Pb-210 dating and lead deposition in the ombrotrophic peat bog, Draved Mose, Denmark

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Pb-210 dating has been tested in an ombrotrophic peat bog in S-W Denmark. The favourable conditions in ombrotrophic systems facilitate the evaluation of a continuous time/depth scale, using a combination of Pb-210 and C-14 datings. The age determination has improved the contemporary prospection of the processes in the bog and of the deposition of heavy metals, reflected in the peat. A detailed description of lead deposition is given. – Since A.D. 1300 the lead deposition in Draved Mose has increased from 0.5 mg Pb $m^{-2}y^{-1}$ to about 50 mg Pb $m^{-2}y^{-1}$ (A.D. 1970-1978). It has been made render that approximately 70% of the recent lead deposition derive from alkyl-lead petrol whereas the rest originate from lead manufacturing industries and other sources.

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The impact of toxic substances on man and his environment is very well recognized. Consequently, efforts have been devoted in recent years to acquire more knowledge of the distribution of chemical elements in the environment to be able to control the overall effect of toxic substances.

Lead is conjectured as a neurotoxin, which acts on the central nervous system and is liable to produce disorders of mentation. This results in social and educational effects in populations which appear normal by conventional health criteria (Bryce-Smith et al. 1978).

Deposition of lead has been calculated from e.g. bulk precipitation (Hovmand 1973 and 1976) and from grass crops harvested on fields (Hovmand and Tjell, pers. commun.). Comparisons of deposition levels found by the two methods show that the two »samplers« have different collecting efficiency, the field being the most efficient. This result stresses the importance of methodical considerations when comparing deposition levels.

Present deposition rates of lead must be related to the preindustrial deposition to evaluate the recent level of pollution. Information of deposition rates in the last decades contributes towards an improved estimate of the relative importance of different lead emittants. Deposition rates in the past have been obtained from material collected years ago (e.g. herbarium material; see Persson et al. 1974; Johnsen and Rasmussen 1977; Rasmussen 1977) and from deposition in peat (Damman 1978; Pakarinen and Tolonen 1977) and in sediments (e.g. Benninger 1978).

In general the deposition rates are based on concentration values only as a consequence of an inadequately determined annual increment.

The C-14 dating method produces reliable results at age determination of ombrotrophic peat exceeding 200 years whereas useful information about peat layers younger than 200 years have been highly delayed by a methodical threshold. Pb-210 methods for dating sediments (e.g. Pennington et al. 1976; Pheiffer-Madsen 1979) have shown an advance towards dating young depositive materials. As a result of the Pb-210 dating procedure it has been possible to calculate a detailed time/depth scale over the last 200 years in ombrotrophic peat. Calculation of a continuous lead deposition for extended periods must require investigation areas with very stable environmental conditions. Hence, only few curves of the lead deposition development are available at present.

Extreme stable environmental conditions are known to have existed for centuries in some ombrotrophic bogs in Denmark (Aaby 1976; Aaby and Jacobsen 1979).

In the present study Pb-210 and C-14 dates are used in combination with an accurate slicing technique to calculate the lead deposition rates in the past 600 years.

Investigation area

Draved Mose is situated approx. 20 km from the North Sea, in the oceanic southern part of Jutland between Løgumkloster and Tønder (fig. 1). The bog covers approx. 500 ha and has an almost circular shape. Most of the area has been disturbed due to peat exploitation during the first part of this century. About 3.5 ha of the central bog plain is left in natural condition, and the sampling site is located in this area, at an altitude of 19.5 m a.s.l. Mean annual precipitation was measured at Draved meteorological station 1 km east of the bog to about 830 mm per year (1952-1978, range of variation 530-1240 mm).

The undisturbed area is rather flat and open with a distinct hummock-hollow structure (fig. 2). A *Calluna vulgaris – Eriophorum vaginatum* sociation dominates the hummock vegetation whereas a *Sphagnum cuspidatum – Rhynchospora alba* sociation is the most frequent in the hollows. A detailed description of the vegetation has been given earlier (Hansen 1966).

