INTERACTIONS OF SPHAGNUM WITH WATER AND AIR

R.S. Clymo

School of Biological Sciences, Queen Mary College, London E1 4NS

ABSTRACT

Peat-accumulating wetlands occupy 2-3% of the Earth's land surface. Sphagnum, an important constituent of much of the peatland vegetation, is responsible for initiating acid conditions in ombrotrophic bogs and, because it decays disproportionately slowly, becomes over-represented in peat. Several features of Sphagnum physiology are important: (1) the plant produces poly-uronic acids which, by cation exchange, release H^+ into the bog water; (2) it is sensitive to the combination of high pH and high Ca^{2+} concentration together, though not to each separately; (3) it is sensitive to even moderate concentrations of o-phosphate, NO_3^- and NH_4^+; and (4) it is sensitive to moderate concentrations of HSO_3^-.

Cation exchange may be an important source of acidity in some bogs but is probably less important generally than was once thought. The role of coloured organic acids as primary sources of acid is not clear. Acid rain sensu stricto has not been shown to affect Sphagnum, but atmospheric pollution in the wide sense is responsible for its disappearance from badly polluted areas of the southern Pennines.

Since the last glaciation, peatlands have been a 'sink' for atmospheric carbon, but some bogs in Europe, at least, are becoming less effective as they approach the natural limit to their growth. Death of their vegetation, where it occurs, and mining of peat both contribute to increasing atmospheric CO_2 concentration, the extent of which can only be guessed. Nor do we know how peatlands would respond to increased concentrations of CO_2 in the atmosphere.

INTRODUCTION

Estimates of the area covered by peat-accumulating systems have tended to increase. A recent one (Kivinen and Pakarinen 1981) of 420 Mha - about 3% of the Earth's land surface - was obtained by summing national estimates by other authors who used a variety of criteria. Olson et al. (1983) used similar methods and recorded 90 Mha of bog and mire, and 380 of low-arctic tundra. Their central estimate of phytomass carbon in these two components was 2.0 and 3.8 Gt in a world non-ocean total of 560 Gt. Estimates of the phytomass of forests, which cover 4000 Mha, include that in trunks and branches of trees. However, the estimates for peatlands ignore the peat, which has almost as important a role in these ecosystems as trunks and branches do in forests. A crude estimate of peat mass can be made. Assuming that the mean bulk density of dry matter in peat, taken to be of average composition CH_2O, is 0.1 g.cm^{-3} and that the mean depth of peat is 1 m, then the total carbon in peat and its surface vegetation

(using cm for calculation) is about $420 \times 10^{14} \times 0.1 \times 100 \times (12/30) / 10^{15} = 170$ Gt. The value of 1 m for peat depth is little better than a guess, but it seems possible that perhaps 1/4 to 1/3 of readily accessible vegetable carbon is in peat-lands. These ecosystems have usually been considered as a sink for carbon, so a substantial change in the rate at which peat is accumulating might have noticeable effects of the concentration of CO_2 in the air.

Among peat-forming plants, one of the most important is Sphagnum - the bog moss. A general account of its ecology and physiology is given by Clymo and Hayward (1982). Of the 200-300 species about twenty are quantitatively important. Each species has its own range of tolerance of water supply and solute concentrations, but all are able to make their environment unusually acidic by cation exchange, and most have an unusually low rate of decay. Most Sphagnum-dominated peatlands are ombrotrophic, even if they rely to some extent on focussed drainage from a larger catchment to keep them in hydrological balance in dry periods. Two factors contribute to the vulnerability of peatlands to atmospheric pollutants when compared with many mineral sites: (1) the depen-dence of peatlands on precipitation, and (2) the sensitivity of Sphagnum to atmospheric pollutants because of its one-cell thick, uncuticularized leaves. The vulnerability of peatlands to inor-ganic compounds of S and N in areas with relatively high pollu-tion has been convincingly shown; the evidence is reviewed by Lee et al. (this volume). They also give reasons for suspecting that there may be sub-lethal effects in less heavily polluted areas.

In this article I consider some general interactions between Sphagnum and water chemistry, and some possible effects on the peat-accumulation process.

EFFECTS OF SPHAGNUM ON WATER CHEMISTRY

One of the most obvious effects of Sphagnum plants is that they make the surrounding water acidic. Some, and probably most, of the initial effect is a consequence of cation exchange. Up to about 30% of the plant dry mass is uronic acid residues in long polymers. There seem to be two uronic acids in about equal amounts: galacturonic acid and 5-keto-D-mannuronic = D-lyxo-5-hexosulopyranuronic acid (Painter 1983a). The latter is unusual among naturally occurring sugars in its ability to crosslink glycan chains. The cation-exchange capacity of Sphagnum is close to that predicted from the measured polyuronic acid concentration (Clymo 1963; Spearing 1972). Both are related to the dryness of the microhabitat; hummock species have values about twice those of pool species. The same tendency is found among individuals of the same species in different microhabitats. Not all plant species of oligotrophic acid habitats have a large cation-exchange capacity. Roots of Eriophorum angustifolium, for example, have a capacity about 1/10 that of Sphagnum. There is no obvious explanation for these trends and differences.

