

# Calcareous groundwater raises bogs; the concept of ombrotrophy revisited

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## Summary

**1** Raised bogs are traditionally regarded as being solely dependent upon atmospheric influences. However, these terrestrial carbon stores may also be affected by calcareous (bicarbonate-rich) groundwater, which is often found in deeper peat layers.

**2** Field data from a bog area in the Netherlands were used to select appropriate levels of bicarbonate supply for an aquarium mesocosm experiment. The effects of 0, 0.1, 0.5, 1 and 2 mmol  $\text{HCO}_3^- \text{ l}^{-1}$ , and 1 mmol  $\text{HCO}_3^- \text{ l}^{-1} + 2 \text{ mmol SO}_4^{2-} \text{ l}^{-1}$ , on the biogeochemistry of peat monoliths, including their *Sphagnum* vegetation, were investigated.

**3** Slightly increased alkalinity rapidly stimulated buoyancy of living *Sphagnum* due to higher inorganic carbon concentrations in the water layer. Moderate  $\text{HCO}_3^-$  concentrations also stimulated buoyancy of the entire peat monoliths after 3 weeks, because of increased methane production rates. High alkalinity, however, led to rapid internal phosphate mobilization, peat disintegration and *Sphagnum* die-off. This detrimental effect was stronger when sulphate was supplied simultaneously.

**4** The results are discussed with respect to the carbon dynamics and overall functioning of peat bogs, in relation to hydrology and hydrochemistry (groundwater influence, sulphate pollution).

*Keywords:* bicarbonate, carbon dioxide, eutrophication, hydrology, methane, peatlands, sulphur, *Sphagnum*

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## Introduction

Peatlands have received much attention because of their role in global carbon (C) cycling, where they are important as both terrestrial sinks and sources for greenhouse gases such as carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ) (e.g. Harriss *et al.* 1985; Khalil & Rasmussen 1990). There is therefore much concern about the effects that changes in temperature and precipitation, which may result from global climatic changes, may have on the exchange of these two gases between peatlands and the atmosphere (Gorham 1991; Moore & Roulet 1993; Yavitt *et al.* 1993; Silvola *et al.* 1996; Saarnio *et al.* 1998). However, far less research has focused on the role of  $\text{CO}_2$  and  $\text{CH}_4$  within peatlands, although both gases undoubtedly play such an internal role.

Raised bogs constitute a significant part of the world's peatlands. Recently, Moore (1997) questioned the generally accepted idea that these acidic peatlands are ombrotrophic and are therefore no longer influenced by mineral-rich groundwater. His statement was based on the findings of Glaser *et al.* (1997), who discovered an unexpected upward movement of water from the mineral base in raised bogs during dry periods. Similar groundwater flow reversals in bogs have been reported by Devito *et al.* (1997). One result of this reversed flow is that minerals supplied from below may reach the roots of the vegetation.

The contact between calcareous [(bi)carbonate-rich] groundwater and acidic peat will, however, also influence geochemical and microbial reactions that control gas production. The bicarbonate ( $\text{HCO}_3^-$ ) involved originates from calcareous deposits in deeper layers (minerotrophic peat and mineral soil) and biogeochemical reduction processes.

Moreover, this contact may lead to an increased upward flow of inorganic carbon, which can then serve as a nutrient in the acrotelm.

Many peatlands, including bog areas, are currently suffering from pollution by sulphate originating from the atmosphere, groundwater and surface water. The increased availability of sulphur compounds not only affects the functioning of characteristic plant species but also the biogeochemical fluxes of nutrients in peatlands (Ferguson & Lee 1983; Heathwaite 1990; Freeman *et al.* 1993; Smolders & Roelofs 1993; Lamers *et al.* 1998). We expect that sulphate pollution will in addition interfere with gas production in bog systems.

To test the effects of the influence of buffered groundwater and of sulphate pollution on the biogeochemistry and vegetation of bogs, we analysed a groundwater profile in a bog area in the Netherlands and conducted a mesocosm experiment in which the supply of  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  was manipulated. The results are discussed against the background of current theories on raised bog functioning.

### Materials and methods

The study was performed in the Haaksbergerveen Nature Reserve (52°9'N, 6°53'E) in the Netherlands. The reserve is a cut-over peatland where bog restoration, which is being carried out by the State Forestry Service, involves flooding as a result of ditch-blocking and the construction of sand bunds. Before regeneration the heaths were characterized by an *Ericion tetralicis* community (Ellenberg 1988) often dominated by *Molinia caerulea* (L.) Moench, *Betula pubescens* Ehrh. and *B. pendula* Roth. Flooding caused the death of *Molinia* and *Betula*, and within 10–15 years a characteristic hummock-hollow vegetation (*Sphagnion magellanici* and *Rynchosporion albae*; Ellenberg 1988) dominated by several *Sphagnum* spp. (including *S. magellanicum* Brid. and *S. papillosum* Lindb.) and characteristic ericaceous species (*Andromeda polifolia* L., *Oxycoccus palustris* Pers., *Erica tetralix* L.) had established successfully on peat remnants that had begun to float (Fig. 1). However, *Betula* spp. and *M. caerulea* also rapidly colonized this floating bog, as observed in many other bog areas in the Netherlands (Schouwenaars *et al.* 1997) and in other Western European countries (Aaby 1995). This is a source of great concern for bog management.

