History of Particulate Atmospheric Pollution from Magnetic Measurements in Dated Finnish Peat Profiles

Report

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An ombrotrophic bog is nourished entirely by precipitation rather than by groundwater. It is therefore excluded from all non-atmospheric inputs of particulate matter. Moreover, since water movement at or near the bog surface is slow and limited, any deposited matter remains largely *in situ*. A history of particulate atmospheric pollution is therefore preserved as the peat accumulates.

Rapid non-destructive magnetic measurements of recent Finnish peats are used here in combination with annual moss increment dating to derive patterns of particulate pollutant deposition over the past 150–200 years.

The results indicate an accelerating increase in magnetic particulate fallout from 1860 AD (around the beginning of the Industrial Revolution) to peak values after World War II. Values are directly related to distance from major industrial complexes, though the increase above pre-industrial levels is over two orders of magnitude even at remote sites in Finnish Karelia. Deposition of ferrimagnetic iron oxides (predominantly Fe_3O_4, magnetite) in the form of spherules known to be the product of fossil fuel combustion, appears to contribute significantly to total iron accumulation in post-war years, especially at sites close to industrial activity. Comparison of the present results with those obtained from British peats in a wide range of situations confirms that major industrial and urban complexes are the dominant source of magnetic particulate fallout. The methods used here provide a useful additional approach to studies of particulate atmospheric pollution, especially its spatial and temporal variations and its cumulative effects.

Most of the evidence that the particulate content of the atmosphere has changed during the last two centuries comes either from observatory records (1) or from ice cores (2, 3). In most cases, problems involved in differentiating particulates from different sources or in establishing detailed chronologies have limited the confidence with which the anthropogenic component can be defined against naturally fluctuating background levels.

At the present day, a significant part of the particulate content of the atmosphere in temperate latitudes comprises magnetic spherules arising from the combustion of fossil fuels (4–6). The observed ferrimagnetic behavior of the oxides present in these spherules indicates a chemical composition close to magnetite, Fe_3O_4. Oldfield *et al* have shown (4) that ombrotrophic peat bogs, (*ie* those excluded from groundwater drainage and entirely dependent on atmospheric inputs) preserve a record of changing spherule concentrations and hence of the particulate output from fossil fuel combustion. Since these mires are not associated with flowing water, particulate matter deposited on the plant surfaces remains approximately *in situ* to be incorporated in the peat as successive layers of vegetation accumulate. Thus a peat profile will contain a record of particulate deposition from the atmosphere.

In order to estimate the concentrations of magnetic spherules at each depth in the peat profiles, dried samples of known weight were packed into 10 ml polystyrene sample holders for measurement. Mass specific magnetic susceptibility (χ) could be measured for the most strongly magnetic samples using a Digico meter. For the majority of samples, susceptibility was too weak to be measurable. In these cases Saturation Isothermal Remanent Magnetization (SIRM) was measured by first placing each sample in a field of 1 Tesla in an Electro magnet, then measuring the intensity of induced remanence with computerized Digico fluxgate magnetometer. Both types of measurement are simple, cheap, rapid (50–200 measurements per hour) and completely non-destructive. SIRM and χ are directly proportioned in all samples where both could be measured, thus allowing the use of either in further calculations. The magnetic properties of the spherules (in particular, coercivity of SIRM and quadrature χ) allow their confident differentiation from other magnetic particulates.

Preliminary results from three sites in Britain (4) confirmed an increase in SIRM of between two and three orders of magnitude since 1800 AD and a spatial distribution of peak surface values directly related to distance from major conurbations. The value of this initial study was limited by the lack of precise dating (4, 8). A further problem arose from the portrayal of magnetic fallout simply in terms of changing concentrations, since short-term fluctuations in the rate of peat accumulation may have been responsible for 'diluting' or 'concentrating' the samples.

A subsequent study (9) in northwest England partially overcomes these problems by calculating the magnetic influx for a given surface area of peat above a clearly synchronous horizon, in this case the first increase in SIRM above pre-industrial levels. This provides values which, once adjusted for within-site hummoc *vs* hollow variations, can be compared from site to site and used to map the distribution of anthropogenic magnetic fallout. These and subsequent studies indicate that post-industrial atmospheric inputs give rise to an order of magnitude increase in the concentration of magnetic minerals even in the least industrially affected parts of the British Isles, and that close to major conurbations the increase is at least 3–4 orders of magnitude (10).

