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Experimental investigation of drought induced acidification in a rich fen soil

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Abstract. Intact rich fen soil cores with controlled water levels near the surface were installed in an open greenhouse. To simulate short term summer drought, water levels were lowered (20 cm) after two weeks in half of the cores (experimental cores) and remained near the surface in the other half (blanks). After two more weeks, the water levels were brought back to the surface in the experimental cores and remained there for another two weeks. In the blanks, reduction and alkalinization of the top peat layer occurred. In the experimental soil cores oxidation and acidification started within one week after drawdown. An indication for a drought induced rise in soluble reactive phosphorus has been found. The velocity of the acidification process illustrates the dynamic nature of the hydrochemical conditions in fen soils during drought. The processes controlling the acid/base status of rich fen, the effect of drought induced acidification on P availability and the significance for the vegetation are discussed.

Abbreviations: Amac – ammoniumacetic acid; Oxac – ammonium oxalate-oxalic acid

Introduction

In many intensively used landscapes of Europe, large wetland complexes have been lost or were damaged. What remains are small entities, often relicts of larger units, that are susceptible to external influences. These scattered wetlands have little functional value on the global or regional scale, other than the habitat they provide for threatened species (Wheeler 1988; Bournerias 1990; van Wirdum 1993; Fojt 1995). Their disappearance or further deterioration will gravely affect biodiversity in Europe. In this study we focus on rich fens, particularly the low-productive, species rich variants with *Caricion davallianae* vegetation. This vegetation type has almost disappeared from lowlands of Europe, although it is still more common in northern and premontane areas (ECC 1991). It may be expected that lowland relicts will experience extra stress from climate changes.

If global climate change proceeds as predicted, wetlands around the world undoubtedly will respond. Wetland reaction is important for the greenhouse effect itself (Gorham 1991; Freeman et al. 1993) and for effects on downstream water quality, on local economies, on the regional hydrological cycle etc. Under a doubling CO_2 scenario, Schneider et al. (1992) predict winter temperature increases over Western and Northern Europe of 4 to 10 °C (towards the poles) and summer increases of 2 to 6 °C. The Intergovernmental Panel on Climate Change (Houghton et al. 1992) expects average yearly temperature changes in this region to be 2 to 4 °C. Winter precipitation is predicted to increase, summer precipitation to decrease. It is likely that seasonal variations will be enhanced, increasing the frequency of summer droughts.

Although the habitat requirements of many rich fen species are not at all well known, base richness and low fertility undoubtedly are involved in the mechanisms producing species richness (Wassen et al. 1990; van Wirdum 1991; Wheeler & Shaw 1995). The dependence of these characteristics on ground-water discharge, makes them vulnerable to water-level changes. Decreased ground-water discharge will diminish the supply of base cations to the fen and lead to acidification in climates with a precipitation surplus (Kenoyer & Anderson 1989; Webster et al. 1990; Cook et al. 1991). In addition, increased water-level variation will affect the redox potential of the soil. While the first effect determines the long-term evolution of average hydrochemical conditions, expressed in the zonation of mire vegetation types, the second effect is much more dynamic.

In this study, two main objectives were distinguished. First, the relation between summer drought and the acid/base transition of a circumneutral rich fen soil that was chemically intermediate between soft and hard water systems was assessed. The second objective was to investigate how these transformations influence P dynamics. Analyses of ground water (Boeye et al. 1994) and soil water (Boeye & Verheyen 1994) in our study area, indicated an acid/base transition related to drought. Kemmers & Jansen (1988) similarly found HCO_3^- consumption and SO_4^{2-} production associated with low ground-water levels under field conditions. LaZerte (1993) studied the chemical budget of a minerotrophic conifer swamp and found downstream export of SO_4^{2-} and base cations following summer droughts.

Apart from acid/base chemistry, low ground-water levels may affect a peat soils' fertility. Biological processes like mineralization, microbial uptake and release and chemical processes controlling P availability are known to depend on redox and/or acid/base status. Previous research in the study area revealed strong P limitation in the vegetation (unpublished) and an indication for increased P concentration in the soil solution during summer drought (Boeye et al. 1996).

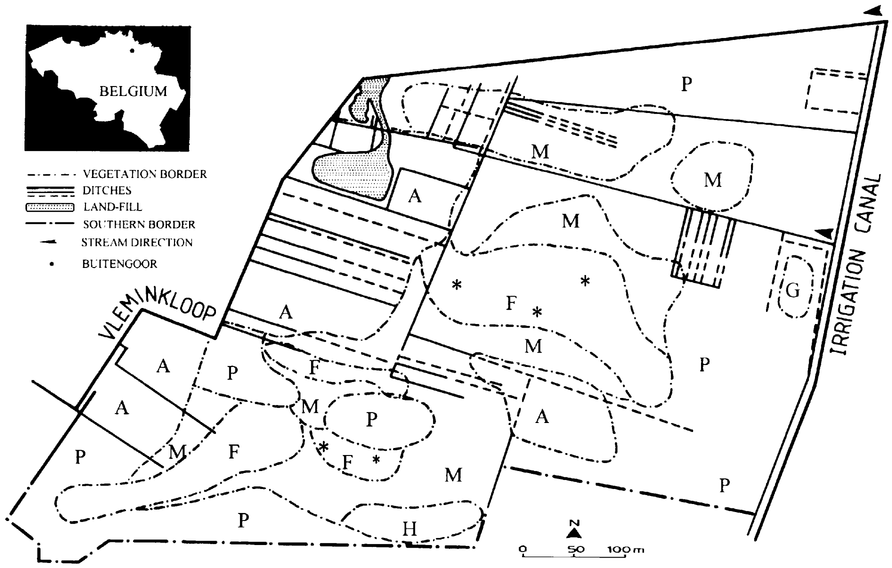

Figure 1. Location of the soil sampling sites in the Buitengoor (∗: sample sites; A: alder wood; F: fen vegetation; G: grassland; M: molinia; P: pine forest).