### PROFILE SAMPLING

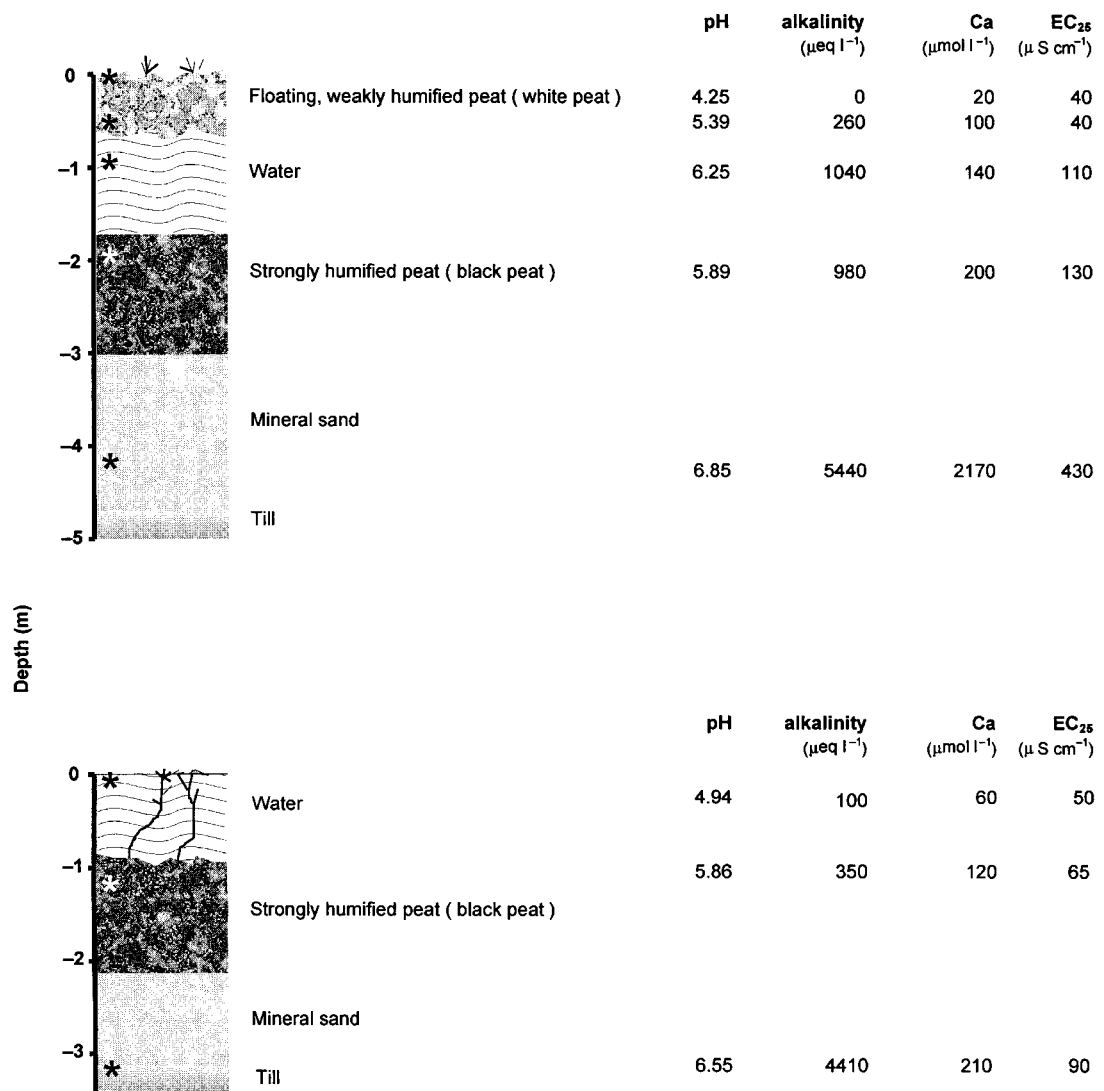
Groundwater samples were collected from sites in the regenerated bog from PVC piezometers ( $\phi$ 32 mm tubes with nylon filters) with filters at different depths, using a peristaltic handpump. Samples were

taken both from an area with floating peat and from an adjacent area dominated by open water. Moisture samples from the top peat layer (at 10 cm below surface level) were taken with ceramic soil moisture sample cups (Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands) connected to vacuum serum bottles.

### EXPERIMENTAL DESIGN

A location was selected close to the profile sampling sites, where the rewetting measures had yet to be taken. The soil and vegetation type were therefore characteristic of the conditions before restoration. Peat monoliths were collected from this site in November 1995. In total, 18 monoliths were cut (20 × 20 cm, depth  $\pm$  13 cm) and on the same day were placed in glass aquaria (24 × 24 cm, depth 32 cm) with an overflow at 5 cm from the top (volume 15.5 l; Fig. 2.). The vegetation on the cores consisted mainly of *Sphagnum cuspidatum* Hoffm. (75–90% cover) along with some *Eriophorum angustifolium* Honckeny and *Molinia caerulea*. At the beginning of the experiment, the water level was about 20 cm above the cores. All aquaria were placed in a water bath and maintained at 20 °C in a climate control room with a light level of 100  $\mu\text{mol m}^{-2} \text{s}^{-1}$  at the vegetation level, and a daily photoperiod of 12 h. Each aquarium received water from its own polyethylene stock container (100 l, stored in the dark) through black silicon tubes, at a flow rate of 15.5 l week<sup>-1</sup> that was maintained by peristaltic pumps. The basic composition of this 'groundwater' (Table 1) was based on that of the upper groundwater in the Haaksbergerveen, with either 0, 0.1, 0.5, 1 or 2 mmol l<sup>-1</sup>  $\text{HCO}_3^-$  (added as  $\text{NaHCO}_3$ ). These concentrations are within the range found in the field. In addition, some aquaria were supplied with 1 mmol l<sup>-1</sup>  $\text{HCO}_3^-$  + 2 mmol l<sup>-1</sup>  $\text{SO}_4^{2-}$  (as  $\text{Na}_2\text{SO}_4$ ). Each experimental treatment consisted of three replicates, randomly distributed over the water bath. The water inlets (Pasteur pipettes connected to the tubes) were placed under the monoliths. A thin hook was used to determine the position of the underside of each monolith, to assess buoyancy.

