

MALHAM TARN MOSS: THE SURFACE-WATER CHEMISTRY OF AN OMBROTROPHIC BOG

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ABSTRACT

Malham Tarn Moss is an ombrotrophic raised bog, entirely dependent for water and solutes on rain and other atmospheric inputs. All the nutrient requirements of the bog-surface vegetation must be met from these sources. The vegetated surface lies at the interface between the rain (and other airborne inputs) which vary widely in composition from day to day, and the water in the underlying peat which hardly varies through the year. The major-ion composition of water in surface pools or sample pits approximates to the average composition of rainwater, somewhat concentrated by evaporation and somewhat modified by ion exchange. The inorganic solutes in this water derive from, (1) a marine component (most of the Na⁺, Cl⁻ and Mg²⁺), (2) a terrestrial component (much of the Ca²⁺ and K⁺) and (3) a gaseous pollutant component (much of the SO₄²⁻, NH₄⁺ and NO₃⁻). In bog waters, total cations generally exceed total inorganic anions, especially in summer; the balance is made up by the anionic groups of the dissolved organic matter (DOM). Broad seasonal trends can be seen in the concentration of univalent and (especially) divalent cations, iron, pH, water colour and anion deficit (both reflecting DOM), and in the ratios Na⁺/Mg²⁺, Na⁺/Cl⁻ and SO₄²⁻/Cl⁻. These reflect seasonal changes in, *e.g.*, average temperature and evaporation, and biological activity. They are often much obscured by shorter term variation, arising from the changing weather and, to a lesser extent, from the chemistry of individual rainfall events. Changes in cation concentrations are strongly influenced by interactions with the ion-exchange sites of the peat. Helwith Moss, in Ribblesdale, shows the same factors operating at rather lower altitude and rainfall, and with higher inputs of terrestrially-derived cations from nearby quarrying.

INTRODUCTION

Malham Tarn Moss is a typical raised bog - a more-or-less lenticular mass of acid peat built up above the level of the mineral-rich drainage water of the surrounding country, and receiving all its water and solutes from rain and other atmospheric sources (Tansley, 1939; Proctor, 1995). Such a bog is described as ombrogenous ('formed by rain') or ombrotrophic ('fed by rain'). The water table in an active, undamaged ombrogenous bog is seldom far beneath the surface; the surface layers of peat and the vegetation mat are more-or-less saturated with water for most of the year, and bogs are often dotted with pools of open water. What is the chemical composition of this water? How does it vary with the seasons and with other factors? And what kind of a habitat for plant growth does an ombrogenous bog provide? This paper, which is based on water analyses from the Tarn Moss at approximately monthly intervals between 1992 and 1997, sets out to provide some answers to these questions.

The topography and history of the Tarn Moss

The Tarn Moss, some 30 ha in area, occupies the western part of the basin of Malham Tarn (Fig. 1; Pigott & Pigott, 1959; Sinker, 1960; Cooper & Proctor, 1998), 7 km northeast of

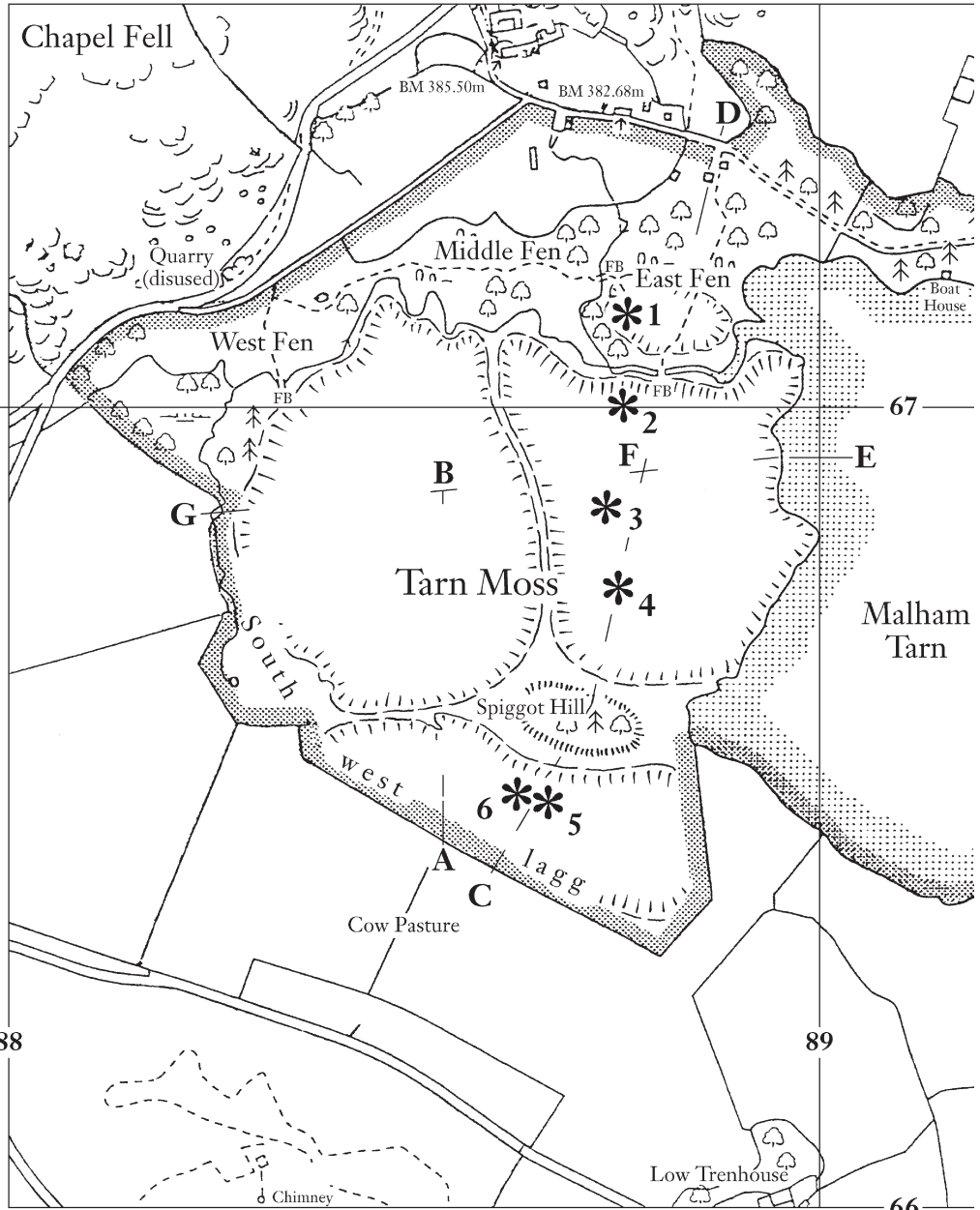


FIG. 1

Location of the Tarn Moss in the western part of the basin of Malham Tarn. The main inflow stream to the Tarn ('Cow Beck') is fed by a series of springs along the foot of the limestone scarp just to the north, with a southern branch fed by a rising at a prominent 'well-eye', and by drainage from the narrow belt of fen along the rest of the south-west lagg. The margins of the three main ombrotrophic peat domes making up the Tarn Moss are sketched in approximately. Capital letters A–G and associated lines show the ends and intersections of the straggraphical transects of Pigott & Pigott (1959). Asterisks (*) mark the approximate positions of the water-sampling points

Settle, North Yorkshire (OSGB Ref. SD 886 667; Lat. 54° 06' N, Long. 2° 11' W), at an altitude of ca 375–380 m above sea level. The main part of the bog, south of the west inflow stream (Cow Beck), consists of three more-or-less coalesced raised-bog domes, bounded by the Tarn to the east and separated from the predominantly drift-covered and calcareous surrounding country by a belt of 'lagg' fen. South of the prominent drift hillock of Spiggot Hill, the ombrotrophic peat surface merges almost imperceptibly with the narrow lagg and adjacent pasture, but most of its periphery shows a more-or-less obviously sloping 'rand', steepest where the northern edge of the Moss borders the Cow Beck; the edge adjacent to the Tarn is an erosion cliff a couple of metres high, formed by cutting back of the edge of the bog by some 15–20 m following the raising of the Tarn water level in 1791 (Pentecost, 2000). The eastern dome of the Moss, bordering the Tarn, rises to some 5 m above the level of the Tarn. It is separated from the broad western dome, bordered westwards by the Cow Beck and the south-western lagg, by a broad seepage, partly straightened by ditching in the past, running northwards from the patch of wet fen at the north-west corner of Spiggot Hill to join the Cow Beck. A third elongated dome lies south and west of Spiggot Hill. In addition to this large area of ombrotrophic peat, small areas of bog grew up in the meanders of the Cow Beck. The largest and most intact of these lies astride the boardwalk between Sand Hill (Miss Hilary's) Cottage and the East Fen bridge. The birch wood in the Middle Fen has grown up on another formerly ombrotrophic area, partly flooded with calcareous water when the level of the Tarn was raised in 1791, and several other small areas of ombrotrophic peat can be recognised in the West Fen

The underlying deposits show that the Tarn Moss has grown up mainly over lake sediments and fen peats, spreading to some extent over adjacent mineral ground as the thickness of the peat built up. Its history is outlined by Cooper & Proctor (1998), and described in more detail by Pigott & Pigott (1959). This is essentially the classical pattern of origin of a raised bog as envisaged by Weber (1907) a century ago. Clays and calcareous marl deposited in open water are succeeded by fen peats, often, especially near the top, with abundant woody remains. Around 7000 years ago, probably roughly coinciding with the filling of the North Sea basin and the switch to a more oceanic climate, a thin woody layer of birch and increasing abundance of *Sphagnum* remains mark the beginning of ombrogenous bog growth. Ombrotrophic peat then accumulated progressively over the ensuing millennia, building up to a depth of 5–6 m over much of the area of the bog. This represents an average rate of accumulation of a little less than a millimetre a year.

The Tarn Moss, as it now stands, bears many marks of human activity, in the shape of peat cuttings, drainage ditches and boundary banks, and farming and other activities over the last few centuries have certainly had a great impact on its vegetation, and on the rate of accumulation (or loss) of peat. Evident traces of peat cuttings can be seen on the East Fen, in the Spiggot Hill peat pools, and towards the western edge of the western dome; some are shown very clearly in the stratigraphic sections of Pigott & Pigott (1959). Shallow drainage ditches ('grips') were dug in many places, as was commonly the practice on the blanket bogs of the hills. In the 18th Century, the Tarn Moss was divided between three ownerships, and a boundary bank north of Spiggot Hill shown on the plans in Thomas Lister's estate book (Anon, 1785–6) is still discernible on the ground. When the Malham Tarn estate was acquired by the National Trust in the 1940s, the main area of Tarn Moss had been heavily (and probably frequently) burnt. The vegetation was dominated by *Eriophorum vaginatum*, with an abundance of *Deschampsia flexuosa* and the mosses *Poblia nutans* and *Tetraphis pellucida*, but very little *Sphagnum* except in the Spiggot Hill peat pools. Since then, many

of the old grip drains have been blocked so that the surface is now wetter, and moving towards what would be seen on an undamaged bog - though still with a long way to go to match such bogs as Glasson Moss in Cumbria or Cors Tregaron in mid-Wales. Peat processes are slow and, though obstacles to recovery can be removed, recovery itself cannot be hurried. Time is the greatest healer of all.