In order to test both empirical relations, chemical changes in soil and soil solution were investigated in soil cores of the Buitengoor with experimentally lowered water levels.

Methods

Study area

The Buitengoor is located in the eastern part of the province of Antwerp, Belgium (51°12′53″ N, 05°10′07″ E, Figure 1). The region has a normal annual precipitation of 727 mm and an annual potential evapotranspiration of 500 mm (Bultot and Dupriez 1974). It is situated on the western slope of the Campine Plateau. The water table follows the regional topography, which decreases gradually from east to west (Cnudde 1978). Because of the depression in this slope, the ground water in the Buitengoor reaches the surface most of the year (Boeye & Verheyen 1992).

In the higher parts of the Buitengoor, acid podzol soils covered with pine forest are found (Figure 1). In the lowest part of the valley, alder wood on top of a thin (20–30 cm) peat soil is present. In between lies a zone of ground-water discharge with herbaceous vegetation. Here a humified peat layer with a thickness of up to 40 cm is present on top of a pure sand (Mol sand).

The major part of the ground-water discharge zone is dominated by *Molinia caerulea* and *Myrica gale*. In three depressions, a mixture of low productive herbaceous rich-fen vegetation (*Caricion davallianae*) and poor-fen vegetation (*Caricion curto-nigrae*) with *Sphagnum*-blankets is present. The supply of base rich water to the Buitengoor originates from a small irrigation canal (Figure 1) that runs through the depression from south to north, just upward from the ground-water discharge zones (Boeye et al. 1995). This canal is nourished by shipping canals, which are supplied with calcareous water from the river Maas. It supports growth of many calcicoles of the *Caricion davallianae* (e.g. *Carex demissa, Eriophorum latifolium, Juncus alpino-articulatus ssp. arthrophyllus, Campylium stellatum, Drepanocladus lycopodioides*).

Soil core sampling and experimental design

At the beginning of June 1995, twenty-five intact soil cores were collected at five different sites in the Buitengoor (5/site, Figure 1). On top of all cores, a similar vegetation with *Carex demissa, Eriophorum latifolium, Juncus alpino-articulatus ssp. arthrophyllus, Campylium stellatum, Drepanocladus lycopodioides* was present. The monoliths were sampled using PVC pipes of 60 cm length and 11 cm diameter. To reduce short distance variability within sites, the cores were taken next to each other. A soil description at the end of the experiment showed that within the cores of one site, the same conditions occur. Twenty soil cores (4/site) were used in the experiment. The five remaining cores were immediately analysed (controls). The top of each core was left open, allowing a free exchange of gases between the soil and the atmosphere. The base of each pipe was sealed with a cap, which was drained by an 8 mm diameter tubing and connected with a reservoir filled with weekly renewed ground water from the Buitengoor (pH: 7.1, 100 mg/l SO_4^{2-}, 0.9 mg/l Fe, 38 mg/l Ca, 35 μg/l PO_4^{3-}). The chemical characteristics of the ground water in the reservoirs remained stable, apart from variable HCO_3^- (29 mg/l s.e. 11) concentrations. By raising or lowering the water level in the reservoir, the height of the ground-water table inside the soil cores could be manipulated. Loss of soil material out of the columns was prevented by a layer of fine filter gravel (Eijkelkamp Agrisearch Equipment) on top of a layer of marbles. Into the pipe walls three holes were drilled at 5–15–25 cm below soil surface. Through these holes Rhizon Soil Moisture Samplers (Rhizon SMS) were horizontally inserted into the soil. The samplers are produced from a hydrophilic porous polymer, which is connected to a PVC tube. To obtain a soil-water sample, the Rhizon SMS is connected to a vacuum tube (0.01 atm). These Rhizon SMS allow porewater sampling from within the core under wet and dry conditions with a minimal disturbance. The twenty soil cores (4/site) were put in an open greenhouse, where temperature and light:dark cycle were comparable to outdoor conditions.

Half of the cores (2/site) were maintained with the ground-water table near the surface (blanks). The water table in the remainders (2/site) was gradually lowered during the third week of the experiment to a depth of 20 cm below the soil surface. The water table was maintained at that depth for two more weeks. At the end of the drought period, five experimental (1/site) and five blank soil cores (1/site) were dismantled and the soil in different horizons was analysed. During the fifth week, the ground-water table in the five remaining experimental soil cores (1/site) was raised to the surface and kept there for the last week of the experiment. At the end of the experiment the ten remaining soil cores were dismantled and analysed.

