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## ELEMENT RETENTION AND REMOVAL IN OMBROTROPHIC PEAT OF HÄÄDETKEIDAS, A BOREAL FINNISH PEAT BOG

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We determined the rate elements are sequestered in hummock peat of an ombrotrophic bog. The peat below 65 cm was radiocarbon dated and the upper 65 cm was dated using the acid insoluble ash (AIA) content and *Polytrichum strictum* growth increments. Peat produced during the last 9 yrs contains roughly all the N, P, Ca, and Mg, and about twice the K, deposited during this period. However, these nutrients are depleted from older peat at rates that depends on mineralization and adsorption properties of the ions. Changes in inorganic chemistry occur mostly while peat is in the acrotelm. Therefore, only peat in the catotelm will show the true accumulation rate of elements. In peat below 65 cm, the annual accumulation rate, as a percent of the present annual input, is: N-38, K-2.5, P-18, Na-1.5, Ca-3, Mg-51 and S-3.5%. Dust fall increased 4-fold about 500 yrs ago and has remained at this level. Therefore, the annual accumulation of elements in peat below 65 cm, or older than 522 yrs, presumably underestimates present accumulation in the catotelm of soil-derived elements, especially Ca and P, and elements that have increased due to pollution such as N and S. This increased dust fall probably changed the floristic composition of the vegetation as well as production and decay.

Keywords: Accumulation, dating, element retention, input changes, nutrient dynamics

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### INTRODUCTION

In most ecosystems organic matter decays within years or decades. In peatlands, decay is very slow and peat can accumulate over thousands of years. Palynologists (Birks & Birks 1977) and bryologists (Janssens 1988) have used these deposits to show long-term changes in vegetation, and others (Clymo 1984, Tolonen et al. 1992) to determine changes in peat accumulation or decay during bog development. Peat deposits can also show chemical changes in the peat during decay (Waks-

man & Stevens 1928) or changes in atmospheric input (Aaby et al. 1979, Livett 1988).

Trends in chemical changes with depth are rather well-documented (Mattson & Koutler-Andersson 1954, Damman 1978, Shotyky et al. 1990, 1992). However, the interpretation of chemical changes with depth is confounded by leaching, redistribution, and uptake by plants as well as by decay and variations in growth. Therefore, the fate of some elements deposited on peatlands is still poorly known or controversial, as for instance

that of nitrogen (Damman 1988a, Malmer 1990) and lead (Damman 1978, Aaby et al. 1979, Livett 1988). The effect of decay, removal, enrichment, and stagnation of peat growth on element concentrations in the peat is illustrated in Fig. 1.

Separating actual from apparent enrichment and removal requires a reliable timescale. From an ecological point of view, this is most important for peat deposited during the last 200–300 years. Unfortunately, this is outside the range of conventional radiocarbon dating and there are problems associated with other dating methods for surface peat. Peat age increases with depth, but depth is not a reliable indicator of age because of local variations in production and decay (Tolonen 1971, Wallén et al. 1988, Johnson & Damman 1993), even in similar microsites within the same bog.

The purpose of this paper is to determine the accumulation rate of elements in peat and to examine the changes in removal and accumulation over time. We will use well-dated cores from an ombrotrophic bog so that inputs are restricted to atmospheric deposition and so that unquantified inputs from weathering or seepage cannot confound the results. We will determine the proportion of the input sequestered in the peat during bog development and show how data on removal and accumulation can provide an insight into biogeochemical processes in peatlands.

## METHODS AND MATERIALS

### Field work

We collected peat cores from the center of Häädetkeidas (62°05'N, 22°45'E; altitude 150 m), a large patterned ombrotrophic bog in a forested region about 15 km WNW of Parkano, N.-Satakunta, in western Finland (Aario 1932). We took two cores from the upper 60 cm of a *Sphagnum fuscum* hummock using a stainless steel cylinder (d = 11.5 cm) with teeth at the lower end. Below 50 cm, we used a Russian peat sampler (d = 10 cm) (Tolonen & Ijäs 1982). We cut the cores at 5 and 10-cm intervals for peat above and below 50 cm, respectively, and at clear stratigraphic boundaries in these cores. These core sections were collected for chemical analysis. We described the stratigraphy and the degree of humification of the peat (von Post 1924) in the field. *Sphagnum fuscum* capitula samples (about 100 cm<sup>2</sup>) were collected from 10 hummocks near the coring site.