Sphagnum is extraordinarily efficient at producing dry mass,

which consists mostly of polysaccharides, with a small investment in cytoplasm. Most of the uronic acid is in the holocellulose fraction, and cation-exchange properties persist after death. It is likely, therefore, that most of the exchange capacity is in the cell walls. The whole plant may be considered as if it were in a cation exchange phase, which would come, if left for a short time into equilibrium with the surrounding solution. This does indeed occur (Fig. 1), showing that in the live <u>Sphagnum</u> plant most, if not all, the uronic acids are manufactured in the free acid form, i.e., as $-COOH$ (or $-COO^- H^+$) rather than as $-COO^- R^+$, where R^+ represents some cation other than H^+.
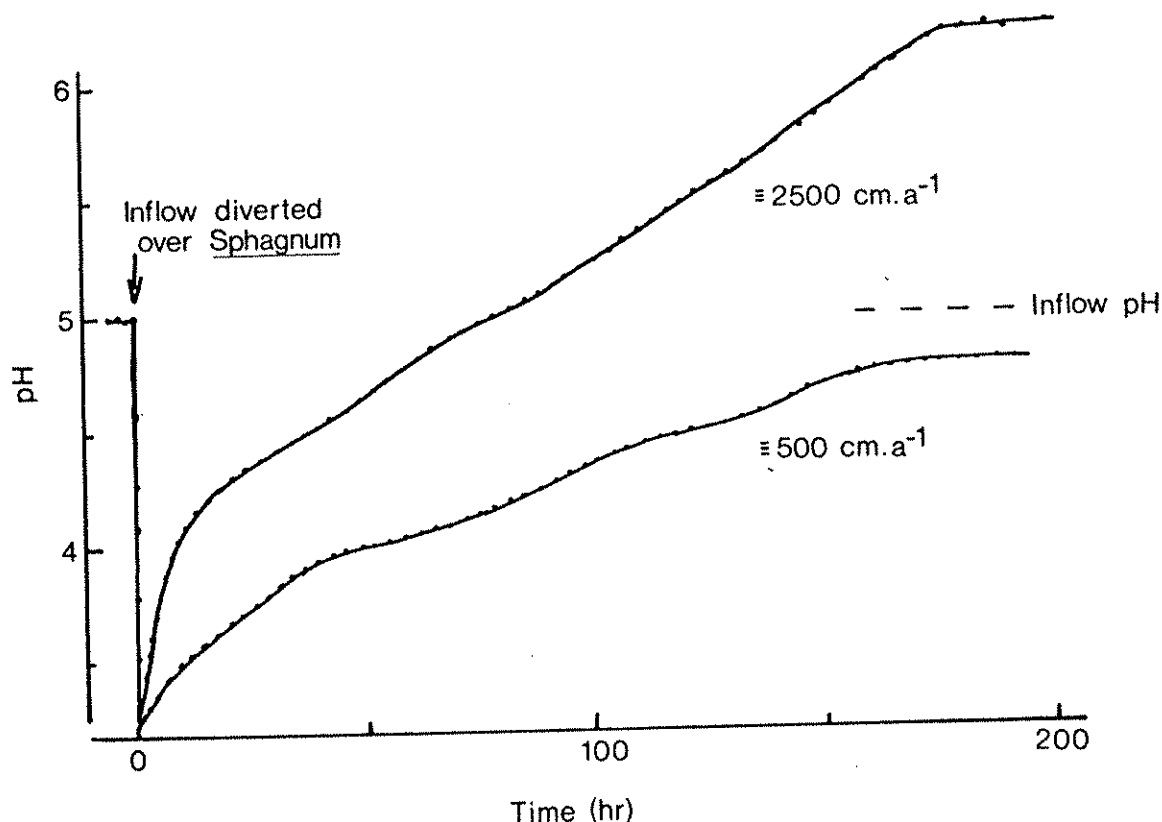

Fig. 1. pH of simulated rain flowing over <u>Sphagnum recurvum</u> at two rates. Both are much greater than normal precipitation averaged over a few days. The plants were in continuous light. At the arrow at t = 0, the solution, which had been bypassing the plants, was diverted over them.

The formation of a uronic acid rather than a sugar may be considered overall as:

$$-CH_2OH + O_2 \rightarrow -COOH + H_2O.$$

Given the presence of O_2, it is not necessary that H^+ be involved in this reaction. It is apparent from Fig. 1 that in the higher flow-rate the pH of the effluent rises as the H^+ on the exchange sites is slowly leached away. Eventually the pH of the outflow exceeds that of the inflow, perhaps as a consequence of photosynthesis (though curious results are found when light and dark alternate). The higher flow-rate, equivalent to 2500 $cm.y^{-1}$, is very much greater than natural rates of precipitation

averaged over periods of more than a day or so. Even though the plants are living and, one assumes, producing new —COOH groups, they cannot produce them fast enough to keep up with the monsoon conditions of this part of the experiment. At the lower rate of inflow (Fig. 1) the plants are able to maintain their pH below that of the inflow. This steady-state pH clearly depends on the plant growth rate and on the solution (precipitation) flow-rate. It also depends on the concentration of solutes. A simple theory (Clymo 1967) shows that with measured growth rates, effective precipitation and solute concentrations, a mean pH of about 4.2 could be maintained in an unpolluted atmosphere. An extension of the theory (Clymo 1984b) allows the effects of acidified rain, evaporation, rain composition and temporal and spatial variations of Sphagnum growth to be calculated. At Moor House (575 m altitude in the northern Pennines of England), during the year in which detailed measurements of growth and rain chemistry were available, Sphagnum contributed about half of the measured acidity. The rest came in the rain, which had a volume-weighted mean pH of 4.1.

The pH of Sphagnum hummocks at the Moor House site in the period 1968–70 showed autumn and spring values of from 4.2–4.5, with a summer pH depression to 3.4, but with a sharp return to higher values with the heavy autumn rains. At that time the pools became, for a short time, more acid than the hummocks. The values of pH calculated for the hummocks from the measured properties of precipitation and from measured plant growth rates agreed fairly well with the measured values except during drought. This is assuming cation exchange to be the only process contributing to further acidification of the bog water.

