SOME CHEMICAL ASPECTS OF WETLAND ECOLOGY*

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Abstract

The chemical properties of fen and bog soils are examined in relation to ion supply from the mineral soil and from the atmosphere. As the influence of the mineral soil wanes through accumulation of organic material, exchangeable hydrogen ions replace exchangeable metallic cations upon the adsorptive complexes of peat deposits, the level of dissolved calcium in peat pools declines to less than 2 mg./l., and acidity rises very sharply--with pH often falling below 4. The source of this acidity may be oxidation of organic sulphur compounds in the peat, air pollution by sulphuric acid, or displacement of adsorbed hydrogen ions by metallic cations supplied through atmospheric precipitation. Weather conditions and geographical location are shown to have a considerable effect upon the chemistry of rain and bog waters.

The productivity of the plant cover of fens and bogs is shown to be related in some degree to the balance between silt and atmospheric precipitation as sources of nutrients.

Introduction

A major characteristic of wetlands is the accumulation, under waterlogged and anaerobic conditions, of muck and peat deposits built up of silt and the remains of plants such as reeds, sedges, grasses, mosses and a variety of shrubs and trees. Often peat deposits originate with the filling in of a lake, which in northern regions may be followed by a swamping of extensive areas of surrounding mineral soil (25). As the deposits increase in area and depth they commonly become more organic, through a decline in the inwash of silt from surrounding mineral soils. Peat surfaces which are subject to some degree of silting or drainage from mineral soils are said to be minerotrophic, but when the peat surface no longer receives any inflow of water from the mineral soil, and depends for its mineral supply wholly upon atmospheric precipitation, it is said to be ombrotrophic (2, 3, 25). Current Swedish usage, which is accepted here, designates minerotrophic sites as fens and ombrotrophic sites as bogs. The differentiation, therefore, rests upon the nature of mineral supply and not upon vegetation, although fens are commonly dominated by reeds, sedges, grasses and hypnoid mosses, while bogs are usually dominated by *Sphagnum* mosses, cottongrasses, deersedge and heaths.

The present review deals mainly with the chemical properties of peat and water which differentiate minerotrophic fens from ombrotrophic bogs in the British Isles. For a more general coverage of wetland ecology broader review may be consulted (6, 11).

Influence of organic accumulation upon the chemistry of waterlogged soils

The increase in soil organic matter ensuing upon the succession from lake through fen to bog has profound consequences for the chemical properties of the soil, as may be seen by an examination of the average ion-exchange characteristics of a series of soils from lakes, fens and bogs in the English Lake District (7). Fig. 1 shows that as organic content (per unit dry weight) rises, the capacity of the soil to adsorb and exchange cations is greatly increased, up to a level of about 1 milli-equivalent per gram dry weight as soils become almost wholly organic. In the less organic soils most of the exchange capacity is saturated by metallic cations (Ca, Mg, Na, K) from soil minerals, but as organic content rises both the amount and percentage of exchangeable hydrogen ions increase slowly. As fens give way to bogs and the influence of soil minerals declines, concentrations of exchangeable metallic cations fall steeply; at the same time the concentration of exchangeable hydrogen rises equally steeply and it comes to predominate strongly among the adsorbed cations. The transition from fen to bog occurs at about 80-90% organic matter, although a few fen peats exceed 90%. The picture given by exchangeable cations is reflected by soil pH, as measured by direct insertion of a glass electrode (see 14). A slow decline from pH values above 6 to values of about 5 occurs as organic matter accumulates to about 85% dry weight. Then as the cation balance shifts sharply toward hydrogen ions, pH drops to almost 3 in the highly organic bog peat.

Plant composition is strongly influenced by, and in turn influences, soil properties. While the mineral ash content of underwater plants averages about 18% dry weight, the fen plants average 5.9% and the bog plants only 2.5%. Presumably these differences reflect differences in the availability of mineral nutrients in the substratum, although the exceptionally high levels of mineral ash in underwater plants are probably partly due to low contents of carbonaceous supporting tissue.

Changes in other important soil properties are also evident. For example Fig. 2 indicates that the total nitrogen content of soil organic matter is above 4% dry weight in the least organic soils, and declines rather sharply to less than 2% as fens give way to bogs. This general trend reflects the levels of nitrogen in contributing vegetation, which are above 4% in underwater plants and below 1% in Sphagnum mosses.

The changes which are demonstrated here by a comparison of surface soils in several different stages of evolution can also be seen in examining peat profiles. Fig. 3 illustrates the characteristic decline in soil pH which occurs as bog peats accumulate over fen peats in the southern part of the English Lake District (5). It is accompanied, as expected, by a decline in the proportion of metallic cations to hydrogen ions adsorbed on the soil exchange complex (percentage neutralization). It is of some interest that the acidity of the topmost sample is considerably greater than that of the next beneath, despite similar values for percentage neutralization. This suggests the presence of stronger acids in the surface peats, and, as will be seen later, surface peats tend to be high in sulphuric acid either from oxidation of organic sulphur compounds or from air pollution.

Both calcium and iron exhibit a similar upward decline, as shown in Fig. 4, and bear further witness to the insulating effect of a blanket of peat upon the chemical influence of the mineral soil.