Three soil moisture samplers (Rhizon SMS-10 cm; Eijkelkamp Agrisearch Equipment) were placed in each monolith to allow collection of representative peat moisture samples. Peat moisture was collected by connecting vacuum infusion flasks (30 ml) to each sampler. The first 5 ml collected was discarded to exclude the internal stagnant sampler water. The three subsamples were pooled after the flasks had been almost completely filled. Surface water was collected using PVC syringes (60 ml). The response of the vegetation was monitored by counting the num-



**Fig. 1** Depth profile for pH, alkalinity, Ca concentration and electric conductivity (EC<sub>25</sub>) for two locations in the Haaksbergerveen reserve. Top: floating bog with *Sphagnum magellanici* and *Rynchosporion albae* vegetations. Bottom: slightly buffered open water characterized by *Potamogeton polygonifolius* Pourr. and *Potentilla palustris* (L.) Scop. Sampling depths are indicated by asterisks.

ber of *Sphagnum capitula*, and by estimating the cover and vitality of the different plant species.

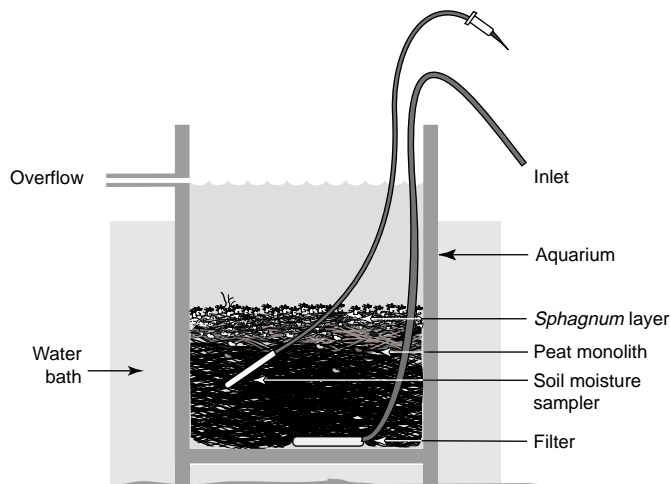
The vegetation in the aquaria was sprayed three times per week with artificial rainwater (Table 1), at a rate equivalent to 750 mm precipitation year<sup>-1</sup>.

#### ANALYSIS OF SURFACE WATER AND PEAT MOISTURE

The pH was determined with a standard KCl pH electrode, and alkalinity and acidity were estimated by titrating part of the sample down to pH 4.2 using HCl, or up to pH 8.2 using NaOH, respectively. Electric conductivity was determined with a Yellow Springs Instruments 33 SCT conductivity meter (Yellow Springs, Ohio, USA), and standardized to T = 25 °C (EC<sub>25</sub>). Colour at 450 nm (E<sub>450</sub>) was mea-

sured for colorimetric background correction and as an estimate for humic substance concentration (dystrophy), after a few grains of citric acid had been added to get a pH of 3.5 (to prevent precipitation of metal ions). The samples were stored (for a maximum of 3 weeks) in iodated polyethylene bottles (100 ml) at -20 °C until further analysis.

Free sulphide was determined in a 10-ml subsample fixed immediately after collection with sulphide anti-oxidant buffer, and measured as described earlier (Lamers *et al.* 1998). The concentrations of o-phosphate, nitrate (and nitrite) and ammonium in the samples were measured colorimetrically, potassium by flame photometry, and total concentrations of calcium, magnesium and sulphur (sulphate) by inductively coupled plasma emission spectrometry, as described earlier (Lamers *et al.* 1998). The data



**Fig. 2** Experimental set-up for one aquarium. The peat monolith (including its vegetation) is shown in the initial position.

were corrected for colour caused by humic substances.

Methane evolution was measured 30 weeks after the aquaria had been set up. Rubber stoppers were carefully placed in the outlets and two layers of parafilm over the tops so that the aquaria were hermetically sealed. At  $t = 1, 2.5$  and  $4$  h, a 50-ml gas sample was carefully taken from the headspace (1800–3400 ml) through the stopper using a syringe, and analysed for  $\text{CH}_4$  on a Pye Unicam gas chromatograph (Unicam, Cambridge, UK) equipped with a flame photometric detector and a Porapak Q (80/100 mesh) column (Waters Chromatography, Etten-Leur, The Netherlands). The low initial  $\text{CH}_4$  concentrations showed that there had been no extra  $\text{CH}_4$  ebullition due to disturbance during the sealing procedure. As the concentrations showed a linear increase with time, the data could be used to calculate the net  $\text{CH}_4$  emission.