The concentration of other ions in the water around the plants was also measured. During the summer, there were strong correlations in hummock samples within the group H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cl^- and SO_4^{2-}, implying that evaporative concentration may have been important. On the assumption that Cl^- is relatively biologically inert, Cl^- concentration was used to assess the extent of this process. The result was that the solution around the plants had, in the extreme cases, been concentrated 7.9-fold. Theoretically, a pH of 2.9 would be predicted while the measured value was actually 3.4. Some of this discrepancy can be accounted for if it is allowed that the last rain before the drought probably drained down the plants first, equilibrating with them as it did so, and then moved up again as evaporation began. This was simulated as a 'batch' of rain (Fig. 2) moving down through ten layers of Sphagnum then back up again, equilibrating with each layer as it moved. The simulation used measured values of ion concentration in the rain and measured values of Sphagnum growth. The immediate effect of the 'last' rain, which had a lower concentration of cations than that in the previous 3 months, was to allow the pH to rise by about 0.1 unit. After evaporation to the point at which the sum of cation concentrations in the top layer was 7.9 times that in the 'last' rain, and after replacement of solution from below, there was a very steep concentration gradient at the surface. This sort of thing occurs naturally as well; after long dry periods one may find the

surface of Sphagnum encrusted with brown tarry concentrates of what was once dissolved organic matter, or even (although rarely) with crystalline salts. The surface layer is very different from all the others, but the volume-weighted mean pH is 3.5, compared with the measured 3.4. (The choice of 10 layers was arbitrary, but the number of layers has only a tiny effect on the result because the 'last' rain is distributed among as many layers as are chosen.) This simulation is crude, but it does serve to show the sort and magnitude of effects that Sphagnum may have on the water around it. It is this water, of course, that eventually runs off into the surrounding streams.
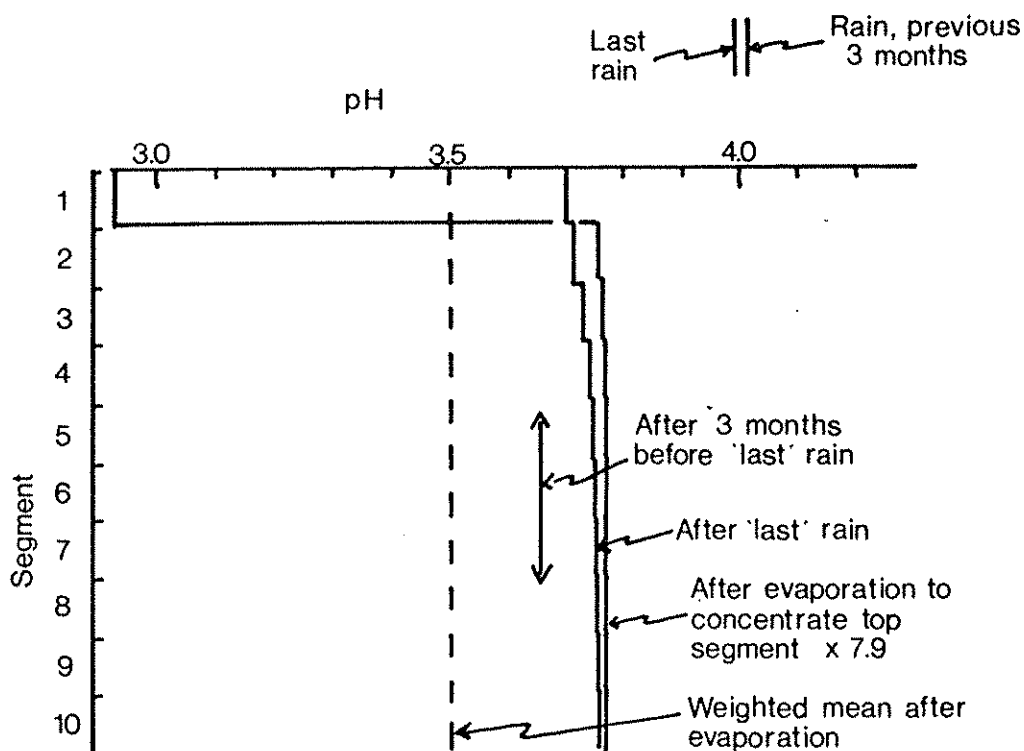

Fig. 2. Simulation of the consequences of cation exchange in a Sphagnum hummock. During April - June, the plants produced 2.4 $g.dm^{-2}$. This has been arbitrarily allocated to segments 2 - 9 and equilibrated with the measured 330 mm of rain of volume-weighted pH 4.01 and concentration of mono-, di- and tri-valent metallic cations 0.07, 0.16 and 0.04 $mmol.L^{-1}$. In the next three weeks, plants grew 0.27 $g.dm^{-2}$ (segment 1) and received 39 mm of rain, pH 3.94, and cation concentrations 0.03, 0.06 and 0.5 $mmol.L^{-1}$. This rain was first assumed to flow down, displacing solution from the segment below and reaching a new equilibrium, in 10 equal aliquots. The following drought, which resulted in a 7.9-fold increase in the Cl^- concentration, was simulated by allowing the solution to move upwards in aliquots, equilibrating at each stage with each segment. This, of course, produces a steep con-centration gradient at the surface because solutes accumulate there.

While the concentrations of most ions in the solution around hummock-Sphagnum were strongly correlated with each other (and much more so than in rain) they were almost uncorrelated with those of NH_4^+ and NO_x^- (NO_3^- + NO_2^-), which were themselves correlated at r = 0.74, n = 38. The quotient NH_4^+/NO_x^- was 0.9 in rain, 7 in pools, and 9 in hummocks. It seems clear that there must be rapid and extensive interconversions of nitrogen-containing compounds – a conclusion supported by detailed studies reported i.e., by Hemond (1983). That these may be directly attributed to Sphagnum or to its associated microflora is shown by the work reviewed by Lee et al. (this volume).

Cation exchange is not the only possible cause of acidity in the surface water of Sphagnum bogs or, perhaps more importantly, in the runoff from them. From time to time it is claimed that high concentrations of CO_2 are found in bog water, and that these may cause the pH to fall to less than 4.0 (e.g., Villeret 1951). If CO_2 is bubbled through bog water the pH falls; conversely, for some samples, if the CO_2 is flushed out by bubbling N_2 gas through the sample then the pH rises to values of about 6.0. In only 5 of 29 samples of water around live Sphagnum from Moor House did the pH rise by more than 0.5 unit when treated in this way – a result similar to that recorded by Gorham (1956a). These five samples were all from places in which the water was probably static and may have been effectively subsurface drainage. They were the only samples that were visibly coloured yellow or brown. It may very well be that microbial activity in peat produces substantial amounts of CO_2; the concentration in peat 1-4 m below the surface was 1-10 $mmol.L^{-1}$ (Claricoates, pers. comm.). This could contribute to the observed pH of about 4.0. But a peat-accumulating system must, on balance, be a sink for CO_2. If there are high concentrations in the catotelm (Ingram 1978) then there cannot also be high concentrations in the surface acrotelm. The CO_2 in the catotelm is thus a secondary, not a primary, source of acidity.

