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Reviewed work(s):
Source: *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, Vol. 327, No. 1240, Palaeolimnology and Lake Acidification (Mar. 12, 1990), pp. 331-338
Published by: The Royal Society
Stable URL: http://www.jstor.org/stable/55393
Accessed: 23/07/2012 05:16

Phil. Trans. R. Soc. Lond. B **327**, 331–338 (1990)
Printed in Great Britain

The record of atmospheric deposition on a rainwater-dependent peatland

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Rainwater-dependent peatlands retain a record of atmospheric deposition. Unlike lake sediments they record both particulate and soluble influxes, and they are not complicated by processes in the catchment or by mineral particle influx from the catchment. They do, however, have their own difficulties some of which are considered here.

The timescale for cores from a suitable peatland in Southwest Scotland was established by a combination of ^{14}C 'wiggle matching', pollen events, ^{210}Pb dating and the ^{241}Am event. Retention of deposited elements varied greatly from less than 1% (Na) to complete retention (N). Hummocks retained more than hollows: the quotient was 1.2–1.8 for elements such as Al (associated with particles) and up to 5–10 for Mn, Fe and Zn. The vertical scale in profiles should be as cumulative dry mass or, better, as dry mass after reconstructing losses by decay. These give vertical scales that are approximately linear with age. Elements differ greatly in the shape of their concentration profile as a result of varying influx and as a result of relocation in the peat.

Introduction

The record of deposition of atmospheric contamination in lake sediments may be difficult to read because the constituents have reached the sediments by a variety of processes and by paths of differing tortuosity at different speeds from different parts of the catchment. Atmospheric deposition is often swamped by the contribution to sediments of mineral particles from the catchment soils and rocks. Rainwater-dependent (ombrotrophic) peatlands do not have these problems and, because of their high cation-exchange abilities, may retain solutes that would never reach lake sediments at all. But they have their own difficulties connected with uptake by plants, with decay of the peat, with chemical change in the peat, and with flow of water in the peat. Here we report an exploration of the possibilities. We consider timescales (essential for calculating fluxes), retention efficiency, how best to present results, and a few of the 50000 results that this work has generated.

Site and methods

Fifteen cores were collected from an ombrotrophic raised bog, Ellergower Moss (National Grid reference NX 482795), at the northeast outlet of Loch Dee, Galloway, southwest

Scotland. The bog is approximately elliptical with radii of about 330 and 350 m. At its centre, where we took samples, it is about 6 m deep. Basal samples have low concentrations of pollen of *Corylus*, and may be cross-referred to a similar site on a peninsula in Loch Dee with a ^{14}C age of 9000 years (P. Newell, personal communication) similar to basal dates for peat in a small basin in the catchment of Round Loch of Glenhead close by (V. Jones, personal communication). Most of the Ellergower peat is humified and homogeneous. The surface has a variety of hummocks and hollows and a few small pools. It contrasts with the nearby Silver Flowe on which pools are abundant.

Cores EM1–EM15 of 20 cm diameter and about 50 cm depth were taken from surface features of various sorts by using apparatus (Clymo 1988) that retains the water in place. They were later cut into 1 cm thick slices and the values of about 60 variables measured including dry bulk density, water content, pH, E_{H5}, the concentrations of about 45 elements, activity of ^{210}Pb, ^{137}Cs, ^{241}Am and several magnetic properties.

Comparisons are possible with the adjacent Loch Dee sediments (B. Rippey, personal communication) but are too complex for this article.

Core structure

The cores all show a downward increase in dry bulk density as a result of compaction (figure 1 *b*). This is associated with the development of waterlogging and anoxia (Clymo 1987). It is convenient to recognize two layers. The upper one, extending down to the maximum depth reached by the water-table in dry summers, is porous and is called the acrotelm (Ingram 1978). The lower, much thicker and anoxic layer is the catotelm. In the acrotelm aerobic decay is relatively rapid and water movement, both vertical and horizontal, is rapid. In the catotelm anaerobic decay and water movement are very slow. At the boundary are high concentrations of sulphide, with which many metals form highly insoluble salts.