### Sample preparation and analysis

We dried the samples in a drying room at 40°C, and weighed them to determine bulk density. Major roots and rhizomes were removed before

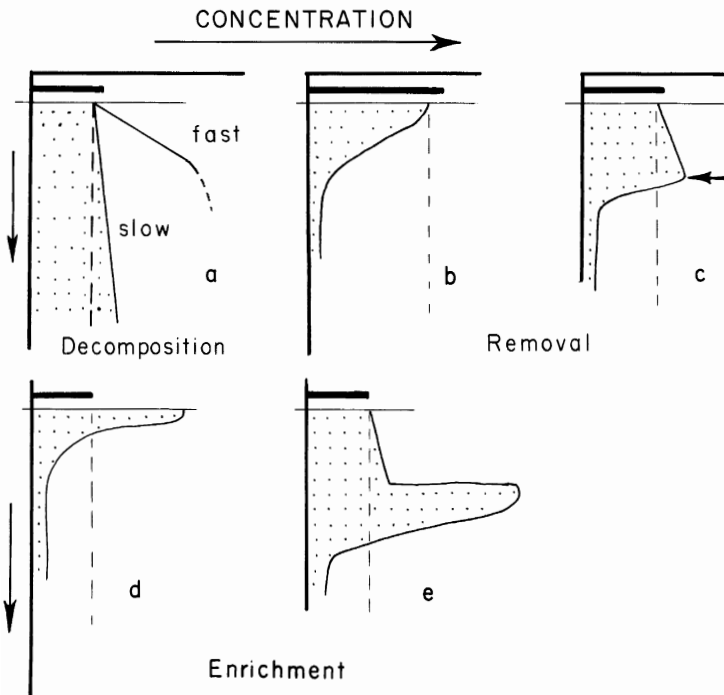


Fig. 1. The effect of various processes on changes in total element concentration in peat with depth. Organic matter decomposition increases elemental concentrations with depth (a), and thus age of the peat. The concentration of mobile elements such as K and Na, decreases from the surface (b). Others are removed below the water table (c). When peat growth stagnates, the detritus cycle increases concentration at the surface (d) for most elements, e.g. N, P, Ca, Fe, Al, Mn, Pb, Zn, but not Na or Mg (Damman 1978). The concentrations of elements such as Fe, Al, Pb and Zn, increases in the zone of water level fluctuation (e). The black bar indicates the concentration of the element in the *Sphagnum* capitulum. Note that the concentration exceeds or equals that of the surface peat in actively growing peat but not in stagnant peat (d).

weighing and grinding. Samples of the ground material were ashed in a muffle furnace at 450°C for 4 hrs or until all organic matter was completely ashed. We treated the ash with 6 N HCl, and the acid insoluble ash (AIA) was collected on a filter, re-ashed and weighed. The filtrate was diluted to volume and analyzed for Na, K, Ca, Mg, Mn, Fe, Pb, Zn, Cu, and Ni by atomic absorption spectrometry and for P by the molybdenum blue method. Nitrogen was determined by macro-Kjeldahl and S on a Leco-analyzer. All results are expressed on an oven-dry weight (100°C) basis.

**Dating of peat profile**

We took samples for radiocarbon dating at 60–65 cm, 97–100 cm, and then at 50 cm intervals up to 5 m. Mineral soil was at 5.13 m in the core. The samples were radiocarbon dated by Dr. H. Jungner, Dating Laboratory, University of Helsinki. Radiocarbon dates were converted to calendar years using the calibration program of Stuiver and Reimer (1986).