Chemical analyses

The soil water in the cores and the ground water in the reservoir was sampled weekly. Four subsamples were taken. pH, electrical conductivity (EC_{25}) and redox potential were determined on the first subsample. HCO_3^-, SO_4^{2-} and Cl^- were immediately measured in the second subsample with a continuous flow auto-analyser. The third subsample was acidified with HNO_3^- and analysed for cations (Al, Ca^{2+}, Fe, Mg^{2+} and Na^+) with a plasma-emission spectrophotometer. The last sample was analysed for NH_4^+, NO_3^- and NO_2^- with a continuous flow auto-analyser. Before using the samplers in the experiment, their contaminating and/or adsorptive influence on water samples was tested. For most elements, the Rhizon SMS samples proved satisfactory. Only the determination of soluble reactive phosphorus (SRP) was unreliable due to the adsorption of PO_4^{3-} on the Rhizon SMS. Therefore, unlike the other elements, PO_4^{3-} could not be monitored continuously. Because the behaviour of PO_4^{3-} during temporal drought was of main interest here, PO_4^{3-} was sampled instantaneously after rewetting the cores. The Rhizon SMS were temporary replaced by small drainage pipes that allow free drainage of pore water from the saturated cores. These post-drought samples were analysed for PO_4^{3-} after filtering over a Millipore 0,45 μ m and acidification with HNO_3^-. The Rhizon SMS were inserted again after the collection of these samples. During the experiment air and soil temperature were continuously measured.

Before analysing the soil, horizonation, texture and presence and distribution of roots were noted. From each horizon, an undisturbed sample with known volume was collected. Water content and bulk density of these samples were determined by weighing before and after drying at 105 °C for 24 hours. Afterwards, these dry soil samples were crushed in a mortar and used for an acid destruction (Houba et al. 1989). The remaining fresh soil of each horizon was used for the determination of the pH-H_2O (1:1) and for an ammonium oxalate-oxalic acid (Oxac, Houba et al. 1989) and ammoniumacetic acid (Amac, Cottenie et al. 1989) extraction.

Statistical techniques

The differences were tested for significance with a Repeated Measures Anova (Statistica 5.0 1995). Sites were treated as individuals and readings from cores within sites as repeated measures. A full factorial design was used with drought treatment (1 df), time (6 df) and horizon (3 df) as factors. For the soil analyses, the results of the control soils (analysed at the start of the experiment, 1/site) were substracted from those analysed at the end of the experiment (experimental (drought treated, 1/site) and blank (1/site)). These calculated values for blank and experimental soils were used to test the significance of difference between both. Also here a Repeated Measures Anova was conducted.

Results

Soil solution analyses

A first glance at Figures 2 and 3 clearly shows the evolution of the soil-water quality in the upper horizon. Because the drought treatment evoked no differences in the lowest water samples, both figures represent only the results of the 5 and 15 cm depth samples. In nearly all variables, drought interacted significantly with time, while in some the separate factors were significant (Table 1). In the blank soil cores, the redox potential decreased during the experiment (Figure 2c). Other variables in the blanks' upper horizon increased gradually: pH, HCO_3^-, Ca^{2+}, Fe and Mg^{2+} (Figure 2a, 2e and Figure 3c, 3e, 3g). The onset of low water levels induced in the upper horizon a decrease in pH, HCO_3^-, and Fe (Figure 2b, 2f and Figure 3f) and an increase in redox, SO_4^{2-}, Al, Ca^{2+}, and Mg^{2+} (Figure 2d, 2h and Figure 3b, 3d, 3h). There were notable differences in the timing. Redox, HCO_3^- and Fe reacted immediately and Fe almost reached zero levels within one week after drainage, whilst other variables did not react until the second sampling occasion after onset of drought. Ca^{2+} and Mg^{2+} concentrations even decreased during the first week of low water levels after which they started to rise. All variables evolved in the direction of pre-drought levels after the rise of the water table.

Because the Rhizon SMS samples were not usefull for the determination of SRP, the samplers were temporary replaced by small perforated drainage pipes, after rewetting the experimental soils. We failed to sample soil water

Table 1. Values of *F* and *p* of a Repeated Measures Anova of soil water parameters at 5 cm depth. PO_4^{3-} values result from a single post-drought sample (n = 4, see text). *p* values < 0.05 are considered statistically significant.

	df	*F*/*p*-value				
		pH	Redox	HCO_3^-	SO_4^{2-}	
Time	6[1]	**5.97/0.001**	**9.27/0.000**	2.29/0.105	**9.79/0.000**	
Drought	1	0.97/0.381	**26.66/0.007**	5.71/0.139	**32.28/0.005**	
Time × drought	6[1]	**4.61/0.003**	**14.22/0.000**	**6.47/0.003**	**9.57/0.000**	
		Fe	Al	Ca	Mg	PO_4^{3-}
Time	6	**3.32/0.016**	**4.43/0.004**	**7.52/0.000**	**5.00/0.002**	
Drought	1	4.73/0.095	**9.60/0.036**	0.03/0.881	0.00/0.969	0.16/0.720
Time × drought	6	**4.16/0.005**	**5.49/0.001**	**3.28/0.017**	2.08/0.904	

[1] df value for redox is 5

with these pipes in 2 of the blank soils (both at 15 cm depth) and in 1, 2 and 2 of the drought treated columns respectively at 5, 15 and 25 cm depth. Analyses of the remaining samples indicated that the concentration of SRP in all horizons of previously drained soils was higher than in those of the blank soils (Figure 4). The strongest effect was found in the deeper horizons, therefore no significant difference was found for the soil water samples at 5 cm depth (Table 1).