Helwith Moss is a smaller raised bog, a little over 20 ha remaining in a more-or-less natural state, in the Ribble valley 9 km north of Settle (OSGB Ref. SD 805696; Lat. 54° 07' N, Long. 2° 18' W), at an altitude of ca 220 m. The surface has been much cut for peat in the past, but for the most part the peat diggings seem to have been relatively small individual allotments (of which some boundary stones remain), and the patchy vegetation retains a good raised-bog flora with much *Sphagnum magellanicum* and *Andromeda polifolia*, along with some dull tussocky *Molinia* areas. Helwith Moss lies between two large quarries in the Silurian slates of the south-east corner of Ingleborough. Both quarries have probably been major sources of dust input to the bog surface, and the spoil heaps of the southern one, Dry Rigg quarry, encroach onto the southern edge of the bog. In spite of (and in part because of) the many human impacts upon it, Helwith Moss remains a rich and interesting site.

The structure of a raised bog: acrotelm and catotelm

An ombrotrophic bog is not simply a uniform mass of peat. An intact bog typically shows a clear division between the surface layer, often ca 30 cm deep, within which the water table fluctuates and which is therefore at least periodically oxygenated. Most biological activity takes place in this surface layer or acrotelm (Ingram, 1978). Plant remains are still readily distinguishable close to the surface, becoming progressively more broken down towards the base of the acrotelm, and water can move freely through the little-humified dead plant material so the hydraulic conductivity of the surface layers is high. The acrotelm can be visualised as a composter in which fresh plant material, added on or near the surface, is progressively broken down, with more or less humified peat as the product at the base. In the permanently waterlogged peat, or catotelm, below the base of the acrotelm, plant remains are still recognisable but are much more fragmentary, and are embedded in a colloidal matrix produced by microbial decomposition of much of the original organic material. (Pollen grains are particularly resistant to decay; together with seeds and other 'macrofossils' they provide a historical record of the vegetation on and around the bog as the peat accumulates.) The catotelm peat in an actively growing raised bog has a bulk density ca 0.1; that is, its water content is around 90% (the bulk density and physical properties of humified peat are similar to porridge). In spite of the high water content, water cannot move freely through the colloidal matrix, and the hydraulic conductivity of catotelm peat is several orders of magnitude less than in the acrotelm. Thus once an ombrotrophic bog is established it forms a largely waterproof seal over the surface beneath.

The addition of new peat to the top of the catotelm depends on the rate of production of new organic matter by the surface vegetation exceeding the rate of breakdown in the oxygenated acrotelm. Peat formation, even at its most active, seldom exceeds 5-10% of primary production. If water level falls through drainage or drought, breakdown of organic matter may equal or exceed production, so that peat growth may cease or become negative. The Holme Post, in the Cambridgeshire fens, provided a famous example of this (Godwin, 1978).

If an ombrotrophic bog surface dries out, or the vegetation is persistently burnt or heavily grazed, the acrotelm/catotelm structure is lost and the plant cover is, in effect, rooted in the surface of partly dried catotelm peat. Restoration of active bog vegetation

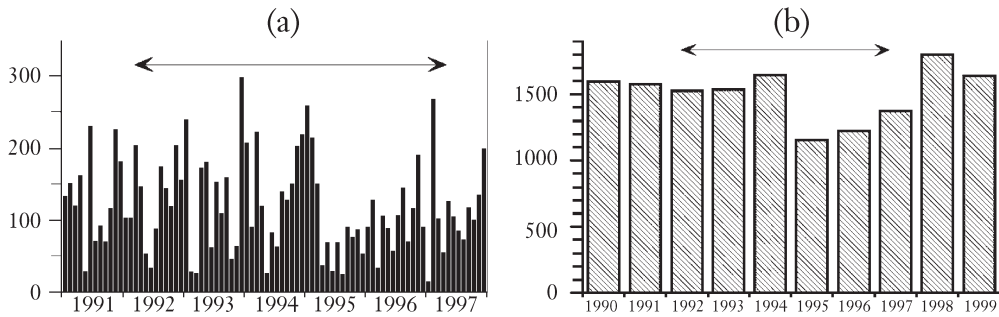


FIG. 2

(a) Monthly rainfall totals (mm) at Malham Tarn, 1991–1997, and (b) Annual rainfall totals (mm) at Malham Tarn through the 1990s. The arrowed bars show the period covered by the water analyses.

then depends on recreation of a functional acrotelm. This happens within a few decades in a small peat cutting. Over an extensive raised-bog surface it may take a century or more; there is no really satisfactory short cut to hasten the process.

Rainfall and the chemistry of rainwater

Average annual rainfall at Malham Tarn Field Centre from 1990 to 1999 was 1507.3 mm, well distributed around the year but varying greatly (and irregularly) from month to month, with a tendency to a maximum from November to February and a minimum from May to July (Fig. 2); the average in the wet winter months was almost double that in late spring and early summer. From 1986 to 1988, Malham Tarn was one of a network of 59 monitoring stations for the chemistry of wet deposition in the United Kingdom (UKRGAR, 1990). We are thus fortunate in having good data for average rainwater composition and total deposition at the Field Centre during those three years for all the major ions except potassium (K^+). Monitoring has continued at a reduced number of sites, including two in the Pennines, Cow Green Reservoir in upper Teesdale, some 60 km north of Malham Tarn, and Wardlow Hay Cop in the Derbyshire Dales 90 km to the south, and at Bannisdale Head in the eastern Lake District, 50 km to the north west. 1986–88 means for the four sites are compared in Table 1. In what follows, I have used the 1994 data from Cow Green

TABLE 1.

Average composition of rainwater, 1986–88, at Cow Green Reservoir, Teesdale (OSGB ref. NY 817 298, alt. 510 m), Bannisdale, Cumbria (NY 515043, alt. 265 m), Malham Tarn (SD 894 672, alt. 384 m) and Wardlow Hay Cop, Derbyshire (SK 177 739, alt. 350 m). Ionic concentrations in mille equivalents per litre ($\mu\text{equiv litre}^{-1}$), $\mu\text{mol ionic charge litre}^{-1}$. Data from UKRGAR (1990). Potassium was not included in the UKRGAR 1986–88 averages, but earlier data from seven sites in the north of England gave an average of 7.1 $\mu\text{equiv. litre}^{-1}$ (for authors, see Proctor, 1992).

Site	Rainfall (mm)	H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺
Cow Green Reservoir	1161	31	9	15	60	76	47	22	21
Bannisdale	2150	28	13	26	106	131	54	20	31
Malham Tarn	1282	31	14*	24	98	124	60	22	28
Wardlow Hay Cop	885	53	53	19	70	104	90	31	37

* mean for 1987 and 1988, excluding a very high figure (50) for 1986

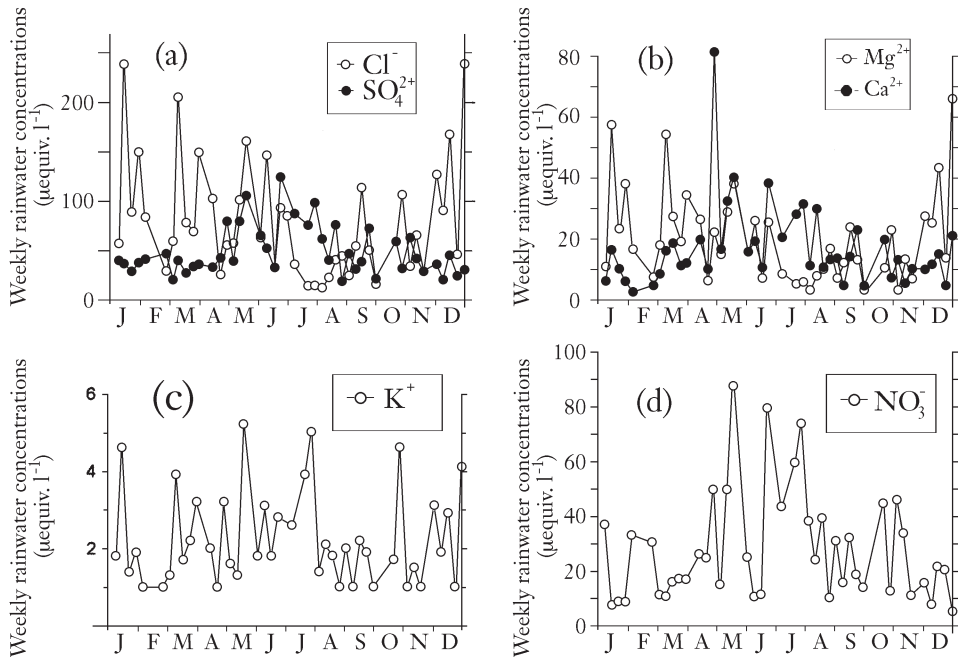


FIG. 3.

Weekly rainwater analyses from Cow Green Reservoir, Upper Teesdale, 1994 (data of Vincent *et al.*, 1995 omitting the very high values in the 2mm rainfall of week beginning 29 June). (a) chloride and sulphate; (b) magnesium and calcium; (c) potassium (cubic regression); (d) nitrate (quadratic regression). See text for further explanation.

(Vincent *et al.*, 1995) to illustrate some general points about rainwater chemistry.

The chemical composition of rainwater is extremely variable. Fig. 3a shows the concentration of chloride (Cl^-) and sulphate (SO_4^{2-}) in weekly samples from Cow Green; both ions show wide variations and there is little correlation between them. Over the year, there is some tendency for Cl^- (and also sodium, Na^+) be higher during the winter months, and SO_4^{2-} higher in summer, but this is far less than the week-to-week variation. Magnesium (Mg^{2+}) and Calcium (Ca^{2+}) paint a similar picture (Fig. 3b). K^+ is widely variable but the general level changes little round the year, though there is a weak tendency to a maximum in spring and a minimum in autumn (Fig. 3c). By contrast, the concentrations of ammonium (NH_4^+) and nitrate (NO_3^-) (Fig. 3d) are markedly higher in summer.

TABLE 2.

The major-ion composition of seawater, calculated from the data of Libes (1992).

The last two rows of the table are quotients relative to chloride and sodium in terms of ionic charge.