In hummocks the porous acrotelm is relatively deep and one might expect substantial relocation of solutes. In hollows the acrotelm is much shallower. In the work reported here the boundary between acrotelm and catotelm is defined as the point where E_{H5} became negative. The cores were all collected in early November when the water-table was probably within 2 cm of its mean position (Bragg 1982).

Timescales

The ^{14}C 'wiggle-matching' method was applied to one core (EM3) from a *Sphagnum capillifolium* hummock. This method relies on the pattern of fluctuations in ^{14}C in the atmosphere over the most recent 400 years. The ^{14}C age of a single sample in this range is ambiguous at best, but a series may allow the pattern of fluctuations to be matched with that known from tree-rings (Stuiver & Pearson 1986). The results are shown in figure 1.

The calibration curve shows troughs at 1712 and 1900, both now in the catotelm. These were matched with what seem to be corresponding points in the sequence of peat samples. The other peat samples are distributed in proportion to the cumulative mass. The matching of *shape* is fairly good, though some of the ^{14}C ages are rather high.

The most conspicuous local pollen event is the great increase in *Pinus*. It is shown as a proportion of the sum of *Pinus*, *Alnus*, *Betula* and *Corylus* (figure 1 *b*). The depth at which this

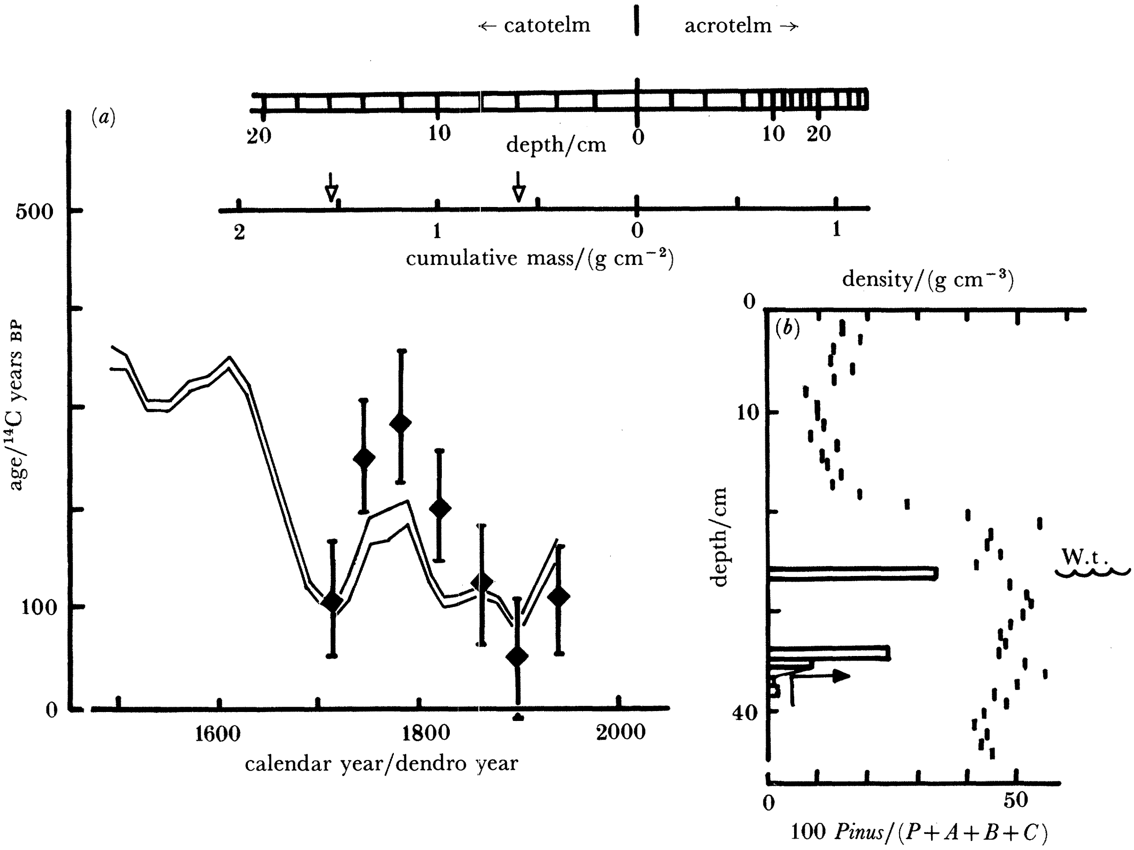

FIGURE 1. Hummock core EM3; (*a*) outer bounds of the relation between ^{14}C age and true (dendro) age. Superimposed lozenges and counting precision bars are for core EM3. Above is a horizontal scale of cumulative mass. Arrows show points at which the EM3 and calibration lines were forced to coincide. At top, the corresponding (nonlinear) scale of depth. Each block represents 2 cm. Both upper scales start at the acrotelm–catotelm boundary. (*b*) Profile of dry matter bulk density (vertical bars) and (histogram) of the pollen quotient *Pinus*/(*Pinus*+*Alnus*+*Betula*+*Corylus*). The point where this rises above 5% is shown by a reflecting arrow. (W.t., watertable.)

variable rises above 5% can be located in all the cores to within 1 cm. The wiggle-matched ^{14}C dates this to about 1835.

The results of ^{210}Pb dating of a core from a hollow are shown in figure 2*a*. The 1835 *Pinus* rise agrees fairly closely with the ^{210}Pb chronology, confirming the assumption implicit in this method that there is relatively little redistribution of Pb in this core with a shallow acrotelm. The assumption of uniformity of processes is confirmed in figure 2*b* where the same results are plotted against cumulative mass. The line is almost straight, with a slight concavity at the top where the decay rate might be expected to be rather higher. Also consistent are the recent rise in conifer pollen (as a result of planting) in about 1973 and of the peak in ^{241}Am attributable to peak influxes from aerial nuclear weapons testing in 1954 and especially in 1963.