Soil analyses

The results are summarized in Table 2 and Figures 5, 6 and 7. During the experiment, no differences of horizonation or root distribution were found between blank and experimental soils. However after the drought period, the colour of the peat layer was more reddish. When the experimental soils were rewetted, the reddish became less intense. In all soil columns, roots were dominant in the upper horizon. A general soil profile is shown in Figure 5. The soil temperature of the cores showed a strong daily fluctuation (±11 °C), which followed the air temperature (mean day temperature 21.5 °C). Drought influenced some soil chemical characteristics. Values of pH showed significant drought and horizon effects (Table 2). The pH values of the blank soil cores increased during the first half of the experiment and remained more or less stable afterwards (Figure 6). In the experimental soils, pH values at the end of the experiment were comparable to, but slightly lower than start values (Figure 6). pH values measured after drought are not shown, because they showed an erratic pattern due to instrumental problems. After Amac extraction, the significant drought effect on the Al concentration was due to the low

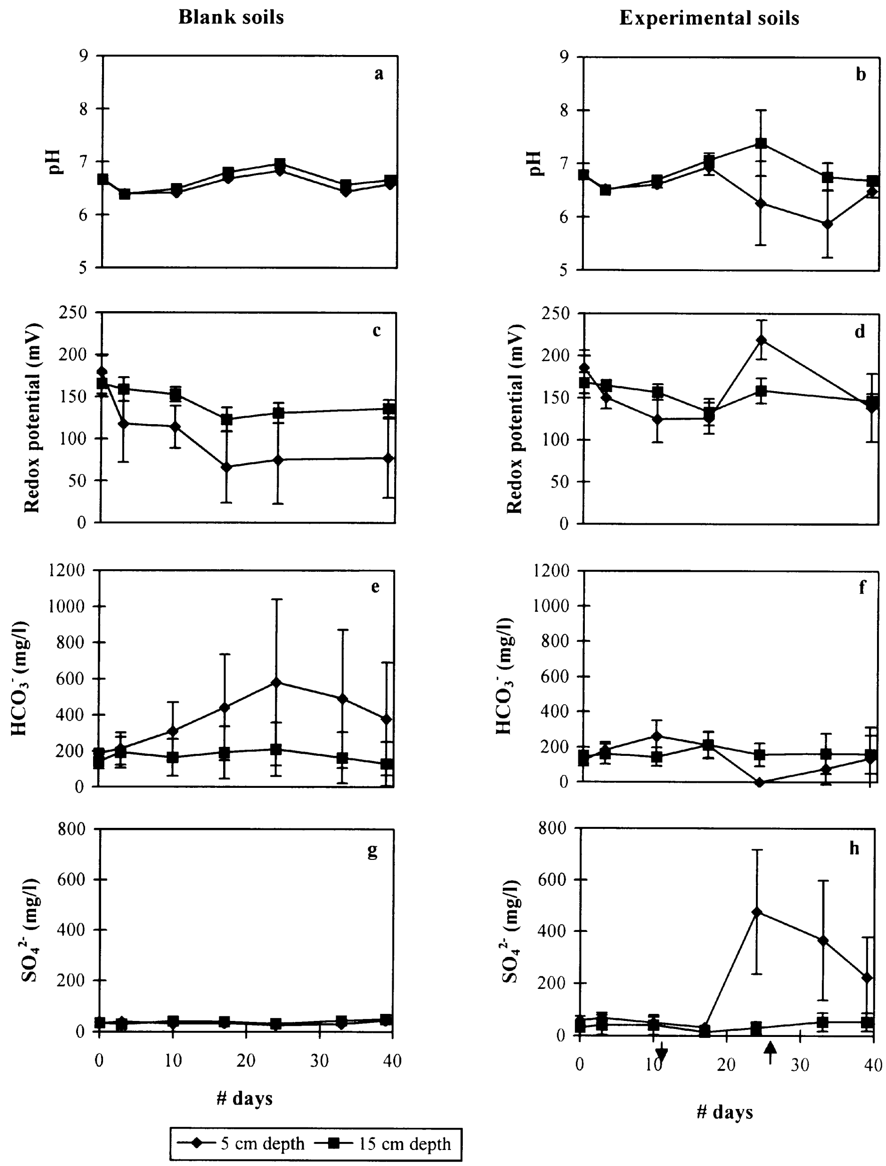

Figure 2. pH, redox potential and HCO_3^- and SO_4^{2-} concentration in the soil solution of blank and experimental soil cores during the experiment. Values are means from 5 replicates ($\pm$ s.e.; $\downarrow$: fall of ground-water table; $\uparrow$: rise of ground-water table).

values found in the blank cores (Figure 7a). Ca^{2+} showed a complex picture with a significant time effect and various interactions (Table 2 and Figure 7c). In general it tended to decrease and the decrease was stronger in the blank

