 0.48^a$ | $0.51 \pm 0.19^b$ | $0.29 \pm 0.05^b$ |

to the control in the pots with *Anthoxanthum*; the bare pots showed no differences with the control (Table 5). P($H_2O$) and N(KCl) did not differ among treatments, nor did Total N and Total P. The difference in N(KCL) at the start (Table 1) and at the end of the experiment (Table 5) was probably due to plant uptake. A significant drop in pH was found between the start and the end: $pH_{water}$ decreased from 6.1 ± 0.01 to 5.4 ± 0.2 and $pH_{KCl}$ from 5.5 ± 0.02 to 5.1 ± 0.1, respectively.

*Table 5.* Experiment 2. Soil analyses for extractable N (N(KCl)) and Bio-Available P (BAP) (mg kg$^{-1}$) and Total N and P (mg g$^{-1}$) at the end of the experiment. Values are means of 10 samples ± SD. Significant differences are denoted by different letters.

| Treatment | BAP | N(KCl) | Total P | Total N |
|---|---|---|---|---|
| *Anthoxanthum odoratum* | | | | |
| $Na_2SO_4$ | 41.3 ± 7.3$^a$ | 3.4 ± 3.3 | 0.72 ± 0.06 | 12.3 ± 1.0 |
| NaCl | 50.9 ± 11.7$^a$ | 3.7 ± 4.6 | 0.70 ± 0.04 | 12.6 ± 0.8 |
| Control | 17.7± 7.4$^b$ | 9.0 ± 8.2 | 0.69 ± 0.06 | 11.8 ± 0.7 |
| Bare (no plants) | | | | |
| $Na_2SO_4$ | 54.6 ± 12.9$^a$ | 2.0 ± 4.9 | 0.85 ± 0.18 | 14.1 ± 3.2 |
| NaCl | 59.3 ± 13.2$^a$ | 1.1 ± 1.5 | 0.78 ± 0.10 | 13.6 ± 1.0 |
| Control | 53.6 ± 19.3$^a$ | 2.2 ± 5.5 | 0.83 ± 0.05 | 13.7 ± 0.8 |

### *Experiment 3*

BAP, Total-N and Total-P did not differ significantly among treatments (Table 1, Figure 1). Water-extractable N and P were very low. *Anthoxanthum* plants showed a significantly higher biomass production for the two treatments compared to the control (Figure 2). The concentrations of P and N in shoots and roots before the experiment showed no significant differences. Total N content in the plants did not differ among the treatments but total P content was significantly higher in the sulphate and chloride treatments than in the control (Figure 3).

## Discussion

All three experiments showed that the percolation procedure did not increase Bio-Available P (BAP) directly and had no impact on water-soluble P. P release is apparently a slow process in these peat soils. This contrasts with the direct release from minerals, as measured by Geelhoed et al. (1997b).

All three experiments provided indications that the anion treatments resulted in a release of P in the peat soil. BAP increased as a result of most of the chloride treatments in vegetated as well as bare soil in experiment 1, whereas this occurred in the chloride and sulphate treatments in vegetated soil only in experiment 2. The higher availability resulted in a higher P uptake by the phytometers: *Epilobium hirsutum* had a higher P content in the chloride-treated soils in experiment 1 and *Anthoxanthum odoratum* in the chloride –

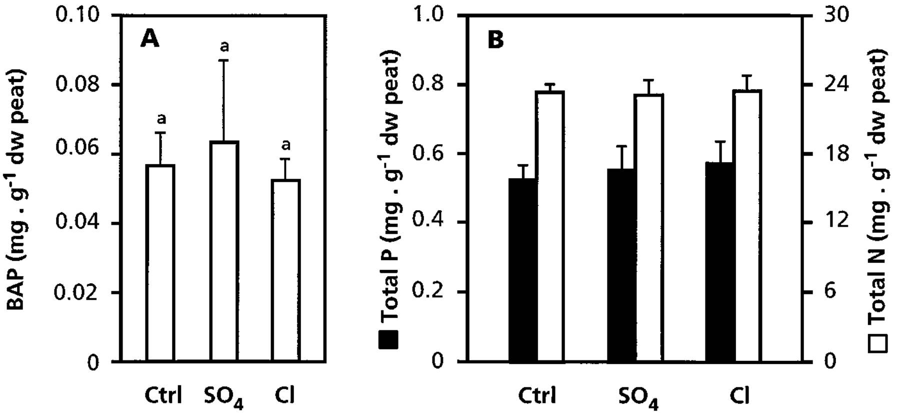

*Figure 1.* A. Bio-Available P (BAP, mg kg$^{-1}$) for peat soil (60% LOI) and B. Total N and P concentration of peat soil (mg g$^{-1}$) after percolation with distilled water (control), 3 mmol$_c$ l$^{-1}$ sodium sulphate and 3 mmol$_c$l$^{-1}$sodium chloride. Same letters mean no significant differences.