RESULTS FROM FINNISH PEAT PROFILES

The data reported here come from four widely separated sites in Finland (Figure 1). Chronological control is provided by analysis of the annual moss increments in peat cores as previously described by Pakarinen and Tolonen (11). The time scale thus derived, together with measurements of bulk density and SIRM, provides a firm basis for dating and calculation. The magnetic measurements can then be converted to estimates of magnetite concentration and influx rate by reference to Parry's study of the magnetic properties of synthetic magnetite of varying crystal diameter and concentration (12).

The results of these calculations are summarized in Figures 2 and 3, and in Table 1. In view of the uniform nature of the *Sphagnum fuscum* peats sampled, the lack of any relationship between total iron concentrations and water table (see Figure 3), and the published (13–15) and unpublished (16) evaluations of total iron profiles in comparable peats, we conclude that the values in Figure 3 and Table 1 are a good reflection of the changing rate of iron accumulation.

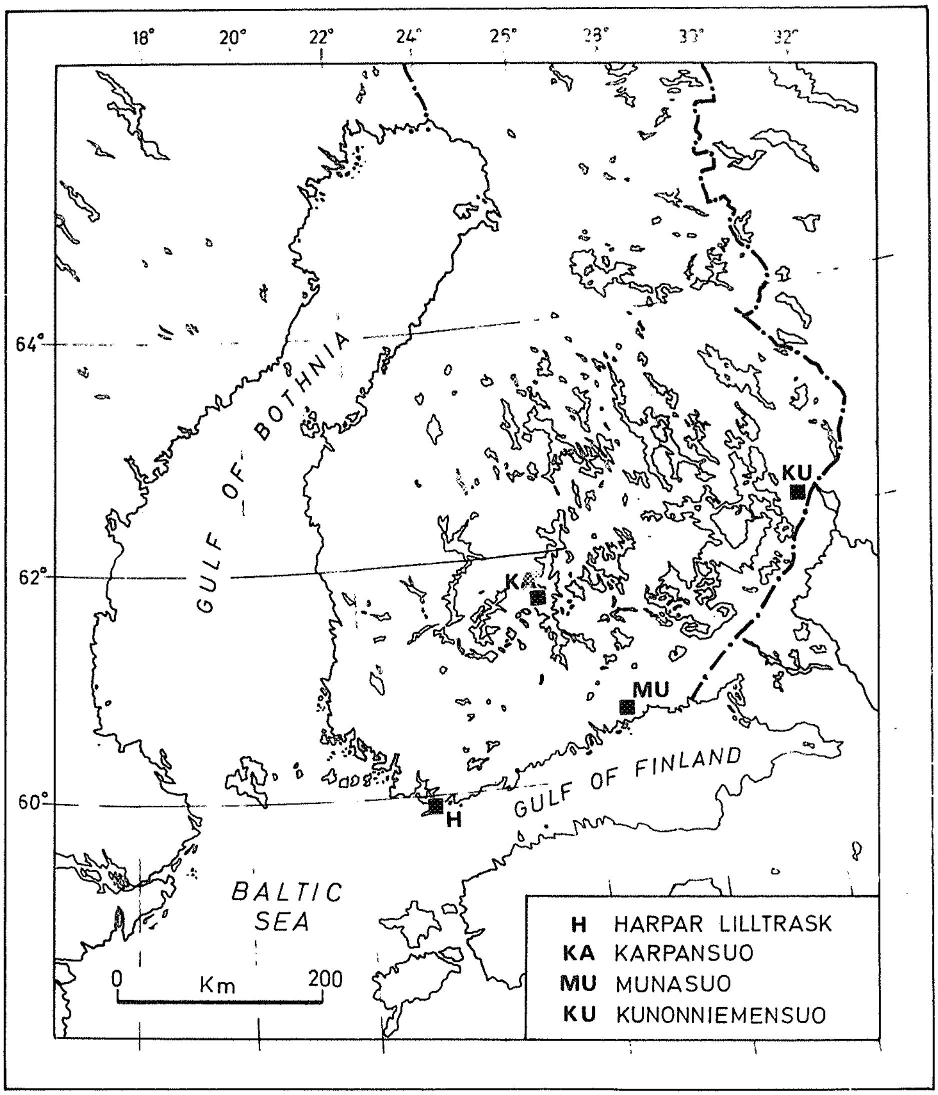

Figure 1. Location map.