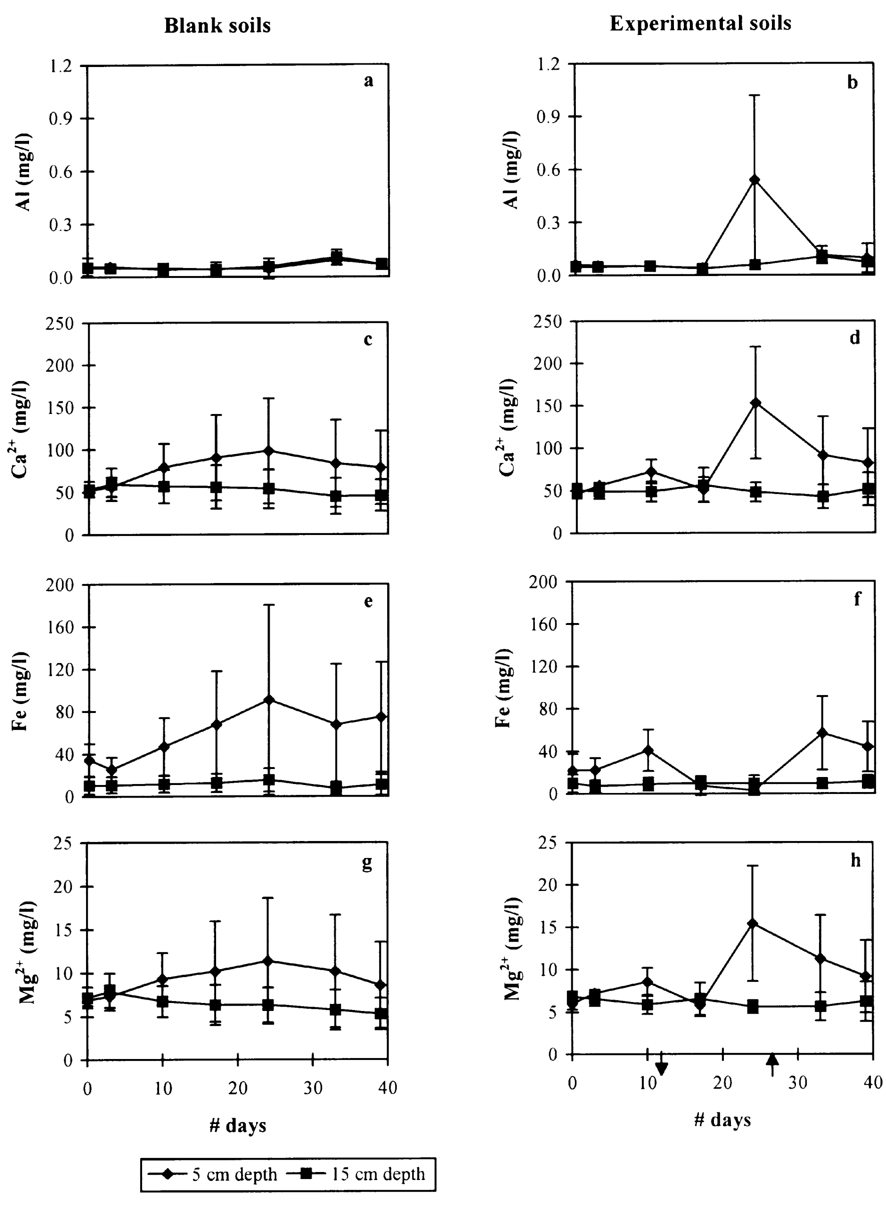

Figure 3. Concentration of Al, Ca^{2+}, Fe and Mg^{2+} in the soil solution of blank and experimental soil cores during the experiment. Values are means from 5 replicates (± s.e.; ↓: fall of ground-water table; ↑: rise of ground-water table).

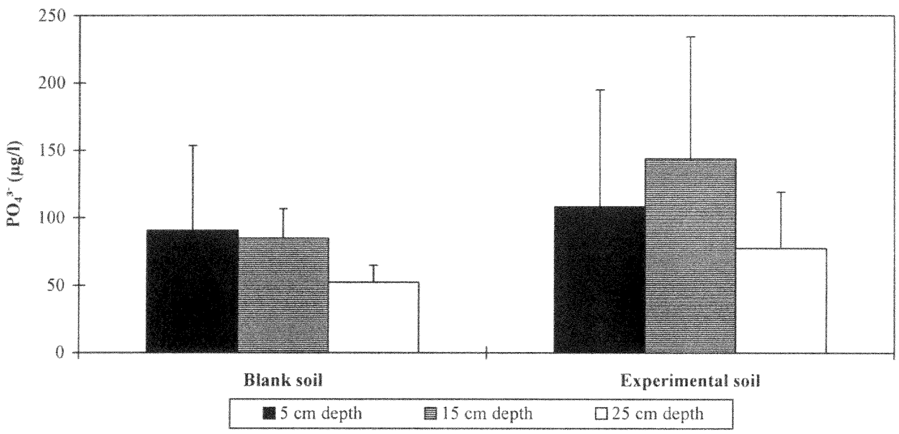

Figure 4. PO_4^{3-} concentration in blank and experimental post-drought soil cores, sampled with mini-drainage pipes. Values are means ± s.e. from 5 replicates with exception of blank soil at 15 cm depth (3 replicates) and experimental soils at 5, 15 and 25 cm depth (4, 3 and 3 replicates respectively).

than in the experimental soils. The upper and lowest horizon of the experimental cores were an exception in which there was an increase of Ca^{2+} after drought. Fe increased strongly in the upper horizon of the blank cores, while it remained low in the experimental cores (significant horizon and drought × horizon effect, Table 2 and Figure 7e). P decreased in experimental and blank cores (significant time effect, Table 2 and Figure 7g). The Oxac extraction revealed no significant drought effects, significant effects were limited to the horizon factor and time × horizon interaction (Table 2 and Figure 7b, 7d, 7f, 7h).