#### DATA ANALYSES

As samples were collected several times from the same units, a repeated measures analysis was used (Potvin *et al.* 1990). The data were analysed using the SAS procedure GLM, model one-way ANOVA, for repeated measures (SAS 1989). Data were log-transformed to make the variances less dependent on the sample means, and for a better fit to the normal distribution. To compensate for uneven time intervals, an orthogonal polynomial transformation was used. Differences at a given time were analysed by a Tukey post-test at the 0.05 confidence limit (SAS 1989). Log-transformed  $\text{CH}_4$  flux data were analysed by ANOVA, and compared to the control values using a Dunnett post-test at the 0.05 confidence limit (SAS 1989). For clarity of presentation,

the means and standard errors are presented as non-transformed data.

## Results

### GROUNDWATER PROFILE IN THE FIELD

Groundwater quality in the Haaksbergerveen site showed a distinct depth profile for bicarbonate alkalinity and pH (Fig. 1). In contrast to the surface layer of the floating peat mat, which was unbuffered and acidic, peat moisture was slightly buffered ( $260 \mu\text{eq l}^{-1}$ ) at only 30 cm below surface level (BSL). The water between the mat and the sediment (sampled at 1 m BSL) was moderately buffered ( $1 \text{ meq l}^{-1}$ ). The chemical analyses showed that this alkalinity was mainly due to calcium bicarbonate and magnesium bicarbonate (results not shown). On sites without a floating raft, the surface water was slightly buffered and covered with plant species indicative of this condition. Hydrological research has shown that the buffered water at both types of site originated from local groundwater flowing towards the peat base (Streefkerk *et al.* 1997).

### EFFECTS OF EXPERIMENTAL BICARBONATE BUFFERING AND SULPHATE ADDITION IN MESOCOSMS

Low levels of experimentally increased alkalinity ( $0.1$  and  $0.5 \text{ mmol l}^{-1}$ ) rapidly induced higher  $\text{CO}_2$  concentrations in the water layer, due to contact between the added  $\text{HCO}_3^-$  and acidic peat. Living *Sphagnum cuspidatum* that had originally been on the top of the monolith began to float within 1 week, unlike the plants in control aquaria, which remained on the top of the submerged peat monolith. At higher levels of  $\text{HCO}_3^-$  the pH of the surface water increased (from 4 to about 5 for the  $0.5 \text{ mmol}$

**Table 1** Chemical composition of the artificial groundwater and rainwater (in  $\mu\text{mol l}^{-1}$ )

	Groundwater	Rainwater
CaCl <sub>2</sub>	150	16
MgCl <sub>2</sub>	30	9
KCl	30	12
NaHCO <sub>3</sub>	0, 100, 500, 1000 or 2000	–
Na <sub>2</sub> SO <sub>4</sub>	0 or 2000	5
NaCl	–	79
NH <sub>4</sub> NO <sub>3</sub>	–	30
Na <sub>2</sub> HPO <sub>4</sub>	–	0.1
pH	7.5	5.0

$\text{l}^{-1}$  treatment, and to 6.5–7 for the higher concentrations; Fig. 3 and Table 2). This shift in pH led to CO<sub>2</sub> concentrations becoming lower as HCO<sub>3</sub><sup>–</sup> concentrations rose above 0.5 mmol  $\text{l}^{-1}$ , although total inorganic carbon (TIC) increased, as shown by the alkalinity (bicarbonate) data.

Unexpectedly, buoyancy of the complete peat monoliths was also stimulated by HCO<sub>3</sub><sup>–</sup> (Fig. 3 and Table 2), indicating increased production and storage of gas in the peat. Treatment resulted in no significant changes in acidity of the peat moisture and the observed effect could therefore not be attributed to increased production of CO<sub>2</sub>. There was, however, a strong increase in CH<sub>4</sub> production, up to nine times the control values for the 1 mmol  $\text{l}^{-1}$  treatment, indicating the role of this gas in buoyancy (Fig. 4).

Peat moisture became more strongly coloured by humic substances with higher concentrations of bicarbonate (indicated by extinction values at 450 nm; Fig. 3 and Table 2). Addition of sulphate increased alkalinity and pH above the levels observed with 1.0 mmol  $\text{l}^{-1}$  HCO<sub>3</sub><sup>–</sup> alone. PO<sub>4</sub><sup>3–</sup> concentrations, both in peat moisture and surface water, increased for those monoliths treated with sulphate or with 2 mmol  $\text{l}^{-1}$  HCO<sub>3</sub><sup>–</sup>. All treatments resulted in decreased NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> concentrations during the experiment, while NO<sub>3</sub><sup>–</sup> levels remained as low as 2–5  $\mu\text{mol l}^{-1}$  (data not shown). Of the 2000  $\mu\text{mol l}^{-1}$  SO<sub>4</sub><sup>2–</sup> added, only 1600  $\mu\text{mol l}^{-1}$  was recovered. The free sulphide concentration rose to levels as high as 60  $\mu\text{mol l}^{-1}$  in the SO<sub>4</sub><sup>2–</sup> treated group, whereas it remained below 5  $\mu\text{mol l}^{-1}$  in the others (data not shown).