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Concentration (g l^{-1})	10.51	0.389	1.26	0.402	18.87	2.646	0.139
Concentration (mequiv. l^{-1})	457	9.95	103.7	20.0	533	55.7	2.27
Relative to Cl^-	0.857	0.019	0.195	0.038	1.000	0.105	0.004
Relative to Na^+	1.000	0.022	0.227	0.044	1.166	0.122	0.005

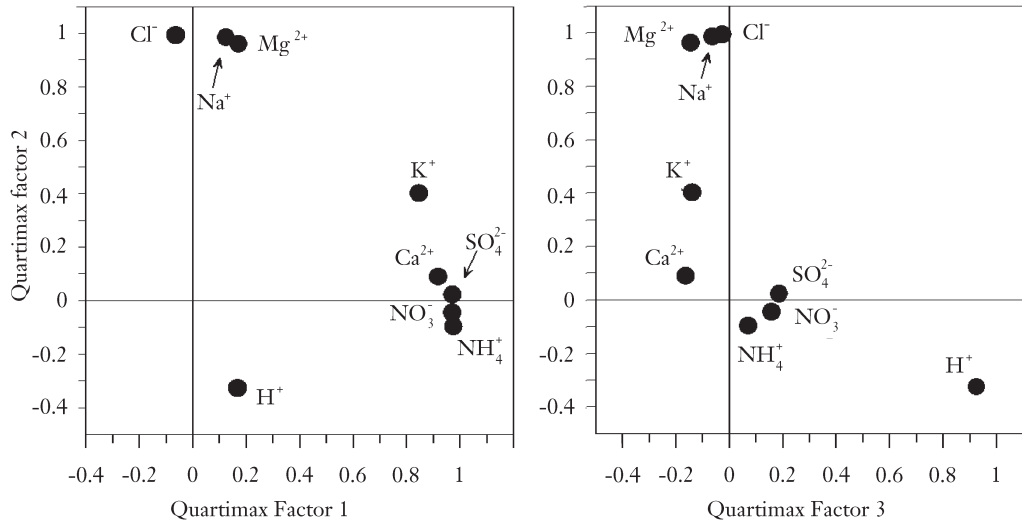


FIG. 4.

Factor analysis (Quartimax rotation) of ion concentrations in weekly rainwater samples from Cow Green Reservoir (Teesdale, northern England) during 1994 (data of Vincent *et al.*, 1995). Note the correlated clusters of marine-derived (sodium, magnesium, chloride) and pollutant-derived (sulphate, nitrate, ammonium) ions, and the more independent behaviour of hydrogen, potassium and calcium. For a comparable analysis of the 1992 Cow Green data, see Proctor (1997).

The solutes in rain come from three main sources; entrained sea spray, dust of terrestrial origin, and pollutant gases. These can be seen in principal components or factor analyses of rainwater data (Fig. 4). Na^+ and Cl^- , both almost entirely marine (Table 2), are closely correlated and come out close together in the analysis. In Britain and Ireland (where our most extensive limestones are nearly pure calcium carbonate, CaCO_3), Mg^{2+} is also mostly of marine origin and is also correlated with them. The ions of predominantly pollutant origin, sulphate (SO_4^{2-}), NO_3^- and NH_4^+ , form a second cluster because their sources, although more diverse, are all mainly land-based and associated with the more populated and economically-active areas of the country. Ca^{2+} and K^+ tend to behave independently of the pollutants and of one another, and the position of hydrogen (H^+) in the diagram reflects a combination of the influence of atmospheric carbon dioxide (CO_2), the acidic pollutant gases, and neutralising cations. Many of the elements present in smaller amounts in rainwater, such as iron (Fe), manganese (Mn), zinc (Zn), copper (Cu) and aluminium (Al) must also come from terrestrial dust. Their maximum possible average concentration in surface waters is limited by their rate of deposition (Cawse, 1981), and measured concentrations in surface waters and peats broadly reflect this (Livett, Lee & Tallis, 1979). The exact relationships between the different components in rainwater varies from site to site. As Table 1 shows, rainwater at Cow Green, remote from large towns and largely surrounded by acid moorland and blanket bog, contains somewhat less SO_4^{2-} and about two-thirds as much Ca^{2+} as at Malham Tarn, while rainwater at Wardlow Hay Cop, in the less rainy limestone Derbyshire Dales midway between Manchester and Sheffield, contains 50% more SO_4^{2-} and around four times as much Ca^{2+} as at our site.

Rainwater, surface water and some physical and chemical principles

How does the composition of rainwater translate into the composition of water in pools, sample pits or permeate the surface layers of an ombrotrophic bog? The first (and obvious) point follows from the law of conservation of matter; solutes in the bog surface water can come only from airborne sources - and these solutes must go somewhere. Water can evaporate; most of the solutes cannot - with the important caveat that compounds of carbon (C), nitrogen (N) and, to a lesser extent, sulphur (S) can undergo chemical transformations releasing the element in gaseous forms to the atmosphere. Apart from rainwater, solutes may enter the system through dry deposition of dust or gases, and through animal movements (spectacularly so in places where a gull colony has taken up residence on a bog). However, as a first approximation, bog surface waters can be thought of as rainwater, averaged over a period of time, and somewhat concentrated by evaporation (Proctor, 1992).

In a natural water (or any other solution), the total positive charges on the cations must balance the total negative charges on the anions, so that the solution as a whole is electrically neutral. In rainwater, there are only inorganic ions to consider: the major cations are Na^+ , K^+ , Ca^{2+} , Mg^{2+} , H^+ and NH_4^+ , and the major anions are Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- (bicarbonate). In bog waters, there are almost always substantial amounts of dissolved organic matter (DOM). This colloidal organic material (responsible for the brownish colour of peaty waters) carries ionisable carboxyl and phenolic groups, and behaves as a mixture of weak acids typically making up a significant fraction of the total anions in bog waters. The ionic balance adjusts through the buffering action of weak acids. In rain, it is buffered by the CO_2 (H_2CO_3) - HCO_3^- system (as it is in calcareous fens); in acid bog waters it is buffered by the organic acids of the peat colloids. Adjustments in the ionic balance typically show up as changes in pH.

The peat colloids function as an efficient cation-exchange medium (Stumm & Morgan, 1981). The quantity of cations associated with a given volume of peat much exceeds those in the same volume of water. The affinity of cations for the exchange sites increases with valency. The peat/water ratio for univalent cations is often in the range 10-20, and that for divalent cations 50-100; the trivalent cations Fe^{3+} and Al^{3+} are almost entirely associated with the organic matter. Divalent cations displace monovalent cations most strongly at low concentrations.

With changing concentration, the ratio of $\log\Sigma(\text{divalent cations})$ to $\log\Sigma(\text{univalent cations})$ follows a line with gradient 2.0. One effect of this is that the ratio $\text{Na}^+/\text{Mg}^{2+}$ is on average slightly lower in bog surface waters than in the rain, even where there is no addition of Mg^{2+} from non-marine sources.

The composition of bog surface waters is also influenced by chemical processes in the peat, especially oxidation-reduction processes involving S and N. Uptake and release by organisms is important too for elements that are limiting nutrients for plant growth or microbial activity, notably N, P (phosphorus) and K.

METHODS***Sample collection***

Water samples were taken from six points on the Tarn Moss, shown by asterisks on Fig. 1, and from three points on Helwith Moss - in a pool on the eastern side of the bog at ca SD 80746951 ('E'), in a long-recolonised peat cutting towards the northern edge of the bog at ca SD 80626968 ('N'), and in a pool on the southern slope of the bog facing the quarry spoil heaps at ca SD 80616949 ('S').

TABLE 3.

Summary statistics of water-analysis data from Malham Tarn Moss, 1992-1997 (n = 55). Values for ions in $\mu\text{mol l}^{-1}$ ($\mu\text{mol ionic charge litre}^{-1}$). A_{320} is measured as optical absorbance (no units). $\kappa_{25^\circ\text{C}}$ is total measured electrical conductivity, corrected to 25°C but not 'corrected' for hydrogen ions. NH_4^+ was measured only from January to November 1994: mean $3.2 \mu\text{equiv. l}^{-1}$, s.d. 1.7, median 3.1, maximum 6.2, minimum 0.9, upper quartile 4.4, lower quartile 2.0 (n = 12). Note that a number of the quantities measured are very variable, with skewed distributions, so the median is a better measure of central tendency than the mean. In general, the number of significant figures given reflects the precision of the individual measurements; the standard deviation is a measure of the (often wide) variation between sampling occasions.

Statistic	pH	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	H ₂ PO ₄ ⁻	DEF	A ₃₂₀	Fe ($\mu\text{g l}^{-1}$)	Zn ²⁺	$\kappa_{25^\circ\text{C}}$ ($\mu\text{S cm}^{-1}$)	Na ⁺ / Mg ²⁺	Na ⁺ / Cl ⁻	Ca ²⁺ / Mg ²⁺	SO ₄ ²⁻ / Cl ⁻
Mean	3.94	31.2	47.7	8.8	168.4	181.8	117.5	3.22	0.49	76.5	0.546	304.9	0.56	79.6	3.98	0.97	0.68	0.67
s.d.	0.14	15.5	24.2	5.7	50.0	66.2	97.7	6.2	0.61	47.8	0.288	153.9	0.32	26.8	1.32	0.22	0.16	0.48
Median	3.96	26.6	41.9	6.75	159.4	175.3	78.3	0.78	0.30	79.9	0.505	294.7	0.51	72.6	3.48	0.95	0.68	0.54
Maximum	4.28	102.9	150.7	31.6	322.8	399.0	560.4	38.40	3.05	182.8	1.344	765.3	1.37	195.7	7.00	1.42	1.22	2.31
Minimum	3.54	9.4	13.2	1.3	83.0	66.5	21.6	0.00	0.00	[0]	0.030	14.0	0.01	41.5	1.71	0.55	0.34	0.16
Upper quartile	4.02	38.6	58.9	12.3	201.0	215.5	140.6	3.70	0.67	105.1	0.688	385.8	0.72	89.3	4.85	1.15	0.75	0.99
Lower quartile	3.86	21.5	30.7	4.23	131.4	134.3	61.6	0.29	0.02	45.7	0.342	195.4	0.31	61.2	3.07	0.81	0.60	0.31

The samples were collected in 150 ml screw-top hard polyethylene bottles. Most were returned by car or by post to Exeter within a few days of collection, and were then refrigerated (ca 5 °C) until analysed, generally within 1-2 weeks (but occasionally longer). Tests on long-stored samples indicate that, for most ions, storage for periods up to at least a few months makes little difference to the results (Proctor, 1993).

Chemical analysis

Analysis methods were the same as in Proctor (1994). Univalent cations (Na^+ , K^+) were determined by flame emission and other cations (Ca^{2+} , Mg^{2+} , Zn^{2+} , Fe) by atomic absorption spectroscopy. Water pH was measured as soon as possible after return of the samples to the laboratory with a glass-electrode pH meter; pH was calculated from conductivity and the analyses of individual ions as a check. When both were measured, the discrepancy between pH measured in the field and in the collected samples was generally very small. NH_4^+ was measured by the indophenol blue method in samples from November 1993 to November 1994. Inorganic anions (Cl^- , SO_4^{2-} , NO_3^- , H_2PO_4^-) were determined by ion chromatography. Conductivity was measured on the collected samples with a conductivity bridge, calibrated against a KCl conductivity standard, and corrected to 25 °C. Optical absorbance at 320 nm was measured by spectrophotometer, with a measurement at 650 nm as a check for turbidity (in general very low; high concentrations of DOM also have measurable absorbance at 650 nm).

