

# Ion Exchange in *Sphagnum* and its Relation to Bog Ecology

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With five Figures in the Text

## ABSTRACT

In *Sphagnum cuspidatum* unesterified polyuronic acids form 12 per cent. of the dry weight; in *S. acutifolium* 25 per cent. of the dry weight. A good correlation has been found for *Sphagna* between the content of unesterified polyuronic acid and the cation exchange ability, and between cation exchange ability and height of normal habitat above the water table. Anion exchange ability in *Sphagna* is less than 0.0026 m.eq./g. D.W. compared with about 1.2 m.eq./g. D.W. for cations at pH values above 7. In natural conditions the exchange sites are, however, only partly dissociated. The production of new plant material in a bog dependent on rainwater for nutrients can be sufficient to maintain the pH below 4.5, but on average in England only of the order of 2 per cent. of the monovalent cations other than H<sup>+</sup> could be retained in exchangeable form. A greater proportion of polyvalent cations could be retained.

The kinetics of cation exchange are consistent with a heterogeneous exchange phase containing regions of high charge density and regions with lower charge density. At equilibrium the proportions of different cations in the exchange phase are largely explicable by a Donnan distribution, but there are notable exceptions. Two estimates based on Donnan distribution suggest that with low external pH and/or low cation concentration the apparent concentration of exchange sites may be 2-3 eq./l., falling with rise in pH and/or increase in cation concentration to 0.9-1.5 eq./l. The apparent dissociation coefficient also varies in these conditions from  $2 \times 10^{-3}$  to  $1 \times 10^{-4}$ .

## INTRODUCTION

PLANTS of the genus *Sphagnum* have long been known to flourish in unusually acid habitats, and to be largely restricted to these habitats. Since the work of Skene (1915) it has been known that *Sphagnum* can take up cations selectively from salt solutions, and Williams and Thompson (1936), Ramaut (1954), and Anschutz and Gessner (1954), showed that other cations are exchanged for hydrogen ions. The details and importance of the process remain obscure (Bell, 1959; Puustjarvi, 1955, 1959). The present work was carried out in an attempt to establish the source of ion exchange phenomena in *Sphagnum*, the laws governing exchange, and to estimate the importance of these properties in the natural habitat.

### General

### MATERIALS AND METHODS

Plants were collected from natural habitats and stored in a cool place in large polythene bags. Plants taken from these bags and brought into a warm room would continue growing.

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In an early experiment it was found that the properties of the stem, 'terminal' rosette, and fully expanded leaves plus branches are different. Most of the experiments were made with fully expanded leaves plus branches, in which the ratio of leaf dry weight to branch dry weight was about 6:1.

All treatments were made in Pyrex glassware or polythene ware with continuous shaking unless otherwise stated.

### *Chemical analyses*

The following methods of chemical analysis were used:

$Na^+$ ,  $K^+$ , and  $Ca^{++}$  were estimated with an EEL flame photometer. Acid concentrations were kept below the 3 per cent. interference level (Collins and Polkinhorne, 1952).

$Fe^{+++}$  and  $Al^{+++}$  were estimated by a slight modification of Davenport's (1949) method using Ferron.

$Mn^{++}$  was estimated as described by Mayer and Gorham (1951).

$PO_4^{--}$  was estimated by Kaila's modification (1955) of the phosphomolybdic acid method.

$Cl^-$  was estimated turbidimetrically in 0.05 N. nitric acid with 0.025 per cent. silver nitrate, warmed at 40° C. for 35 minutes in the dark.

*Uronic acids* were estimated by a modification of the method of McComb and McCready (1952), which depends on the production of a red colour with carbazole. For reliable results the hydrolysis time was critical and it was found necessary to heat the plant material, originally in 95 per cent.  $H_2SO_4$  at 1° C., in the boiling-water bath for  $10 \pm 1$  minutes and then return it immediately to a refrigerator. The time for maximum colour production at 20° C. after adding carbazole was found to be  $37 \pm 4$  minutes. The optical density at 520  $m\mu$  of the brown colour formed in the initial hydrolysis both of standards and samples was additive with the carbazole colour, and, by measuring optical density before and after adding carbazole, it could be allowed for. Duplicates which differed by more than 5 per cent. were rejected and the estimation repeated.

*The measurement and expression of exchange ability.* The structure of *Sphagnum* leaves makes it difficult to achieve reproducible fresh weight or volume measurements, so results were expressed on a dry weight basis.

The ability to exchange cations cannot be characterized by a single quantity, since it varies for a given material with the nature and concentration of the cation and with the pH. The non-committal term  $E_a$  with superscript for cation concentration in m.eq./l. and prescript for the solution pH will be used: for example  ${}_{5.9}E_a^{Ca^{++}=7.4}$  standing for the exchange ability in m.eq./g. dry weight at equilibrium in a solution containing 7.4 m.eq./l. of  $Ca^{++}$  and of pH 5.9.

The measurement of  $E_a$  involved four steps.

First, the cations already present on the exchange sites were displaced with four 30-minute changes of 0.05 N.  $HNO_3$  with a solution weight to plant dry-

weight ratio of at least 100. The success of this treatment depends less on competitive displacement of other cations by  $H^+$  than on the suppression of ionization of the exchange sites (see p. 316).

Secondly, the plant materials were shaken in three 60-minute and one overnight changes of a salt solution. The pH, anion, and cation concentrations of the solution were measured at the end of the last change.

Thirdly, the plant materials were removed, blotted to remove as much surplus solution as possible, and put into a known volume of 0.05 N.  $HNO_3$  in which the solution weight to plant dry-weight ratio was not less than 120. In some cases the plant material was rapidly weighed before transfer. After 2 hours the concentration of cations and anions transferred from the second step and displaced into solution were estimated. The success of this step again depends more on suppressing the ionization of the exchange sites than on competition of  $H^+$  with other cations. Experimentally it was found that less than a further 2 per cent. of the cations were displaced by further treatments with 0.05 N.  $HNO_3$ .