Water chemistry in fens and bogs

Owing to their dependence upon atmospheric mineral supply, bogs in the English Lake District exhibit very low levels of calcium in their waters, the concentrations always being less than 2 mg./l. Fen sites transitional to bog, in which carpets of *Sphagnum papillosum* and *S. recurvum* often grow luxuriantly (the lacustrine bogs of Pearsall, 22), usually range between 1 and 4 mg./l. Normal fens range from 3 to 23 mg./l. in non-calcareous sites. Calcium levels are shown in relation to pH in Fig. 5 (data from 18). It is evident that calcium concentration rises slowly between pH 4 and 6, and rapidly above pH 6 as the influence of the mineral soil becomes pronounced. In fen sites the calcium ions are balanced by bicarbonate ions from the weathering of mineral soils (9). The pH range of bog waters is from 3.8 to 4.4, while transitional sites range from 4.1 to 6.0 and normal non-calcareous fens from 4.8 to 6.9.

An extreme example of the effect of a peat blanket upon the chemistry of surface waters can be seen at Malham Tarn in Yorkshire, where the main inflowing stream contains 80 mg./l. of calcium, the lake itself 47 mg./l., and pools on deep bog peat beside the lake only 0.5 mg./l. (16).

It should be remarked here that most of the ions in peat are strongly adsorbed on the soil exchange complex. Table 1, which presents data from Irish bog peats (Sjörs and Gorham, unpublished), shows that this is especially true of hydrogen ions, with only traces present in the free state, and of the divalent metallic cations magnesium and calcium, which are about 99% absorbed. Even about nine-tenths of the divalent sulphate anion appears to be present in the adsorbed state. The monovalent ions sodium and chloride, relatively abundant because of sea spray in these maritime peats, exhibit the lowest degree of adsorption.

Acidity of bogs

Much of the free acid in British bogs appears to be sulphuric acid (13), either from air pollution (12) or from oxidation of organic sulphur compounds in the peat (10). Fig. 6 shows the relationship between hydrogen and sulphate ions in waters from five inland bogs with a living <u>Sphagnum</u> cover in northern England, Scotland and Wales; and it may be noted that the two highest acidities are observed in the sites closest to the great industrial areas of Britain. The cross represents rain in the English Lake District, which is subject to considerable air pollution. An extreme example of the influence of air pollution is the case of Ringinglow Bog on the outskirts of Sheffield, where sulphate ions reach a level of 0.96 milli-equivalents per litre and hydrogen ions 0.58 milli-equivalents (pH 3.24).

Another source of acidity may also have considerable importance, namely, the exchange of metallic cations brought down in rain for hydrogen ions adsorbed by bog plants and peats. The hydrogen ions are produced metabolically either by the living bog plants or in the course of their decomposition. Gorham and Cragg (17) have suggested such a mechanism to account for part of the acidity of peat pools in the Falkland Islands, and Clymo (1) has calculated from growth rates of Sphagnum that such a source of hydrogen ions may also be a very significant factor in British bogs.

Atmospheric ion supply to bogs

The atmospheric nature of ion supply to bog surfaces can be illustrated by a comparison of ionic concentrations in rain from the English Lake District (8) and bog waters from Moor House in the Pennine mountains nearby (10). This comparison is given in Table 2, from which it is clear that in wet weather bog pools approximate rainwater in composition. During dry weather ionic levels in the bog pools rise considerably owing to evaporation, as in the case of chloride which nearly doubles its concentration. Other ions may exhibit further rises in concentration owing to other causes. For example, sulphate increases nearly fourfold, and shows the greatest increases in the smallest pools most subject to drying out (10). It seems reasonable to ascribe much of the increase in sulphate to the oxidation of reduced sulphur compounds in the peat to sulphuric acid. Some of the hydrogen ions so produced may then exchange with metal cations adsorbed on the peat, thus raising concentrations of these metal cations above the levels which might be ascribed to evaporation. Calcium and magnesium are much more affected by such an exchange than are sodium and potassium, because the divalent metal cations are much more abundant than the monovalent cations on the adsorptive complexes of the peat. This greater abundance of adsorbed divalent cations is shown in Table 3, which presents data for natural bog peats at Moor House (4).

The location of a bog exerts a marked effect upon the type of atmospheric mineral supply to which it is exposed. The influence of air pollution upon water chemistry has already been mentioned in the discussion of acidity in peat bogs. The influence of sea spray also depends very much on geographical location, as may be seen in Table 4, which presents data on the water chemistry of ombrotrophic bogs from different parts of the world (17). The sites in the Falkland Islands, Western Ireland and Northern Scotland are distinctly maritime and exhibit very high levels of sodium and chloride. The last site, in Poland, is the most continental, and is extremely low in both these ions.

Even within one site the direction of rain-bearing winds may have a profound influence upon atmospheric ion supply. Fig. 7 (modified from 12) shows the effect of wind direction upon the amount of ion supply per unit area of ground at a site in the English Lake District. The site is nearest the sea in a southwesterly direction, while the nearest centres of population and industry lie to the south and east. As expected, the largest amounts of chloride come from the southwest and the largest amounts of sulphate (and nitrate) from the southeast. An increase in wind speed also has an effect in raising the level of ion supply by atmospheric precipitation, especially in the case of chloride where the difference between calm periods and gales may be more than tenfold. This is not only because the transport of sea spray inland is increased by high winds, but also because the actual entrainment of spray droplets into the air is favoured by stormy weather.