DISCUSSION

Pre-industrial deposition of magnetite in the peat profiles at Karpensou and Kunonniemensuo varies between 0.197 and 0.057 × 10^{-6}kg/m^2/y. The lower value is for Kunonniemensuo peat which has been pollen-analyzed in detail and dated to the 11th century AD by both moss increment counting and three ^{14}C, dates (17). The higher value is for early 19th-century peat from Kunonniemensuo. The mean value of ten pre-1869 samples from both sites is 0.113 × 10^{-6}kg/m^2/y. Both these sites show about the same pattern—deposition rates increase from about 1860 onwards, and by 1900, mean annual deposition rates are two to five times the 1850 level. By 1935, the values are twenty to fifty times those of 1850, and maximum post-war values at these two sites are over 200 times those of 1850 AD. The profiles from Harpar Lillträsk and from Munasuo cover a shorter time span, but all show dramatic increases during the last 40–50 years. Harpar Lillträsk lies 7.8 km northwest of the steelworks at Koverhar, which began iron production in 1961 and steel production in 1971. The extremely high rates of magnetite deposition calculated for the last decade may thus be directly related to the nearby industrialization. The peak annual deposition rate at Harpar Lillträsk (424 × 10^{-6}kg/m^2/y) is about 3800 times the mean pre-1860 AD rate in central and eastern Finland.

Table 1 allows the total magnetite input resulting from the anthropogenic increases in atmospheric fallout to be compared with that recorded in British sites. These results together with previous studies confirm that both temporal and spatial variations in magnetite influx as estimated by the present methods show consistent patterns which can be directly related to the combustion processes associated with industrialization.

Figure 3 allows some assessment of the impact of these processes on rates of total iron accumulation. For the period prior to World War II the evidence shows little correlation between total iron accumulation and atmospheric deposition rates. Iron derived from magnetite deposition seems never to have provided more than about 20 percent of the total iron accumulated during this period at any of the sites. Indeed, during the period prior to 1860 its proportional contribution was at least an order of magnitude less than this. For the period after 1950, all sites show some direct correlation between magnetite deposition rates and total iron accumulation.

The proportion of the iron contributed by atmospheric magnetite decreases from industrial centers such as the steel works close to Harpar Lillträsk. At this latter site, the values, once adjusted for the percentage of Fe by weight in magnetite crystals, indicate that around 40 to 50 percent of the iron recently accumulated in the peat may be spherules from anthropogenic combustion. The estimated proportion in the sites of Munasuo and Karpansuo in central Finland ranges from 18 to 26 percent, and averages around 15 percent in the two profiles from Kunonniemensuo. These rough estimates coupled with the generally strong parallel between post-1950 magnetite deposition rates and iron accumulation (Figure 2) suggest that the recent increase in total iron accumulation at all sites are directly related to magnetite fallout resulting from combustion processes. At Harpur Lillträsk it seems probable that fallout from the nearby steelworks has been the major factor behind the five-fold increase in total iron accumulation rates over the last two decades.

The estimated post-1850 influx of

magnetite at the Finnish sites ranges from 730×10^{-6}kg/m^2 at Harpur Lillträsk, where a full estimate is not yet possible. The values can be compared with the estimates for British sites shown in Table 1.

The values given above for Karpansuo and Kunonniemensuo are respectively 3.7 and 2.6 times the lowest estimate obtained from British peats from Achnahaird. The Achnahaird sites lie on a peninsula on the northwest coast of Scotland, remote from urban and industrial activity. The post-1950 influx at Harpur Lillträsk is 4.5 times the mean value of *total* anthropogenic influx for the eleven profiles from northwest England coming from three valleys midway between the northern fringe of industrial and urban development some 10–30 km south of the sites, and the rural area of the English Lake District to the north. It is already 50 percent of the total anthropogenic influx for Ringinglow Bog, in an area of extensive urbanization and industrial development on the southern boundary of Sheffield.