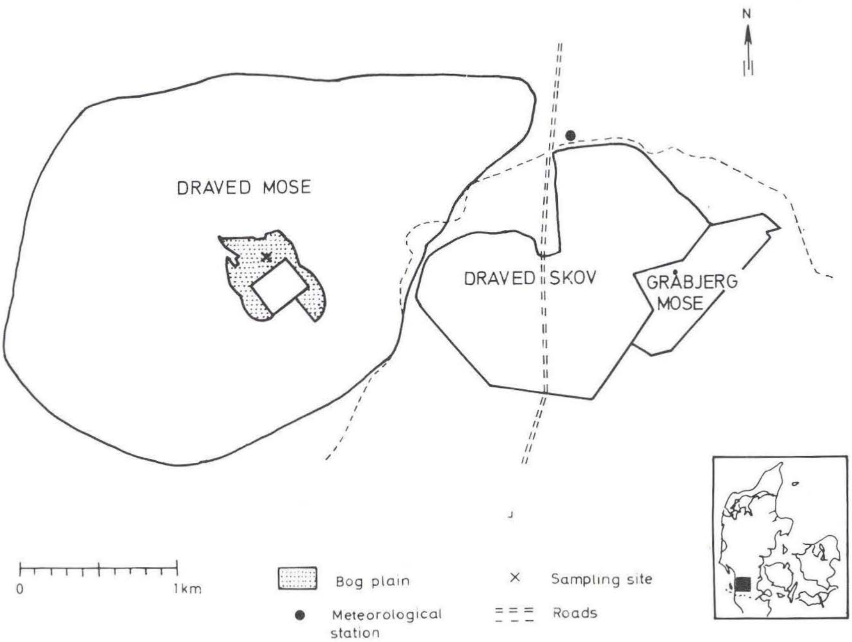


Fig. 1. The localization of the investigation area in Draved Mose.

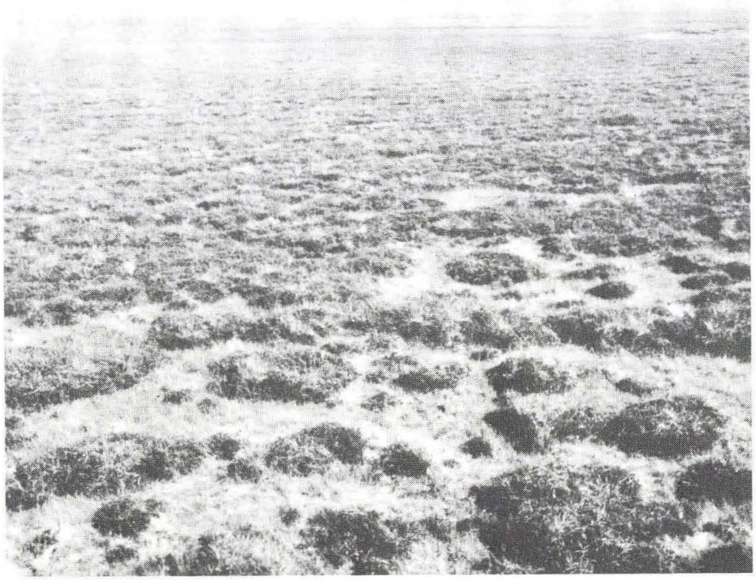


Fig. 2. The sampling site in Draved Mose. The bog surface consists of hummocks (dark areas) and hollows (bright areas).

Methods

Sampling procedure

In September 1978, a profile was excavated from the centre of a hollow to the central part of an adjacent hummock (fig. 3).

After peat stratigraphy analyses, a vertical peat column was taken from the hummock (hummock column I) and another from the centre of the hollow (hollow column I). The columns were stored in polyethylene bags which were prewashed with nitrogen, and after filling more nitrogen was added to prevent oxidation of the stored material.

In addition a peat column (hollow column II) was cut out of the wall close to the previous sampling site. The column was stored in a plastic container.