RETENTION IN PEAT

The inventory in cores EM3 and EM4 down to the 1835 *Pinus* event is compared with the precipitation influx from 1981–1988, provisionally assumed to hold for the 150-year period (table 1). Less than 1 % of Na is retained in either core. For the group of elements K, S, Mg and Ca the hollow retains 4–10 % and the hummock 12–29 %. Bomb-test ^{137}Cs is more effectively retained, and there is more N in the cores than calculated from recent precipitation. It may be that the influx of $NH_4^+ + NO_3^-$ has declined recently or that there is significant influx from (unrecorded) dry deposition. The peat does not hold a complete record of influx for many elements. This need not invalidate its use to indicate changes in influx provided that the proportion retained does not alter independently.

Table 1. Percentage retention of elements in peat[a]

	Na	K	S	Mg	Ca	^{137}Cs	N
hollow EM4	0.3	4	10	6	10	25	120
hummock EM3	1	12	16	23	29	63	250

[a] Precipitation (except ^{137}Cs) variables measured for the Solway River Purification Board from 1981–1988 (F. M. Lee, D. J. Tervet & J. C. Burns, personal communication). The calculation assumes that these values are representative for the whole period 1835–1984 of the peat inventory. The ^{137}Cs influx to 1984 was calculated (P. Cawse, personal communication) from values at Milford Haven and local precipitation, with allowance for decay.

More is retained in the hummock than in the hollow of all elements measured, not just those in table 1. The extent varies: for the 1835–1984 inventories the quotient hummock:hollow ranges from 1.2 to 10. At the low end (1.2–1.8) are acid-insoluble ash, insoluble ^{137}Cs, Al, Ti, Ce, Sc as well as S and Li. The first six are plausibly associated with particulate influx. The systematically higher inventory for hummocks may indicate greater interception in windy weather. The next group (2.1–2.8) includes Mg, the 'metabolic' elements K, soluble ^{137}Cs, P and N and Pb and Cu. In the range 3.5–5.0 are Cd, Na, Ca, Sr and Ba. Finally, with large differences, are Mn (5.1), Fe (7.7) and Zn (10.0). The main difference between the cores is that the hummock has a deeper unsaturated layer than the hollow has. Retention of some elements is very dependent on processes in the unsaturated layer.