Another possible source of acidity is related to the supply and interconversion of S- and N-containing compounds. In Sphagnum bogs there are few of the neutralization reactions that exist in calcareous fen peat and mineral soils. Therefore, after the modifications imposed by cation exchange, most of the H^+ in precipitation contributes directly to the observed acidity. The anions may, however, undergo conversions which also affect the acidity. One example, simplistically:

$$2H^+ + SO_4^{2-} \text{ (anaerobic)} \rightarrow \leftarrow \text{(aerobic)} \ H_2S + 2O_2,$$
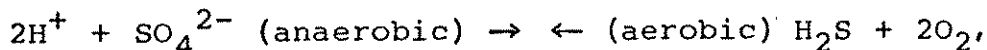
is probably microbiologically mediated. Gorham (1956b) was the first to suggest that the reverse reaction might account for the observed approximately four-fold higher concentration of SO_4^{2-} in bog pools during dry weather. At the same time, the pH fell to below 4.0. The method used for analyses of SO_4^{2-} included organic anions (Gorham, pers. comm.). The concentration of other ions was also higher after dry weather: Na^+ and Cl^- by about two-fold; Ca^{2+} and Mg^{2+} by about four-fold. Evaporation may, therefore, have been partly responsible in the way already discussed. The mechanism of sulphide oxidation itself remains

plausible. Hemond (1980, 1983) and Urban et al. (this volume) have made the most detailed attempts yet recorded to calculate the effects on acidity of assimilation of S and N into organic combination. In effect, when N in NH_4^+ is incorporated into neutral organic molecules, there is a concomitant acidification. The reverse is true of NO_3^- and SO_4^{2-}.

The last primary source of acidity may be loosely called excreted free organic acids. Ramaut (1955) extracted small amounts of an acid from Sphagnum recurvum and identified it as succinic acid or one of its polymers. He thought it might be excreted and might be at least partly responsible for the acidity of bog water. It is easy enough to identify a variety of organic acids in Sphagnum by chromatography, but in the only reported experiments in which C-14 was supplied to Sphagnum the rate of appearance of organic compounds in the water was tiny; over 1 day less than 0.1% of the C-14 fixed by the plants in soluble organic form appeared in the water, and most of that was in sugars (Clymo 1967). The rate of release of organic compounds is notoriously dependent on the environmental conditions, however, so perhaps this possibility should not be dismissed. More interesting is the recent demonstration (Hemond 1980; Gorham et al. 1985; Urban et al., this volume) that a very wide geographic range of North American bog waters contained organic anions at concentrations of 0.05-0.3 $mmol.L^{-1}$ - a result foreshadowed by Malmer (1963). This may be represented as pA 4.3-3.5 to allow comparison with pH. The concentration was strongly correlated with that of dissolved organic carbon and with the absorbance at 320 nm. On photo-oxidation the pH, in most cases, rose to 6.0 or above. This is a convincing demonstration that some of the H^+ is associated with these yellow or brown 'humic' or 'fulvic' acids of unknown chemical constitution. Painter (1983b) has recently shown that the coloured organic anions in one sample of peat water are probably derived from carbohydrates rather than from lignins. But whether or not these are the source of H^+ is a much more difficult question to answer. The dissolved organic anions are probably products of breakdown. Some might be colourless chunks of original plant material liberated from polymers in pieces small enough to be soluble. Small carbohydrates of this kind are usually rapidly attacked by microorganisms. Most of the yellow and brown anions are probably new productions by microorganisms. In the first case, the associated H^+ is scarcely new: the 'source' is the original plant. In the second case, it may be 'new', but one still has to account for the original H^+, both that in the water and that left in the exchange phase. This requires a clear model of the structure and processes in the surface layers - approximately the top 30-50 cm - of a peat bog.

Suppose the surface of a bog is Sphagnum-dominated. New material is added to the top few centimetres, while aerobic decay occurs down to the water table at perhaps 2-30 cm depth. Because the rate of diffusion of O_2 in water is only 10^{-4} that in air, the peat below the water table becomes anoxic as long as microorganisms are active, and the rate of decay then drops by several orders of magnitude. Aerobic decay in the acrotelm, and the accumulation of mass, eventually cause macroscopic structure at

the base of the acrotelm to collapse. (The first snows of winter, at a time when the surface is not frozen solid, may be particularly important.) After collapse, the spaces between elements are very much smaller; therefore, hydraulic conductivity decreases by several orders of magnitude. Most excess water, therefore, flows laterally rather than through the newly collapsed structure and all that lies beneath it. It is this process that is the main cause of the high water table in bogs. Capillary forces are of secondary importance (Ingram 1983). This model is not universally applicable of course, but it will serve to direct attention to the fate of the organic matter.

Any particular piece of organic matter has to wait in aerobic conditions, during which the rate of decay is relatively great, until it collapses and passes into the catotelm. During this time perhaps 90% of the dry matter is lost (Clymo 1984a). Carboxylic acids may disappear by reactions that have the overall effect: $4COOH + O_2 \rightarrow 4CO_2 + 2H_2O$. There is an implied change in the concentration of H^+ insofar as the concentration of COOH was itself buffering H^+. But the acids associated with a metal cation, $-COO^-R^+$, cannot simply abandon the R^+ without a counterion. Their charge might be balanced if microorganisms use the $-COO^-$ as a substrate and release in its place equivalent amounts of alternative (yellow or brown) acid anions. Organic acids might also be produced using neutral plant carbohydrates (just as uronic acids are produced by plants). These would be new acids. The main possibilities are summarised in Fig. 3.