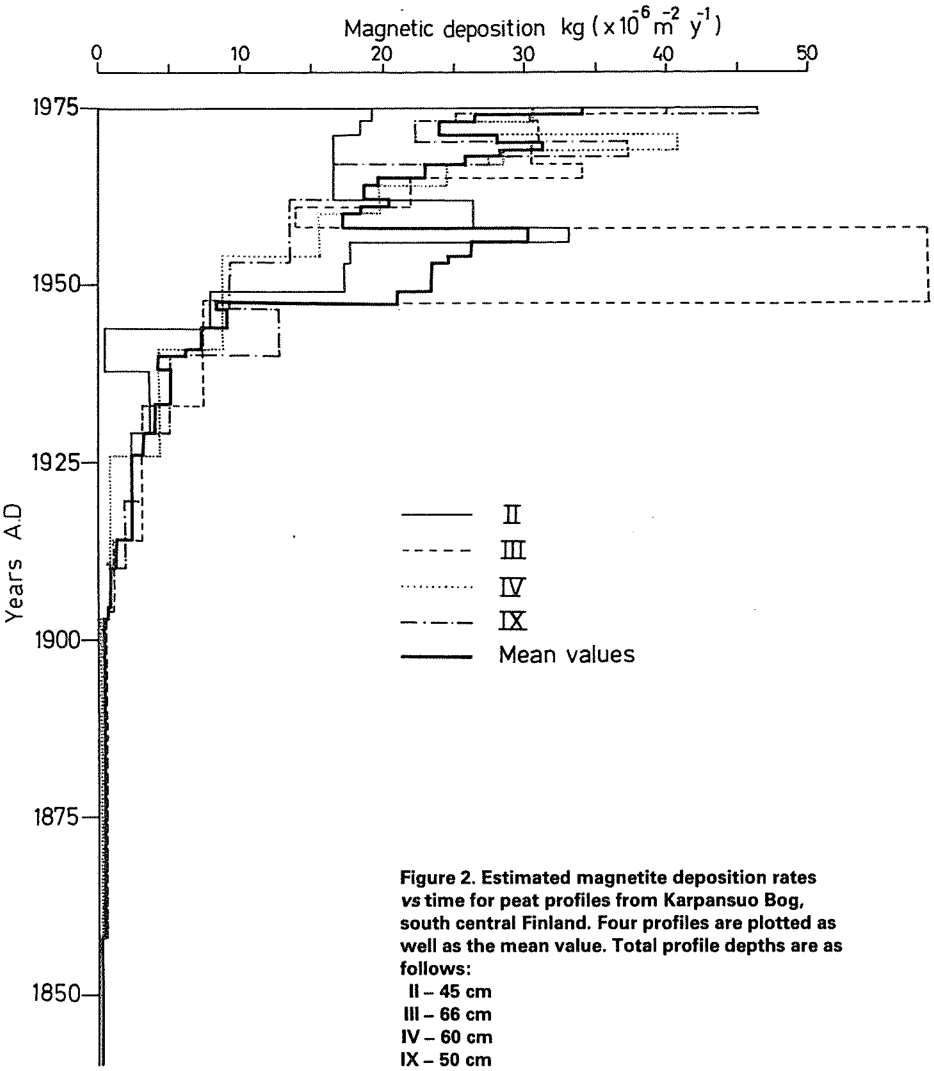

Figure 2. Estimated magnetite deposition rates *vs* time for peat profiles from Karpansuo Bog, south central Finland. Four profiles are plotted as well as the mean value. Total profile depths are as follows:
II – 45 cm
III – 66 cm
IV – 60 cm
IX – 50 cm

Figure 3. Estimated magnetite deposition rates and measured total iron deposition rates *vs* time for six peat profiles from four ombrotrophic mire sites. Total profile depths are given below followed by the mean water level in each profile in brackets.
Harpar Lilltrask – 28 cm (22 cm)
Karpansuo III – 66 cm (30 cm)
Munasuo I – 24 cm (10–15 cm)
Munasuo II – 24 cm (10–15 cm)
Kunonniemensuo 7 – 40 cm (40 cm)
Kunonniemensuo 9 – 45 cm (40 cm)