Some effects of disturbance upon the chemistry of bog peats

The changes in bog vegetation which are brought about by human interference have been discussed at length by Pearsall (23). When bogs are drained and burned repeatedly, so that their *Sphagnum* cover is replaced by heather (*Calluna vulgaris*) and cottongrass (*Eriophorum vaginatum*), or in extreme cases by pine (*Pinus silvestris*), the chemical properties of their peats are greatly affected. For example, in the English Lake District (15) peat pH averages only 3.0 under pinewood on bog peat, while under regenerating *Sphagnum* the pH averages 3.6, much the same as in the more acid of undisturbed ombrotrophic bogs. Also, concentrations of both mineral ash and nitrogen in the peat are about 40% higher in the damaged Lake District bog surfaces than in the average intact *Sphagnum*-covered surface. Presumably a greater degree of oxidative decomposition has been induced by the draining and burning, with much organic matter having disappeared as carbon dioxide while nitrogen and mineral material have been conserved.

Productivity of wetlands

Presently available data are insufficient to provide accurate comparisons of annual plant productivity in fen and bog communities of diverse types. However, some indication of differences can be derived from terminal harvest of above- ground standing crops (24), as shown in Table 5. The range is from 4,000 to 11,000 kg dry weight per hectare. In a general way the table proceeds from productive stands to unproductive ones, and from circumneutral silted sites to acid peaty habitats. For example, the reedswamps represent a fen type of vegetation most characteristic of rich silted habitats along lake shores. Grass fens of the *Deschampsia*, *Calamagrostis* and *Phalaris* types generally occur in drier silted sites. However, grass fens of the *Molinia* type are an exception and occur frequently on quite highly acid peats similar to those inhabited by *Trichophorum* fen and bog.

The estimate for *Sphagnum*, based on data from two sources (1, 24), is rather high in comparison to the *Molinia* and *Trichophorum* values, and cannot be regarded as definitive. However, it may be noted that in this case above-ground is equivalent to total productivity, whereas in the other cases it is not. Moreover, *Sphagnum* appears to have an exceptionally low demand for nutrients such as phosphorus and nitrogen (19, 20, 21). If either of these nutrients limits growth in bog habitats, and there is evidence that both can do so (26), then *Sphagnum* may be able to produce more dry matter per unit of nutrient uptake than other bog plants with a greater nutrient demand. The autecology of *Sphagnum* species is urgently in need of study, with particular reference to the factors controlling growth and productivity.

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Table 1. Ions dissolved in the interstitial water as a percentage of total (dissolved + adsorbed) ions in surface peats from Irish bogs.

Na	K	Ca	Mg	H	SO_4	Cl
30	8	1.4	0.9	0.03	11	ca. 70

Table 2. Ionic composition of rain and bog waters from northern England.

	Na	K	Ca	Mg	Cl	SO_4	pH
	(milligrams per litre)						
Rain, Lake District	1.9	0.2	0.3	0.2	3.3	3.2	4.45
Bog pools, Moor House							
Wet weather	1.7	0.17	0.30	0.20	3.2	4.0	4.21
Dry weather	4.3	0.33	1.17	0.82	5.9	15.2	3.85
Ratio $\frac{dry}{wet}$	2.5	1.9	3.9	4.1	1.8	3.8	2.4

Table 3. Exchangeable cations in natural bog peats from northern England.

Na	K	Ca	Mg	H
(milliequivalents per 100 grams dry weight)				
0.68	1.13	4.29	4.79	150

Table 4. A comparison of bog waters from the Falkland Islands and various European areas.

	pH	Total cations	Cations (milligrams per l.)				Anions	
		(m. equiv./l.)	Na	K	Ca	Mg	Cl	SO_4
Falkland Islands	4.10	2.35	38.6	1.6	2.1	5.4	72.0	13.4
Gowlan East, W. Ireland	4.40	0.783	12.5	0.5	0.8	1.8	20.6	7.7
Sutherland, N. Scotland	4.51	0.760	13.9	0.6	0.5	1.1	23.6	5.3
Coom Rigg, N. England	3.90	0.508	5.3	0.5	1.0	1.1	9.3	10.9
Moor House, N. England	3.91	0.371	3.4	0.3	0.9	0.6	5.0	11.4
Rannoch Moor, W. Scotland	4.50	0.169	2.2	0.1	0.3	0.3	4.3	2.7
Eastern Sudeten Mts., Poland	3.92	0.169*	0.2	0.2	0.5	0.3**	0.3	7.7

* Anion sum, Mg not done on all samples

** Single sample

Table 5. Above-ground standing crop in British wetlands.