There appear to be differences in the bogs of England and those of North America with respect to organic anions. Hemond (1980), Gorham et al. (1984), and Urban et al. (this volume) all report substantial concentrations of yellow or brown organic anions in summer samples of bog water from North America. Hemond's samples were probably from the catotelm but the others were above or just below the water table. However, in similar midwinter samples from bogs in England Gorham et al. (1985) and Urban et al. (this volume) found no more than a very low concentration of organic anions perhaps because these pools had been flushed by recent rain (Gorham, pers. comm.). Clymo (1984b) reported that the concentration of cations and inorganic anions in an English blanket bog were close to equilibrium. The balance was maintained even in summer. It may be that the relatively high concentration of marine and pollution solutes masked the organic anions and that the relatively great excess of precipitation over evaporation prevented summer concentration of the organic anions in pools to the extent found in North America (Gorham, pers. comm.).

As Gorham et al. (1985) point out, the higher concentrations of organic anions are generally found in those areas in which precipitation is little more than evaporation, and perhaps below it in summer when the samples were collected. Not only is the lateral flux of water small, but solution around the lower part of Sphagnum plants may be drawn up to the apices by evaporation and concentrated there to the surprising extent already mentioned.
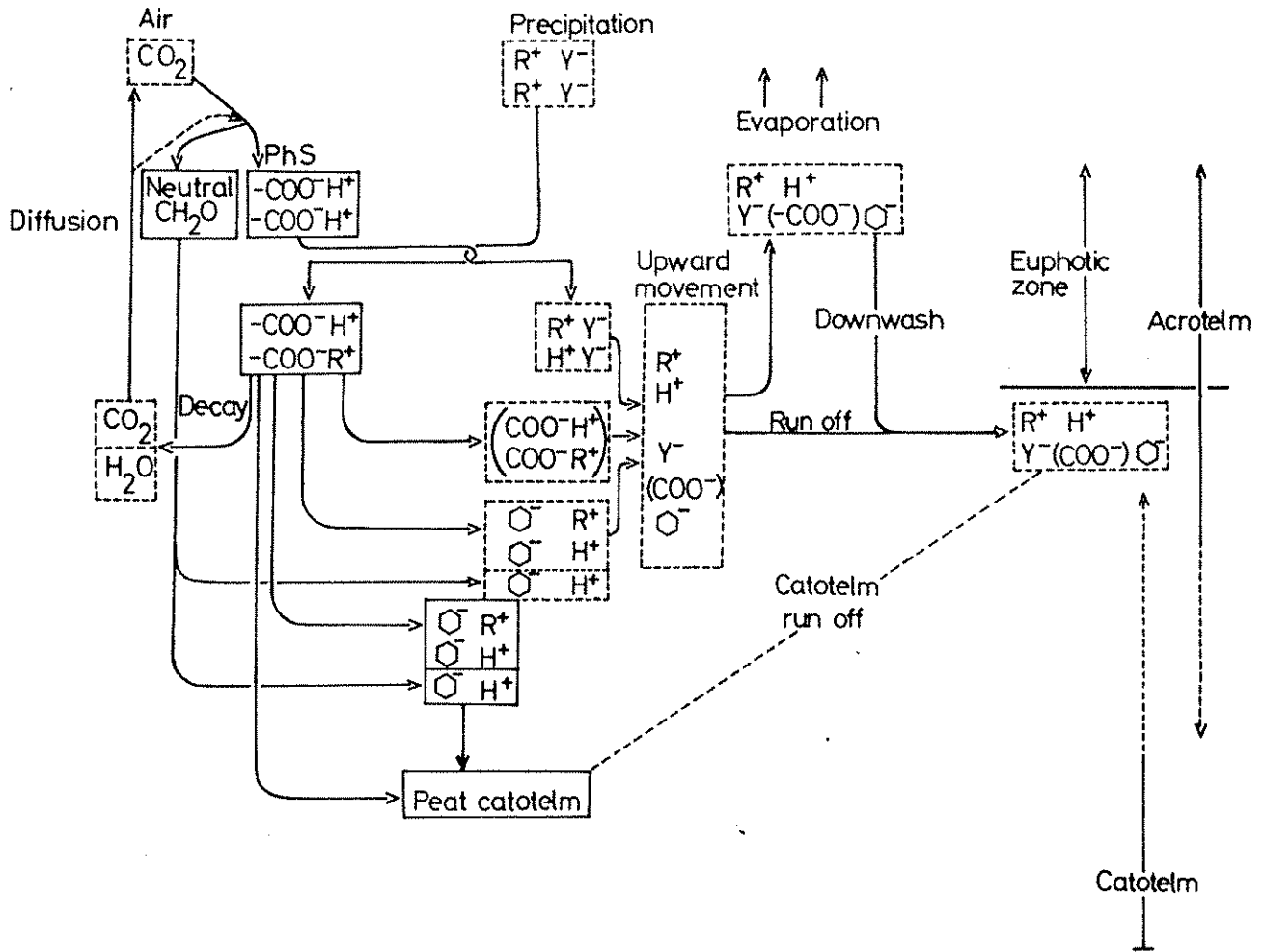
Fig. 3. Some of the processes involved in acid production in bog waters around Sphagnum. The effects of CO_2, of direct acid precipitation, of some forms of cation and anion uptake into plants, and of the interconversion of the various forms of N and S are omitted. Soluble forms are surrounded by broken lines, insoluble ones by a continous box. The symbol R^+ indicates a cation other than H^+; Y^- is an inorganic anion; $-COO^-$ represents uronic acid; $\bigcirc^-$ represents yellow or brown coloured 'fulvic' or 'humic' acid, perhaps aromatic, but perhaps derived from carbohydrate (Painter 1983b) and shown in parentheses. Some of the CO_2 produced during decay may be taken up again at the plant apex without escaping to the air. Decay does continue in the catotelm and some water does flow through it. These three processes are shown by broken lines.