Finally, the dry weight of the plant materials after drying at 105° C. for 12–24 hours was determined.

Some part of the cations estimated in step 3 will have been transferred in the residual solution. It will be shown that the concentration of exchange sites is not less than 0.4 M., and with solution concentrations less than 10 mM./l. the concentration of diffusible anions in the exchange phase (calculated with the simple model and Donnan theory explained in section 5) will be less than 2.5 per cent. of that in the solution. The solution anions are, in fact, virtually excluded from the exchange phase. Knowing the concentration of cations and anions in the salt solution, and the amount of solution anions transferred in step 3 in the plant material, the amount of cations transferred could be calculated and subtracted from the total cations estimated in step 3. When the final pH of the salt solution was over 5 this correction was less than 10 per cent. of the total cations estimated.

The overall accuracy of duplication was usually better than  $\pm 2$  per cent. More widely divergent results were rejected.

## EXPERIMENTS AND RESULTS

### 1. *The origin of acidity in solutions surrounding Sphagnum plants*

Two hypotheses have been put forward to account for the production of acid conditions in the medium by *Sphagnum*. The first involves the excretion of complete organic acid molecules into the medium and the second the exchange of  $H^+$  originally in the plants for other cations in the solution. The following experiment was made to distinguish between these.

*Sphagnum recurvum* plants were shaken in 0.02 N. HCl for 30 minutes. The plants were washed four times in distilled water. One-half were transferred to 0.1 N. KCl and the other half to distilled water with pH adjusted to that of the KCl with 0.01 m.eq./l. of HCl. Both lots were shaken mechanically

for 24 hours. Measurements of pH and conductivity were made before and at the end of the experiment. The measurements are shown in Table 1.

Only in the case where there were cations other than  $H^+$  in the solution did the solution become markedly more acid. The cycle of loading with  $H^+$  and displacement of  $H^+$  in 0.1 N. KCl was repeated twelve times on the same plants, the solution pH falling to 3.50 on the last occasion. About 0.5 m.eq./g. dry weight of  $H^+$  was released at each exchange, and this would correspond

TABLE 1

The effects on pH and conductivity of two solutions produced by addition of  $H^+$ -treated *Sphagnum recurvum*

Solution	pH		Conductivity ( $\mu$ mhos at 20° C.)	
	Start	Finish	Start	Finish
0.1 N. KCl	4.96	3.45	12,700	12,900
$1 \times 10^{-6}$ N. HCl	4.92	4.70	5	12

to the loss of about a quarter of the total plant weight ( $12 \times 0.5 \times 46$  mg./g.) if even the simplest organic acid was being excreted. The measured loss was less than 5 per cent., much of which occurred in the manipulations.

A similar though smaller change of pH was obtained using 3 cycles of 0.01 N. HCl and 5 m.eq./l. KCl for 30 minutes each with *Sphagnum recurvum* plants, which afterwards resumed growth.

## 2. Anion exchange

The anion exchange ability was examined in the following experiment.

*Sphagnum palustre* branches and leaves were used with a method similar to the measurement of  $E_a^+$ . The 0.05 N.  $HNO_3$  was replaced by 0.01 N. NaOH and the amount of  $PO_4^{--}$  taken up from 10 m.eq./l.  $K_3PO_4$  estimated. The amount of  $PO_4^{--}$  transferred in residual solution was estimated from the fresh weight—dry weight. With this correction  ${}_{4.5}E_a^{PO_4} = 10$  was less than 0.0026 m.eq./g. dry weight.

At this pH any anion exchange groups should be almost completely dissociated and this estimate is probably near the maximum of anion exchange ability.

Radioautographs on X-ray film of plants given  $P^{32}O_4^{--}$  in a total  $PO_4^{--}$  concentration of 1.0 m.eq./l. showed considerable uptake by leaves of live *Sphagnum palustre*, but no detectable uptake by dead leaves.

## 3. The nature of the cation exchange sites

The titration curve of *Sphagnum papillosum* in 0.1 N. NaCl with 0.01 N. NaOH (Fig. 1) shows the behaviour found with weak acids, with an apparent pK of about 4. Recent evidence (Jansen, Jang, Albersheim, and Bonner, 1960; Dainty, Hope, and Denby, 1960; Knight, Crooke, and Inkson,

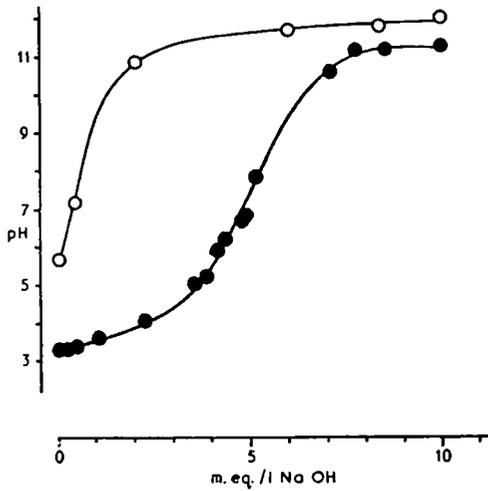


FIG. 1. Titration curves of 0.1 N. NaCl with NaOH (open circles) and of 1.35 g. dry weight *S. recurvum* in 0.1 N. NaCl with NaOH (closed circles).