RESULTS

Patterns in a 5-year data run

As Table 3 shows, all the chemical and physical quantities measured in the Tarn Moss water samples are variable, some of them extremely so. How much of this variation is regularly seasonal, and how much relates to other, more irregular causes? The monthly pattern for Ca^{2+} over the five-year span of the data (Fig. 5a) looks at first sight rather clearly seasonal, with peaks in summer and lower values in winter. Closer inspection shows that the pattern is, in fact, rather irregular; the highest peaks can occur at any time from spring to late autumn, with no predictable regularity and low values, though commonest in winter, can occur at any time of year. The data for the two major marine-derived cations, Na^+ and Mg^{2+} (Fig. 5b), show a generally similar picture, but the curve for Na^+ is disrupted by the after-effects of the dry summer of 1995 to the extent that the pattern in 1996 is completely out of phase with what would be expected as 'normal'. The curve for pH (Fig. 5c) shows (perhaps surprisingly) little sign of a regular seasonal pattern. The lowest values occurred in midsummer in 1992 and 1994, in late winter and early spring in 1993, and in the late autumn of 1995, all preceded by periods of low rainfall (Fig. 2a). The two most important anions, Cl^- and SO_4^{2-} , both give rather irregular graphs. It is hard to see any regular seasonal pattern in Cl^- , but SO_4^{2-} shows a tendency to high values in late summer. Peaks in SO_4^{2-} generally correspond to low values of pH and follow spells of dry weather (Fig. 2a).

Two variables with very clear seasonal patterns are shown in Fig. 6. Nitrate, with an average concentration around 22 $\mu\text{equiv. l}^{-1}$ in rain, is seldom present in more than trace concentrations in surface waters, except in winter weather cold enough to suspend almost all biological activity, resulting in a clear peak every winter (Fig. 6a). The optical absorbance at 320 nm (A_{320} , Gorham *et al.*, 1985; Gorham & Detenbeck, 1986), which is a measure of the brown colour of peat waters due to dissolved organic matter, is (apart from the aftermath of the 1995 drought) consistently high in summer and low in winter (Fig. 6b).

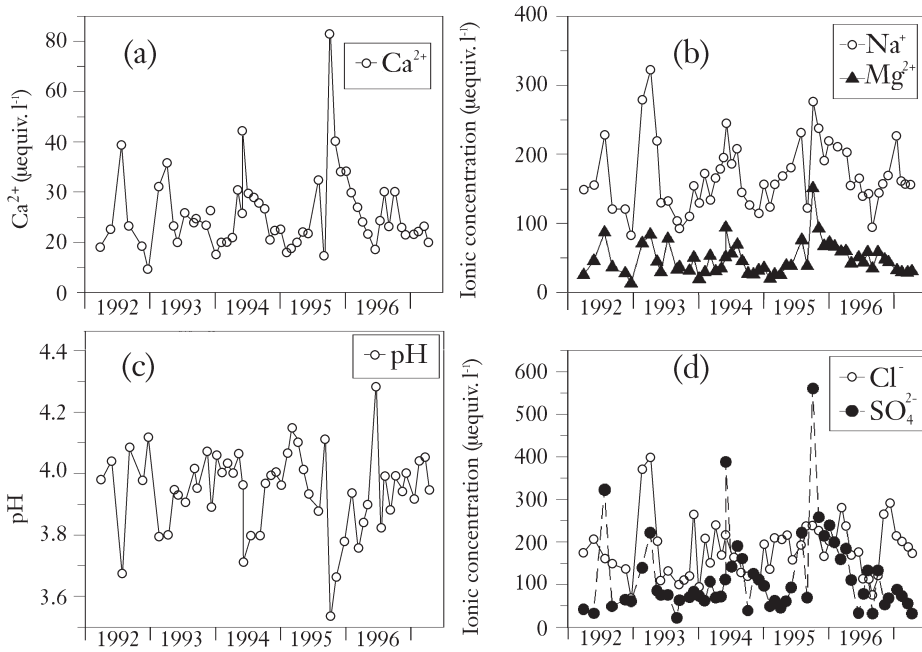


FIG. 5.

Ionic concentrations in surface-water samples from Malham Tarn Moss, March 1992-April 1997. (a) calcium; (b) the two marine-derived cations, sodium and manganese; (c) pH; (d) the two most abundant anions, chloride and sulphate. Note the close coincidence of peaks in the curves in (b) and the total lack of correspondence between the two curves in (d).

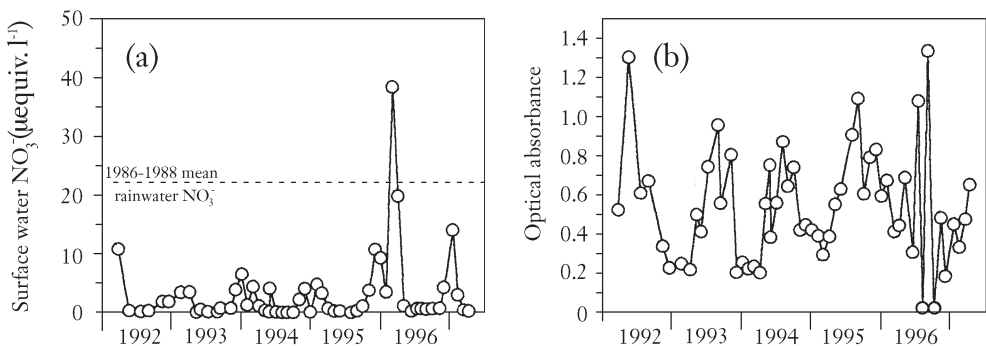


FIG. 6.

Nitrate and water colour in surface water on Malham Tarn Moss, 1992-97.

(a) nitrate: the concentration in surface water is almost always much less than the rainwater average, with the highest values during cold weather in winter or immediately after heavy rain; (b) Optical absorbance at 320 nm, a measure of water colour, and of the concentration of dissolved organic matter.

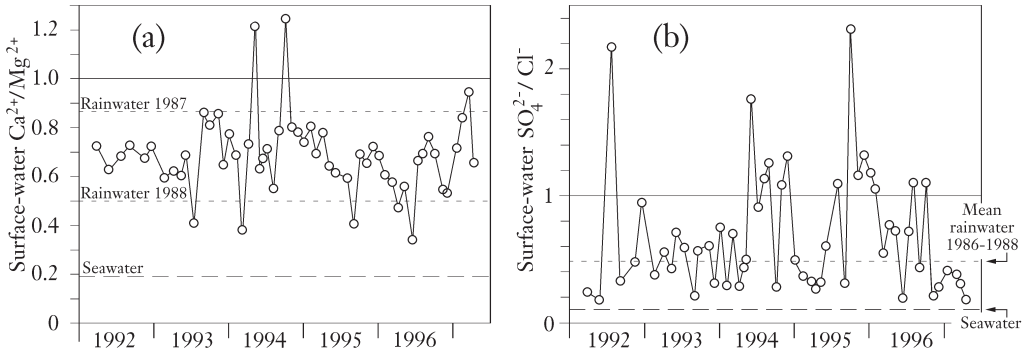


FIG. 7.

Ionic quotients in seawater, rainwater and bog surface water, Malham Tarn Moss, 1992-97.

(a) calcium/magnesium approximates to the average rainwater value, with a tendency to higher values in winter and lower values in summer; (b) sulphate/chloride varies widely around the rainwater mean, with occasional high peaks in (mostly summer) periods of low water level.

Two ionic quotients are plotted in Fig. 7. The ratio of Ca^{2+} to Mg^{2+} fluctuates around its average of 0.68, which is probably close to the long-term rainwater average, without showing any obvious seasonal pattern (Fig. 7a). The ratio of SO_4^{2-} to Cl^- is very widely variable around its median value of 0.54 (which is not greatly different from the rainwater mean). SO_4^{2-} often exceeds Cl^- in dry summers, with high peaks generally coinciding with low values of pH; the ratio falls to compensating low values during wet periods of high water level. The ratio $\text{SO}_4^{2-}/\text{Cl}^-$ is not uniformly distributed across the bog. As Fig. 8 shows, the lowest median values (less than the mean in 1986-88 rainwater) occur at the sample site in the detached area of bog north of the inflow stream, and south of the centre of the main eastern dome of the Tarn Moss, while the highest values are in the area south of Spiggot Hill.

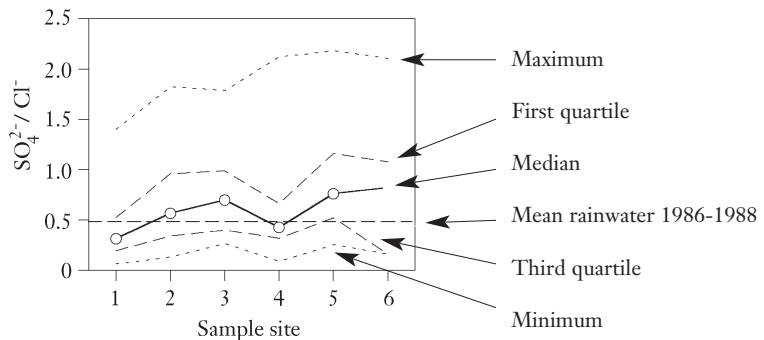


FIG. 8.

Median sulphate/chloride at the six sample sites on Malham Tarn Moss, Feb. 1993-Dec. 1994. Broken lines show the first and third quartiles, and dotted lines the maxima and minima over this sampling period ($n = 21$). The horizontal broken line shows the mean rainwater sulphate/chloride at Malham Tarn for 1986-88. Site 1 is on the detached area of bog north of the inflow stream; sites 2-4 are on the main East Dome of Tarn Moss, and sites 5-6 are on the South Dome, south of Spiggot Hill (see Fig. 1). Differences between sample sites and between months (not shown) are statistically significant ($P < 0.001$).

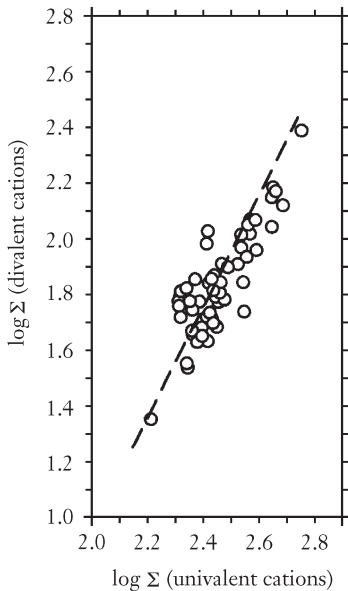


FIG. 9.
Logarithmic relation of the sum of divalent cations to the sum of univalent cations for all sampling occasions from March 1992 to April 1997. The broken line passes through \bar{x} and \bar{y} means, with a slope of 2.0.