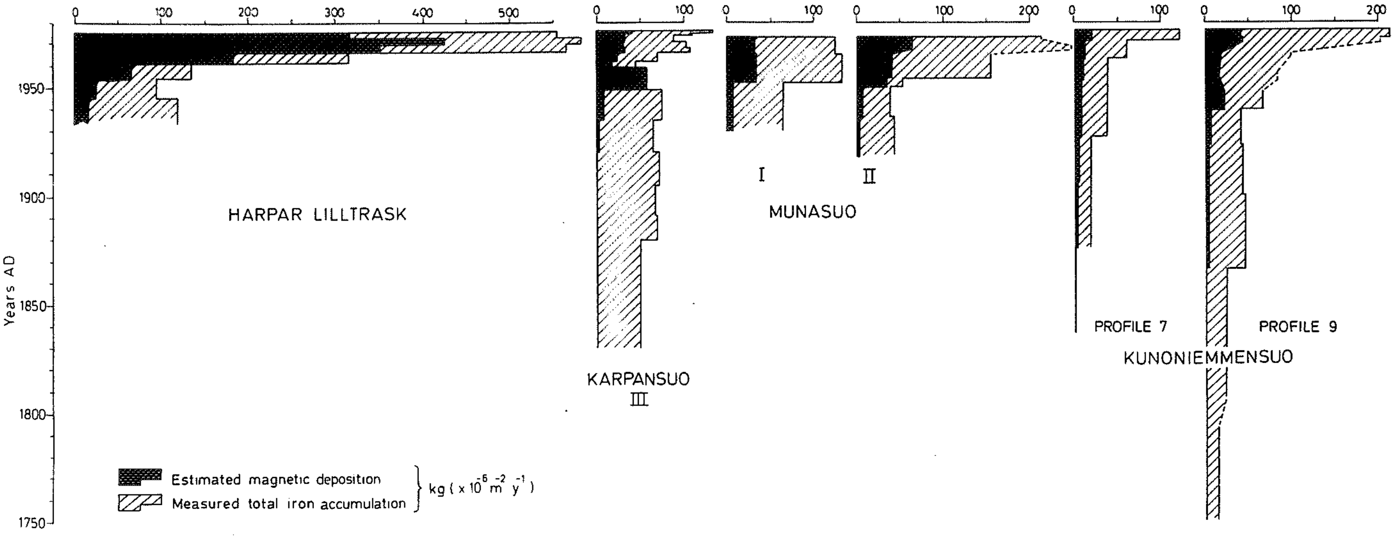

Table 1. Estimated magnetite and measured total iron deposition at sites of ombrotrophic peat growth in Finland and Britain. The Table summarizes (A) annual deposition rates for atmospheric magnetite and total iron deposition rates for the years 1850, 1900, 1935 and 1973 at each site; (B) the total cumulative post-1850 and post-1950 deposition of atmospheric magnetite and total iron at each site, and for comparison: (C) total post-industrial deposition of atmospheric magnetite at British sites using the sampling methods described in Oldfield et al (9) and the estimation procedure outlined in the text.

Annual influx and accumulation rates	Harpar Lillträsk			Karpansuo				Munasuo					
				Profile III			[mean of 4]	Profile I			Profile II		
M	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$	M	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$
A 1973	314	567	1.8	31	88	2.8	24	31	125	4.0	64	213	3.3
B 1935	16	122	7.6	7.5	74	9.9	5	6.6	65	9.8	2.7	40	14.8
C 1900	–	–	–	0.7	67	95.7	0.4	–	–	–	–	–	–
D 1850	–	–	–	0.3	49	163	0.2	–	–	–	–	–	–
$^{A}/_{B}$	20	4.6	0.2	4.2	1.2	0.28	4.7	4.7	1.9	0.40	24	5.3	0.22
$^{A}/_{D}$	–	–	–	113	1.8	0.02	101	–	–	–	–	–	–
Cumulative influx	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$	[mean of 4]	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$
Post 1950*	6051	10 227	1.7	980	1767	1.8	710	630	3252	5.2	–	–	–
Post 1850*	–	–	–	1230	8107	6.6	1030	–	–	–	–	–	–

Annual influx and accumulation rates				Kunoniemmensuo								
	[mean of 2]			Profile 7			Profile 9			[mean of 2]		
M	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$
A 1973	47	169	3.6	22	119	5.4	40	213	5.3	31	166	5.4
B 1935	4.6	53	11.5	7.6	38	5.0	6.6	40	6.1	7.1	39	5.5
C 1900	–	–	–	2.3	18	7.8	1.9	44	23.2	2.1	31	14.8
D 1850	–	–	–	0.4	–	–	0.3	23	76.7	0.3	–	–
$^{A}/_{B}$	10	3.2	0.31	2.9	3.1	1.1	6	5.3	0.87	4.5	4.3	1
$^{A}/_{D}$	–	–	–	55	–	–	133	9.3	0.07	94	–	–
Cumulative influx	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$	M	Fe	$^{Fe}/_{M}$
Post 1950*	–	–	–	380	1849	4.9	–	–	–	–	–	–
Post 1850*	–	–	–	730†	4053	5.6	–	–	–	–	–	–