The existence of high concentrations of coloured organic anions serves to buffer the pH of the water at about 4.0, but it does not per se tell us about the primary origin of the H^+. We need to know to what extent these coloured anions are chemically equivalent to the $-COO^-R^+$ that have been destroyed, and to what extent they are new products in the H^+ form.

An approximate calculation of the chemical nature of the coloured anions can be made. Suppose Sphagnum productivity is 300 $g.m^{-2}.y^{-1}$ with 20% of dry mass as polyuronic acid. Suppose also that 50% of the H^+ is exchanged for other cations. This proportion will be greater the larger the value of P - E (precipitation - evaporation) and the greater the concentration of non-H^+ cations in the precipitation. Suppose further that 90% of the plant mass is lost during passage through the acrotelm (Clymo 1984a). The molecular mass of a uronic acid residue is 176; therefore the rate of destruction of those $-COO^-$ associated with non-H^+ cations is 300 x 0.2 x 0.9 x 0.5 / 176 = 150 $mmol.m^{-2}.y^{-1}$. For dissolved 'fulvic' and 'humic' acids the mean negative charge density, on a carbon basis, of many samples was 10 $mmol.g^{-1}$ (Oliver et al. 1983). If the lost non-H^+ uronic acids were all replaced by coloured organic anions in solution in this way then the mean concentrations would be:

P - E	$(cm.y^{-1})$	1	10	100
Coloured anions	$(mmol.L^{-1})$	15	1.5	0.15
Coloured anions as DOC	$(mg.L^{-1})$	1500	150	15

Most of the recorded concentrations lie toward the right hand side. On the other hand, as Gorham and Urban (pers. comm.) point out, for 14 samples in a transect across North America (Gorham et al. 1985) the mean concentration of H^+ was 107 $\mu mol.L^{-1}$, of other cations was 75, of $Cl^- + SO_4^{2-}$ was 21, (and of the anion deficit, probably mostly coloured organic anions, was 157 $\mu mol.L^{-1}$). This indicates a minimum of (107 - 21) / (107 - 75) = 0.47 $\mu mol.L^{-1}$ of 'new' coloured organic acids. However, this makes no allowance for undissociated acids.

In short, it is possible that the coloured organic anions are no more than microbially-produced replacements for non-N^+ associated carboxyl groups originally formed by the plants as polyuronic acids. One calculation indicates that they may all be replacements, but another indicates that half or more may be 'new'. We need more studies of the chemistry and microbiology of peat-forming ecosystems.

EFFECTS OF WATER CHEMISTRY ON SPHAGNUM

Most species of Sphagnum are unable to survive prolonged submergence in most, and particularly calcareous, groundwaters. From observations of their field behaviour as colonists in fens, it would seem that a few species, have a greater tolerance than most (e.g., S. squarrosum, S. fimbriatum). Is it the high ionic strength, more specifically Ca^{++}, or the pH to which the plants respond? Wilcox (1984) showed that S. recurvum continued to grow

in NaCl at 40 mmol.L^{-1}, although at a reduced rate, and Paul (1908), recorded by Skene (1915), showed that several species of Sphagnum were able to grow in CaSO$_4$ solutions as concentrated as 15 mmol.L^{-1}, equivalent to a 1/2 Ca of 30 mmol.L^{-1}. Experimental work is bedevilled by the high cation-exchange capacity of the plants: any attempt to change the ambient concentration of cations is 'resisted' by the plants. It is necessary to flush them with large volumes of solution if approximate control concentrations in the solution are to be imposed. When this was done (Clymo 1973), it became clear that pH and Ca^{2+} concentration had independent effects, but also interacted. It was the combination of pH 7.5 and 1/2 Ca^{2+} concentration of 5 mmol.L^{-1} that reduced most species to bare survival. Two groups of species emerged in these experiments. The more tolerant were Sphagnum inundatum, S. squarrosum, S. subnitens, and S. recurvum. Less tolerant were the 'high moor' species S. papillosum, S. capillifolium, S. magellanicum, and S. cuspidatum.

Concentration gradients in the field can sometimes be very steep. For example, at Sunbiggin Tarn in northern England (National Grid reference NY 6808) 60-cm tall hummocks of S. fuscum rise apparently directly from mineral soil flushed by water so calcareous that tufa forms. The pH in water around the plants falls in adjacent 4-cm thick samples from 7.3 at the base to 4.1. The 1/2 Ca^{2+} concentration falls from 1.45 to 0.07 mmol.L^{-1} at the same time (Bellamy and Rieley 1966).

Rate of supply may be just as important as concentration (Pearsall 1950). Species such as Sphagnum inundatum and particularly S. recurvum may grow extremely rapidly (more than 50 cm.y^{-1}) in the flushed habitats of slow flowing ditches or drainage lines on hillsides. Flushing at rates up to the equivalent of precipitation at 30 cm.day^{-1} (3 L.dm^{-2}) increased growth by up to 15% (Clymo 1973). This increase is probably much less than that produced by favourable conditions in the field.