We determined the age at 5 cm using the growth increments of *Polytrichum strictum* (Pakarinen & Tolonen 1977). From the amount of acid insoluble ash (AIA) in the 0–5 cm core segment and its age, we calculated the average annual AIA input. The age of peat at any level above

a 65-cm depth could then be determined by dividing the AIA content of the peat above that level by the annual AIA input. This dating of the surface peat assumes that: 1) AIA is not dissolved or redistributed in the peat, and 2) AIA input into the bog has not changed over time. The validity of this assumption will be discussed later in this paper.

**RESULTS**

**Peat stratigraphy**

The core consists of ombrotrophic *Sphagnum* (section *Acutifolia*) peat to a depth of 4.50 m. *Sphagnum fuscum* is the dominant species in at least the upper 50 cm. The peat from 33–50 cm is more humified and darker colored than the peat above or below it. Bands of *Eriophorum vaginatum*–*Sphagnum* peat occur at several places in the core (Fig. 2). A layer of *Sphagnum*–*Scheuchzeria* peat occurs from 3.32–3.38 m. At 4.5 m the peat becomes minerotrophic. It changes from woody *Eriophorum*–*Carex*–*Sphagnum* peat to *Carex*–*Equisetum* peat, separated by a layer of *Sphagnum*–*Scheuchzeria* peat (Fig. 2). The peat becomes muddy at 5 m and is underlain by sand at 5.13 m. The peat at 5 m is 9120 ± 120 B.P.

The changes in peat accumulation rates during the development of the bog are noteworthy. The

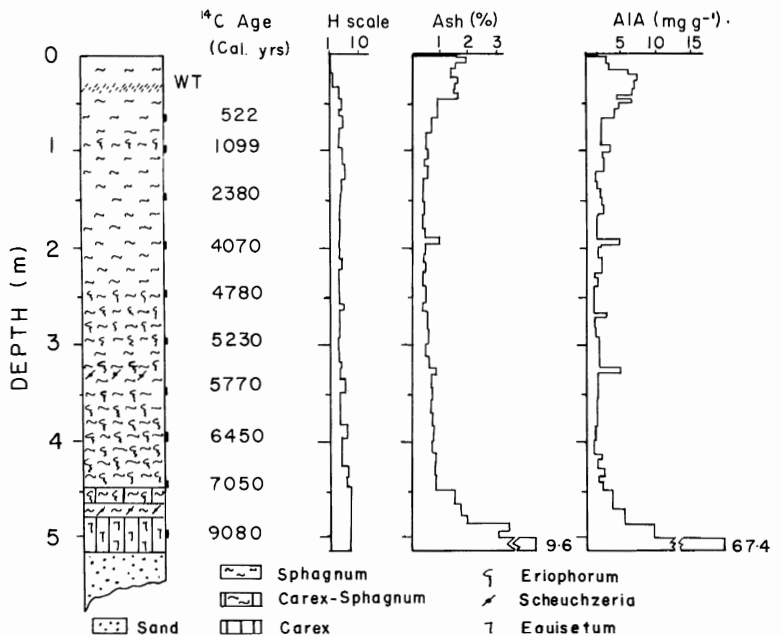


Fig. 2. Stratigraphy, ash, and acid insoluble ash (AIA) content from hummock in center of the raised bog Häädetkeidas. The peat turned ombrotrophic at 4.50 m. Radiocarbon dates are converted to calendar years. Black squares indicate where radiocarbon samples were taken. WT = water level at time of sampling (Oct. 1989).

peat was radiocarbon dated at 50 cm intervals, but the time necessary to accumulate 50 cm of peat varied considerably (Fig. 2). In the minerotrophic peat, peat accumulation is very slow; it required 2 000 yrs to build up 50 cm of peat. The ombrotrophic peat accumulated 3–4 times as fast until about 4 000 years ago when accumulation slowed down to about 2 times that in the minerotrophic peat. Much of the peat in the upper 1 m is still actively decaying so that we cannot make direct comparisons with the older peat.