The addition of 2 mmol  $\text{l}^{-1}$  HCO<sub>3</sub><sup>–</sup>, and of 1 mmol  $\text{l}^{-1}$  HCO<sub>3</sub><sup>–</sup> + 2 mmol  $\text{l}^{-1}$  SO<sub>4</sub><sup>2–</sup>, resulted in a significant die-back of *Sphagnum cuspidatum* within 14 weeks. The peat monoliths lost their texture and there was a strong development of filamentous algae. In the other treatments, *Sphagnum* remained healthy and the monoliths did not disintegrate. At the time of CH<sub>4</sub> sampling (after 30 weeks), the sulphate treatment had almost completely blocked methane evolution (Fig. 4).

## Discussion

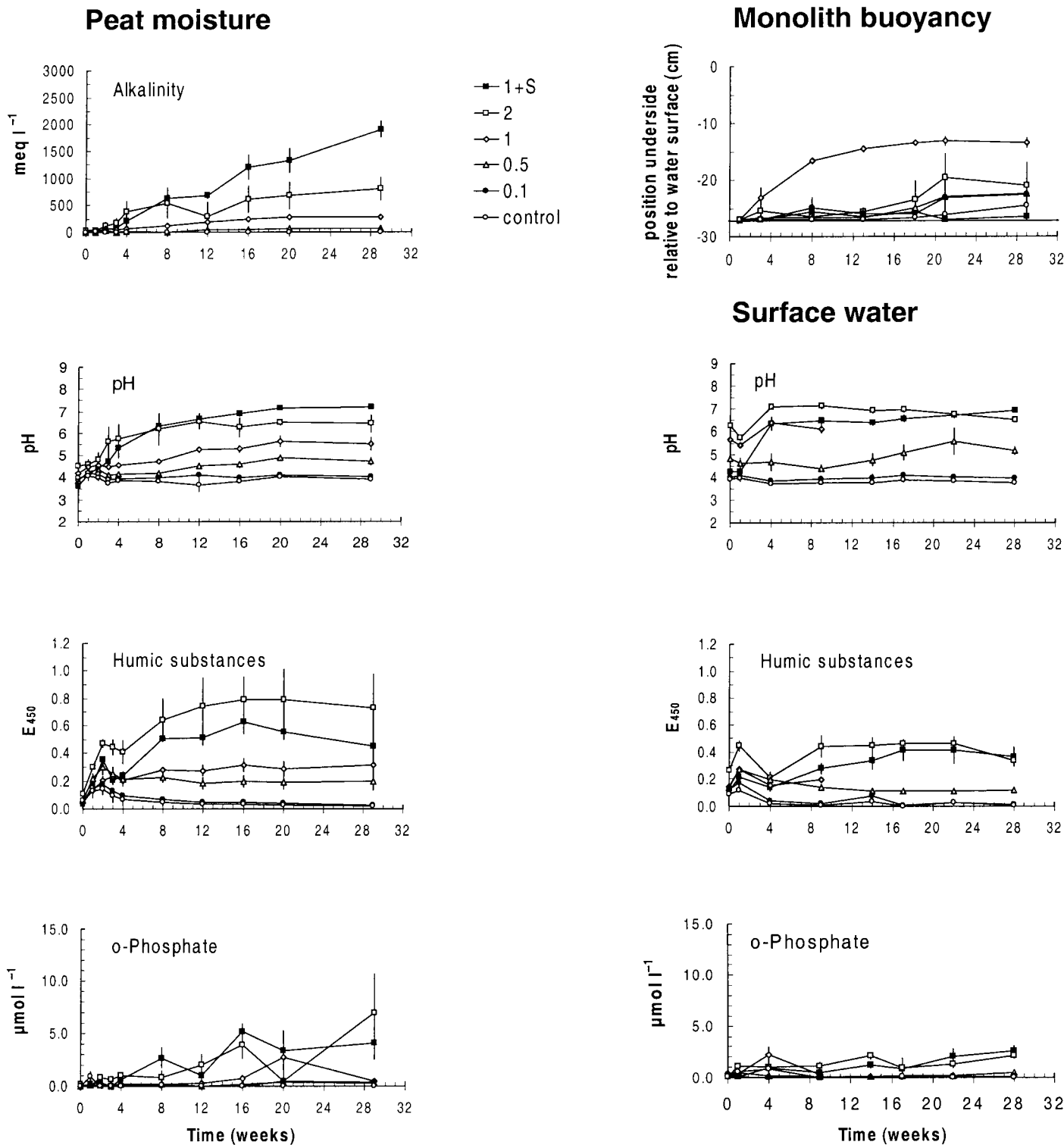
The strong depth-related increase in alkalinity and pH found in the Haaksbergerveen reserve was similar to the results found in other bogs (Siegel & Glaser 1987; Devito *et al.* 1997; Glaser *et al.* 1997). We demonstrated that the acid buffering by bicarbonate in deeper peat layers, as found in the gradient analysis, was of functional significance, due to the stimulation of CH<sub>4</sub> and CO<sub>2</sub> production.