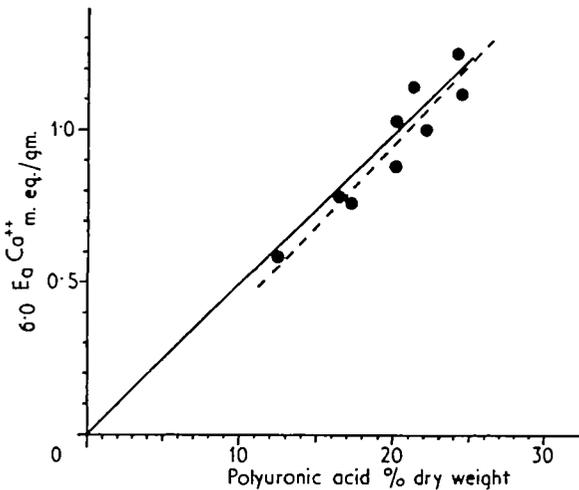


FIG. 2. Relation between  ${}_{6.0}E_a^{Ca^{++}}$  and unesterified polyuronic acid content for 9 species of *Sphagna*. The dashed line is the calculated regression  $y = 0.053x - 0.10$  (excluding the point 0, 0). The full line is the calculated  ${}_{6.0}E_a^{Ca^{++}}$  for given proportions of unesterified polyuronic acid of concentration and pK equal to those of *S. papillosum* in section 5.

1961) has indicated that in some plants at least the exchange sites are probably unesterified polyuronic acids in the cell walls.

The  ${}_{6.0}E_a^{Ca^{++}}$  and unesterified polyuronic acid content of a number of species of *Sphagna* are shown in Fig. 2.

There is a good correlation ( $r = 0.93$  with  $P < 0.001$ ) between  $E_a^{Ca^{++}}$  and uronic acid content. If the equivalent weight of a polyuronic acid residue is taken as 176 and allowance made for the measurement of  ${}_{6.0}E_a^{Ca^{++}}$  being

less than the maximum (see p. 316) there is a good correspondence between the measured exchange ability and that calculated for pH 6.0 from the unesterified polyuronic acid content.

#### 4. *The kinetics of exchange*

The following experiments were made with fully expanded leaves plus branches of *Sphagnum papillosum*. The exchange sites were saturated as far as possible (confirmed by  $E_a$  values of greater than 1.0) with either  $\text{Na}^+$  or  $\text{Ca}^{++}$  by shaking in 0.05 N.  $\text{HNO}_3$ , followed by two 3-hour changes of  $\text{NaCl}$  or  $\text{CaCl}_2$  (50 m.eq./l.) with pH adjusted to 10 with  $\text{NaOH}$  or  $\text{Ca}(\text{OH})_2$ . The plants were given a third change of  $\text{Na}^+$  or  $\text{Ca}^{++}$  at pH 10 and of concentration equal to that to which they were eventually transferred for exchange measurements. In these conditions the exchange sites should be almost completely dissociated (see later). The plants were then blotted dry, weighed, and about 0.3 g. fresh weight transferred to 250 ml. of another cation chloride solution which was magnetically stirred at constant speed. Samples of 3 ml. were taken at intervals and analysed for  $\text{Na}^+$  or  $\text{Ca}^{++}$ .

In one experiment the leaves and branches were separated and exchange followed on each separately.

The results are shown in Fig. 3. The use of a semi-log plot will be explained.

The exchangeable cations appear to be in two main fractions. About 70 per cent. of the  $\text{Na}^+$  is replaced with a half-time ( $t_{\frac{1}{2}}$ ) of the order of 1 minute, and about 20 per cent. with a half-time of the order of 10 minutes. The separation of the fractions is less clear than for isotopic exchange in *Chara australis* (Dainty and Hope, 1959). There appear to be at least four possible sources for the different fractions.

Firstly, the fast fraction might be those cations transferred in the film of pretreatment solution. From measurements of the fresh weight, dry weight, solution concentration and volume, it can be calculated that less than 5 per cent. of the fast fraction could have arisen in this way.

Secondly, the slower fraction might be cations from the central parts of the branches which have an average diameter of about 200  $\mu$ . Curves G and H in Fig. 3, which are for leaves alone and branches alone, show that two fractions are still found with leaves only. The curve for branches alone approaches that to be expected of an uncharged volume, and is rather surprising. It cannot, however, account for the slower fraction of exchange from leaves plus branches.

Thirdly, the slower fraction might come from some more remote and isolated cellular compartment. The reduction of the slower  $\text{Ca}^{++}$  fraction from 70 to 10 per cent. of the total (curves E and F) when the exchange is with  $\text{H}^+$  rather than with  $\text{Na}^+$  would not be easily explained on this basis.

Lastly, the slower fraction might be those cations retarded in regions of high electrostatic charge density. The observed increase in rate of exchange of the slow fractions of  $\text{Na}^+$  and  $\text{Ca}^{++}$ , and the reduction in size of the slower fraction of the more highly charged  $\text{Ca}^{++}$ , when the exchange is made with  $\text{H}^+$

in place of  $\text{Na}^+$  (curves B, C, and E, F) are both to be expected in this case if the effect of the  $\text{H}^+$  is to reduce the dissociation of the polyuronic acid exchange groups.