### Ash and insoluble ash

The ash concentration is 1.5–2.0% in the upper 45 cm and mostly below 1% in the remainder of the ombrotrophic peat. This decrease could result from removal of soluble ash components by leaching or uptake by plants. Acid insoluble ash (AIA) which consists of inert ash component, mostly quartz and silicates, is unlikely to be removed from the peat and, thus, should increase with depth as the peat decays. Initially AIA does increase (Fig. 2), but then it decreases abruptly between 50 and 75 cm to concentrations comparable to those at the surface of the core.

If we assume that AIA input at the bog center remains constant and that AIA does not move

in the profile, then the average annual AIA input can be calculated for the last 522 yrs, the  $^{14}\text{C}$  age of peat at 60–65 cm, from the amount of AIA in the upper 65 cm ( $181.37 \text{ g m}^{-2}$ ), i.e.  $0.35 \text{ g m}^{-2}\text{yr}^{-1}$ . The present annual input can be derived from the AIA in the upper 5 cm ( $1.80 \text{ g m}^{-2}$ ) and the age of the peat at 5 cm; it is  $0.39 \text{ g m}^{-2}\text{yr}^{-1}$ . The difference between these two values is mainly due to lower AIA input in the peat below about 50 cm. Thus AIA input appears to have remained at about the same level during most of the last 500 yrs (Fig. 2, Table 1).

Similar calculations for the peat below 65 cm show that AIA accumulation in this peat is only about 1/3 of the present AIA input (Table 1). Is this because AIA is removed from the anoxic peat layers or was input so much lower at the time this peat was deposited?

Biogenic silica, the most easily dissolved fraction, makes up only about 5% of the AIA throughout the ombrotrophic hummock peat of south Finnish bogs (Eustis 1992). This biogenic silica fraction includes diatoms and vascular plant silica as well as dissolved silica in pore water and adsorbed on the peat. The remainder is mineral silica. The extremely low solubility of silicates and quartz at the pH of the peat (Stumm & Morgan 1981), and the low hydraulic conductivity of the

Table 1. Present input compared to average annual accumulation ( $\text{mg m}^{-2}\text{yr}^{-1}$ ) for dated sections of core from Häädetkeidas bog center. Input based on bulk deposition for Jämijärvi (1971–1988), except K and Na which were based on wet and dry deposition at Jokioinen (1980–1986). Ash and Acid Insoluble Ash (AIA) inputs were calculated from amounts in and age of the 0–5-cm horizon.

Depth (cm)	Period (yrs)	Ash	AIA	N	P	K	Na	Ca	Mg	S	Peat type	Rate of peat accumulation
0-20	50	1115	394	450	24.4	97.2	9.2	128	34	59	Ombrotrophic peat ↓	Slow
20-65	472	782	342	582	20.6	17.7	5.0	42	61	77		
65-100	577	237	85	323	6.7	3.9	3.6	9	30	32		
100-150	1285	193	75	292	5.2	2.6	3.1	10	22	26		
150-200	1690	165	68	196	3.5	2.0	2.4	11	17	18		
200-250	710	240	65	224	4.0	3.8	4.2	30	34	22	Ombrotrophic peat ↑	Fast
250-300	450	362	82	622	5.4	4.5	4.7	52	41	40		
300-350	540	556	152	331	6.0	4.3	4.7	90	48	47		
350-400	680	446	91	358	7.1	2.5	2.8	69	30	46		
400-450	600	714	124	486	18.0	3.2	3.9	115	33	60		
450-500	2030	517	139	440	11.4	1.7	1.6	45	9	51	Minerotrophic	Slow
Present input ( $\text{mg m}^{-2} \text{yr}^{-1}$ )		2604	394	860 <sup>1</sup>	36.8	155	234	310	59	920		

<sup>1</sup>  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  input; total N input is  $1032 \text{ mg m}^{-2} \text{yr}^{-1}$ .

peat in the catotelm (Ivanov 1981) make it highly unlikely that the low AIA accumulation rate below 65 cm is caused by dissolution and removal of AIA.