		Terminal Harvest dry weight (kg/ha)
REEDSWAMP	*Typha latifolia*	11,000
	Phragmites communis	7,600
GRASS FEN	*Deschampsia caespitosa*	10,000
	Calamagrostis lanceolata	8,800
	Phalaris arundinacea	8,700
	Molinia caerulea	4,000
SEDGE FEN	*Carex acutiformis*	6,300
	Carex lasiocarpa	5,100
	Carex rostrata	4,200
DEERSEDGE FEN AND BOG	*Trichophorum caespitosum*	4,500
SPHAGNUM FEN AND BOG	*Sphagnum* spp.	~6,500

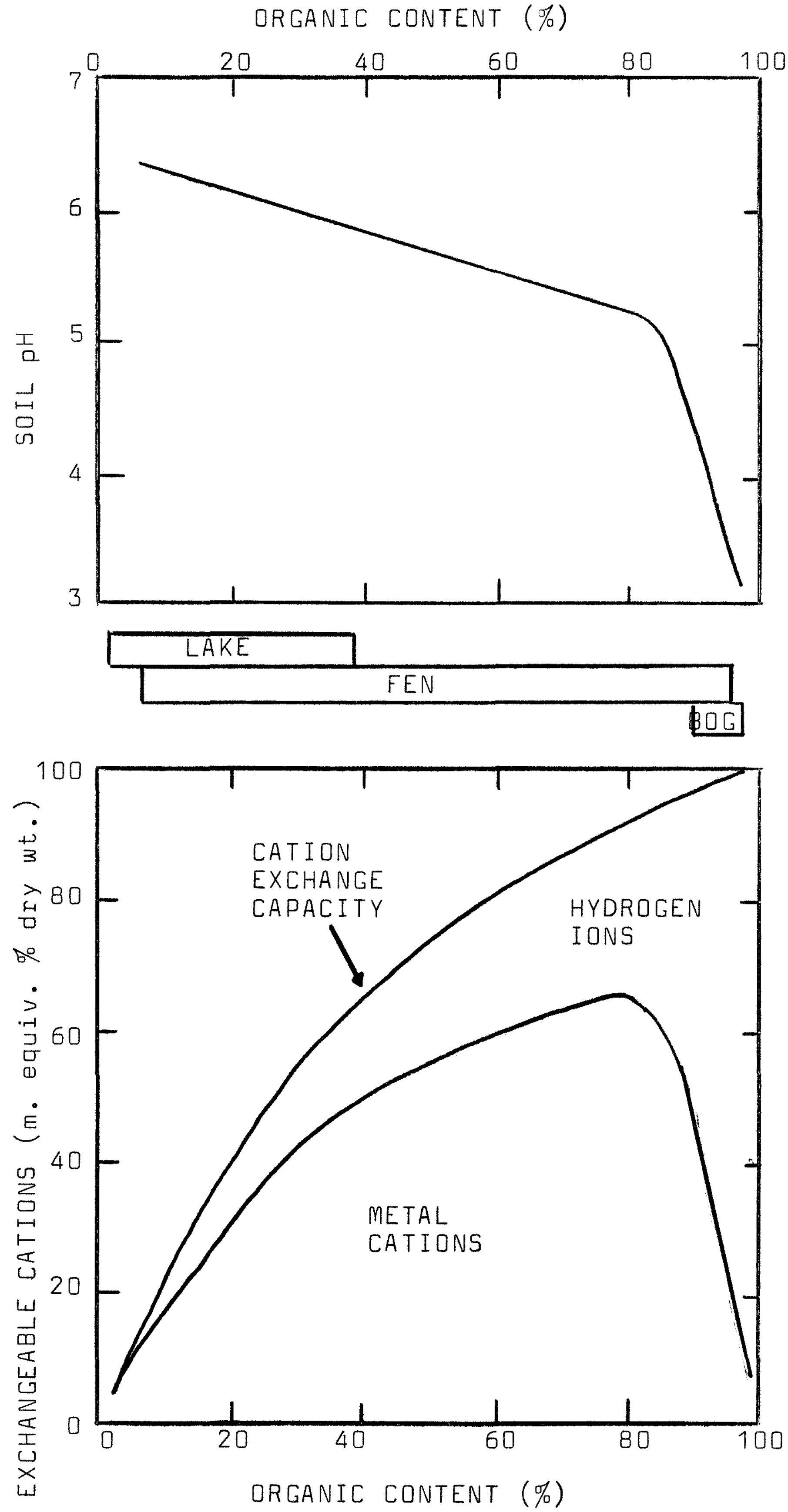

FIGURE 1. pH AND EXCHANGEABLE CATIONS IN RELATION TO ORGANIC CONTENT OF LAKE, FEN AND BOG SOILS