Presenting concentration profiles

Lake sediment profiles are usually shown with depth as distance. In peat, however, compression may make this very misleading. Figures 2*a*, *b* and 3 show this effect. Cumulative mass is easily measured and involves no assumptions. But even this can be misleading. During the time that it takes for the catotelm to rise and engulf a piece of organic matter, originally at the surface, aerobic decay will have removed a lot of the matter. Estimates (Clymo 1984) give values of about 90 % loss. If an element were conserved in position its concentration on a dry mass basis would increase tenfold. There are two solutions: firstly, one may use only those cores, such as in figure 2*b*, where there is a linear age against cumulative mass relation. (The most plausible, but not the only possible, explanation of such linearity is constant rate of peat accumulation.) Secondly, one may try to reconstruct the lost mass. In figure 3*c*, for the hummock core EM3, is shown a case where this would be essential. The top 32 cm of this profile (strongly condensed by the choice of axis in figure 3*c*) would have had a much steeper slope than the lower part. On the assumptions that, in the acrotelm, $dm/dt = -\alpha m$ and $dM/dT = p - \alpha M$, where m = dry mass of peat, t = time, M = cumulative dry mass on an area basis below a datum, T = time in the past below the same datum, p = rate of addition

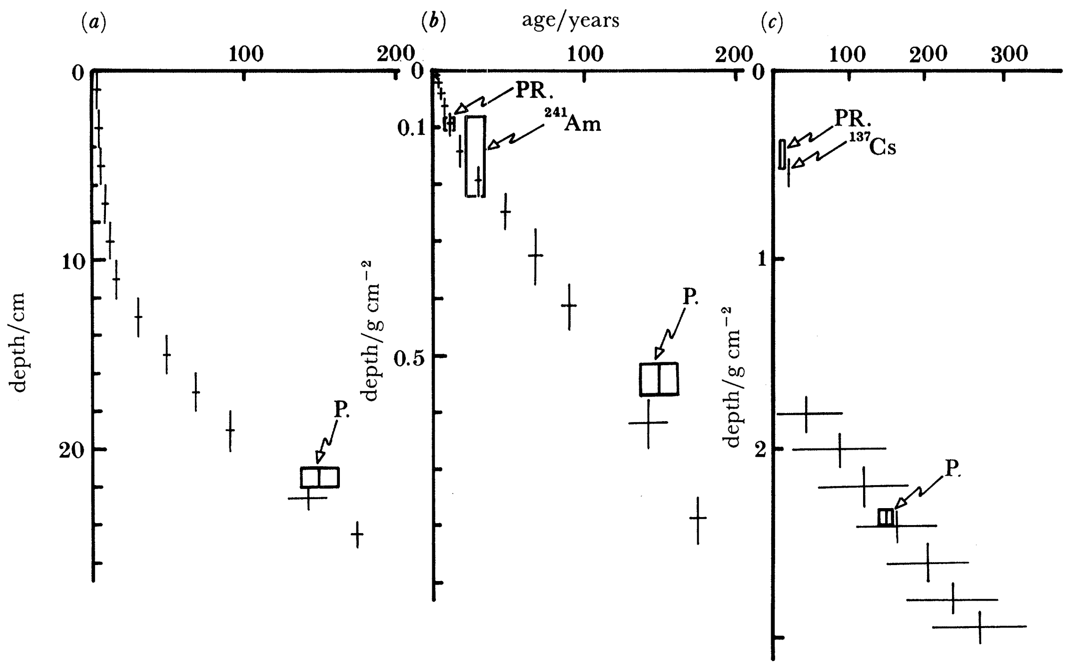

FIGURE 2. Profiles of age against depth. (*a*) Hollow core EM4, ^{210}Pb derived age. (P., *Pinus* event (see figure 1).) (*b*) Same data as in (*a*) but plotted against depth as cumulative dry mass. Not shown in (*a*) are PR., a recent increase in conifer pollen attributed to Forestry Commission plantings, and ^{241}Am, attributed to aerial nuclear weapons testing. (*c*) Axes as in (*b*) but for the hummock core EM3 by using the ^{14}C derived ages from figure 1. The vertical ^{137}Cs line is for acid-insoluble (probably particulate) material, but may be unreliable. Note that though (*b*) shows only a small concavity near the origin, (*c*) has a marked break in slope even though the effects of compression and differing bulk density are removed by this sort of plot. The remaining effect is attributed to decay in the acrotelm (see figure 3).