The area of all the columns were about 150-250 cm^2.

Measurements

Measurements of pH and redoxpotentials (Eh) were carried out in the field using a portable pH-meter, Radiometer type 29, connected to a combinated glass-elec-

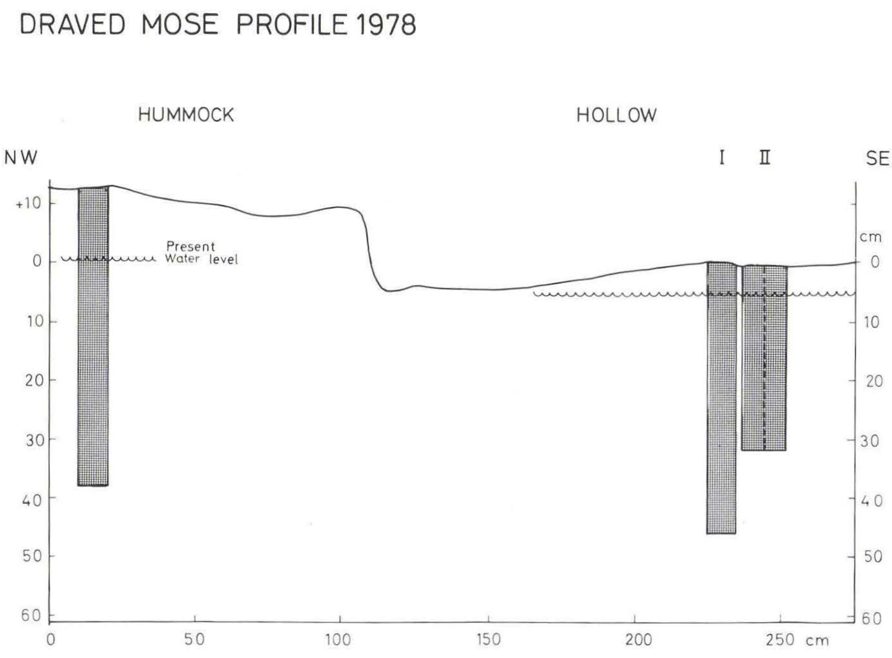


Fig. 3. Excavated profile, 1978, showing the location of the peat columns.

trode for pH measurements and to a special produced platinum electrode with a calomel reference for redoxpotential measurements (Hargrave 1972).

The surface area of the platinum electrode was less than 2 mm^2 which made it possible to carry out Eh-measurements fast and with a minimum of disturbance of the peat material. The electrodes were injected 5 to 10 cm into the water-logged peat just after the excavating of the peat profile. The equilibration time needed for each read-out was less than $2\frac{1}{2}$ min. for both pH and Eh measurements.

Laboratory procedure

Description of peat types and macrofossil analysis

The peat layers have been characterized (p. 53); the degree of humification (H) is given, using the method of v. Post (1924). The composition of the *Sphagnum* material is shown on the macrofossil diagrams (fig. 4 and fig. 5).

The procedure used in determining the frequencies of leaves from different *Sphagna* and epidermis cells of *Rhynchospora alba* and Ericales has been described earlier (Aaby and Jacobsen 1979).

Slicing technique

The entire hummock and hollow columns were frozen to -18^0 C before they were sliced. The freezing procedure facilitates a high slicing accuracy as the ice stabilizes the *Sphagnum* material. Solid *Calluna* twigs and tussocks of *Eriophorum vaginatum* are therefore easily cut without displacing the adjacent *Sphagnum* material. In addition, a high degree of accuracy in volumetric measurements has been secured.

Hummock column I and hollow column I were sawed into approx. 2 cm thick (unfrozen value) segments by hand. The hollow column II was sawed longitudinally into two identical sub-columns. One of these was stored and the other was cut into 3 mm thick slices (unfrozen value) on a circular saw which produced no saw-dust.