With materials of the dimensions of *Sphagnum* leaves which have cell walls 3 to 15  $\mu$  thick the rate of exchange may well be controlled by film transport

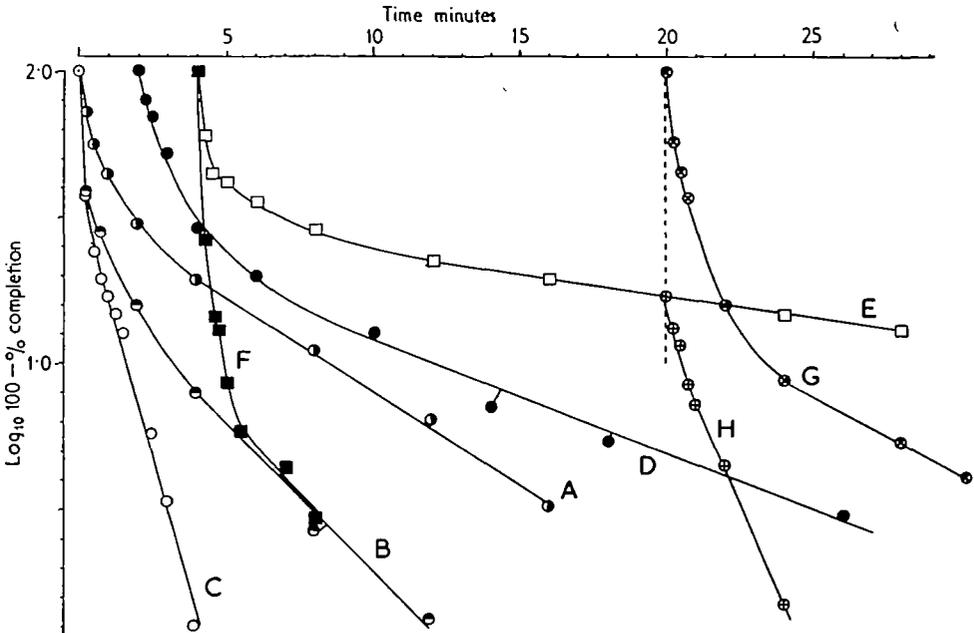


FIG. 3. The kinetics of exchange. Vertical scale is  $\log_{10}$  of 100-per cent. completion of establishment of equilibrium.

Replacement of:

- A  $\text{Na}^+$  by 5.8 m.eq./l.  $\text{K}^+$  at pH 10.
- B  $\text{Na}^+$  by 22.3 m.eq./l.  $\text{K}^+$  at pH 10.
- C  $\text{Na}^+$  by 20.0 m.eq./l.  $\text{H}^+$  at pH 1.7.
- D  $\text{Na}^+$  by 2.50 m.eq./l.  $\text{Ca}^{++}$  at pH 10. Time zero displaced by 2 min.
- E  $\text{Ca}^{++}$  by 20.0 m.eq./l.  $\text{Na}^+$  at pH 10. Time zero displaced by 4 min.
- F  $\text{Ca}^{++}$  by 20.0 m.eq./l.  $\text{H}^+$  at pH 1.7. Time zero displaced by 4 min.
- ⊗ G  $\text{Na}^+$  by 10 m.eq./l.  $\text{K}^+$  at pH 10—leaves only. Time zero displaced by 20 min.
- ⊕ H  $\text{Na}^+$  by 10 m.eq./l.  $\text{K}^+$  at pH 10—branches from G. Time zero displaced by 20 min.

(Bircumshaw and Riddiford, 1952; Briggs, Hope, and Robertson, 1961). If this were so the logarithm of the mean concentration in the internal phase would vary linearly with time, and for isotopic exchange in a phase with relatively high concentration of exchange sites  $t_{\frac{1}{2}}$  would be inversely proportional to the external solution concentration. If  $\text{Na}^+$  and  $\text{K}^+$  behave similarly in the exchange phase, then  $\text{Na}^+$  can be considered analogous to an isotope of  $\text{K}^+$ . The curves in Fig. 3 are only approximately linear for the faster fractions. For curves A and B the concentrations of  $\text{K}^+$  are 5.8 and 22.3 m.eq./l. (1:3.9). For the faster fraction the values of  $t_{\frac{1}{2}}$  are 40 seconds

and 12 seconds (3.3:1), and for the slower fractions 270 seconds and 180 seconds (1.5:1). It appears that film-controlled transport may account for the faster fraction of  $\text{Na}^+$  exchange, but is unlikely to do so for the slower fraction.

The kinetics of exchange indicate an exchange phase similar though less clearly defined than that of *Chara australis* (Dainty and Hope, 1959), in which there are groups of exchange sites giving local volumes of high-charge density. The fine structure of the wall of *Sphagnum* leaves does not appear to have been described, so the regions of high-charge density cannot be correlated with any specific structure.

### 5. The effects of pH and cation concentration on exchange ability

Since the habitat of *Sphagnum* is usually of pH less than 5 and may occasionally be below 3.0, and the cation concentrations in natural habitats are

TABLE 2

External solution concentrations and  $E_a$  for *Sphagnum papillosum*

External solution		$E_a^{\text{Na}^+}$ (m.eq./g. D.W.)	External solution		$E_a^{\text{Ca}^{++}}$ (m.eq./g. D.W.)
$\text{Na}^+$ (m.eq./l.)	pH		$\text{Ca}^{++}$ (m.eq./l.)	pH	
3.30	3.62	0.11	..	..	..
2.94	5.02	0.27	4.90	3.54	0.31
2.44	5.94	0.49	0.84	4.46	0.44
1.60	6.12	0.50	3.64	5.00	0.73
2.13	7.36	0.78	3.52	5.72	0.96
2.08	7.86	0.90	1.30	6.36	0.99
13.2	3.29	0.13	2.12	6.84	1.11
18.9	4.48	0.43	2.56	7.05	1.11
18.0	4.96	0.48	26.8	4.34	0.66
18.0	5.60	0.57	27.3	4.86	0.86
18.0	7.12	0.78	26.8	5.52	1.05
18.5	8.02	0.84	26.4	6.24	1.07
17.2	9.02	1.00	25.5	7.22	1.20

of the orders 0.01–1.0 m.eq./l., it seemed important to attempt to estimate the effect of variation in pH and of low cation concentration on the amounts of cations held in the plants in readily exchangeable form.