Discussion

Drought induced acidification

Oxidizing effects of water-level flow have been reported for mire surface water (Sparling 1966) and near lake shore ground water (Schafran & Driscoll 1990), while ponding of surface water has been reported to cause reduction of the water column and upper peat layers (DeVito & Dillon 1993). The experimental set-up used here, isolated the cores from horizontal water movement. This probably caused the reduction and concomitant alkalinization of the top peat layer (Roelofs 1991). The effect of drought is exactly opposite: entrance of oxygen caused oxidation and acidification in the pore-water solution. The drought effect was reflected in the first sample collected after lowering the

Table 2. Values of F and p of a Repeated Measures Anova of pH-H_2O (1:1) and ammoniumacetic acid and ammonium oxalate-oxalic acid soil extraction. p values < 0.05 are considered statistically significant.

	df	F/p-value				
		pH-H_2O(1:1)	Al (Amac)	Fe(Amac)	Ca(Amac)	P (Amac)
Time	1		0.28/0.626	0.61/0.478	**9.97/0.034**	**14.15/0.020**
Drought	1	**28.27/0.006**	**36.72/0.004**	5.88/0.072	3.52/0.134	5.25/0.084
Horizon	3	**3.85/0.039**	2.31/0.128	**14.92/0.000**	1.93/0.179	0.56/0.653
Time × drought	1		2.55/0.185	4.81/0.093	**9.51/0.037**	1.32/0.315
Time × horizon	3		0.40/0.754	1.39/0.294	**3.98/0.035**	0.61/0.619
Drought × horizon	3	1.51/0.263	0.07/0.973	**7.47/0.004**	**4.44/0.026**	0.62/0.614
Time × drought × horizon	3		1.63/0.234	3.47/0.051	0.97/0.438	0.19/0.902
			Al(Oxac)	Fe(Oxac)		P (Oxac)
Time	1		4.21/0.109	5.06/0.88		3.28/0.145
Drought	1		2.05/0.225	1.97/0.233		0.92/0.393
Horizon	3		0.16/0.713	**3.98/0.035**		**14.80/0.000**
Time × drought	1		0.16/0.713	0.06/0.819		0.20/0.678
Time × horizon	3		0.76/0.540	**3.70/0.043**		**4.70/0.022**
Drought × horizon	3		0.41/0.752	0.34/0.800		0.20/0.897
Time × drought × horizon	3		0.49/0.696	0.50/0.691		0.28/0.840

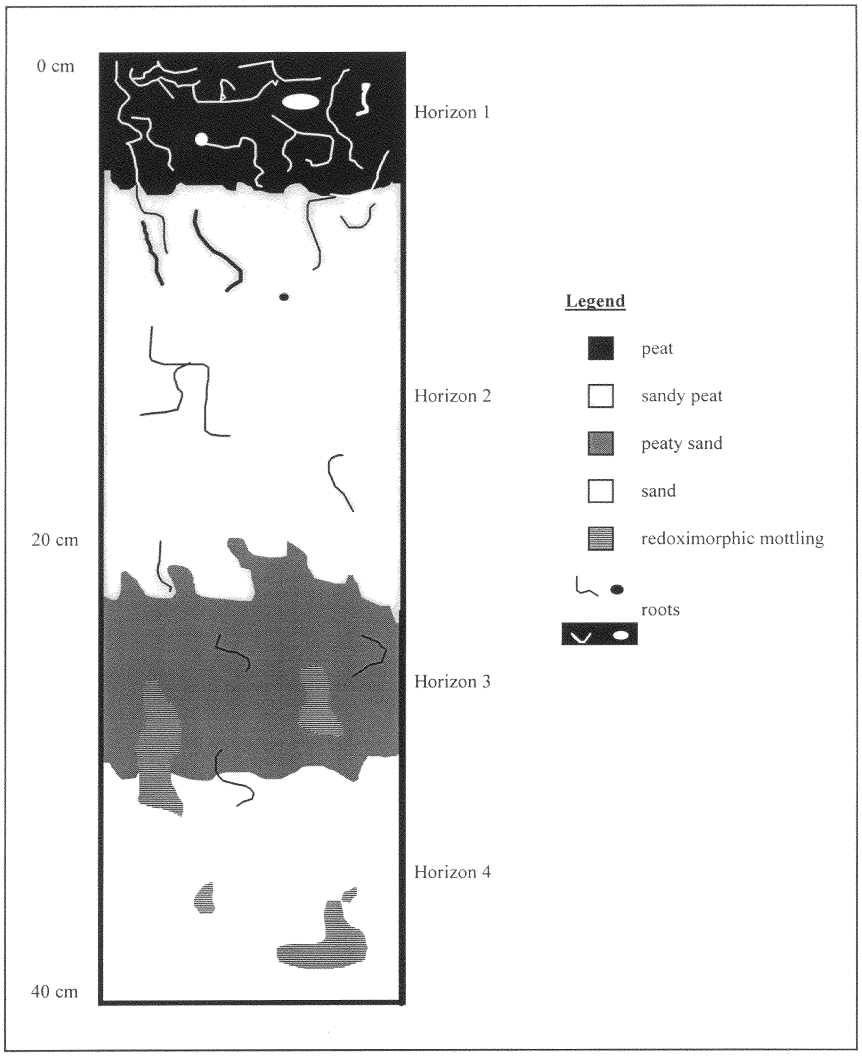

Figure 5. General soil profile.