This comparison of rate and concentration was further investigated in an experiment with S. papillosum. Single plants, initially 4.0 cm long, were supported in a test tube with the capitulum top about 1 cm above the level of 17 mL of solution. The solution was either left in position and topped up with distilled water as necessary to compensate for loss by evaporation, or replaced (equivalent to flushing) every 2 or 3 days. The solutions contained one or more of NaNO$_3$, NH$_4$Cl, and NaH$_2$PO$_4$. No attempt was made to control the pH, but it was measured and varied between 4.1 and 5.2, tending to be lower in the unreplaced solutions. The most concentrated solutions of the two forms of N were 30 mmol.L^{-1}, and of ortho-P 6 mmol.L^{-1}. These were calculated to supply, in 17 ml, about 100 times the amount initially in the plants (i.e., x100 treatment). Dilutions to supply x50, x20, x10, x1, x0.1 and '0' (distilled water) were also used. Each treatment was duplicated and the tubes were randomized in racks, protected from rain, and put on a north-facing windowsill of a building in the relatively unpolluted Hampstead area of northwest London. The experiment ran from January to June 1981. As expected all plants in the x100 and x50 treatments of all three
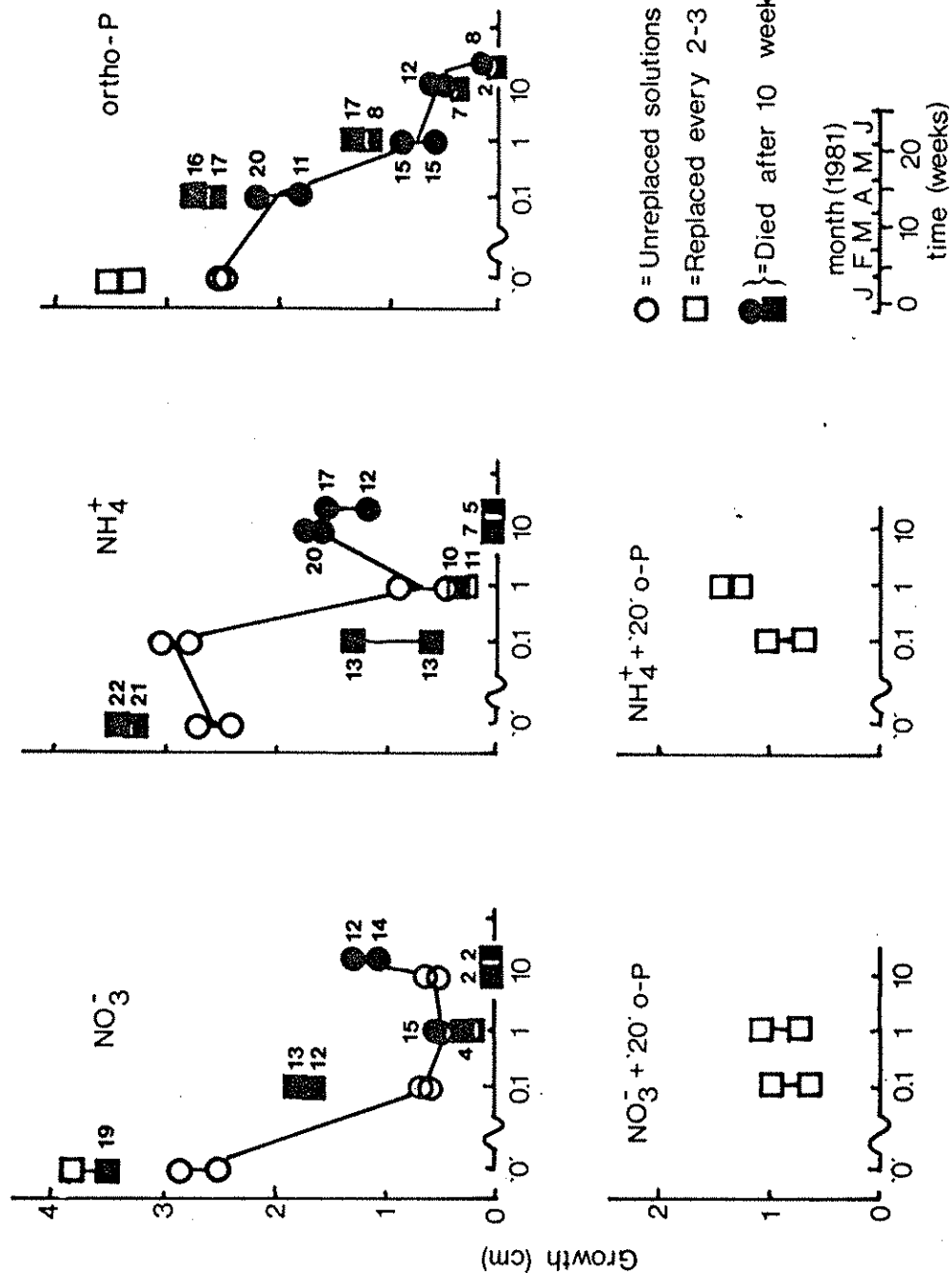
solutes died within 2-3 weeks. Results for the rest are shown in Fig. 4. Separate '0' treatments were included for all three single-solute series, but these are in fact all the same treatment. The results of all six agreed well, as did most of the duplicates throughout the experiment. The results showed the following:

(1) In the unreplaced series all the treatments reduced growth, compared with the nominal '0', except perhaps that which was most dilute in NH_4^+.

(2) Replacing distilled water - the nominal '0' - increased growth, although in three of the six cases the plants died shortly before the end of the experiment in mid-summer. It may be that N and P had been removed to such an extent that the plants could not survive during active growth.

(3) Most of the other results are consistent with the hypothesis that, within the range of concentrations and rates of supply used, a higher supply reduces growth, although there may have been an initial stimulation, followed in spring by death.

(4) The x0.1 treatment with unreplaced NH_4^+ was less inhibitory than the similar one with NO_3^-.

(5) The mixtures of solutes allowed the plants to survive better than might have been predicted from the single-solute results, but the plants still grew poorly.

These results are consistent with field observations that dilute solutions of inorganic N and P compounds kill Sphagnum - at least those species in the 'high moor' group. But all these experiments lasted for a relatively short time. It is interesting, therefore, that the same effect is seen on hummocks where owls or grouse have perched and defecated: Sphagnum in the immediate vicinity dies, but that a little distance away may grow faster. A similar chance observation of increased growth of Sphagnum around ground rock phosphate applied in a fertilizer trial was made by McVean (1959). These two field observations extend the time scale over which effects may occur. Lastly, the growth of S. fuscum in the field is stimulated by balanced fertilization with N and P (Gardetto, pers. comm.).

The lowest concentrations supplied deliberately in the present experiments were 30, 30 and 6 $\mu mol.L^{-1}$ for NO_3^-, NH_4^+, and otho-P, respectively. The N concentrations are similar to those in rain in the UK and southern Norway (Barrett et al. 1983). No attempt was made to exclude gaseous dry deposition, although particulate deposition must have been much reduced if not completely prevented by the transparent covers. Even so, if unintended supplies had been important then one might not have expected the lowest deliberate rates of supply to have had such a depressing effect as did, for example, NO_3^-.