A series of experiments was made on *Sphagnum papillosum*. The  $E_a^+$  of fully expanded leaves plus branches was measured in solutions containing various concentrations of  $\text{NaCl}$  or  $\text{CaCl}_2$ , and with pH variants produced by adding freshly made up  $\text{NaOH}$  or  $\text{Ca}(\text{OH})_2$ , the pH and cation concentration at equilibrium being measured. The results are given in Table 2.

In attempting to account for the results the following simple model has been used, using the theory of Donnan (1911).

External solution  
Cations  $\text{H}^+$ ,  $\text{x}^+$   
Anions  $\text{Cl}^-$ ,  $\text{OH}^-$

Internal solution = exchange phase  
 $\text{H}^+$ ,  $\text{x}^+$   
 $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{A}^-$

In this model,  $x^{+v}$  is any cation (other than  $H^+$ ) of valence  $v$ , and  $A^-$  is the indiffusible polyuronic acid anion. All the ions except  $A^-$  can diffuse freely in either phase. A similar model has been used by Mattson (e.g. 1929, 1948) for soils and by Briggs and others (1961) for plant tissues. A more fundamental approach, based on the Boltzmann distribution at a charged interface has been developed by Eriksson (1952), Bolt (1955), and Dainty and Hope (1961) which indicates that the errors in the simple Donnan approach may tend in defined conditions to cancel one another out. The electric double layer model is more difficult to deal with and the Donnan system model has been preferred for a first approach.

The Donnan theory predicts that, at equilibrium, the activities of the cations in mols./l. will be related:

$$x_e^+/x_i^+ = (x_e^{++})^{0.5}/(x_i^{++})^{0.5} = (x_e^{+++})^{0.33}/(x_i^{+++})^{0.33}$$

or, in general, 
$$= (x_e^{+v})^{1/v}/(x_i^{+v})^{1/v}. \tag{1}$$

With certain limits on the ratio of  $H_e$  to  $x_e$ , and for a single cation type, combination of this with the Henderson–Hasselbach equation (appendix) shows that, where  $K_a$  = apparent dissociation coefficient,  $r$  is the factor converting the units of  $E_a^{+v}$  from m.eq./g. dry weight into eq./l., and the prescripts 1 and 2 refer to measurements in the different sets of conditions 1 and 2, then

$$\frac{K_a}{(r)^{1/v}} = \frac{{}_1H_e^+({}_1E_a^{+v})^{1+1/v}/({}_1x_e^{+v})^{1/v} - {}_2H_e^+({}_2E_a^{+v})^{1+1/v}/({}_2x_e^{+v})^{1/v}}{({}_2E_a^{+v}) - ({}_1E_a^{+v})}. \tag{2}$$

Representing  $H_e(E_a^{+v})^{1+1/v}/(x_e^{+v})^{1/v}$  by  $P^+$  for univalent ions and by  $Q^{++}$  for divalent ions then for measurements over the same range of  $P^+$  and  $Q^{++}$

$$r = (E_a^{++}/E_a^+)^2 \tag{3}$$

and 
$$K_a = r(P^+/E_a^+) = r^{0.5}(Q^{++}/E_a^{++}). \tag{4}$$

Fig. 4 shows logarithmic plots of  $P^+$  or  $Q^{++}$  vs.  $E_a$ . Over short distances the  $Na^+$  and  $Ca^{++}$  lines are nearly parallel which facilitates the calculation of  $r$ , shown in Table 3. These values of  $r$  give apparent concentrations of the exchange sites from about 3.2 eq./l. to about 1.6 eq./l. The calculated value of  $r$  does depend on the parts of the curves which are compared. If instead of the same range of  $P^+$  or  $Q^{++}$  the same range of  $H_e^+$  is used a slightly different value of  $r$  results, but further assumptions are involved, and in the absence of a good theoretical reason for using the same internal pH range the simpler method has been preferred.

The value of the apparent dissociation coefficient calculated from the  $Na^+$  data decreases from  $1.9 \times 10^{-3}$  at high values of  $P^+$  or  $Q^{++}$  (low external pH and/or cation concentration) to  $1.0 \times 10^{-4}$  at low values of  $P^+$  or  $Q^{++}$ .

These calculations ignore variations of concentration *within* the regions of high-charge density, activity coefficients, and changes of volume which at concentrations of this order are probably important. The activities in the exchange phase are not known, but a test was made using values of activity

coefficients appropriate to solutions in water, when the value of  $r$  calculated was reduced from 1.6 to 0.75.

A different estimate of  $r$  is also shown in Table 3 based on average exchange site concentration in the volume from which  $\text{Cl}^-$  was excluded. It confirms the general order of concentration of the exchange sites, the important differences of activity and concentration and the apparent increase of concentration at low pH and low concentration of other cations.

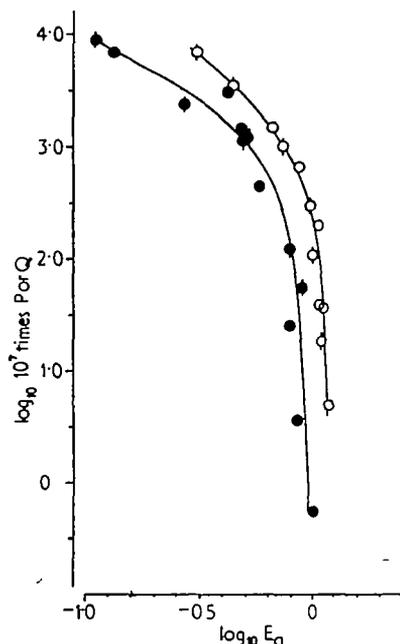


FIG. 4. Relation between  $\log_{10} 10^7 P^{++}$  and  $\log_{10} E_a^{Na+}$  (full circles) and  $\log_{10} 10^7 Q^{++}$  and  $\log_{10} E_a^{Ca++}$  (open circles) for *S. papillosum*. Barred circles are from external concentrations of  $\text{Na}^+$  or  $\text{Ca}^{++}$  less than 5.0 m.eq./l. Unbarred circles from external concentrations greater than 13 m.eq./l. See text for further explanation.