of dry mass on an area basis and α = proportional rate of decay then it follows that $M_a = (p/\alpha)[1-\exp(m_a/m_0)]$, where the subscript 'a' indicates conditions at the acrotelm–catotelm boundary. The value of M_a can be measured; m_a/m_0 ('survival') could be measured but in practice must be guessed; and p/α can then be calculated. This is then used in $M = (p/\alpha)[1-\exp(m/m_0)]$ at other positions in the acrotelm to calculate m/m_0 and hence to reconstruct m_0. For the catotelm the rate of decay is so much lower that for periods of a few hundred years (only) one can ignore it. The results of using these three methods of presentation (linear, mass and reconstructed mass) are shown in figure 3. The value $m_a/m_0 = 0.05$ gave a line that points, approximately, to the origin in figure 3*c*. Two points are clear. First, the method of plotting has a substantial effect on the apparent meaning of the results. Secondly, the plot in (*d*) is such that if an element had been coming in at constant rate and had not moved after it was deposited then one would see a straight line parallel to the vertical axis. For iron this is not the case. The peak is associated with the water-table where there are large chemical (and probably microbiological) changes as well. It is unlikely that there was a short-lived 20-fold increase in influx during the 1950s; transport and local accumulation on a large scale within the peat core are likely explanations.

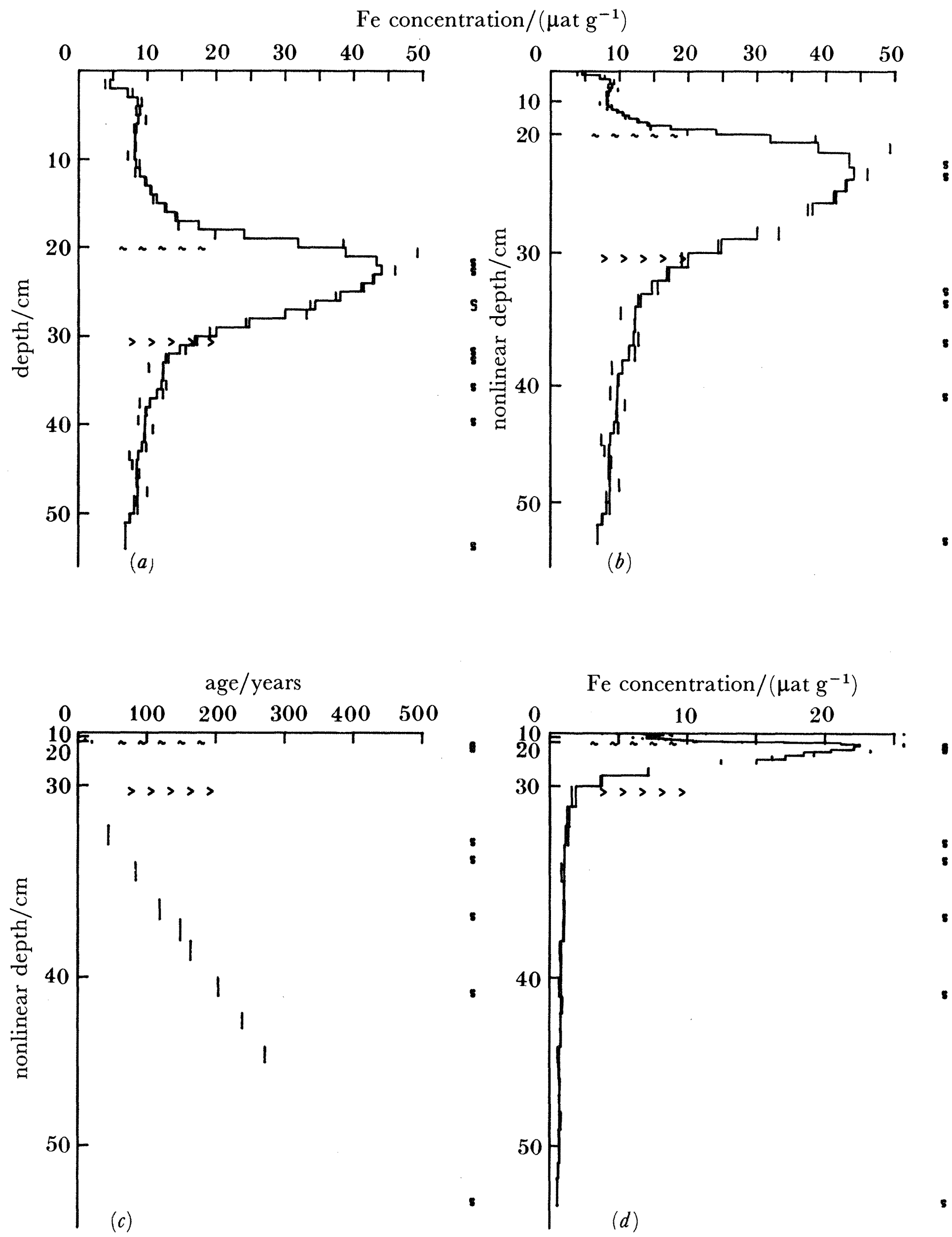

FIGURE 3. Profiles in hummock core EM3 of age (*c*) inferred from figure 1 and of concentration of iron (*a*), (*b*), (*d*). Measured values and a smoothed line are shown. In (*a*) the depth scale is linear distance. In (*b*) depth is linear with cumulative dry mass but has been marked with appropriate distance units (cm). Depth scales in (*c*) and (*d*) are similar to (*b*) but the dry mass includes estimated losses during decay assuming $m_a/m_0 = 0.05$ (see text). The line of (~ ~) indicates the watertable. The line of (>) indicates the depth at which E_{H5} becomes negative. The column of scattered symbols at the right of each graph show where a moderate to strong smell of sulphide was recorded.

BEHAVIOUR OF SELECTED ELEMENTS

An example of the variety of patterns in one hollow is shown in figure 4. The vertical scale is linear with cumulative mass and approximately linear with age (figure 2*b*) and the whole core spans about 600 years.