Therefore, AIA input appears to have been much lower than at present during most of the time the peatland developed and to have increased greatly about 500 years ago, probably because of intensified cultivation, road building or other human activities in the region. Eustis (1992) also found large increases in AIA in the surface peat of ombrotrophic bogs in southern Finland.

### Elements sequestered in peat

Concentration changes with depth can indicate removal and redistribution of elements, but they do not show to what extent elements are sequestered in the peat. We calculated the accumulation rate of elements for the dated sections of the peat profile. A comparison of these accumulation rates in the peat with the present input of these elements (Table 1) shows that for most elements only a small fraction of the present input is stored in the peat below 65 cm. Even N accumulated at a rate less than that of the present input. Accumulation rates in the upper 65 cm are higher than in the older peat for all elements and ash, except N.

This means that either the annual supply of these elements is much higher now than during earlier stages of bog development or that much of the input is removed from the peat. Undoubtedly present inputs of N and S are higher today than in the past because of air pollution. Several other elements associated with agricultural or road dust, e.g. Ca, P, Mg and Fe, probably increased at the same time the AIA input increased. However, increases in inputs cannot explain the low accumulation rates throughout the profile of elements such as K, Na, S and Ca. Clearly, these elements were very actively removed from the peat. We will need to look at conditions in the surface peat in more detail to determine the relative importance of removal and changes in input.

Accumulation rates for several elements (Table 1) tend to be slightly lower during periods of slow peat accumulation (1 000–4 000 yrs ago; 65–200 cm) than in the more rapidly accumulating peat (4 000–7 000 yrs ago; 200–450 cm). This difference is only significant ( $P>0.05$ ) for ash, Ca and Mg. However, the sample size is small because we had relatively few radiocarbon dates. During periods of slow accumulation, peat decays

longer in the acrotelm, where decay is most active. This probably causes the more effective removal of the Ca and ash components.

Accumulation rates, but not concentrations, in the minerotrophic peat below 450 cm are also lower for K, Na, and Mg. Of course, this peat decayed much more rapidly than the ombrotrophic peat and 50 cm of peat represents here 2 000 yrs of peat accumulation. Therefore, this peat stayed for a very long time near the surface where mineralized elements are most easily taken up by plants or leached. Nevertheless, very little of the original nutrient input is sequestered in the peat, especially considering that during this stage of peat bog development the atmospheric nutrient supply was augmented by nutrients in the mineral soil water.

### Retention of input in recent peat

The AIA supply appears to have changed little during the last 500 years. Therefore, we can calculate the age at any depth as the number of years of the present AIA input that has accumulated in the peat above that level. This may slightly underestimate the actual age of the peat since AIA input has increased slightly during that period. The age of peat at 65 cm calculated in this way is 460 yrs. This compares to a radiocarbon age, converted to calendar years, of 522 yrs (95% confidence interval 357–556 yrs). Therefore, the error is relatively small and most of it will be in the peat below 50 cm.

We used this method to date the upper 35 cm of the peat and we used the  $^{14}\text{C}$  date of 522 yrs for the peat at 65 cm. In this way we could calculate the retention of elements also in the recent peat. Fig. 3 shows this for a few contrasting elements; input data and accumulation rates for peat below 65 cm are included for comparison.

Potassium concentrations decrease rapidly with depth and this element is clearly conserved to a very large extent in the living *Sphagnum* (Damman 1978, Malmer 1988). Potassium accumulation is in excess of the input throughout the upper 10 cm and the upper 10 cm contains about 19 x the annual supply, although it represents only 9 years of growth. This is the more surprising since light penetrates less than 1 cm in the dense *Sphagnum fuscum* carpet so that the plants are probably not alive to 10 cm. Below 10 cm the peat contains very little K.