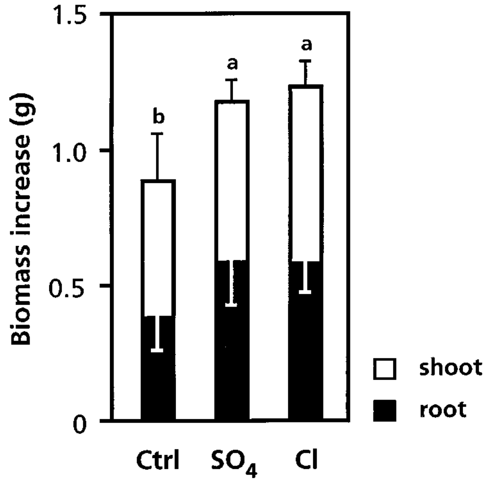

*Figure 2.* Increase in dry weight (g) of *Anthoxanthum odoratum* plants in the control and the treatments with sodium chloride and sodium sulphate solution.

as well as sulphate-treated soils in experiments 2 and 3. In experiment 3, the higher P uptake has resulted in an increase in biomass production. Surprisingly, the $CaCl_2$ treatment increased P availability, which was not expected since Ca is known to precipitate with P (e.g. Appelo & Postma 1993; Boyer & Wheeler 1989; Fixen et al. 1983; Larsen 1966; Richardson & Marshall 1986). This indicates that the anion exchange effect of the chloride is quite strong.

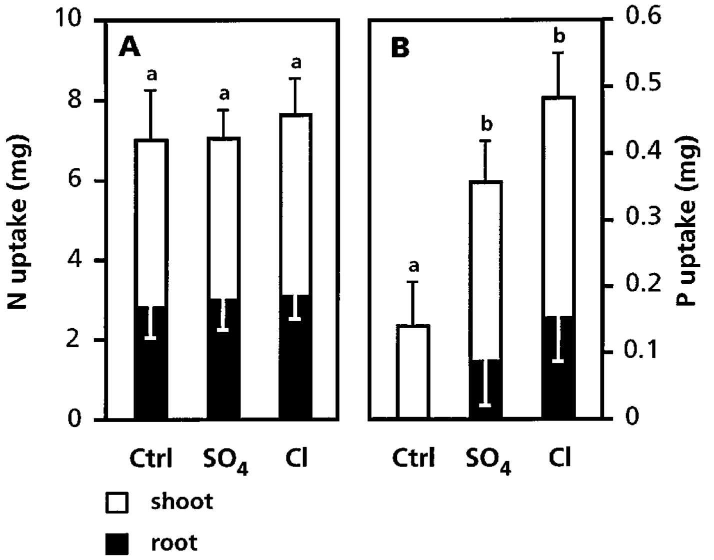

*Figure 3.* Increase in total N (A) and P (B) content of *Anthoxanthum odoratum* in the control and the treatments with sodium chloride and sodium sulphate solution.

The second and third experiments also showed an increased P availability for the sulphate treatments. This is not surprising since there is much evidence for anion exchange between sulphate and phosphate (e.g. Caraco et al. 1989; Smolders & Roelofs 1995). Also, reduction of sulphates to sulfides and subsequent precipitation of FeS might release Fe-bound phosphates (Caraco et al. 1989; Lamers et al. 1996, 1998). It is not clear which of the two mechanisms has worked in our sulphate treatments. Geelhoed et al. (1997a, b) also showed an effect of sulphate concentration ('salt effect') on phosphate adsorption to a mineral adsorbent, i.e. goethite. Their corn plants grown on mineral P suspensions, showed the best uptake of P at high salt levels (2 mmol $l^{-1}$ $SO_4$). Our chloride treatments increased the concentrations from 0.2 to 3 mmol $l^{-1}$, which is in a similar range. However, peat is a complex natural mixture compared to the artificial minerals used by Geelhoed et al. (1997a, b) and their pH (3.7) was far lower than ours. Because of the very low redox potential necessary for the sulphate reduction and the short duration of our experiment, we assume that anion exchange has been the most important mechanism leading to increased BAP and plant uptake in experiment 3.

Internal eutrophication apparently involves increased availability of P, because no effects of the treatments on the N availability were found. By contrast, Koerselman et al. (1994) showed increased mineralisation of N in response to higher chloride and sulphate concentrations. A possible explanation for the absence of an effect on inorganic N pools in our experiment might be that nitrate was denitrified so rapidly that we could not measure it. However, dissolved ammonium was not detected either, while it is common in anoxic organic soils (Verhoeven et al. 1988, 1990). Apart from differences in experimental design, no explanation is available since the analytical procedures were the same.

Internal eutrophication appears to be a complex process in which more than one process might be working at the same time, resulting in enhanced availability of P in the soil pore water. As we worked with highly organic soil, the assumption of a role for the organic chains of humic acids in this process is reasonable. Qualls and Richardson (1995) showed that phosphorus in the peat soils of the Everglades is largely locked up in organic matter. Perez Corona et al. (1996) showed that organic P may be directly available for some plants. In general, there is an equilibrium between the fraction of an ion adsorbed and the fraction in solution, which is impacted by the total ion-strength of the solution (Freeze & Cherry 1979; Geelhoed et al. 1997a; Tipping et al. 1988). This process might also work for binding of ions to organic soils (Tipping & Hurley 1988) but whether this works for the binding of e.g. $PO_4$ to calcium, iron or aluminium sites in humic acids, is not clear yet (see also Beltman et al. 1992). We highlighted that increased concentrations, even of an ion as chloride with a relatively low affinity for adsorption, impacted the release of P from soil binding sites even in calcium-rich peat (c. 40–50 mg $l^{-1}$ Ca in pore water).

The ecological impact of this internal eutrophication process in peat soils is, that P is released from the soil complex, which is often considered as a sink for P in the soil pore water solution (Richardson 1989). Once in inorganic form it is available for more rapid uptake by plants and may also be transported. The extra phosphorus might become washed out from the soil pore water to open water. A point of consideration for a manager might be to accept a short period of drought with possible increased mineralization or emission of greenhouse gases (Aerts & Ludwig 1997) rather than supply river water high in Cl and $SO_4$ to keep water at a fixed level as agreed in laws and legislation from waterboards and impact the soil adsorption processes.

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