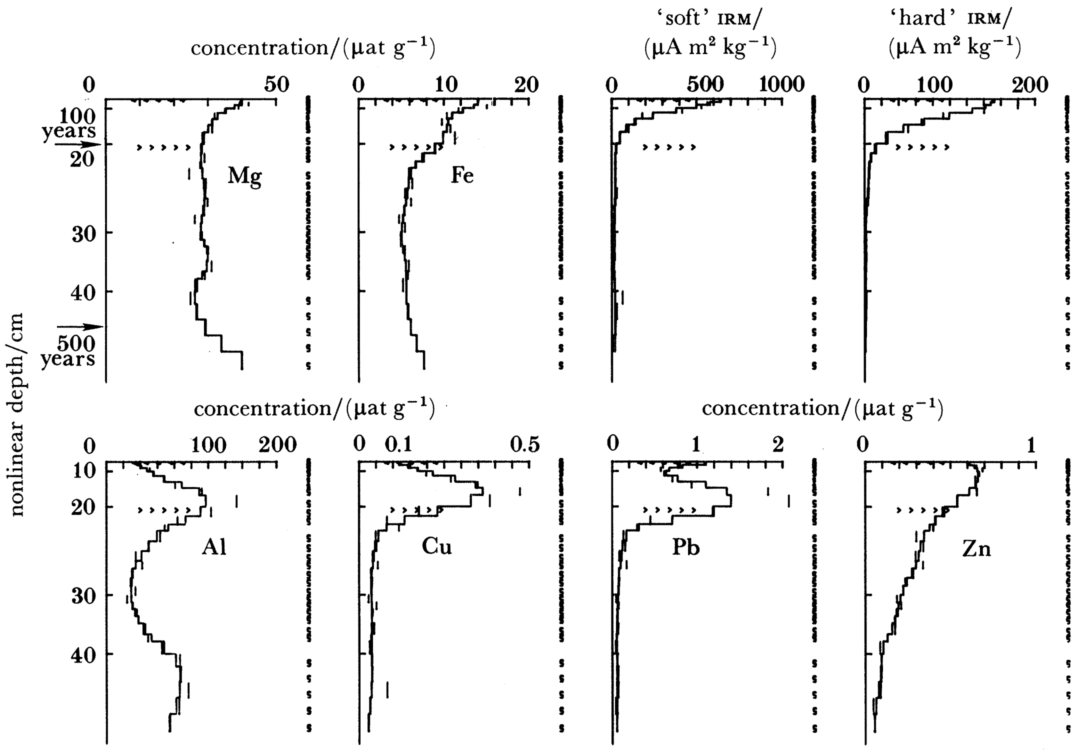

FIGURE 4. Profile of concentrations on a dry mass basis (µat g^{-1}) of six elements and two magnetic variables in hollow core EM4. Conventions as in figure 3. The vertical scale is linear for cumulative dry mass but is marked in (nonlinear) distance units for convenience. For this core cumulative mass is approximately linear with age (figure 2*b*), so on these plots vertical distance on the plot is approximately linear with age too. The arrow at about 19 cm depth is at approximately 100 years; that at about 46 cm depth is five times further down (in cumulative mass) and is therefore at about 500 years (about 1500 A.D.); 'soft' IRM ($SIRM - IRM_{-20 mT}$) reflects changes in the concentration of magnetite; 'hard' IRM ($SIRM + IRM_{-300 mT}$) reflects haematite (Oldfield & Richardson, this symposium). (Isothermal remanent magnetization, IRM; 'saturation' isothermal remanent magnetization, SIRM.)

The concentration of Mg, which we assume to be derived mainly from sea spray, is approximately constant though with small increases at the core base and recently. As barely 6% of the incident Mg is retained (table 1) this relative constancy in concentration of an element whose influx has probably been fairly constant is important. The elements Ca, Sr and Ba (not figured) show a similar pattern to that of Mg except that their concentrations double during the last 50 years.

The profile of Al is similar to Ti and V with peaks in about 1500 and 1880. We suspect these elements arrived mainly as particles, but the decline during the present century suggests that power-station fly ash may contribute rather little compared with other sources. The peak centred on 1880, however, is related to the E_{H5} drop and to a sharp increase in dry bulk density (not shown). The chemistry of Al is not much affected by redox or sulphide concentration, but the movement of particles may be affected by sharply reduced hydraulic conductivity (consequent on increased bulk density).

Both Pb and Cu form very insoluble sulphides, and their downward movement may be retarded in horizons with a high concentration of H_2S thus giving peaks in their concentration profiles. There is a doubling of concentration of Pb (parallel with that of Ba and Sr) during the last 50 years. This is consistent with the increase in emission of these elements.

The retention of Zn in hollows is barely 10% of that in hummocks (table 1). Its profile is consistent with a steady increase over the last 600 years or, more credibly, with an equally persistent loss.

Retention of Fe in hollows is almost as poor as that of Zn, but the concentration of Fe down the core settles towards a value that is about half that at the surface whereas Zn continues to decline to less than 0.1 of that at the surface.

In hummocks the profiles of Fe, Cu, Zn and Pb all show a very large peak in the zone 10 cm above the E_{H5} drop.

Both magnetic variables (Oldfield & Richardson, this symposium) show small increases from about 1800 to 1880 then steeper increases to near the present day. This and other evidence indicates that the changing concentration of magnetic variables reflects a combination of the influx of the magnetic fraction of fly ash and selective dissolution of magnetic minerals in the acidic, sulphidic, reducing, organic environment.

We conclude that the record of atmospheric deposition preserved in peat is biassed, but that the bias in hollows may be fairly uniform so they may, if interpreted with care, be a useful supplement to the record in lake sediments.

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