Bulk density, ignition residue, and degree of humification

The methods used in determining the ignition residue and the degree of humification have been described by Aaby and Jacobsen (1979). Dry matter (DM) was determined after freeze drying until constant weight. The ignition residues were calculated after heating at 550^0 C for 3 hours.

The volume of the peat material was calculated from frozen peat and multiplied by 0.9 prior to bulk density calculation.

Chemical analysis

Samples from hollow column I were divided into subsamples by vertical cutting. One series of subsamples was filtrated in a N_2 membrane filter apparatus using a 300 μm filter to isolate the interstitial liquid. Homogenous portions of the interstitial liquid were centrifuged at 2340 g for 10 min. separating the »particulate« and the »dissolved« fractions.

The lead concentrations in the unseparated interstitial liquid and in the »dissolved« fraction were determined after digestion in HNO_3. Untreated samples from hollow column I and freeze-dried samples from hollow column II were preweighed, digested in HNO_3. The lead concentration in the wet ashing solution was measured by atomic absorption spectrophotometry using a Perkin-Elmer 460 model connected to a HGA-74 graphite furnace.

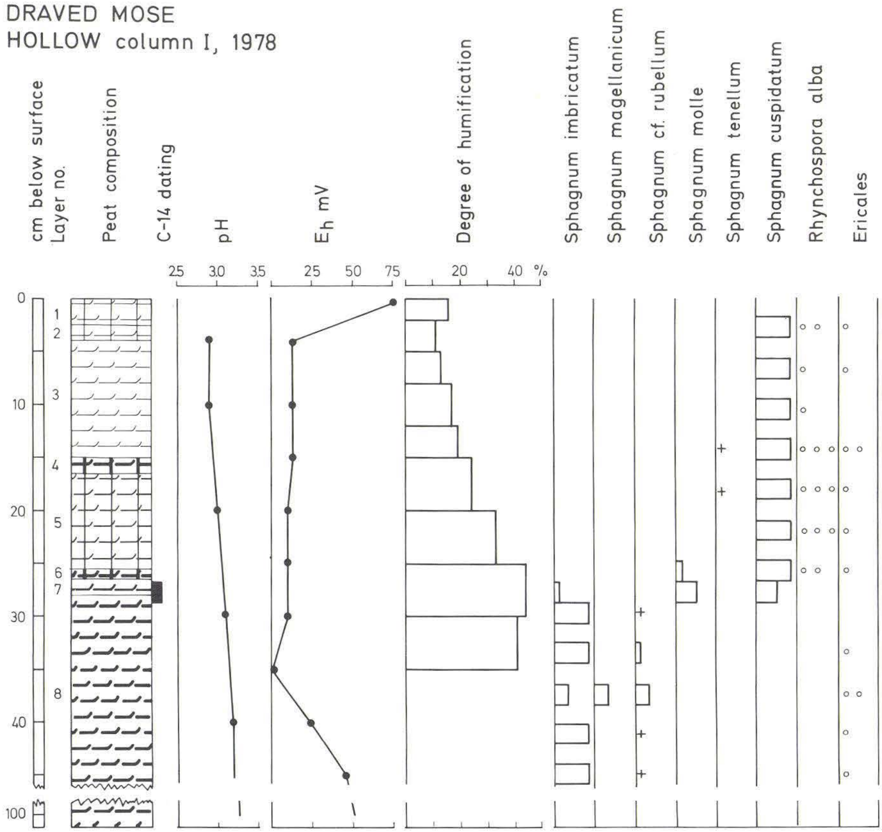


Fig. 4. Hollow column I, 1978. The sediment symbols and the frequencies of *Sphagnum* leaves and Ericales epidermis cells are shown in fig. 5. The thickness of peat symbols indicates degree of humification.