Calcium concentrations stay more or less constant in the upper 40 cm of ombrotrophic hummock peat (Damman 1978), but only the upper

10 cm contains almost all of the input. Below this level, less than 1/3 of the annual input is retained.

Accumulation rates for P show a pattern that closely resembles its concentration changes with depth. Accumulation in the upper 10 cm slightly exceeds inputs. The element is conserved in the living parts (Damman 1978, Malmer 1988), as is K, and is transported to the actively growing parts (Rydin & Clymo 1989). In many respects, P accumulation resembles N, but retention of P in the upper 10 cm is slightly higher than for N. Both elements also show an increase in accumulation between 25 and 65 cm, perhaps because they are immobilized in the microbial biomass to a greater extent at these depths.

Sulfur shows an entirely different accumulation pattern. Sulfur concentrations in the upper 1 m remain more or less constant, but clearly the amount of S stored in the peat represents only a very small fraction of the input (Fig. 3). The retention rate in the upper 5 cm is less than 12% of the annual input and less below this.

**Acid insoluble ash ratios as indicators of element removal with time**

Periodic changes in decay and productivity affect the concentration of elements in the poorly de-

cayed surface peat. Assuming that AIA input is constant, we can use AIA concentrations to correct for variations in production and decay. Elements that are not redistributed will increase at the same rate as AIA during decay. Therefore, element/AIA ratios equal to that in the capitulum will show that all of the element incorporated in the living plant is retained whereas smaller ratios will indicate losses and vice versa.

The element/AIA ratios for the capitula and peat horizons in the upper 65 cm are shown for 4 elements (Fig. 4). Since the capitula contain more N, P, and K than is annually supplied in bulk precipitation, these graphs exaggerate the actual losses. However, when considered with the accumulation rates, these ratios provide an insight into processes in the surface layers of the bog. A further advantage is that these ratios can also be used for elements for which input data are not available.

The Pb/AIA ratio decreases slowly from the capitulum to about 15 cm, but increases sharply at 40–57 cm. The initial decrease with depth is probably a result of lower Pb inputs in the recent past, whereas the increases lower in the profile are clearly caused by redistribution of Pb in the profile.

In the upper 10 cm, all P supplied in bulk precipitation is retained (Fig. 3). However, the

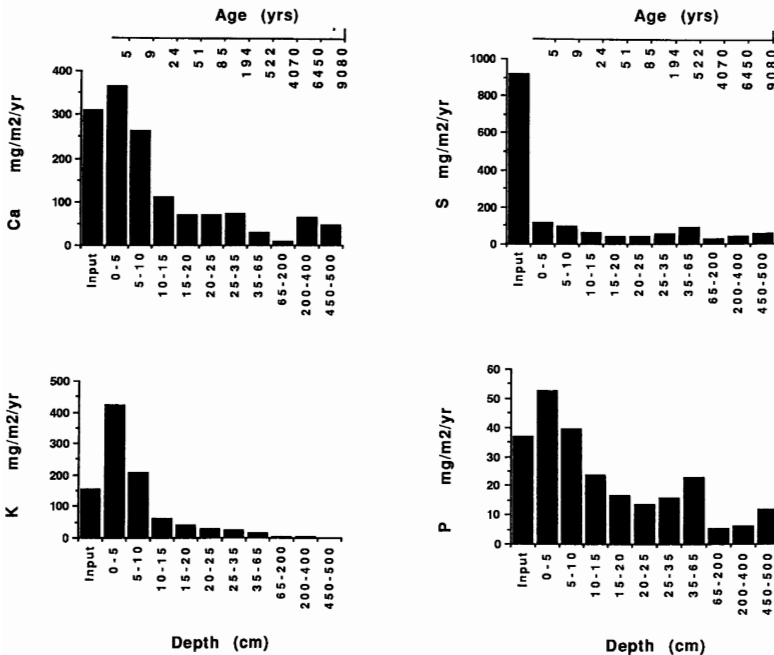


Fig. 3. Annual accumulation of Ca, K, S and P in the peat in comparison to annual input. The annual accumulation in peat below 65 cm and over 522 yrs old is included for comparison.