British Sites					
Northwest Scotland		Northwest England (Head of Morecambe Bay)			Industrial Southern Yorkshire near Sheffield
Achnahaird [4]	L Broom [2]	Duddon Valley [4]	Leven/ Rusland Valley [5]	Lyth Valley [2]	Ringinglow Bog [6]
M	M	M	M	M	M
280	700	2600	390	830	12 400

M = 10^{-6}kg m^{-2} atmospheric "magnetite" (see text)
Fe = 10^{-6}kg m^{-2} total iron
*Surface values extrapolated to end of 1977
† 1876 value extrapolated back to 1850. Figures in square brackets refer to numbers of profiles used.

CONCLUSIONS

Magnetic measurements of ombrotrophic peat provide valuable records of the spatial and temporal variations in particulate atmospheric pollution. The procedures used can be readily combined with methods of monitoring heavy metal pollution based on the chemical analysis of *Sphagnum* (18). The present results can be converted to estimates of changing magnetite influx rates and dated by annual moss increment counting (11).

Magnetite influx rates per unit area begin to increase slowly at about 1860 AD, then rise more steeply during the present century to reach post-war levels which are two to three orders of magnitude greater than those recorded in pre-1860 peat. For the post-war period, the distribution of atmospherically-derived magnitite can be directly related to the proximity of industrial sources. Moreover, the recent iron deposition rates often parallel magnetite deposition in detail from level to level at each site.

Particulate iron in the form of industrially and domestically generated magnetite spherules appears to be a significant component of the iron in recent peat, even at remote sites. The present techniques provide a rapid and extremely informative approach to the study of spatial and temporal variations in the atmospheric fallout of particulates resulting from industrial and domestic combustion processes (19):

References and Notes

1. J M Mitchell in *Global Effects of Atmospheric Pollution* (E Singler, Ed, Riedel, Dordrecht, 1970).
2. C U Hammer *Union Géodésique et Géophysique Internationale. Association International des Sciences Hydrologiques; Commission des Neiges et Glaces, Symposium: Isotopes et impurétés dans les neiges et glaces. Actes du colloque de Grenoble;* août/septembre: 365 (1975). IAMS-AISH Publication No. 118.
3. C U Hammer, H B Clausen, W Dansgaard, N Gunsterup, S J Johnsen, N Reeh *Journal of Glaciology* **20**, 3 (1978).
4. F Oldfield, R Thompson, K E Barber *Science* **199**, 679 (1978).
5. L J Doyle, T L Hopkins, P R Betzer *Science* **194**, 1157 (1976)
6. D W Parkins, D R Phillips, R A L Sullivan *Journal of Geophysical Research* **75**, 1782 (1970).
7. F Oldfield, J A Dearing, R Thompson, S E Garrett-Jones *Polskie Archivum Hydrobiologii* **25**, pp 321–334 (1978).
8. F Oldfield, P G Appelby, R S Cambray, J D Eakins, K E Barber, R W Battarbee, G R Pearson, J M Williams *Oikos* **33**, pp 40–45 (1979).
9. F Oldfield, A Brown, R Thompson *Quaternary Research* **12**, 326–332.
10. F Oldfield, S Hughes, R Thompson, University of Liverpool. Dept of geography, Liverpool *personal communication.*
11. P Pakarinen, K Tolonen *Suo* **1**, 19 (1977).
12. L G Parry *Philosophical Magazine* **10**, 303 (1965). We have assumed the SIRM of magnetite to be 5 Am^2/kg. From the range of grain diameters observed microscopically in magnetic extracts we conclude that, for the present samples, our calculations will yield a close approximation of the magnetite concentrations, though estimates will be low for samples with a modal magnetite grain size larger than 6 microns, and *vice versa.*
13. A Rühling, G Tyler, *Oikos* **21**, 92 (1977).
14. P Pakarinen, K Tolonen *Oikos* **28**, 69 (1977).
15. P Pakarinen, K Tolonen *Suo* **28**, 95 (1977).
16. Unpublished iron analyses from the area around the Koverhar iron works, 1973–78 by T Tuominen and students of plant ecology in the Department of Botany, University of Helsinki.
17. J Vuorinen, K Tolonen, Department of Botany, University of Helsinki, Helsinki, *Personal communication.*
18. P Pakarinen, K Tolonen *Ambio* **5**, 1 (1976).
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