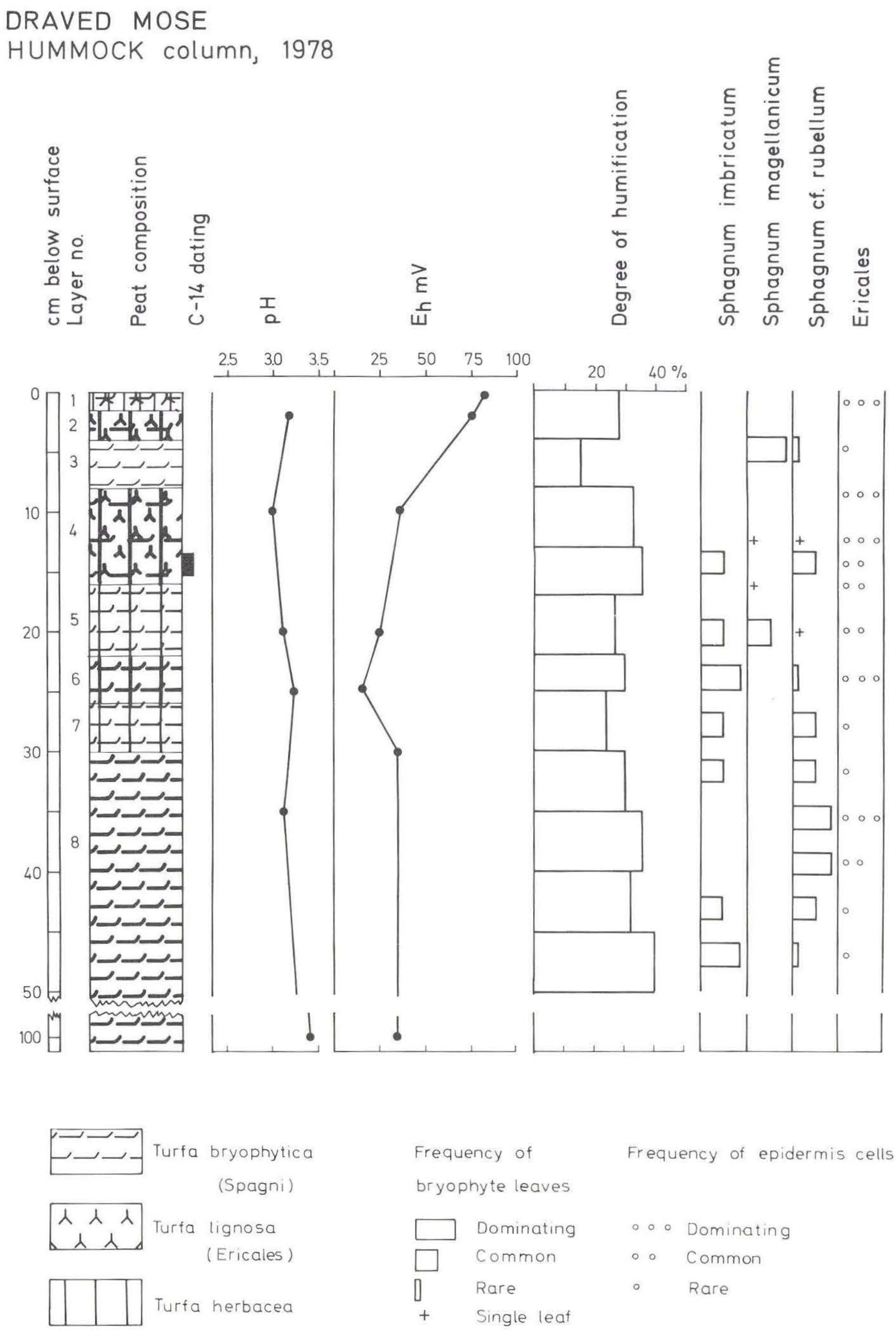


Fig. 5. Hummock column, 1978. The thickness of peat symbols indicates degree of humification.

Dating

The C-14 countings were made by the C-14 Laboratory of the Geological Survey of Denmark and the National Museum using the conventional technique and calibrated to absolute age according to Clark (1975).

The Pb-210 datings were carried out at the Danish Isotope Centre using a modified technique (Pheiffer-Madsen 1979).