P/AIA ratios (Fig. 4) decline gradually with depth to about 25 cm and all ratios are much lower than in the capitulum. In this case the high concentrations in the upper parts of the plants are due to translocation of P to actively growing parts (Rydin & Clymo 1989).

Although S and P differ greatly with respect to retention in the peat (Fig. 3), nevertheless once in the *Sphagnum* plants their ratios with respect to AIA are remarkably similar (Fig. 4) and resemble N/AIA ratios. The ratio for all three elements also increases in the peat at 40–57 cm; probably because they are immobilized in microbial biomass. The rapid removal of K is well illustrated by the K/AIA ratios (Fig. 4). In contrast to S and P, the K/AIA ratios continue to decline with depth. This is very similar to the ratios for Na and Mn in hummock peat.

## DISCUSSION

The deposition of AIA on the bog surface of Häädetkeidas more than quadrupled about 500 years ago. This appears to be the result of major anthropogenic changes that increased dust fall in the region. High concentrations of Si (Chapman 1964, Eustis 1992) and Al (Chapman 1964, Shotyk et al. 1992) of anthropogenic origin have been observed in the surface layers of ombrotrophic peat profiles elsewhere. This is likely to be a wide-

spread phenomenon in many bogs, although obviously the timing differs regionally.

This increased dust deposition must have been associated with an increased supply of other soil-derived elements (Gorham & Tilton 1978), e.g., Fe, Mg, Ca, P, and probably K. These elements are more mobile than AIA, and therefore changes in their accumulation rate in the peat will not accurately reflect input changes. This additional nutrient input must have greatly affected these extremely nutrient deficient ecosystems. Presumably, it increased decay more than production, resulting in lower peat accumulation rates. It probably also changed the floristic composition of ombrotrophic bogs. Recent increases in the deposition of N, S and trace elements may further change these ecosystems.

The major change in peat accumulation rate around 4 000 years (~ 2 m) ago must be attributed to climatic changes affecting bog hydrology rather than changes in nutrient input. The humified horizon with abundant ericaceous rhizomes occurring from 32–35 cm (~ 100 yrs ago) is probably due to local conditions (Tolonen 1971).

In Häädetkeidas, the AIA input appears to have remained relatively stable over the last 500 years, since the average input per year over this period is almost equal to the present input. Therefore, AIA could be used as an effective dating tool for the upper 65 cm of peat of this bog. However, dust blown in from gravel roads and

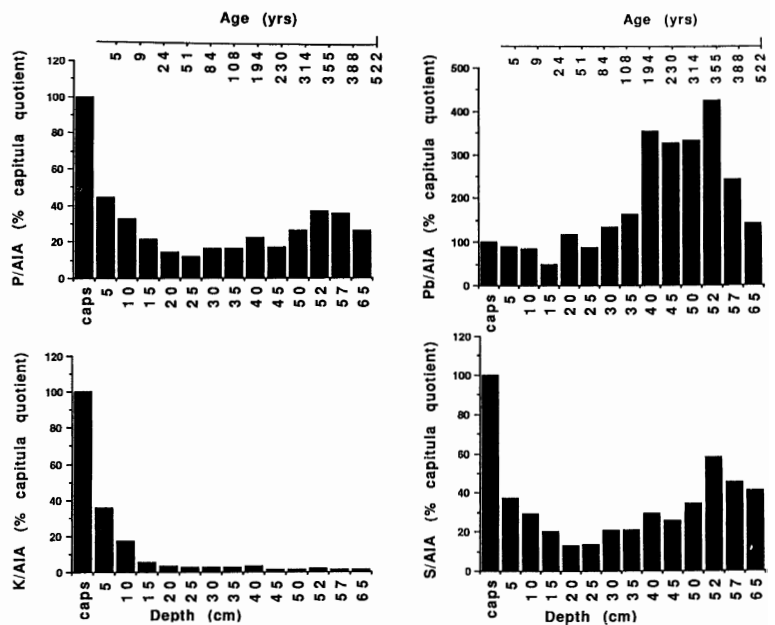


Fig. 4. Removal and accumulation of P, K, Pb and S in the surface peat. Changes in the element/AIA quotient are shown as a percent of that in the capitulum.