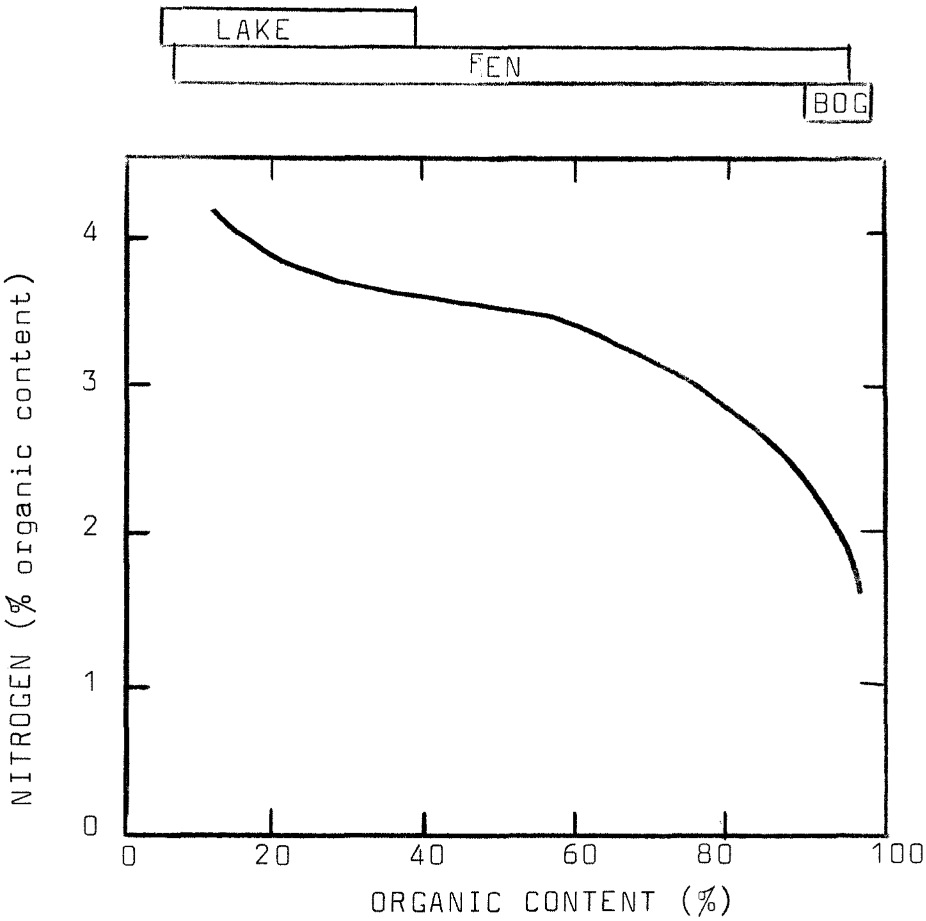

FIGURE 2. NITROGEN IN THE ORGANIC MATTER OF LAKE, FEN AND BOG SOILS WITH DIFFERING ORGANIC CONTENTS

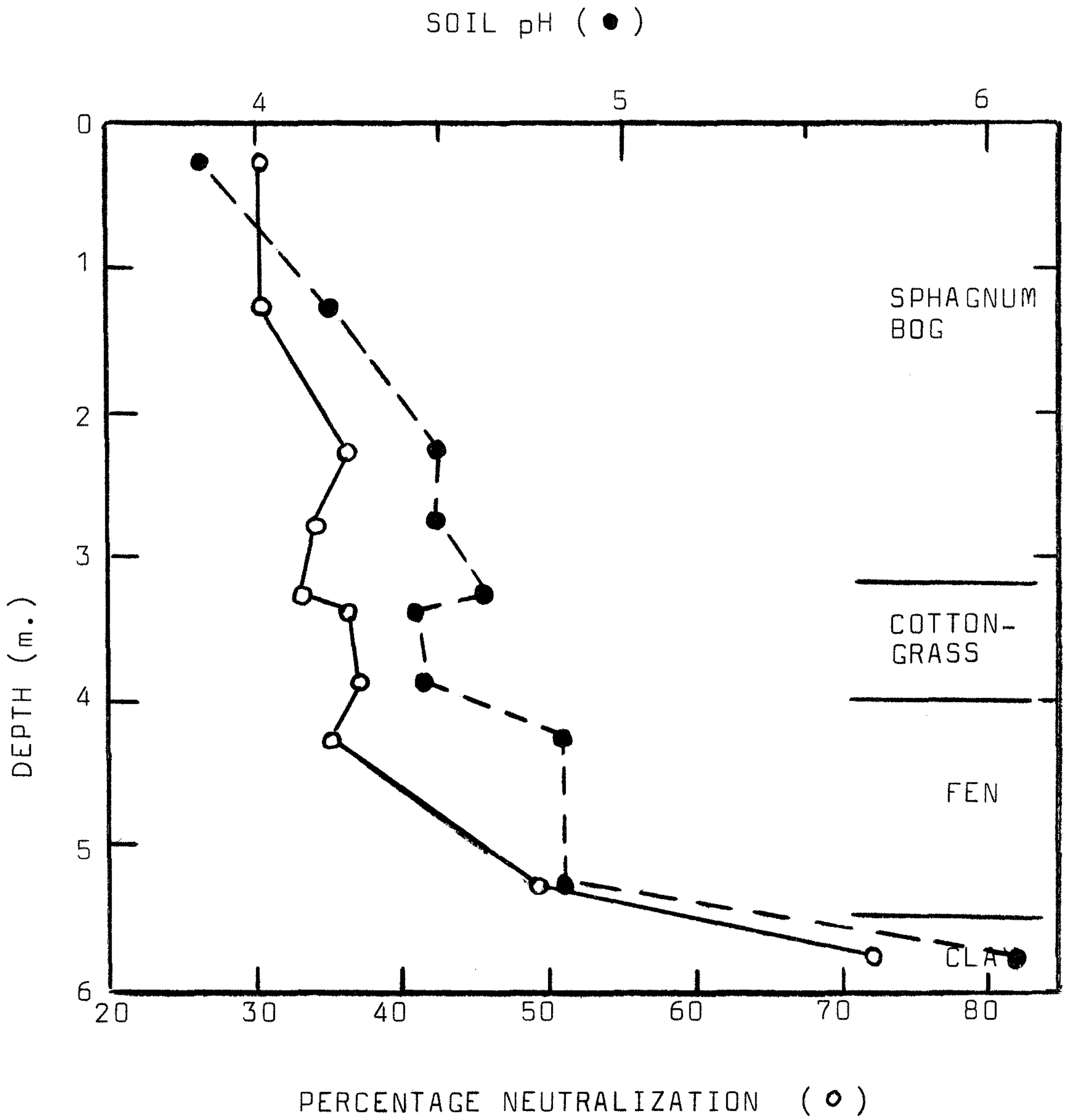

FIGURE 3. pH and % NEUTRALIZATION IN A BOG PEAT PROFILE