Fig. 9 shows the logarithm of the sum of divalent cations plotted against the logarithm of the sum of univalent cations. The points in the graph form an elongated cluster, with an average slope close to the value of 2.0 that would be expected from ion-exchange theory (Stumm & Morgan, 1981).

Monthly means - and annual cycles?

Another view of the seasonality of the changes in water chemistry on the Tarn Moss is given by averaging the values obtained each month over successive years. There is a degree of arbitrariness in this procedure. The samples were not collected on the same day each month, and occasional readings are missing. Nevertheless, this should not obscure major trends. The monthly means for almost all of the measurements show great variation. Error bars have been omitted from most of the subsequent graphs for clarity, but it should be borne in mind that the standard deviation in any one month often equals or exceeds the annual variation of the mean.

As would be expected, water levels were generally higher in winter than in summer,

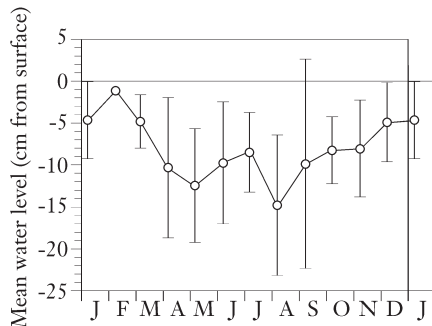


FIG. 10.
Monthly mean water level at six sampling sites on Malham Tarn Moss, September 1993-April 1997.

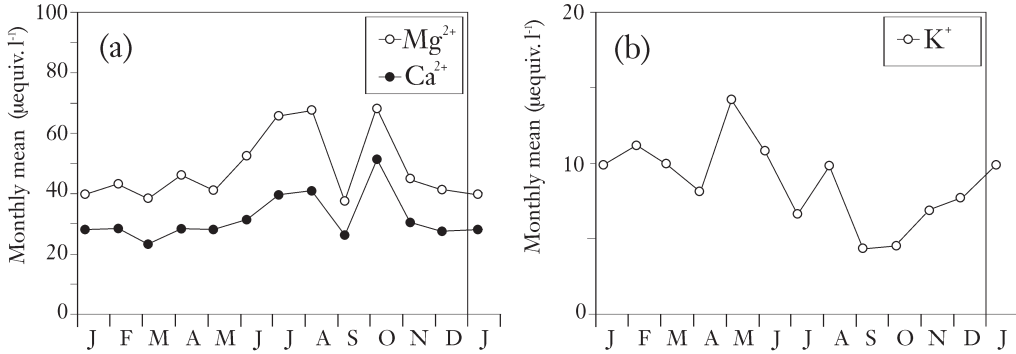


FIG. 11. Monthly mean cation concentrations, March 1992-April 1997. (a) calcium and magnesium; (b) potassium.

when evaporation is at its highest (Fig. 10). However, there was great variation throughout the year, especially in spring and summer. In general, the water table was generally within 5 cm of the surface during winter and early spring, and within 10 cm of the surface for much of the year, occasionally falling to lower levels in dry periods in summer.

Variations in the water chemistry often broadly parallel this annual water-table fluctuation. The two major divalent cations, Ca²⁺ and Mg²⁺, both show higher average concentrations in summer (Fig. 11a), hardly reflected at all by the univalent Na⁺ which, on average, varies little round the year; low September values for all three elements are probably the result of a chance coincidence of three wet sampling days in successive years. A plot of total divalent and total univalent cations on a logarithmic scale (Fig. 13) shows very clearly the greater proportionate variation in the divalent ions, reflecting the ion-exchange effects alluded to above (p. 560).

K⁺, present at much lower concentrations and often a limiting plant nutrient, shows a different pattern from both Na⁺ and the divalent ions. It is highest in May and declines

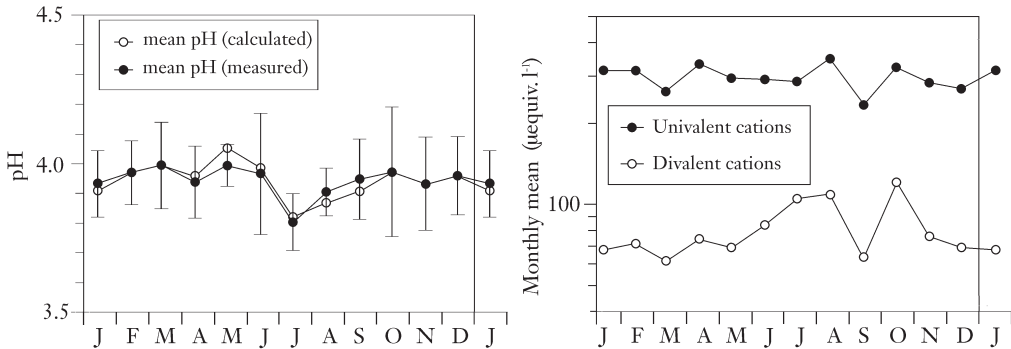


FIG. 12.

Monthly mean pH on Malham Tarn Moss, 1992-97, measured by glass electrode, and calculated from electrical conductivity and the major-ion analyses; pH is somewhat variable at all times of year, with a tendency to slightly lower values in mid-summer.

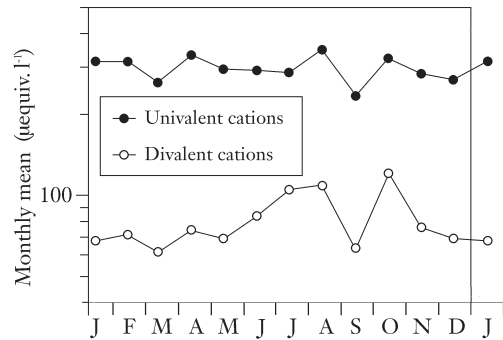


FIG. 13.

Monthly mean sums of total univalent and divalent cations on Malham Tarn Moss, 1992-97, plotted on a logarithmic scale. Note the much larger proportionate changes in the divalent cations, and compare with Fig. 7.

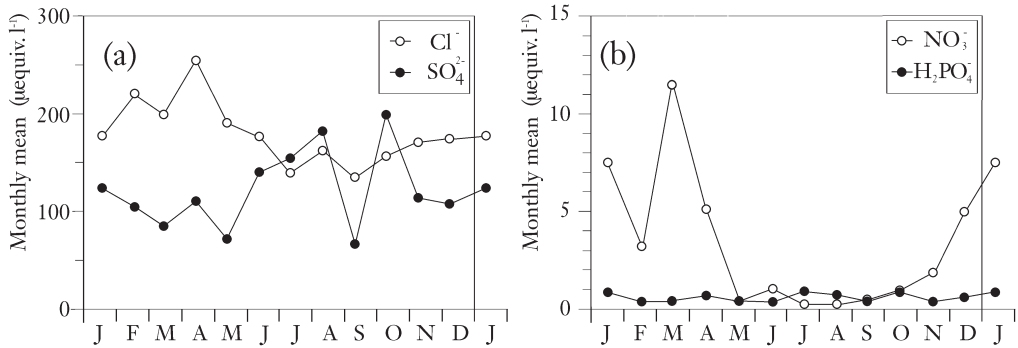


FIG. 14.

Monthly mean anion concentrations on Malham Tarn Moss, 1992-97.

(a) chloride tends to be highest in late winter and early spring and lowest in late summer, while sulphate shows a late summer and autumn maximum; (b) nitrate is highest in periods of low biological activity during the coldest months of the year, with generally very low values through the growing season, while hydrophosphate occurs at similar irregularly low levels throughout the year.

through the growing season to a minimum in September and October (Fig. 11b). Surface-water pH shows less seasonal regularity than might have been expected; it is variable at all times of the year, with only a rather small tendency to a mid-summer minimum (Fig. 12).

The two major anions both show rather clear seasonal patterns (Fig. 14a). Cl^- is highest in late winter and early spring (when it is the predominant anion) and lowest in mid to late summer, while SO_4^{2-} is at its lowest in spring rising to a maximum in late summer and early autumn (when it often exceeds Cl^-). NO_3^- and H_2PO_4^- are present at very much lower average concentrations, and are both limiting plant (and microbial) nutrients (Fig. 14b).

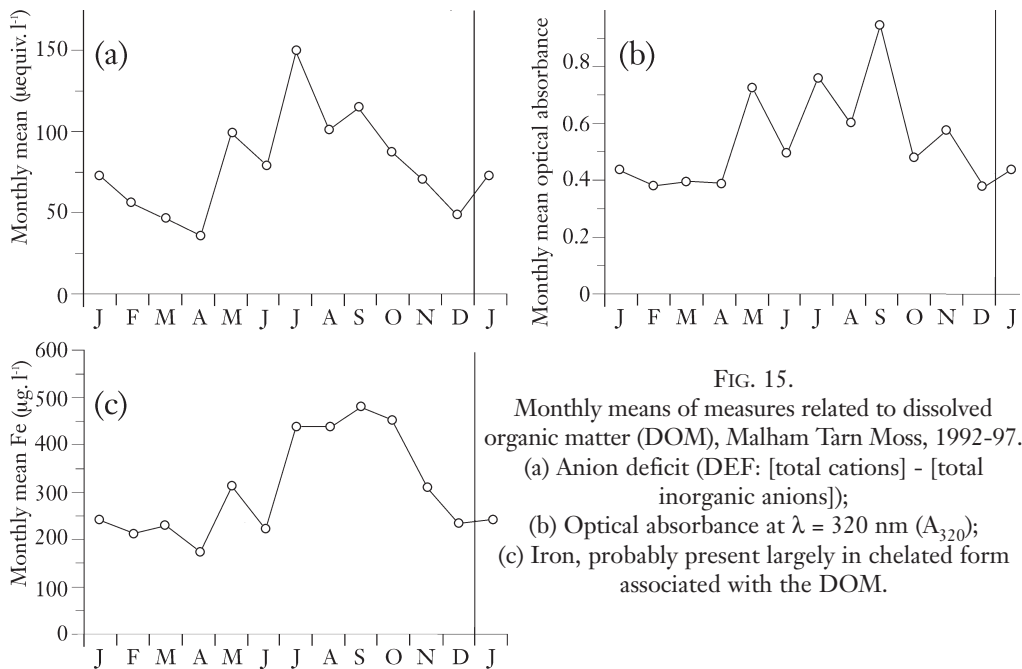


FIG. 15.

Monthly means of measures related to dissolved organic matter (DOM), Malham Tarn Moss, 1992-97.