The same level of alkalinity as found in the field led to buoyancy of peat remnants in the mesocosm experiment, through the strong stimulation of methanogenesis. For floating bogs, the production of CH<sub>4</sub> bubbles must be sufficient to provide buoyancy for the peat in which it is trapped. The bubbles act as a CH<sub>4</sub> buffer between peat and the atmosphere (Fechner-Levy & Hemond 1996). An increase in pH to circumneutral values (due to acid buffering by HCO<sub>3</sub><sup>–</sup>), which occurs in deeper peat layers, is known to accelerate CH<sub>4</sub> production in acidic peat (Phelps & Zeikus 1984; Williams & Crawford 1984; Goodwin & Zeikus 1987; Dunfield *et al.* 1993). This acceleration is caused by increased availability of substrates such as H<sub>2</sub> + CO<sub>2</sub> or acetate due to stimulation of microbial hydrolysis of complex polymers, or by a direct effect of increased pH on methanogenic Archaea. Moreover, increased CO<sub>2</sub> availability has been shown to stimulate methanogenesis in monoliths covered with *Sphagnum* and sedges, or with *Sphagnum* only, probably through the increased production and leaching of organic substances that can serve as substrates for methanogens (Saarnio *et al.* 1998). The simultaneous addition of 1 mmol  $\text{l}^{-1}$  HCO<sub>3</sub><sup>–</sup> and 2 mmol  $\text{l}^{-1}$  SO<sub>4</sub><sup>2–</sup> strongly inhibited CH<sub>4</sub> production (by 99%, compared with the 1 mmol  $\text{l}^{-1}$  HCO<sub>3</sub><sup>–</sup> alone treatment), as could be expected because of substrate competition between methanogens and SO<sub>4</sub><sup>2–</sup> reducers (Lovley & Klug 1983; Fowler *et al.* 1995).

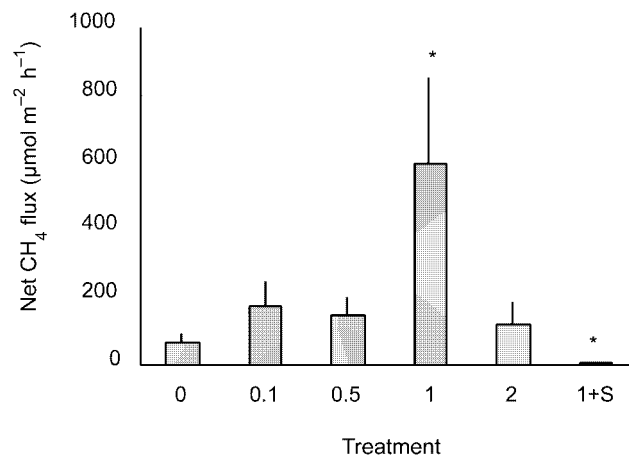
Bicarbonate addition stimulated the production of CO<sub>2</sub> by chemical reaction with abundant organic acids in the peat, and increased decomposition rates (shown by an increase in dissolved humic substances in peat moisture) due to internal pH buffering of organic matter (McKinley & Vestal 1982; Kok *et al.* 1990; Kok & Van de Laar 1991). The observed increase in the concentration of humic substances, and internal alkalinity generation by microbial reduction processes, also contributed to the buffering of the pH. It is known that CO<sub>2</sub> flow from underwater sediments, originating from decomposition, groundwater discharge or moderate artificial liming and subsequent reacidification, regulates photosynthetic rates and thereby growth of peat moss in pools and lakes (Roelofs *et al.* 1984; Wetzel *et al.* 1985; Alenäs *et al.* 1991). For aquatic *Sphagnum* spp., such as *S. cuspidatum*, a high concentration of dissolved CO<sub>2</sub> (> 500  $\mu\text{mol l}^{-1}$ ) has

been shown to be essential for buoyancy (Paffen & Roelofs 1991). Photosynthetic rates must be sufficiently high for the formation of oxygen bubbles (supersaturation), which are trapped in the strongly branched leaves of *Sphagnum*. This is vital for these

mosses in deeper, dystrophic waters (i.e. those strongly coloured due to high concentrations of humic substances), as light penetration below 0.5 m is insufficient for the maintenance of adequate photosynthetic rates (personal observations by the



**Fig. 3** Peat moisture and surface water characteristics during 28 weeks after bicarbonate addition at the concentrations (mmol l<sup>-1</sup>) indicated alone or in combination with 2.0 mmol l<sup>-1</sup> sulphate (1 + S). Means are given, with their standard error ( $n = 3$ ). The horizontal line in the monolith buoyancy figure represents the base of aquarium. Monoliths treated with 1.0 mmol l<sup>-1</sup> HCO<sub>3</sub><sup>-</sup> reached the water surface after 9 weeks, so no surface water was present after this time.



**Fig. 4** Net fluxes of CH<sub>4</sub> in the laboratory mesocosms after 30 weeks treatment, as affected by the addition of bicarbonate ± sulphate. Means are given, with their standard error. \*Significantly different from control (0).