Drying curves for *Sphagnum papillosum* indicate that, at the point where loss in weight ceases to be linear with time, the leaves contain about 4.5

Similar apparent concentrations of exchange sites are found in synthetic cation exchange resins (Samuelson, 1953). In plants a value of 0.6 eq./l. for beet disks has been found by Briggs, Hope, and Pitman (1958) and of 0.8 eq./l. for walls of *Chara australis* by Dainty, Hope, and Denby (1960). These last authors have also indicated that the apparent concentration and volume occupied depend on the external solution concentration, and suggest that this is really owing to the variable ionization of the exchange groups.

The measurements on *Sphagnum* with a range of external solution concentrations show that the percentage ionization is important but indicate a change of apparent concentration even when this has been allowed for, and this effect is difficult to explain with the simple Donnan equilibrium model.

TABLE 3

Values of factor  $r$  for calculating apparent concentration of exchange sites of *Sphagnum papillosum* (calculated by two different methods)

(See text for explanation)

Range of $\log_{10} (P^{++}$ or $Q^{++} \times 10^7)$	3.7-	3.4-	3.0-	2.6-	2.2-	1.8-	1.4-	1.0-
1. Calculated $r$ from Fig. 4	3.4	3.0	2.6	2.2	1.8	1.4	1.0	0.6
2. Calculated $r$ from $\text{Cl}^-$ free volume	3.2	2.3	1.9	1.8	1.7	1.7	1.7	1.6
	2.4	1.2	1.2	..	..	1.0	..	0.85

The concentration of exchange sites in eq./l. is approximately the same as the value of  $r$ , since  $E_a^{\text{max}}$  is about 1.0 m.eq./g. D.W.

volumes of water to every one of other materials. Of these 25 per cent. by weight are polyuronic acid residues—about 46 g./l. If these were uniformly dispersed they might give apparent exchange site concentrations of 0.26 eq./l. Higher apparent concentrations may thus support the picture of locally aggregated exchange sites suggested by the kinetic data.

#### 6. The distribution of mixtures of cations of different type and valency

In natural habitats cations occur in mixtures. The following experiments were made to determine the relative proportions of the commoner cations present in the exchange phase.

Fully expanded leaves and branches of *Sphagnum papillosum* were used.  $E_a^+$  was measured in various mixtures containing chlorides of  $H^+$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{++}$ ,  $Mn^{++}$ ,  $Fe^{+++}$ , and  $Al^{+++}$ . Solution A approximates to that found in the natural habitat. Solution B was expected to give a roughly equal concentration of all cations in the exchange phase. Solution C had large differences of concentration between cations of the same valence. The results are shown in Table 4. (The reciprocal of the Donnan ratio of equation (1) is used for convenience as it is a whole number.)

TABLE 4

#### The equilibrium distribution of mixtures of cations between Sphagnum papillosum and solution

Reciprocal of Donnan ratios calculated with  $r = 1.0$  according to equation (1)

Ion	$H^+$	$Na^+$	$K^+$	$Mn^{++}$	$Ca^{++}$	$Al^{+++}$	$Fe^{+++}$
A. External concentration (m.eq./l.)	0.0282	2.45	0.338	0.0187	0.14	0.0306	0.00446
$E_a^+$ (m.eq./g. D.W.)	—	0.040	0.102	0.010	0.57	0.064	0.053
Donnan ratio reciprocal	—	16	30	23	64	13	23
B. External concentration (m.eq./l.)	0.0038	16.2	15.6	0.64	0.05	0.0984	0.00151
$E_a^+$ (m.eq./g. D.W.)	—	0.127	0.164	0.268	0.48	0.137	0.086
Donnan ratio reciprocal	—	8	11	21	98	11	39
C. External concentration (m.eq./l.)	0.0138	8.35	1.75	1.20	0.30	0.251	0.00188
$E_a^+$ (m.eq./g. D.W.)	—	0.68	0.023	0.366	0.345	0.115	0.061
Donnan ratio reciprocal	—	8	13	18	34	14	32

From equation (1) it follows that if the external solution, containing a mixture of cations of different valencies, is diluted, the *proportion* of higher valency cations in the exchange phase will increase, so that in dilute solutions the polyvalent cations will appear to be selectively concentrated in the exchange phase. The results agree in general with this prediction but there are divergences from the theoretically equal Donnan ratios. These divergences are larger the more dilute the external solution and are generally related to the lyotropic series:  $Na^+ < K^+$ ;  $Mn^{++} < Ca^{++}$ ;  $Al^{+++} < Fe^{+++}$ . A similar series of divergences is found for some synthetic cation exchange resins (Samuelson, 1953). The  $Ca^{++}$  ion appears to be particularly selected in

*Sphagnum* and such observations have also been made on some synthetic ion exchange resins.

Owing to these selectivities the apparent concentration of exchange sites (calculated by the method using cations of different valence) will depend on the species of cation used for the measurements; the values found with  $\text{Na}^+$  and  $\text{Ca}^{++}$  will be amongst the higher estimates.

#### 7. The cation exchange ability of *Sphagnum* in relation to other plants

The results of estimates on a variety of plants are shown in Table 5.