History of vegetation at the sampling site

A *Sphagnum imbricatum* sociation with *Sphagnum rubellum* dominated the lower part of the profile (see figs. 4 and 5). Ericaceous plants were rather scarce. About A.D. 1300 (see K. 3127 on table 2) the *Sphagnum imbricatum* sociation was replaced by a *Sphagnum molle-Sphagnum cuspidatum* sociation in the present hollow area (fig. 4). This vegetation shortly afterwards changed to a *Sphagnum cuspidatum-Rhynchospora alba* sociation which has persisted until the present. The vegetational change about A.D. 1300 indicates that a hollow was formed, and from the profile investigations it is concluded that the location of the hollow area has been rather stable in time.

The *Sphagnum imbricatum* sociation dominated until about A.D. 1600 (see K3126 in table 2) in the present hummock area. A *Calluna vulgaris-Eriophorum vaginatum* sociation replaced the former vegetation, and various *Sphagnum* species were restricted to minor patches (e.g. layer no. 3 in fig. 5), as seen on present day hummocks. Also the youngest layers have been formed by the *Calluna vulgaris-Eriophorum vaginatum* sociation, and the actual hummock vegetation has thus existed for about 400 years.

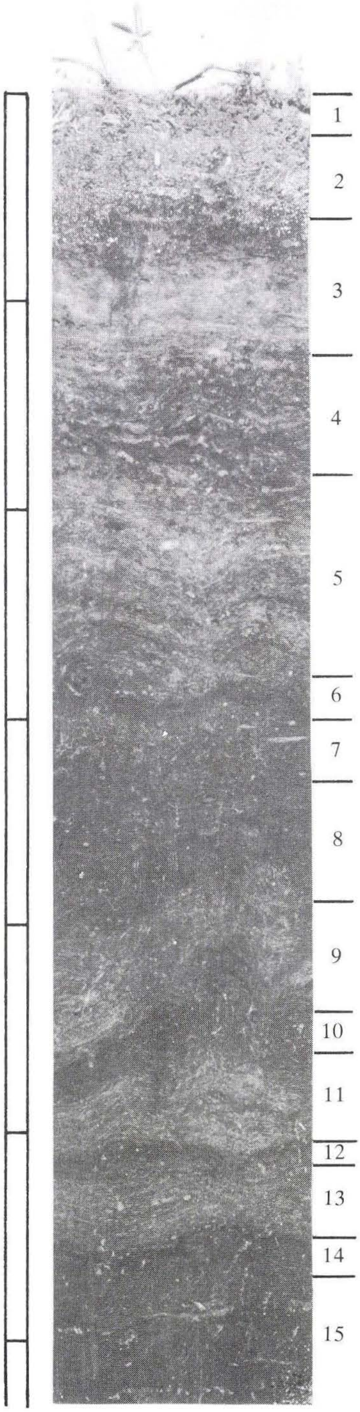
The extinction of the *Sphagnum imbricatum* sociation on the bog has been discussed by Aaby and Jacobsen (1979).

Results

Field measurements

The pH measurements showed small variations only, vertical as well as horizontal (figs. 4 and 5). The mean level is about pH 3 with a slight tendency towards increasing with depth. In the hummock a slightly increased pH was found above the water level. In the deepest part of the excavated profile the pH was between 3.2 and 3.3.

Measurements of Eh seemed to indicate the influence of the water logging.



cm b.s.