water table (i.e., within one week), but became fully evident in the second (i.e., after two weeks). The build up of a reductive potential and alkalinity during the pre-drawdown period undoubtedly slowed the drought response. Ca^{2+} and Mg^{2+} concentrations were illustrative in this respect. Alkalinization as well as acidification resulted in a rise of both concentrations in the soil solution. The first because during reduced conditions, alkalinization supports the replacement of exchangeable Ca^{2+} and Mg^{2+} by Fe^{2+} (Van Breemen 1987). Acidification induced by oxidation, will also increase the dissolved Ca^{2+} and

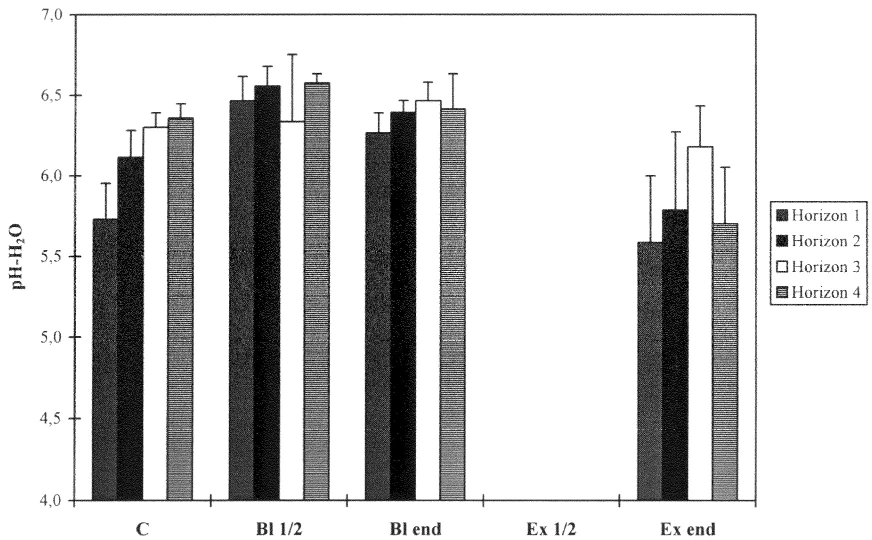

Figure 6. Mean soil pH-H_2O in control, blank and experimental soil cores. Values are means from 5 replicates ($\pm$ s.e.) (horizon legend see Figure 5).

Mg^{2+} in the soil solution because of cation exchange with H^+. Therefore Ca^{2+} and Mg^{2+} concentrations first decreased and then increased again after water-table drawdown. Our experiment showed that drought induced acidification of the soil solution comes into play one to two weeks after moderate (20 cm) water-table drawdown. When the water levels were brought to the surface again, the opposite process occurred, illustrating the reversibility. The soil-water composition proved to be the most sensitive indicator of drought effects. This should not be surprising. Soil water was sampled from an almost undisturbed soil, whilst soil analyses required important disturbance that may mask the subtle changes we were interested in here. Moreover, the high capacity of the solid phase makes it less sensitive to short chemical transitions than the soil-water solution. Nevertheless, significant drought effects on soil pH, Al(Amac), Fe(Amac) and Ca^{2+}(Amac) were observed that are in line with soil-water solution changes.

Both soil and soil-water data show that drought effects were most pronounced in the peat layer. The transitional and the sandy horizons were less strongly influenced by a decrease of the water level. This difference can be explained by capillary rise causing permanent wetting of the transitional horizon. Because the ground-water table was only lowered 20 cm, the lowest part of the soil cores, the sandy horizons, remained wet. As most roots were present in the peat layer, the vegetation readily experiences redox and acid/base shifts.