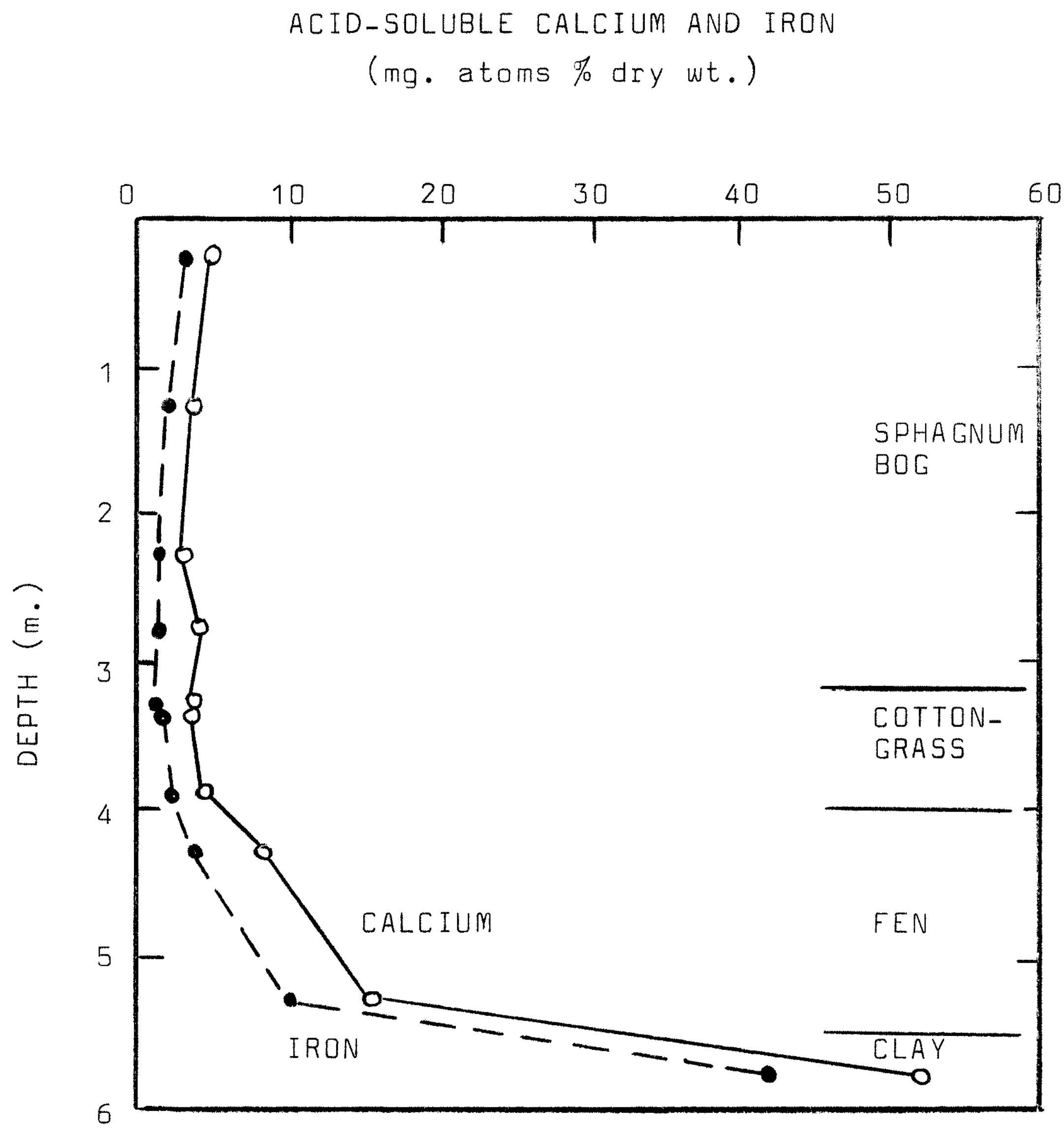

FIGURE 4. CALCIUM AND IRON IN A BOG PEAT PROFILE

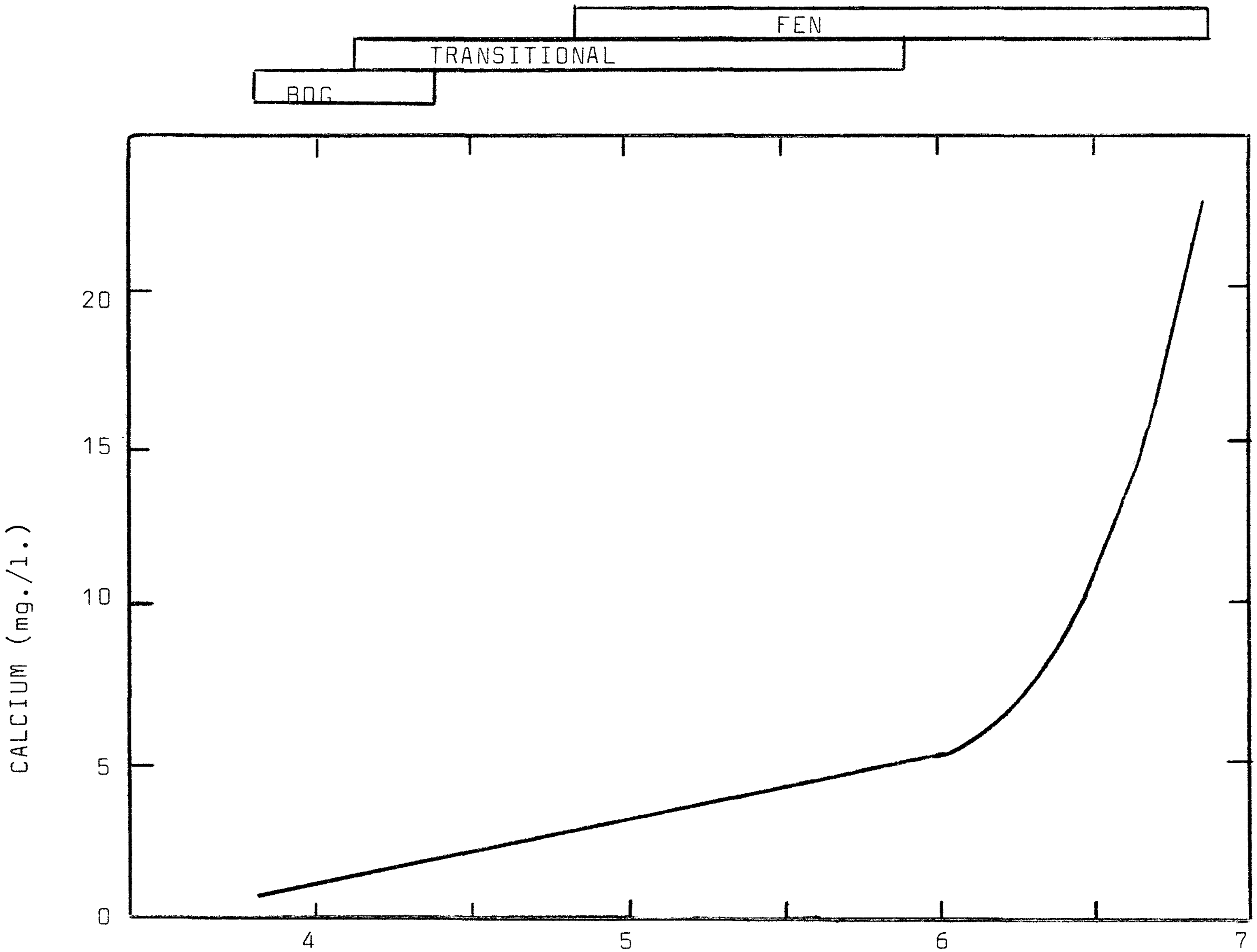

FIGURE 5. THE RELATION BETWEEN CALCIUM AND pH IN FEN AND BOG WATERS

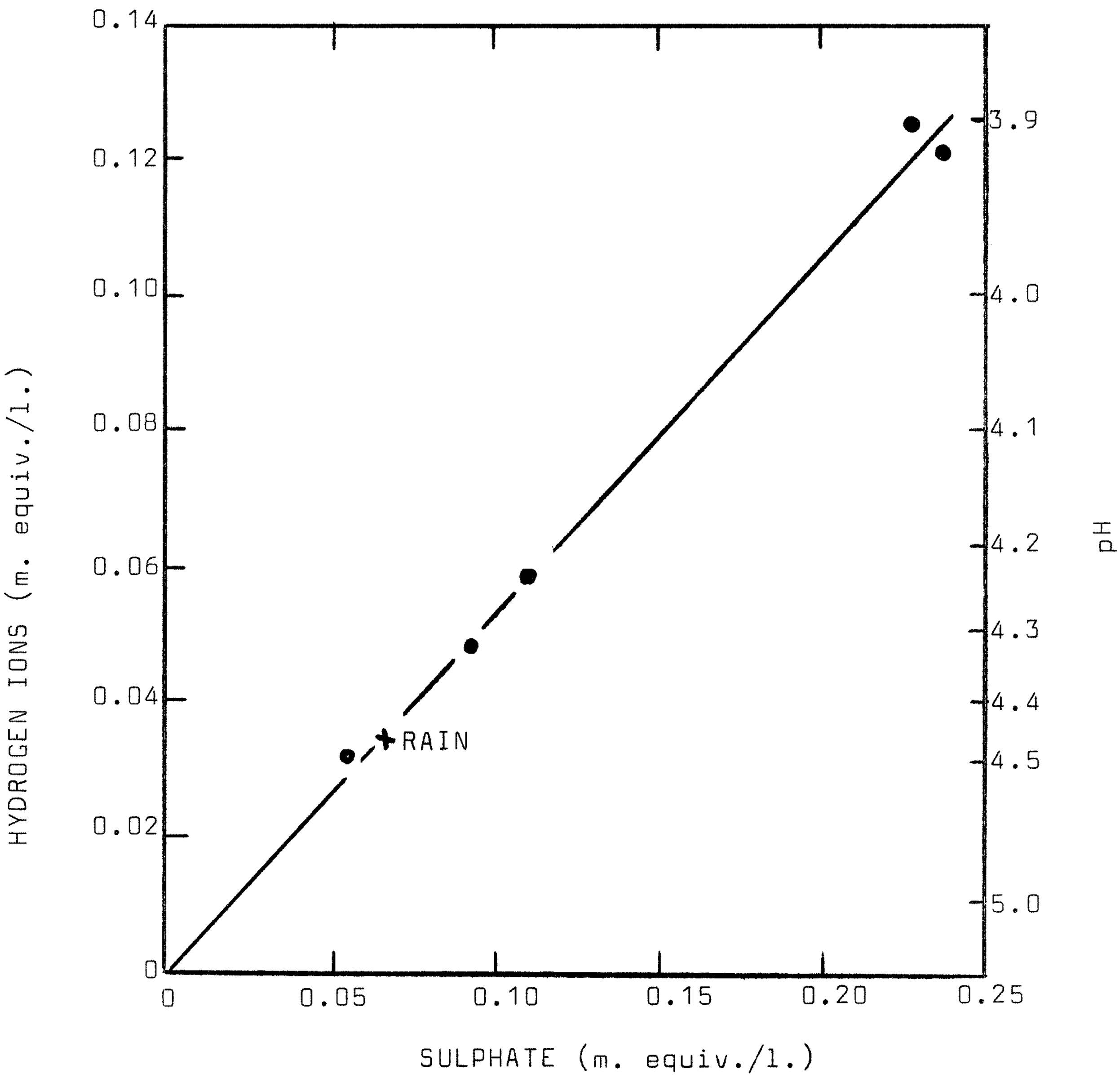