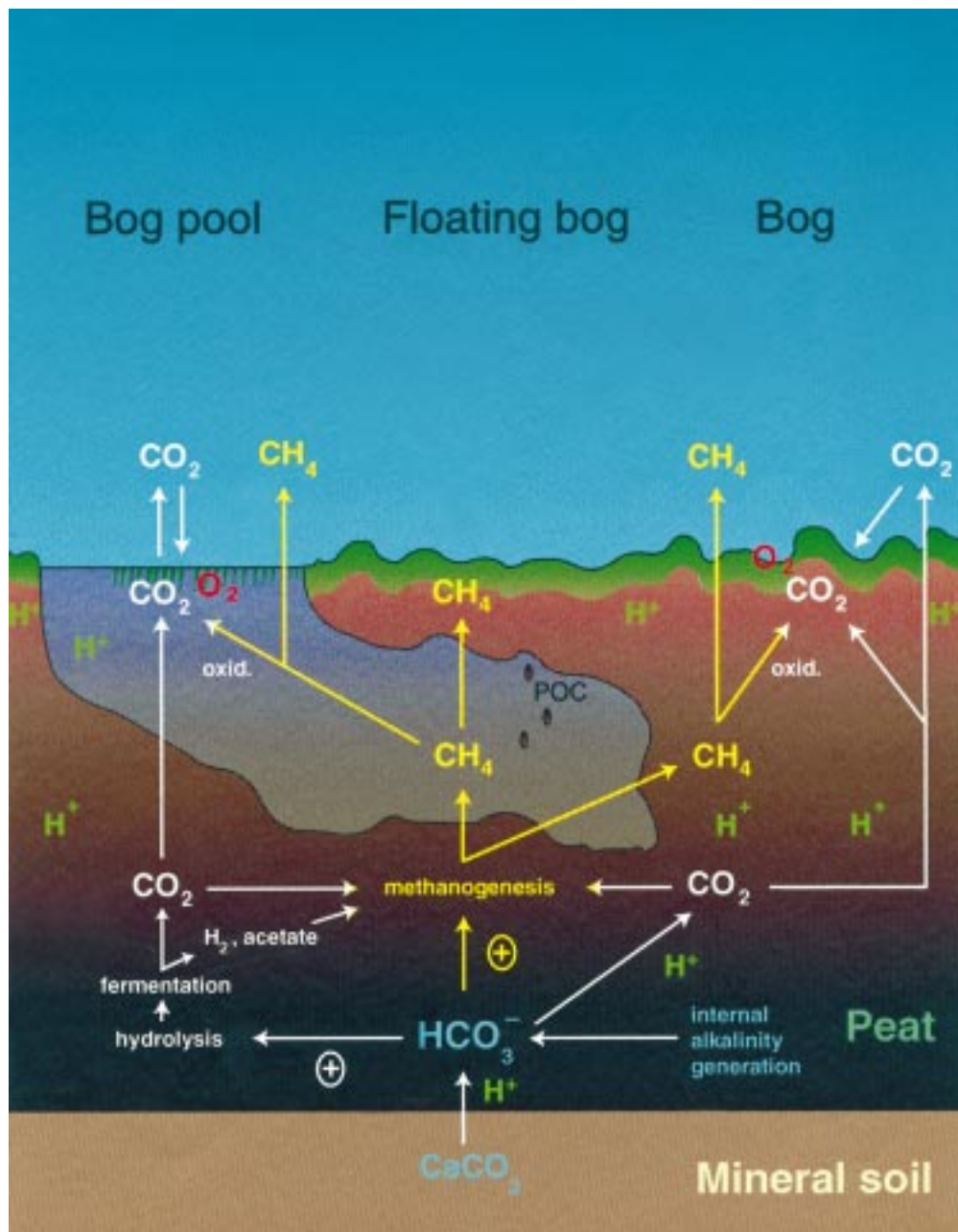
authors). It is very plausible that CO<sub>2</sub> evolution from the peat catotelm also regulates photosynthetic rates and growth of terrestrial, hummock-forming *Sphagnum* spp. The CO<sub>2</sub> concentration needed to saturate photosynthesis of these plants is, unlike that of many vascular plants, much higher than the present ambient atmospheric CO<sub>2</sub> concentration. Levels of four times the ambient concentration, and for water-saturated *Sphagnum* even up to 20 times this value, still stimulate photosynthesis (Silvola 1990). In this way, some of the CO<sub>2</sub> diffusing rapidly from peat moisture due to the strong concentration gradient between this water (several mmol l<sup>-1</sup>) and the atmosphere (*c.* 15 µmol l<sup>-1</sup>) will be fixed by the living top layer, which is sheltered from air movements. Preliminary measurements (by infra red gas analysis) of air inside *Sphagnum* hummocks, taken from between green parts below the capitula of the mosses, showed CO<sub>2</sub> concentrations twice the ambient level above the hummock (personal observations by the authors). As the samples were taken during daylight (after 8 h of photoperiod), this strongly supports the hypothesis that a natural 'CO<sub>2</sub>-enriched greenhouse' is formed by *Sphagnum* in layers and hummocks, trapping soil-derived CO<sub>2</sub>. This theory is supported by the work of Tolonen *et al.* (1992), who estimated from δ<sup>14</sup>C analyses that 20% of the CO<sub>2</sub> fixed by the *Sphagnum* vegetation originated from soil respiration. The partial oxidation of CH<sub>4</sub> by methanotrophs in the upper water and peat layers (Crill *et al.* 1994) forms an additional CO<sub>2</sub> source. The interrelation of these biogeochemical processes in bogs, with the effects of bicarbonate enrichment, is shown in Fig. 5.

High alkalinity in the peat top layer resulted in strong peat degradation and loss of structure, through the stimulation of decomposition rates. Phosphate concentrations in peat and surface water increased, and filamentous algae began to grow.

This type of eutrophication, caused by increased internal nutrient release rates and not by extra nutrient influx, is termed internal eutrophication (Roelofs 1991). Moreover, *Sphagnum* died because of the high alkalinity and the concomitant pH increase above 5 (Clymo & Hayward 1982). These detrimental effects are identical to the observations in bog areas flooded or waterlogged with alkaline surface water in order to compensate for water shortage and desiccation (Roelofs & Cals 1989).