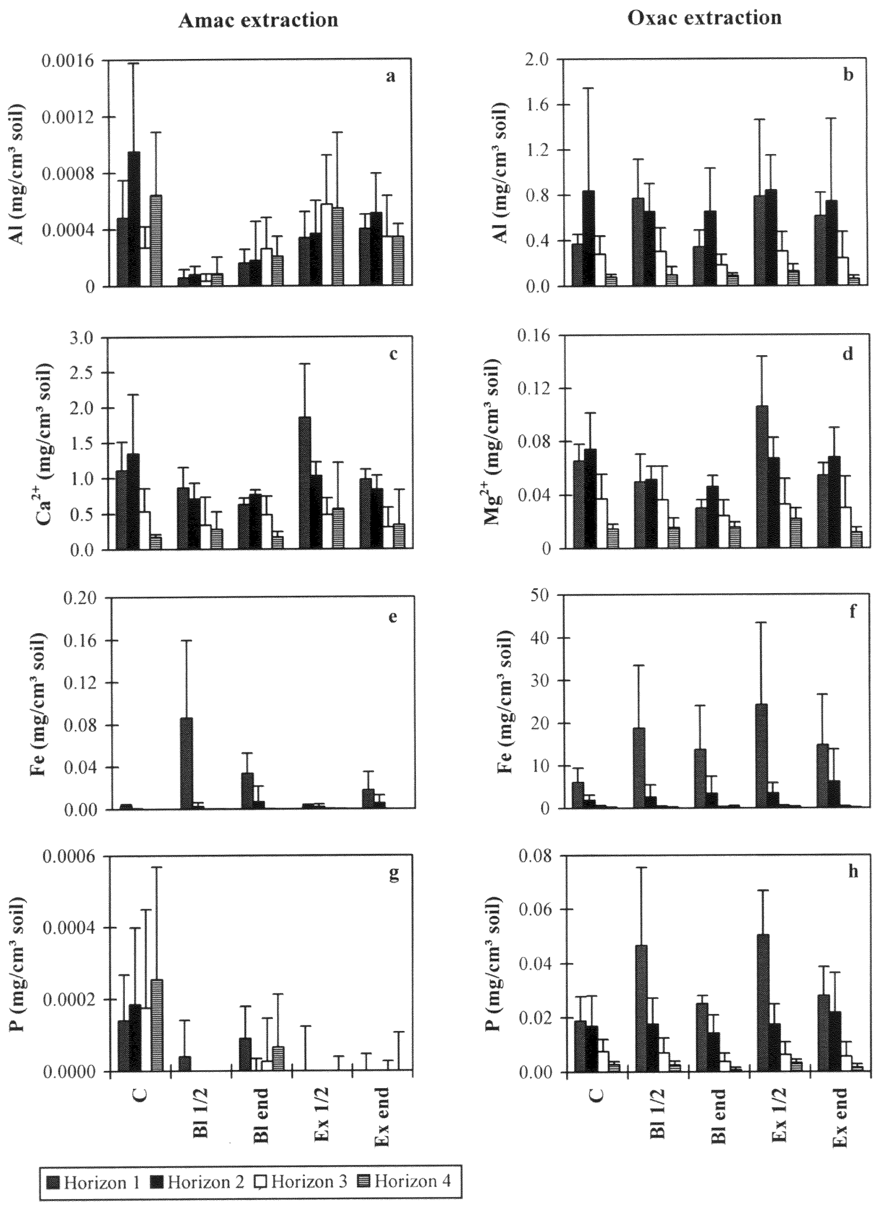

Figure 7. Mean Al, Ca^{2+}, Fe, Mg^{2+} and P concentration after an ammonium oxalate-oxalic acid and ammoniumacetic acid extraction of control, blank and experimental soil cores. Values are means from 5 replicates (± s.e.) (horizon legend see Figure 5).

Effects of acid/base transitions on P dynamics

Apart from the effect on the soil acid/base conditions, we found an indication for a drought induced increase of SRP in the soil solution. This is in accordance with a field observation during summer drought in the study area (Boeye et al. 1996). Grootjans et al. (1985) found available P in *Cirsio-Molinietum* vegetations to be higher during drying than during very wet or very dry conditions. Oxidation has been shown to limit P solubility because of more efficient binding of P by ferric vs. ferrous Fe (Patrick & Khalid 1974). Moreover, the limitation of P solubility by Fe and Al minerals is most efficient at low pH values (Brady 1974; Berkheiser et al. 1980). On the other hand, in hard water systems, P is controlled by Ca minerals, and these are most efficient in binding P at high alkalinity (Stumm & Leckie 1971; Driscoll et al. 1993). Rich fens that lack soil calcite precipitates, are chemically intermediate between soft and hard water systems and are weakly buffered. This means they can easily switch to acid conditions due to processes like we have studied here. In the transient state of drought induced acidification, pH values lie between 5.5 and 6, where P supply from sediments is optimal (Lucas & Davis 1961; Stumm & Morgan 1981; Richardson & Marshall 1986). More insight should be gained by using non-P adsorbing material for Rhizon SMS construction, which will allow continuous P monitoring.

Conclusion

There is little doubt that acid/base and nutrient status of rich fens are important determinants of vegetation composition and distribution (Wheeler & Shaw 1995). However, little is known on the effect of the dynamic behaviour of these factors. Some point to the stable hydrochemical conditions in groundwater discharge fens to explain their high species richness (Wassen et al. 1989), while others attribute it to the large spatial and temporal variability (Vitt & Chee 1990; van Wirdum 1991). We have illustrated here that induced water level fluctuations introduce strong dynamics in the soil hydrochemical system of a weakly buffered fen. Yet it harbours a species rich vegetation with many typical rich fen species (Boeye & Verheyen 1994). An inquiry of the tolerance limits of rich fen species for temporal acidification and of their potential to use available nutrients under these conditions may provide insight in this problem.

Apart from biological effects, the relative short oxidation and acidification periods may have a large impact on annual chemical budgets and thus on downstream water quality (DeVito & Dillon 1993; LaZerte 1993) and on trace gas emissions (Freeman et al. 1993) from wetlands. In view of predicted climate changes, these aspects all merit an evaluation of the significance of temporal acidification for fens in general. A picture of controlling site factors should be composed. An inventory of these factors in different fens over Europe may provide insight in the reaction of the rich fen habitat resource to predicted climate changes.

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