- (a) Anion deficit (DEF: [total cations] - [total inorganic anions]);
- (b) Optical absorbance at $\lambda = 320 \text{ nm}$ (A_{320});
- (c) Iron, probably present largely in chelated form associated with the DOM.

TABLE 4.

Summary statistics of water-analysis data from Helwith Moss, E. sample site, 1992-1997 (n = 46). Values for ions in $\mu\text{equiv l}^{-1}$ ($\mu\text{mol ionic charge litre}^{-1}$). A_{320} is measured as optical absorbance in a 1 cm cell. $\kappa_{25^\circ\text{C}}$ is total measured electrical conductivity, corrected to 25°C but not 'corrected' for hydrogen ions. NH_4^+ was measured only from January to November 1994: mean 1.0 $\mu\text{equiv. l}^{-1}$, s.d. 1.1, median 0.7, maximum 3.0, minimum 0.0, upper quartile 1.7, lower quartile 0.0 (n = 11). As in Table 3, note that a number of the quantities measured are very variable, with skewed distributions, so the median is a better measure of central tendency than the mean. In general, the number of significant figures given reflects the precision of the individual measurements; the standard deviation is a measure of the (often wide) variation between sampling occasions.

Statistic	pH	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	H ₂ PO ₄ ⁻	DEF	A ₃₂₀	Fe ($\mu\text{g l}^{-1}$)	Zn ²⁺	$\kappa_{25^\circ\text{C}}$ ($\mu\text{S cm}^{-1}$)	Na ⁺ / Mg ²⁺	Na ⁺ / Cl ⁻	Ca ²⁺ / Mg ²	SO ₄ ²⁻ / Cl ⁻
Mean	4.34	113.3	112.7	21.4	205.1	219.3	228.2	0.71	0.144	56.9	0.405	612	0.473	74.9	2.24	0.96	1.03	0.938
s.d.	0.25	93.8	96.0	23.2	70.8	80.8	330.7	2.16	0.292	201.0	0.181	365	0.515	40.1	0.73	0.18	0.12	1.065
Median	4.35	86.3	81.3	14.2	181.3	206.4	108.5	0.10	0.000	94.0	0.359	559	0.382	61.4	2.39	0.91	1.04	0.642
Maximum	5.34	579.0	555.0	115.6	394.8	465.0	1519	14.00	1.000	304.7	0.851	2053	3.333	237	3.50	1.42	1.24	5.470
Minimum	3.58	52.5	48.3	1.28	125.7	90.8	13.6	0.00	0.000	(0.0)	0.187	199	0.000	41.8	0.71	0.66	0.61	0.078
Upper quartile	4.43	125.5	126.0	24.7	226.5	245.7	227.2	0.46	0.160	116.8	0.502	708	0.550	87.6	2.79	1.08	1.09	0.892
Lower quartile	4.25	63.1	58.5	7.44	161.7	168.1	59.9	0.00	0.000	57.6	0.247	340	0.222	50.4	1.62	0.84	1.00	0.308

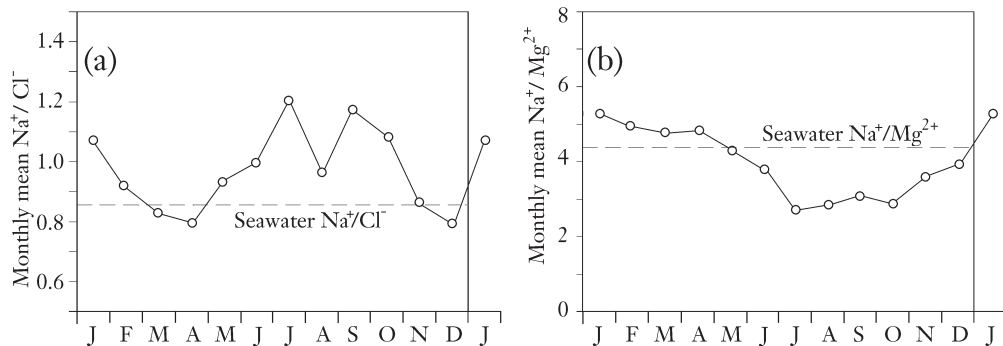


FIG. 16.

Monthly variation in ionic quotients of seawater-derived ions on Malham Tarn Moss, 1992-97.

- (a) sodium/chloride: the summer peak probably reflects the high summer concentration of organic anions displacing Cl^- , and the winter peak is probably an ion-exchange effect;
 (b) sodium/magnesium: the variation is probably largely a concentration and ion-exchange effect.

Average concentrations of NO_3^- are much lower than in rain throughout the year, always less than $1 \mu\text{equiv l}^{-1}$ and often undetectable through the growing season and at greater concentrations only in the coldest months of the year. The average concentration of H_2PO_4^- varies irregularly with no seasonal pattern, and is always less than $1 \mu\text{equiv l}^{-1}$. NH_4^+ , the other source of available inorganic N, was measured for only 11 months, from January to November 1994. It was present at measurable concentrations (ca $1\text{-}5 \mu\text{equiv l}^{-1}$) throughout the year, with a weak tendency to a maximum in summer.

Comparison of the total cations with the total inorganic anions measured in water samples from Tarn Moss shows a deficit of about 20% in anionic charge. This 'anion deficit' (DEF) is made up by the charges carried by the anionic groups on the colloidal dissolved organic matter (DOM), and is probably a general characteristic of acid peat waters (Malmer, 1963; Gorham *et al.*, 1985; Gorham & Detenbeck, 1986; Urban *et al.*, 1989). The anion deficit is generally lowest in winter and peaks in mid summer (Fig. 15a). The brown colour characteristic of peat waters, and here measured by the optical absorbance at 320 nm (A_{320}), shows a similar annual periodicity (Fig. 15b) - in fact, one of the most regular seasonal periodicities seen in the Tarn Moss water samples. The measured concentration of Fe, probably mostly chelated with the DOM, shows a similar seasonal pattern (Fig. 15c).

Quotients of measured ions can display interesting relationships. Fig. 16a shows monthly averages of the Na^+/Cl^- quotient in Tarn Moss waters, which clearly varies widely around the seawater average of ca 0.86. The summer peak (and the generally higher-than-expected average) is probably due to dilution of Cl^- by the organic anions of the DOM. The winter peak probably reflects the seasonal shift in balance between univalent and divalent ions. These relationships will be further discussed later in this paper. A simpler consequence of ion-exchange relationships is seen in the seasonal course of the $\text{Na}^+/\text{Mg}^{2+}$ quotient (Fig. 16b), roughly inverse to the total concentration of divalent ions, DEF and A_{320} .

Some data from a lowland raised bog: Helwith Moss

The concentrations of most ions are higher and, in some cases, very much higher, at Helwith Moss than at Malham Tarn Moss (Tables 3, 4). A notable difference is the very

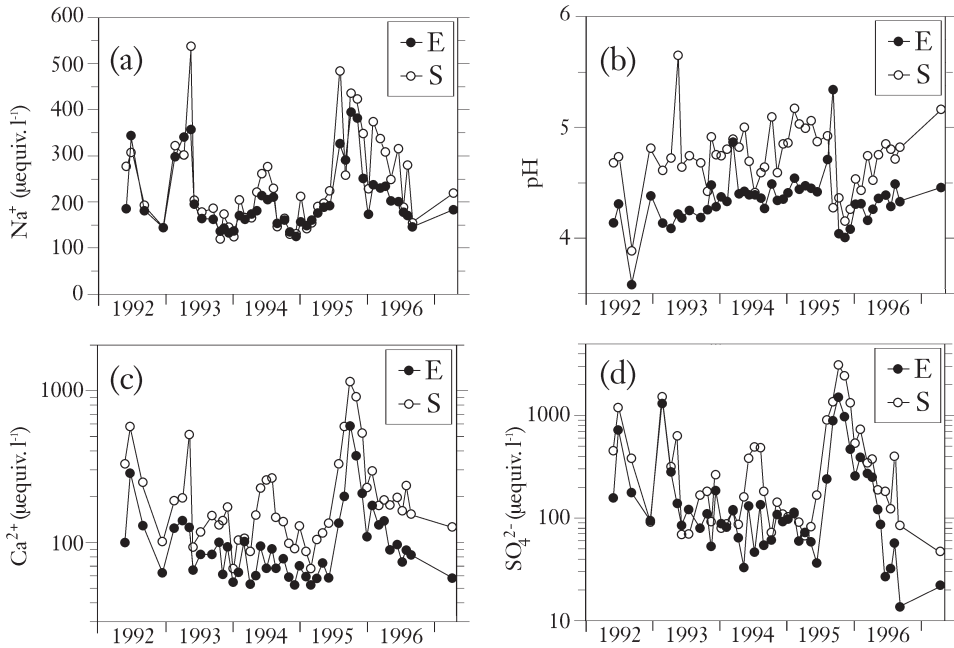


FIG. 17.

Ionic concentrations at the E and S sampling sites, Helwith Moss, March 1992 to April 1997.

(a) sodium: strong seasonal pattern, partly obscured by slow recovery after the 1995 summer drought; (b) pH: an apparent general upward trend, with episodic local peaks, and low values in dry summers from which recovery was slow following the 1995 summer drought; (c) calcium (logarithmic scale): a strong quasi-seasonal pattern, interrupted by the persistent effects of the 1995 drought; (d) sulphate (logarithmic scale): a similar pattern to calcium, but somewhat more irregular and even more widely variable.

much greater variability at Helwith Moss in the divalent cations, Ca^{2+} and Mg^{2+} , and in SO_4^{2-} . Helwith Moss is also influenced by the dustfall from quarrying in its immediate vicinity. The effect of this is greatest on the relatively steep south edge of the bog facing the spoil heaps of Dry Rigg Quarry, but more diffuse effects are apparent in the water chemistry of the whole bog. Table 4 summarises the measurements from a relatively intact and 'natural' area towards the east side of the bog (E); Figs. 17-20 include data from all three of the sites sampled.

Na^+ shows a similar quasi-seasonal pattern to that on the Tarn Moss, but the range of concentrations is greater and the curves from Helwith moss are more 'spiky' (Fig. 17a), especially at the south (S) sampling site. The pattern of pH (Fig. 17b) gave little sign of seasonality, but the already high pH showed a steady increase from 1992 to 1995. The dry summer of 1995 saw a sharp fall in pH of 0.5-1 unit, with gradual recovery over the ensuing 18 months to pre-drought levels. Ca^{2+} and SO_4^{2-} both vary very widely (dictating the logarithmic scale of Fig. 17c, d) with a clear (but not invariable) seasonal tendency to high values in late summer and low values in winter. Both show long-lasting after effects of the 1995 drought.