Layer no.	Description
1	Present vegetation and light yellow *Sphagnum* peat containing *Cyperaceae. Oxycoccus quad., Andromeda poli., Rhynchospora alba* and *Eriophorum ang.* were present (H1).
2	Tangled grey-yellow *Sphagnum* peat with *Cyperaceae. Rhynchospora alba* and *Eriophorum ang.* were present. (H2).
3	Tangled, light yellow *Sphagnum* peat. (H1-2).
4	Similar to layer no. 3, but a little darker. (H2).
5	Tangled, yellow *Sphagnum* peat. *Rhynchospora alba* and *Eriophorum ang.* rather common (H1-2).
6	Distinct dark gray *Sphagnum* peat layer with *Cyperaceae. Eriophorum ang.* remains was frequent. (H5).
7	Light brown *Sphagnum* peat with *Cyperaceae. Rhynchospora alba* and *Eriophorum ang.* roots were found (H3)
8	Similar to layer no. 7, but a little darker. (H4).
9	Similar to layer no. 7. (H3).
10	Distinct dark chocolate brown *Sphagnum* peat with *Cyperaceae. Rhynchospora alba* was present. (H5).
11	Similar to layer no. 7. (H3).
12	Similar to layer no. 10. (H5).
13	Tangled, light brown *Sphagnum* peat. *Rhynchospora alba* was present (H3).
14	Dark chocoloate brown *Sphagnum* peat. Distinct upper limit. (H6).
15	Tangled, brown *Sphagnum* peat. (H5). *Eriophorum vag.* was found.

Sphagnum cuspidatum was the dominating *Sphagnum* species in the upper peat layers (0 – 27 cm b.s.), whereas *Sphagnum imbricatum* was the most frequent downwards.

Fig. 6. Peat stratigraphy and description of hollow column II.

Above the water table redoxpotentials are relatively high (50-100 mV) and below Eh are less than 50 mV. It should be noticed that the Eh values given are at the actual pH conditions. Corrected to pH 7 redoxpotentials varied between 215 and 310 mV.

Lead profile

The lead content on dry matter basis in hollow peat column II varied more than 1.5 order of a magnitude (fig. 7). The uppermost layer (0-4 cm) had a lead content between 32 and 110 μg Pb (g DM)$^{-1}$, ppm. From 4 to 8 cm the lead content reached the highest level, 150-350 ppm. However, the content of adjacent layers varied within 40%, indicating asynchronous deposition and increment rates on perennial basis. A level about 100 ppm was found in the interval from 8 to 14 cm, and below 14 cm the lead content diminished along a smooth gradient to a rather constant level of less than 10 ppm.

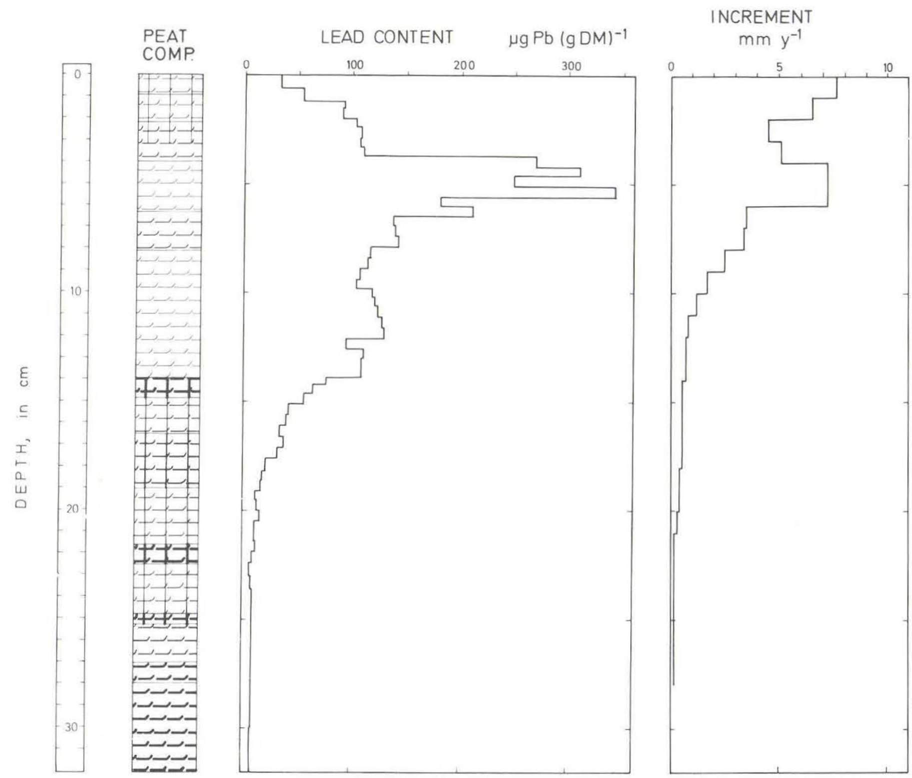


Fig. 7. Peat composition, lead content and increment profile in Draved Mose, hollow column II. Symbols of peat composition are shown in fig. 5. Increment given as 1 cm average.