Results for the broad plant groups in the same relative order, but at pH 7.0

TABLE 5  
*Exchange abilities of plants in various groups*

Plant	$_{3.5}E_a^{\text{Ca}=30}$	Plant	$_{3.5}E_a^{\text{Ca}=30}$
Roots of:		Whole plants of:	
<i>Calluna vulgaris</i>	0.079	<i>Pellia epiphylla</i>	0.110
<i>Fagus sylvatica</i>	0.131	<i>Plectocolea cremulata</i>	0.112
<i>Acer pseudoplatanus</i>	0.162	<i>Nardia scalaris</i>	0.171
<i>Eriophorum angustifolium</i>	0.030	<i>Polytrichum commune</i>	0.069
<i>Juncus bulbosus</i>	0.051	<i>Fontinalis antipyretica</i>	0.121
<i>Juncus squarrosus</i>	0.061	<i>Leucobryum glaucum</i>	0.123
<i>Carex lepidocarpa</i>	0.063	<i>Rhytidiadelphus triquetrus</i>	0.127
<i>Dryopteris filix-mas</i>	0.140	<i>Thuidium tamariscinum</i>	0.131
		<i>Pleurozium schreberi</i>	0.147
		<i>Hypnum cupressiforme</i>	0.154
		<i>Aulacomnium palustre</i>	0.184
		<i>Acrocladium cuspidatum</i>	0.188
		<i>Mnium hornum</i>	0.190
		<i>Sphagnum</i> spp.	{ 0.213
			{ 0.242
		<i>Lobaria pulmonaria</i>	0.039
		<i>Cetraria islandica</i>	0.068
		<i>Cladonia</i> sp.	0.069
		<i>Usnea barbata</i>	0.172

have been reported by Puustjarvi (1955) and by Knight, Crooke, and Inkson (1961). The present estimates show that even at low pH *Sphagna* have unusually large exchange abilities. Synthetic carboxyl-type cation exchange resins have abilities 2–10 times larger per unit dry weight.

#### 8. The variation of cation exchange ability with species and habitat

Samples of *Sphagna* of different species growing at about the same height above water table and within a radius of  $1\frac{1}{2}$  yards were collected from Cranemoor (Grid. Ref. SU 1903—a valley bog in the New Forest—Newbould, 1960) and Hartland Moor (Grid. Ref. SY 9585). Collections were also made of the same species growing close together but at various heights above the water table. Estimates of  $_{6.0}E_a^{\text{Ca}=7.4}$  were made, and the results are shown in Tables 6 and 7.

Two conclusions may be drawn from these tables. Firstly, the exchange

TABLE 6

$6.0E_a^{Ca=7.4}$  for *Sphagna* in relation to water table

Species	<i>S. cuspidatum</i>	<i>S. pulchrum</i>	<i>S. plumulosum</i>	<i>S. papillosum</i>		<i>S. palustre</i>	<i>S. subsecundum</i>	<i>S. magellanicum</i>	<i>S. acutifolium</i> ( <i>rubellum</i> )
..	..	..	..	..	0.91	..	..	..	1.13
..	..	..	..	..	*1.01	..	..	1.13	1.12
..	..	..	0.98	1.03	0.96	..	..	*1.13	*1.25
..	..	0.88	0.97	*1.01	0.95	1.00	†1.04	*1.14	1.22
..	..	*0.87	*1.00	0.99	0.95	*0.93	0.83	1.14	1.19
water	0.73	0.88	0.96	0.89	0.91	0.89	0.68	1.01	1.15
$\frac{w}{table}$	$\frac{w}{0.83}$	$\frac{w}{0.76}$	$\frac{w}{..}$	$\frac{w}{..}$	$\frac{w}{0.78}$	$\frac{w}{0.87}$	$\frac{w}{..}$	$\frac{w}{0.84}$	$\frac{w}{..}$
..	0.73	..	..	..	..	..	..	..	..

\* = most robust plants from this habitat.  
 † *S. palustre* collections were all equally robust.

TABLE 7

$6.0E_a^{Ca=7.4}$  of collections of *Sphagna* from the same site, with pH and conductivity corrected for H<sup>+</sup> ( $\mu$ mhos at 20° C.) at the site, and maximum value from Table 6

Species	Maximum from Table 6							
		1	2	3	4	5	6	7
<i>S. acutifolium</i>	1.25	..	0.93	..	..	..	1.15	..
<i>S. magellanicum</i>	1.14	..	..	..	1.11	1.03	..	..
( <i>S. palustre</i> )	1.04	..	..	..	..	..	..	..
<i>S. papillosum</i>	1.03	0.85	0.80	0.91	1.01	0.87	0.87	0.84
<i>S. tenellum</i>	..	0.83	0.81	..	..	0.82	..	..
<i>S. plumulosum</i>	1.00	..	..	..	0.97	..	..	..
<i>S. pulchrum</i>	0.87	..	..	0.74	..	..	..	0.79
<i>S. subsecundum</i>	..	0.66	..	..	..	0.65	0.72	..
var. <i>auriculatum</i>	..	0.66	..	..	..	0.65	0.72	..
<i>S. cuspidatum</i>	0.83	0.51	..	0.58	..	0.73	..	0.67
pH	..	4.3	4.4	4.3	4.3	4.8	4.7	4.1
K <sub>corr.</sub> <sup>20</sup>	..	84	87	97	104	125	128	155

ability is best developed (on a dry weight basis at least) where the plants appear subjectively to be growing best. Secondly, there is an almost exact correlation between exchange ability and height of the optimum habitat (as found by Ratcliffe and Walker, 1958) above the water table.