Monthly variations in water level on Helwith Moss are of similar magnitude to those on Tarn Moss; as would be expected they are greater at the more sloping S sample site than

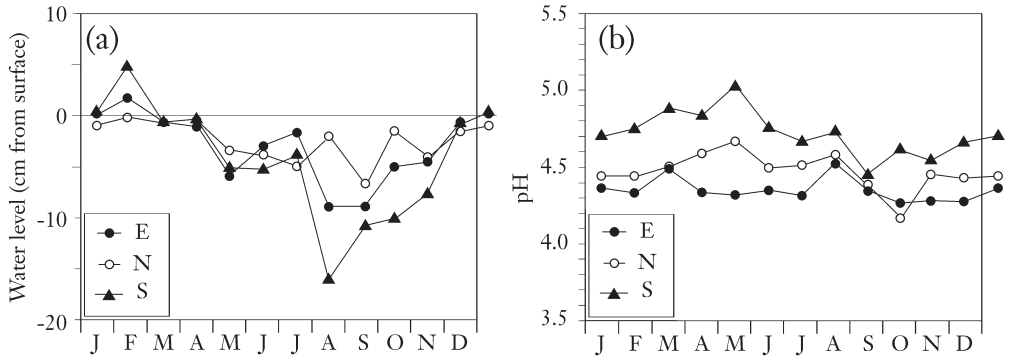


FIG. 18.

Monthly mean water levels (Nov. 1993–April 1997) and pH (May 1992–April 1997) at three sample sites on Helwith Moss. (a) Mean water levels: the N site, in an extensive recolonised peat cutting showed least variation, and the S site near the top of the Rand slope towards the edge of the bog showed the most; (b) pH: the E site, probably the most ‘natural’ of the three, showed generally the lowest values, with very little variation round the year, while the highest values and the greatest variation were from the S site, with greatest fluctuations in water level and closest to the quarry spoil heaps.

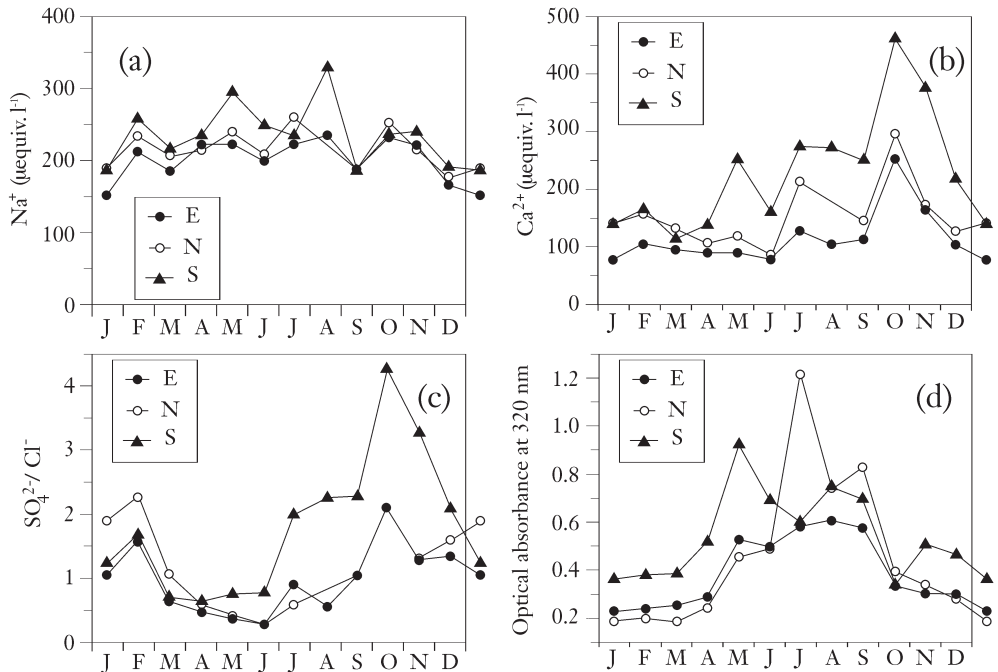


FIG. 19.

Monthly means of ionic concentrations and related quantities, Helwith Moss, May 1992–April 1997 (a) sodium; (b) calcium; (c) sulphate/chloride; (d) A₃₂₀.

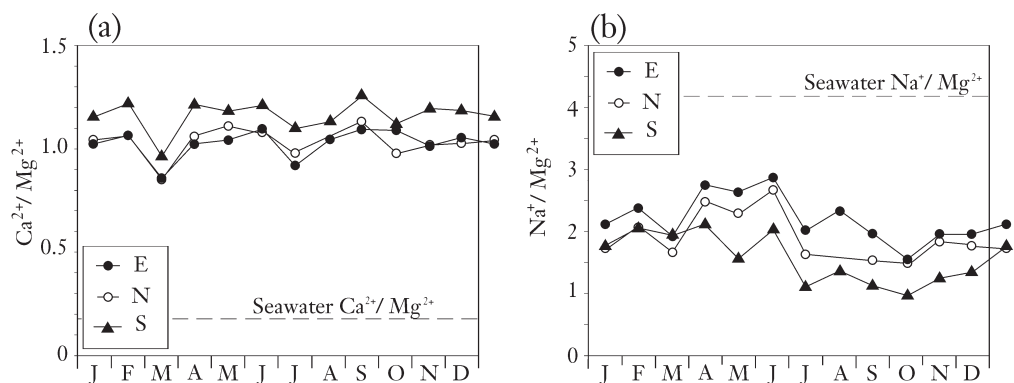


FIG. 20.

Monthly means of ionic quotients, Helwith Moss, March 1992–April 1997.

- (a) calcium/magnesium: higher than at Malham Tarn Moss (compare Fig. 7a), and varying little round the year, with site S (nearest the quarry spoil heaps) consistently higher than E and N;
 (b) sodium/magnesium, showing the effect of added terrestrial magnesium and a somewhat similar seasonal pattern to Malham Tarn Moss (Fig. 16b), but delayed by a few months.

at the other two (Fig. 18a). As on Tarn Moss, there is surprisingly little consistent seasonal variation in pH, but there are substantial systematic differences between the three sites (Fig. 18b). Na^+ shows a much clearer tendency to higher values in summer than at Malham Tarn, and the late-summer and autumn peak in Ca^{2+} is very much more striking than there, with particularly high values at the S sampling site (Fig. 19a, b). The $\text{SO}_4^{2-}/\text{Cl}^-$ quotient (Fig. 19c) is very strongly seasonal, especially at the S sampling site. A_{320} shows much the same range of variation as at Malham Tarn, but some higher maxima were measured at the N and S sites (which did not contribute to Table 4). The $\text{Ca}^{2+}/\text{Mg}^{2+}$ quotient is some 50% higher than at Malham Tarn, indicative of the greater input of calcareous dust (Fig. 20a), varying very little round the year. The $\text{Na}^+/\text{Mg}^{2+}$ quotient runs at rather less than half the corresponding level for Tarn Moss, suggesting that some 50–70% of the Mg^{2+} in the surface water is of terrestrial rather than marine origin (Fig. 20b). NO_3^- was generally at lower levels than on the Tarn Moss during summer, and the winter peaks was less marked but some isolated high values (up to ca 15–25 $\mu\text{equiv. l}^{-1}$) occurred during the 1995 drought and its aftermath. NH_4^+ was also generally at lower levels than on Tarn Moss, especially at the E sample site, which showed a clear summer maximum. The highest levels of NH_4^+ were measured at the S site (mean 2.0 $\mu\text{equiv. l}^{-1}$, s.d. 2.4, maximum 7.0), but there was great variability and only a weak tendency to a maximum in summer.

DISCUSSION

The results nicely illustrate the major points outlined in the introduction. The surface of the Tarn Moss (or any other ombrotrophic bog) lies at the interface between rainwater (and other atmospheric inputs), varying widely in composition from one rainfall event to another (Fig. 3; Vincent *et al.*, 1995), and the water that makes up some 90% of the mass of the underlying peat, which hardly varies in composition at all (Adamson *et al.*, 2001). Comparison of Table 1 with Table 3 shows that median concentrations of most of the major ions in Tarn Moss surface water are between 1.41 (Cl^-) and 1.75 (Mg^{2+}) times the average concentration in rainwater – broadly in the range that would be expected from the relation between rainfall and evaporation. The ratios for the two divalent cations are rather higher

than for univalent Na^+ , an expected ion-exchange effect following from the increased concentration (*cf.* Fig. 9). The high ratio for Ca^{2+} could also reflect some dry deposition of dust from the predominantly calcareous surroundings. Two ions with conspicuously lower average concentrations in surface water than in rain are NO_3^- and (probably) K^+ . Both represent essential, and often limiting, elements for plant growth. The lower concentration of Cl^- relative to Na^+ is probably a consequence of the generation of organic anions by the plant cover.

How far can seasonal cycles be recognised in bog water chemistry?

We are all so keenly aware of the seasons that it is natural to expect seasonal patterns in bog water chemistry. In this respect some of the present results may seem surprising, and possibly even disappointing. There are clear seasonal patterns in the variables related to DOM - water colour (as measured by A_{320}), anion deficit (DEF) and Fe concentration - and in SO_4^{2-} . Weaker seasonal patterns are seen in cation concentrations (especially of divalent cations), pH and Cl^- . All of these show much short-term variability, often equalling or exceeding the average annual variation. There is clear evidence that changes in the concentrations of different cations are closely linked by cation exchange with the peat.

Most seasonal cycles stem from one or other of two causes. The first is the balance between rainfall and evaporation. Rainfall is distributed throughout the year, but on average is greatest in winter and least in late spring and early summer (Fig. 2). Evaporation (dependent on temperature and radiation income amongst other things) is much greater in summer than in winter, with consequences which are obvious in the annual fluctuation of the water table. This also tends to result in generally higher ionic concentrations in Tarn Moss water in summer than in winter. However, the average seasonal variation is much less than might be expected at first sight, probably because concentrations in the water are strongly buffered by ion exchange with the peat. The annual variation in water level can have important secondary effects through changing aeration of the surface peat. When water level falls, peat that was waterlogged and anaerobic becomes aerated and oxidising. The most striking effect of this is oxidation of sulphide (S^{2-}) to sulphate (SO_4^{2-}). As H_2S is a weak acid (and sulphides are often insoluble) and H_2SO_4 a strong acid, low water levels in late summer are typically marked by raised SO_4^{2-} and lowered pH.

The other major seasonal factor is temperature, operating mainly through its effect on biological processes. This lies behind the regular annual variation of DOM (Tipping, *et al.*, 1999, Adamson *et al.*, 2001), and therefore of A_{320} , DEF and Fe. It also has some less direct consequences. N and K are both potentially limiting nutrients for plant (and microbial) growth. For most of the year, NO_3^- is much more abundant in rain than in raised-bog surface water; whatever its precise fate there is no doubt that most of the NO_3^- input is quickly metabolised by plants or microorganisms. However, in winter when the weather is cold enough to bring most biological activity to a standstill significant amounts of NO_3^- appear in the surface water. By contrast, NH_4^+ is found at measurable concentrations throughout the year, tending to a maximum in summer which probably reflects the level of decomposer activity. The tendency for K^+ to peak in late spring and then to decline through the summer is likely to be a consequence of depletion by plant uptake during the growing season.