Increased concentrations of sulphur, not only in atmospheric deposition but also in groundwater and surface water (Heathwaite 1990; Freeman *et al.* 1993), may endanger peatlands because of direct toxicity of sulphur compounds (Ferguson & Lee 1983; Lee & Studholme 1992). In addition, the increased availability of SO<sub>4</sub><sup>2-</sup> often leads to eutrophication and sulphide toxicity, due to increased SO<sub>4</sub><sup>2-</sup> reduction rates (Smolders & Roelofs 1993; Lamers *et al.* 1998). In acidic peat, these rates are generally low, but alkalinity provided by groundwater or microbial reduction processes strongly promotes SO<sub>4</sub><sup>2-</sup> reduction (Roelofs 1991). In addition, the reduction of SO<sub>4</sub><sup>2-</sup> generates alkalinity (Fig. 3), providing a positive feedback. As was shown in our experiment, methane production, necessary for floating bog development, is seriously hampered by sulphate pollution. Internal eutrophication, alkalization and sulphide toxicity combine to make *Sphagnum* growth impossible.

It is striking that the formation of *Sphagnum* hummocks occurs much faster in minerotrophic fens, where peat has grown slightly above the mineral-rich water layer, compared with (former) bog areas. Decomposition rates, and thereby CO<sub>2</sub> evolution, are usually higher in the pH-buffered fens. This is very interesting, as the majority of bogs have originally developed by transition from minerotrophic to acidic peatlands. As groundwater tables



**Fig. 5** Schematic summary of the effects of  $\text{HCO}_3^-$  supply from local or regional groundwater (originating from calcium carbonate  $\text{CaCO}_3$ , and internal reduction processes) on the production and internal exchange of  $\text{CO}_2$  and  $\text{CH}_4$  in bogs. Note that the position of a specific biogeochemical reaction in the scheme does not necessarily represent its exact location in the profile.  $\text{HCO}_3^-$  reacts with acids in the upper layers ( $\text{H}^+$ ) forming  $\text{CO}_2$ , and promotes decomposition and concomitant  $\text{CH}_4$  and  $\text{CO}_2$  production (in deeper peat layers and/or in floating peat mats) because of acid buffering. POC (particulate organic carbon) flow from floating mats to the sediment provides extra C input for decomposition.  $\text{CO}_2$  diffuses from the peat and stimulates photosynthesis (indicated by oxygen,  $\text{O}_2$ ) and growth in aquatic and terrestrial *Sphagnum* spp. (top layer).  $\text{CH}_4$  bubbles, forming a buffer between production and emission to the atmosphere, provide buoyancy of peat in floating bogs. Part of the  $\text{CH}_4$  is oxidized (oxid.) to  $\text{CO}_2$ .

have fallen in many densely populated areas in recent decades, future prospects for bog establishment and restoration are much less favourable. In both fens and bogs, vascular plants like *Juncus effusus* are often overgrown by *Sphagnum*. These plants might not only provide physical support for the

mosses, but also extra C nutrition because of the significant  $\text{CO}_2$  fluxes through the aerenchyma (Thomas *et al.* 1996) and from decomposing standing litter (Kuehn & Suberkropp 1998).

In contrast to the traditional view that bogs are only influenced by atmospheric input (ombro-



**Table 2** Repeated measures analysis of variance (general linear models) of the effects of treatment on peat moisture and surface water characteristics, as shown in Fig. 3. For treatment, d.f. = 5; for time, d.f. = 9 for peat moisture and d.f. = 7 for surface water (monolith buoyancy, d.f. = 6). *F*-values are given, with their level of significance: <sup>a</sup>*P* ≤ 0.01; <sup>b</sup>*P* ≤ 0.001; <sup>c</sup>*P* ≤ 0.0001

Dependent variable	Independent variable		
	Treatment	Time	Interaction
Peat moisture			
pH	17.73 <sup>c</sup>	55.29 <sup>c</sup>	12.40 <sup>c</sup>
Alkalinity	33.25 <sup>c</sup>	26.83 <sup>c</sup>	5.78 <sup>c</sup>
E <sub>450</sub>	15.54 <sup>c</sup>	25.99 <sup>c</sup>	7.93 <sup>c</sup>
PO <sub>4</sub>	23.93 <sup>c</sup>	10.8 <sup>c</sup>	3.93 <sup>c</sup>
Surface water			
pH	438.26 <sup>c</sup>	15.08 <sup>c</sup>	8.68 <sup>c</sup>
Monolith buoyancy	8.10 <sup>a</sup>	16.03 <sup>b</sup>	2.47 <sup>a</sup>
E <sub>450</sub>	58.51 <sup>c</sup>	9.98 <sup>c</sup>	8.42 <sup>c</sup>
PO <sub>4</sub>	23.02 <sup>c</sup>	3.87 <sup>b</sup>	3.04 <sup>c</sup>

trophic), we have shown that groundwater may strongly influence the gas production in these ecosystems, and provide extra C as a nutrient for *Sphagnum* spp. In bogs where groundwater (permanently or occasionally) reaches the rhizosphere of vascular plants, this might also provide an additional source of other nutrients (N, P, K). As the *Sphagnum* layer forms an efficient filter for air-borne nutrients (Malmer *et al.* 1994), this will severely influence species composition in these peatlands. This has important implications for the overall functioning of these systems, and for the evaluation of experimental data on gas exchange and the effects of increased atmospheric CO<sub>2</sub> availability. We therefore hope that this paper will encourage the inclusion of research on the quality of water and peat in hydrological research.

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