FIGURE 6. THE RELATION BETWEEN HYDROGEN AND SULPHATE IONS IN FIVE INLAND BRITISH BOGS

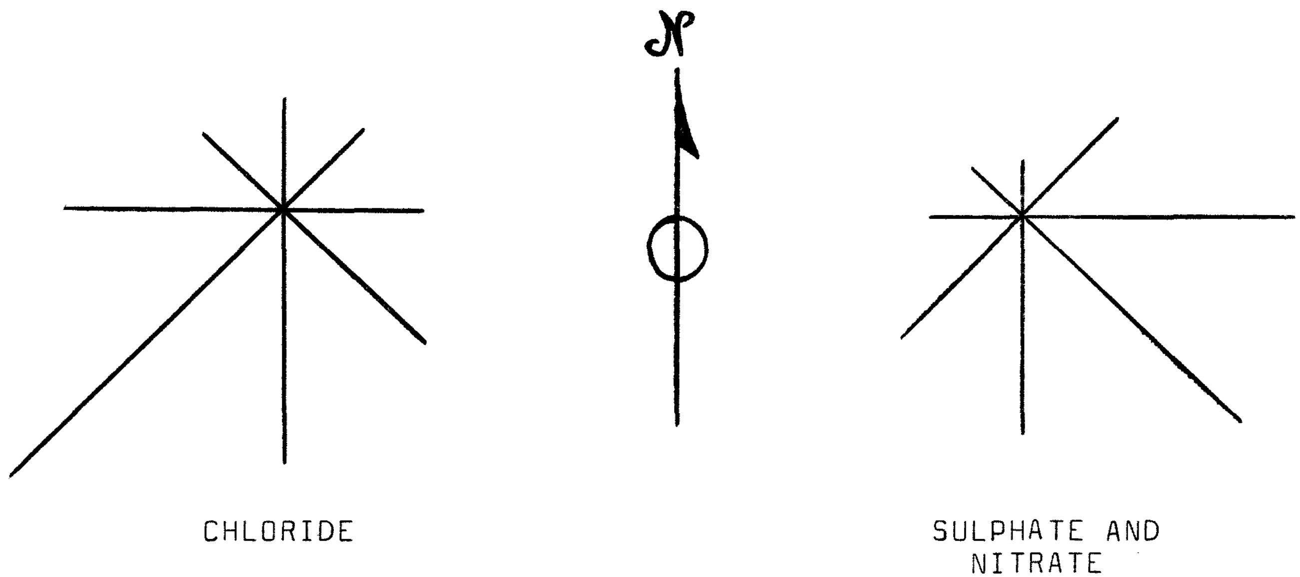

FIGURE 7. THE INFLUENCE OF WIND DIRECTION UPON ATMOSPHERIC ION SUPPLY TO A SITE IN THE ENGLISH LAKE DISTRICT (LENGTH OF LINE PROPORTIONAL TO ION SUPPLY)