DISCUSSION

It seems likely that the cation exchange properties of *Sphagna* are owed to unesterified polyuronic acids—possibly mixed sugar-uronic acid molecules (Theander, 1954). *Sphagna* have a greater proportion by weight of the plant in exchange sites than has any other recorded plant, but in general exchange

ability seems to be correlated more with taxonomic group than with habitat (compare *Sphagnum* and *Eriophorum angustifolium*, for instance). There seems to be no obvious factor present in the mire habitat which would favour the production of  $-\text{COOH}$  rather than  $-\text{CH}_2\text{OH}$  groups.

Within the *Sphagnum* the variation of exchange ability is highly correlated with the height of the habitat above the free-water table *and* with the pH of the water round the plants. One example of a numerous series of measurements on hummock and hollow development is shown in Fig. 5. Where the

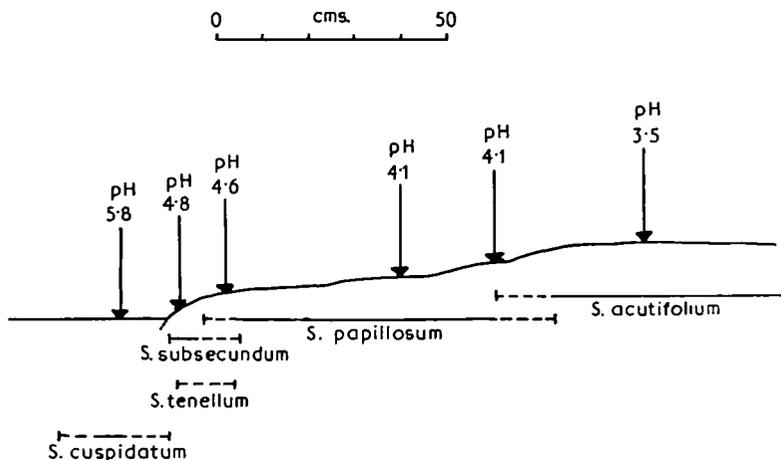


FIG. 5. Profile, distribution of *Sphagnum*, and pH values of water in the top 5 cm. of a hummock and pool at Thursley Common.

concentration of other cations in the water is constant these differences in pH mean that the actual  $E_a$  is roughly constant (at a particular site) whatever the species. In the example shown it was about 0.4 m.eq./g. dry weight.

The question arises, how far can the acidity of the habitat be maintained by the production of new uronic acids? The only data suitable for such a calculation seem to be those of Chapman (1962 and unpublished). Measurements of the growth of marked *Sphagnum* plants at Coom Rigg in Northumberland gave a productivity of about 100 g. dry matter/m.<sup>2</sup>/year. With a rainfall of 125 cm./year averaging 2 m.eq./l. of dissolved cations a pH of about 4.5 could be maintained and with  $E_a$  consequently about 0.5, an average of about one-fiftieth of the cations presented retained within the exchange phase. Polyvalent cations would be more effectively trapped than this. Chemical analyses by Chapman of rainfall and runoff showed a relative decrease in the proportion of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  and increase in the proportion of  $\text{Na}^+$  and  $\text{K}^+$  in runoff, which accords with expectation.

The lower pH of hummocks may be partly owing to equilibrium with material of a higher  $E_a^{\text{max}}$ , partly to greater losses of water by evaporation, and perhaps partly to a higher chemical concentration of exchange sites.

No account has been taken of active uptake of cations and of seasonal

variations, both of which could be important. Chapman showed that water movements do occur in at least the top 20 cm. of the bog, and at least 15 cm. of this, being dead, would be unable to take up cations by active processes. Finally, it is perhaps worth noting that there are at least two other sources of acidity in many British mires (Gorham, 1958). Oxidation of sulphides produced in anaerobic conditions may lead to free sulphuric acid, and sulphur acids are deposited downwind from industrial areas. In parts of the Pennines  $\text{SO}_4^-$  in rain may total 1,000 g./100 m.<sup>2</sup>/year, and rainwater pH may range from 6.0 in late summer to 3.8 in March. (D.S.I.R. Atmospheric Pollution Division Reports.)

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## APPENDIX

*Calculation of  $K_a$  and  $r$* 

USING the model of section 5 and dealing with concentrations; if  $\text{H}^+ + \text{A}^- = \text{HA}$  then the apparent dissociation coefficient

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]. \quad (\text{A})$$

Also 
$$[\text{HA}] = [\text{A}^{-\text{max}}] - [\text{A}^-], \quad (\text{B})$$

where  $[\text{A}^{-\text{max}}]$  is the concentration of  $\text{A}^-$  when the acid is completely dissociated. Representing two different sets of conditions by the prescripts 1 and 2

$$K_a = [{}_1\text{A}^-][{}_1\text{H}^+] - [{}_2\text{A}^-][{}_2\text{H}^+]/[{}_2\text{A}^-] - [{}_1\text{A}^-]. \quad (\text{C})$$

If the factor converting  $E_a^{+\nu}$  to eq./l. is  $r$ , then

$$[x_i^{+\nu}] = rE_a^{+\nu}. \quad (\text{D})$$

From (1), and omitting concentration brackets,

$$\text{H}_i^+ = \text{H}_e^+ \left( \frac{rE_a^{+\nu}}{v} \right)^{1/\nu} \left/ \left( \frac{x_e^{+\nu}}{v} \right)^{1/\nu} \right. . \quad (\text{E})$$

Also 
$$[\text{A}^-] = [x_i^{+\nu}] + [\text{H}_i^+]. \quad (\text{F})$$

If  $\text{H}_e^+ \left/ \left( \frac{x_e^{+\nu}}{v} \right)^{1/\nu} \right.$  is less than 0.05, then less than 5 per cent. error is introduced by putting

$$[\text{A}^-] = rE_a^{+\nu} \quad (\text{G})$$

which simplifies the substitution of G and E in C to give (2).

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