What are the causes of shorter-term variations?

The factors behind broad seasonal patterns can also operate over much shorter time spans.

More or less prolonged spells of wet or dry weather result in changes in ionic concentration on a time-scale of days or weeks which are often much greater than the average seasonal differences seen in the course of the year. Ion exchange is important even at short time scales; most of the variation in the relative concentration of univalent and divalent ions, seen in Fig. 9, reflects short-term changes. The effects of changing aeration as water levels fall and rise again are equally apparent at short time scales. A period of low water level followed by rain is typically marked by a sharp peak in SO_4^{2-} , and a sharp dip in pH, very obvious in Fig. 5 c-d.

The varying composition of rainfall may also have effects, but they are seldom large. The influx of Na^+ when a winter storm blows in from over the Atlantic may also bring about (through ion exchange) peaks in divalent ions (Proctor, 1994). The annual variation in wet deposition of SO_4^{2-} and other pollutant ions, rising to ca 150% of the annual mean in late spring (UKRGAR, 1990), seems almost always to be hidden by other factors. Undoubtedly many of the observed periodicities are a complex result of interacting physical and biological factors. Thus the lack of biological activity which results in a winter peak of NO_3^- may also be the cause of the apparent low winter peak in SO_4^{2-} by slowing its conversion to sulphides.

Surface water and peat: which is the template?

A number of references have been made to ion exchange, and the effect of the peat in determining or buffering the composition of the surface water. What determines the ionic composition of the peat? The answer can only be the rain and other atmospheric inputs falling on its surface. This is only an apparent paradox. Peat accumulates slowly, seldom at more than 1 mm a year. At a typical bulk density of 0.1, this is equivalent to 100 g m^{-2} (which is likely to be some 5-10% of primary production). An annual rainfall of 1282 mm falling on a square metre of the Tarn Moss in the course of a year is equivalent to 1282 litres - nearly 1.3 tonnes. The divalent ions in the annual increment of peat represent no more than 5-10% of the annual deposition, but the quantities in the whole thickness of the active surface layer of the peat (the acrotelm) are equivalent to the rainwater input of many decades. The span of time for the univalent ions is less, but still measured in years. Trivalent ions such as Fe^{3+} and Al^{3+} will be held by the ion-exchange sites most tenaciously of all, but their concentration in rain is generally very low. Thus the ionic composition of the peat reflects the composition of the rainfall integrated over a very long period of time - but in the short run, the peat has a strong controlling influence on the composition of the surface water of the bog. The peat is the template in the short term; in the long run, all is determined by average rainwater composition (Proctor & Maltby, 1998). This simple picture may seem at odds with the undoubted complexity of the processes taking place in the plant cover and the acrotelm layer at the surface of the bog (Damman, 1978, 1986; Malmer, 1988, 1992), but even the most complex 'black box' can have simple inputs and outputs.

The 1995 drought and its effects

The time-span of the measurements included the dry summer of 1995, which over much of England and Wales was one of the most severe short-duration droughts of the 20th Century (Jones, Conway & Briffa, 1997), with a rainfall deficit of 50% or more of the long-term average from the latitude of Malham southwards. The following year, 1996, though less extreme, was also relatively dry. Water levels on Tarn Moss in the first half of 1995 were in no way unusual, but from June to September the water table fell sharply to an average of

over 32 cm below the bog surface. This drop in water level was marked by unusually high concentrations of all the major cations, which then took several months to fall progressively to more normal levels (Fig. 4a, b). It was followed by the highest peak in SO_4^{2-} , the lowest average pH recorded during the survey and by a conspicuous peak in Zn^{2+} (Tipping *et al.*, 2003). Sulphate remained unusually high and pH unusually low through the ensuing winter. From mid-1995 the $\text{SO}_4^{2-}/\text{Cl}^-$ quotient remained above the mean rainwater value (implying a net release of SO_4^{2-} from the peat) for all but three of the ensuing 16 months, returning to normal levels only in the late autumn of 1996. Fig. 5 shows an unusually high peak in NO_3^- in the winter of 1995-96 and a general disruption in the otherwise regular seasonal pattern of A_{320} . The effects of the drought on Helwith Moss were qualitatively similar but more extreme (Fig. 16). It is evident that a drought can have effects which persist at least into the following season, and can be detectable for several years.

The bog surface as a habitat for plant growth

It goes without saying that an ombrotrophic bog is not an easy habitat for plant growth. Problems of nutrient limitation are added to the problems of waterlogging common to all wetland habitats. However, shortage of essential plant nutrients is not necessarily more severe than in some non-peatland habitats, such as heaths or woods on leached siliceous sands or on many of the hard acid rocks of northern and western Britain. Even some of the so-called 'macronutrients', such as Ca^{2+} , are required in relatively small quantities which are adequately supplied by rain; in Britain and Ireland the marine component in rain is likely always to be a sufficient source of Mg, S and probably Ca. Iron and the other 'micronutrients' must be supplied from the atmosphere, but the terrestrial sources from which they come are likely to reflect a substantial area of the surrounding country, yielding a reasonably constant chemical mix - hence ombrotrophic bogs are likely to be relatively free of the deficiencies of particular trace elements which can beset plants growing on some mineral soils. Plants in all of these nutrient-stressed habitats tend to be slow growing, and efficient both at acquiring nutrients from nutrient-poor soils, and in retaining nutrients once they have been taken up (Chapin, 1980).

The three essential elements that are commonly limiting for growth on any soil are N, P and K. Of this trio, K typically makes up ca 0.5-2% of plant dry weight., but is probably almost always available in adequate quantities on ombrotrophic bogs for the slow growth of bog plants. On an ombrotrophic bog, growth is generally limited by either N (ca 1-2.5% of dry weight) or P (ca 0.10.2% of dry weight), or perhaps some combination of the two. There are indications that N may typically be limiting in unpolluted environments, but that P is the limiting element where there is substantial deposition of inorganic N from pollutant sources (Aerts, Wallén & Malmer, 1992). Typically both elements, in their available inorganic forms, are present at only very low concentrations in bog waters. This concentration may give little indication of the availability of the element for plant growth, which will depend much more on the rate of 'mineralisation' - the release of available inorganic forms of the element in the course of decomposition. The usual presumption is that NH_4^+ is the main available form of N on acid soils and peats, and it is indeed generally the first product of mineralisation (tending to be highest at times of high biological activity in summer). However, many bog plants take up N in other ways. *Eriophorum vaginatum* may take up N in the field largely in the form of free amino acids (Chapin, Moilanen & Kielland, 1988), *Calluna vulgaris* is mycorrhizal and acquires organic N through its symbiotic fungi (Read, 1991), while *Sphagnum* shows well-marked nitrate reductase activity and probably

acquires much of its N from rainwater NO_3^- (Press & Lee, 1982; Woodin, Press & Lee, 1985). Mycorrhizal plants on acid, nutrient-poor soils also get much or all of their requirement of P through their mycorrhizas. Both these and the roots of non-mycorrhizal species may rely largely on acid phosphatases secreted from the cell surfaces to release inorganic P from organic phosphates. Thus the amount of free inorganic N or P in the surface water may say rather little about the availability of these elements to the plants (Marschner, 1995).

The water table on Tarn Moss is for much of the year no more than 10 cm below the surface, and often less. The anaerobic conditions that result from waterlogging can affect plants directly by depriving the underground parts of oxygen essential for their metabolism, and sometimes also indirectly through the accumulation of high concentrations of toxic ions (e.g. Fe^{2+} , Mn^{2+} , S^{2-}) and other substances (though metal ions are much less likely to occur at toxic levels on bog peats than on mineral soils). Also, the slowness of molecular diffusion in stagnant waterlogged peat impedes nutrient uptake in an already nutrient-poor substratum. Wetland plants have adapted to these conditions in various ways. Some have shallow root systems confined to the well aerated surface layers. Others (such as *Eriophorum vaginatum*) have systems of air spaces in their stems and roots which allow internal gaseous diffusion of oxygen down into roots in anaerobic peat. Many wetland species have higher resistance to toxic ions than their dry-land counterparts; thus *Erica tetralix* tolerates concentrations of Fe which quickly kill its dry-heath relative *E. cinerea* (Etherington, 1982; Crawford, 1989).

Of course, waterlogging is also a prerequisite for the accumulation of peat. The carbon balance of a peatland is determined by the difference between carbon fixation by the plant cover, and the diverse losses of carbon from the system - aerobic breakdown in the acrotelm (releasing CO_2 to the air), anaerobic breakdown in the catotelm (releasing methane and CO_2), and losses of DOM in solution (which may amount to 10-20% of even high rates of peat accumulation (McKnight, Thurman & Wershaw, 1985; Urban, Bayley & Eisenreich, 1989; Proctor, 1997). To arrive at an accurate carbon balance - to know whether a bog is a net source or sink of CO_2 - is, therefore, not easy. Some indication is given by whether the bog is a net source or sink of SO_4^{2-} . At Malham, the average ratio of $\text{SO}_4^{2-}/\text{Cl}^-$ in Tarn Moss surface water is a little greater than the ratio in rainwater (Tables 1 and 3), suggesting some net loss of C over the site as a whole. However, it is clear from Fig. 7 that the balance varies from one part of the bog to another. At Helwith Moss, the disparity between surface-water and rainwater $\text{SO}_4^{2-}/\text{Cl}^-$ is somewhat greater, suggesting a greater net loss of peat mass.

Chemical 'climate' and chemical 'weather'

In the meteorological sphere, it has been facetiously said that Britain does not have a climate - only weather. We all recognise this as a tongue-in-cheek half-truth, but it is a reminder that (meteorological) 'climate' is an abstraction. Measurements of temperature, rainfall, wind, sunshine at Malham Tarn once a month for five years could begin to give us some preliminary feelings about the climate; they would certainly tell us a great deal about the variability of the weather. Probably we should not expect otherwise of the water chemistry of the Tarn Moss. Tables 3 and 4 should give a good summary of average chemical conditions in surface pools or shallow sample pits on Tarn Moss and Helwith Moss, which is likely to be little altered by further data. The graphs of monthly averages in Figs 9-15 and Figs 17-19 give the beginnings of an insight into seasonal patterns, of which the main features are probably fairly robust but which could undoubtedly be refined in detail by a longer period of observations. But this still leaves room for a great deal of day-

to-day variation. A good deal of this is driven by the capricious weather that surrounds us. We should not be surprised to find that organisms in bog pools experience 'chemical weather' too.

ACKNOWLEDGEMENTS

I am indebted to a succession of placement students at the Field Centre for collecting many of the water samples, in fair weather and foul, to the Field Studies Council and staff at Malham Tarn for the hospitality, cooperation and support which made this project possible, and to Peter Splatt for running the anion analyses.

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