fields greatly affects AIA input, and this creates a problem for AIA dating of many peat bogs. It also cannot be used in minerotrophic peatlands.

Concentration changes with depth cannot be easily interpreted in terms of removal and redistribution of elements because of the confounding effect of decay and variation in productivity on element concentrations. An inert component, such as AIA, can be used to correct for these effects, if it is supplied at a constant rate and stays in place.

We used AIA 1) to calculate accumulation rates of elements in the peat for direct comparison with inputs, and 2) as a tracer to determine removal and accumulation of other elements. These data showed that mobile ions that are non-essential or supplied in excess of demand, such as Na and S, were removed from the time they are deposited. Elements that are in biological demand, e.g., K, N, and P but also Ca and Mg, were retained. The last 9 years of *Sphagnum* growth contained about the total input during this period except that it contained twice the input of K. However, there is a net loss of all these elements from older peat, in this case below 10 cm, the rate of depletion being controlled mainly by mineralization and adsorption. Below 65 cm, the accumulation rates remain more or less constant for all elements, suggesting that removal from this peat is negligible. This indicates that the major changes in the inorganic composition of the peat occur in the acrotelm. Therefore, only peat in the catotelm will show the true accumulation rate of elements.

In peat below 65 cm, the annual accumulation in the catotelm peat amounts to the following percentages of the present annual input: 38% N, 2.5% K, 18% P, 1.5% Na, 3% Ca, 51% Mg and 3.5% S. For other elements no input data were available. This peat was deposited more than 500 years ago, and thus before dust fall in Häädetkeidas increased. This has two implications:

1) Annual accumulations represented probably a larger percentage of the input at that time than at present, certainly for soil-derived elements, such as Ca and P, and for pollutants as S and N.

2) Presumably, data for peat below 65 cm underestimate the present accumulation in the catotelm shown in Fig. 3.

Several elements, e.g., Ca, Fe and Al have much lower concentrations in the catotelm than in the acrotelm of many ombrotrophic bogs (Damman 1978, 1986). Increased dust fall in recent years has probably contributed to the magnitude of this difference. For Ca it could be the cause of the rather sudden decrease in concentration with depth, since it cannot be easily explained by other processes.

Why are ionic concentrations in bog waters so low (Gorham et al. 1985), if nutrients are removed from peat below about 10 cm. Especially since this depletion occurs primarily in a 30–40 cm thick horizon above the catotelm. There are several reasons for this:

- 1) The time interval between a depth of 10 and 50 cm is about 345 years at Häädetkeidas, so that removal takes place over a very long period. Of course, even for highly mobile ions, the annual removal is less than that supplied annually in the precipitation. Therefore, the effect on ionic concentrations will be small.
- 2) During the vegetative season, nutrient ions are actively taken up by the vegetation so that concentrations in the bog water are very low in summer. Therefore, ionic concentrations in bog water show clear seasonal trends. Especially, K and Mg, and to a lesser extent Ca, are highest in spring and fall (Damman 1988b) when the run off from the bog is also highest.
- 3) Sulfate concentrations are highest during dry periods, and most of this sulfate is removed from the bog with the first heavy rain. Other ions may have similar short concentration peaks that could be easily missed in water sampling.

Many nutrients are concentrated in the living biomass, but this does not represent an active sink, since the vegetation pattern of these ombrotrophic bogs is rather stable. At the core site in Häädetkeidas the vegetation had not changed for hundreds of years.

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