It seems clear that the growth of at least the 'high moor' species of Sphagnum is affected by concentrations or rates of supply of inorganic N that are commonly found nowadays in precipitation. Even present supplies may be beyond the nutrient and neutral ranges and into the toxic one. The results reported by Lee et al. (this volume) differ in detail but lead to similar conclusions.

ortho-P

NH₄⁺

NO₃⁻

Growth (cm)

○ = Unreplaced solutions

□ = Replaced every 2-3 days

●□ = Died after 10 weeks

month (1981)
J F M A M J
0   10   20
time (weeks)

NH₄⁺ + '20' o-P

NO₃⁻ + '20' o-P

Supply (as proportion of that in plant at start) [log scale]

Fig. 4. Survival and growth of Sphagnum papillosum plants in relation to supply of NH₄⁺, NO₃⁻, ortho-P, or a mixture. 'Concentration' is in units of the amount in the plants at the start of the experiment. In the replacement series (squares) the solution was replaced every 2 or 3 days. Filled symbols indicate plants that died after the number of weeks shown adjacent to the symbol. Other details are given in the text.

There is one curious exception to this. Boatman and Lark (1971) showed that the protonema of Sphagnum flourished in, and perhaps needed, concentrations of P of about 1 mmol.L^{-1}. In the field protonema is almost unknown, but it has recently been discovered (Clymo and Duckett, in press) that peat below Sphagnum contains abundant spores which can easily be stimulated to germinate and eventually to produce mature gametophytes, which are the plants one normally sees, in situ in low concentrations of solutes. High concentrations are not necessary.

This discussion has been selective, concentrating on pH, Ca, N and P. Other compounds, such as those containing S, have as great or greater effects (Lee et al., this volume.). Yet other compounds, such as those containing Pb and Cd, or AsO$_4$ and F have effects on the ultrastructure and growth of Sphagnum if the concentration is sufficiently high (Simola 1977). Doubtless others do too. Their importance in nature remains to be determined.

It is of some interest to know the cytoplasmic pH of Sphagnum. If it is similar to that of the environment in which the plants normally grow, then either it is unusually low or the proton gradient across the plasmalemma is unusually great. Preliminary results (Clymo and Hawkes, unpub.) with NMR spectroscopy of the ortho-P peak allow one to infer that the cytoplasmic pH of S. cuspidatum growing in a pool of pH 5.5 was also 5.5. This is an improbably low value for cytoplasm, and is being checked by an independent method. The value proved to be strongly 'buffered'; a change of pH of the solution by 2 units in either direction produced a change in the cytoplasm of no more than 0.1 - 0.2 units. These differences were maintained for several days at least, without impairing the ability to grow normally when returned to water of pH 5.5.

Change of pH in the water per se may be of much less importance to Sphagnum than quite small changes in the rate of supply of some inorganic compounds.

SPHAGNUM AND THE PEAT-ACCUMULATION PROCESS

The process by which Sphagnum formed at the surface is submerged by the rising acrotelm and eventually engulfed by the anoxic catotelm has been described. If the acrotelm maintains the same general character then it injects matter into the catotelm at an approximately constant rate, about 1/10 that at which matter is being added to the acrotelm by plant primary production. If this continues without change and decay ceases altogether in the catotelm then peat will accumulate without limit. But if decay continues, however slowly, then as time passes the integrated loss by decay throughout the growing peat column approaches more and more closely the (constant) rate at which it is injected into the top of the catotelm. The true rate of accumulation slows asymptotically towards zero even though the acrotelm surface is healthy and assimilating matter at the same rate that it always has done. There are two reasons for believing that this account is broadly correct. First, the age vs depth relation is

curvilinear in many, but not all, European cases. This implies continued decay (or steadily accelerating productivity). Secondly, the concentrations of CH_4 and CO_2 in the peat increase steadily downwards (Claricoates, pers. comm.) to the base of the peat several metres deep. This is consistent only with continued production of CH_4, and hence of decay. The whole problem is considered in detail by Clymo (1984a). In the present context it is important because some, and perhaps many, peat-forming systems may be reaching the stage at which the true accumulation rate has become very small, so that they are no longer acting as effective sinks for atmospheric carbon. (In most North American bogs for which sufficient data are known (Gorham, pers. comm.) there seems to be, however, little evidence of a curvilinear age vs depth relation). Peat mining ('harvesting' is a euphemism) for burning or horticulture will make peat-bogs sources of atmospheric carbon. Draining may have the same effect as peat mining because it increases the effective depth of the acrotelm and hence the total mass exposed to aerobic decay.

Destruction of Sphagnum, or decrease in its growth rate caused by atmospheric pollution, may have complex effects. Sphagnum itself decays relatively slowly, probably as a direct result of its low N concentration (Coulson & Butterfield 1978). Not only does proportionally more of it survive into the catotelm, but it enables the catotelm to rise faster and hence it increases the fraction of other species that survive into the catotelm too. On the other hand, Sphagnum itself, excepting the aquatic species, usually forms a fairly thick acrotelm while a surface dominated by Eriophorum vaginatum, for example, may have a shallow acrotelm. Whether or not damage to a Sphagnum carpet, or its replacement by vascular plants, would turn peat bogs from sinks to sources of carbon cannot be confidently predicted at present.

The consequences of an increase in the concentration of CO_2 in the atmosphere are also unpredictable. Billings et al. (1983) showed that the direct increase of the rate of carbon storage in tundra was much smaller than the decreases, as a consequence of postulated increase in the temperature and lowering of the water table.

The links between those aspects of atmospheric pollution that most concern us now and those that seem likely to be occupying us by the end of the next decade remain unquantified. Sphagnum-dominated peat bogs may be useful systems on which to begin this task.

Acknowledgements

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