Table. 1. Chemical state of lead in peat from hollow column I

Depth b.s., cm	Bulk content	collodial, dissolved or particulate (< 5 μm)	Particulate 5 - 500 μm	sorbed or chemically bound	Bulk content	collodial, dissolved or particulate (< 5 μm)	particulate 5 - 500 μm	sorbed or chemically bound
	μg (g DM)-1				‰ of total			
0 - 2	65	0.16	0.90	64	1000	2	13	985
2 - 5	112	0.18	1.14	111	1000	2	10	988
5 - 8	110	0.18	1.20	109	1000	2	11	987
8 - 12	104	0.08	0.87	103	1000	1	8	991
12 - 15	61	0.12	0.86	60	1000	2	14	984
15 - 20	26	0.07	1.16	25	1000	3	45	952
20 - 25	9.6	0.08	0.08	9.4	1000	8	8	984
25 - 30	8.8	0.06	0.06	8.7	1000	7	7	986
30 - 35	8.3	0.04	0.04	8.2	1000	5	5	990

The chemical state of lead in the peat column seemed to be correlated to the degree of humification. Lead in solution, colloidally bound or connected to particles (<5 μm) may be regarded as a semi-mobile fraction. In slightly humified peat (0-20 cm), only 1-2 ‰ of the total lead content is present in this fraction (table 1). Below 20 cm the semi-mobile fraction increased to 5-8 ‰ caused by the higher degree of humification.

The particulate bound lead fraction (5-500 μm) made up 8-14 ‰ in the uppermost 15 cm whereas below 20 cm it amounts to 5-8 ‰. In the peat layer from 15 to 20 cm the particulate lead shows an increased value, 45 ‰, probably correlated to intensive rates of humification and particle formation.

The all-dominating part, 990-984 ‰ of the total lead content, is bound or sorbed to the peat, except for the above-mentioned peat layer from 15 to 20 cm b.s.

The maximal concentration of lead found in hollow column I is less than the corresponding concentration in hollow column II (table 1, fig. 7). The areas of the subsamples in column I were 2-3 cm^2 compared to areas of 150-200 cm^2 in hollow column II. Hence the discrepancy in lead concentration can be ascribed to the statistical variation in horizontal distribution as pointed out by Aaby and Jacobsen (1979).

Pb-210 dating

The use of C-14 and Pb-210 as dating elements are based on knowledge of deposition and retention of the radionuclids in the accumulating material. Both isotopes are of non-anthropogenic origin and hence not affected by the activity of man. The C-14 is generated in the upper atmosphere by cosmic radiation of N-14, and Pb-210 is one of the daughter nuclids of U-238. The half-life of C-14 and Pb-210 are 5568 y and 22.26 y, respectively.

Investigations indicate that U-238-containing bedrocks have emitted daughter nuclids with the same ratio during a millennium at least (e.g. Marenco and Fontan 1972). The nuclear weapon let offs during the last decennia have not contributed to a significant increase in emission of U-238 daughter nuclids (Feely 1970).

Due to formation of gaseous Rn-222, which escapes the bedrock, the daughter radionuclids are uniformly distributed in the atmosphere of the originating hemisphere. Thus, a constant amount of Pb-210 has been emitted during an extended period, at least regarding localities of same latitude (Person et al. 1974). By measuring the decrease in areal content of Pb-210 in an accumulating system (sediments, peat, etc.), a calculation on a constant supply rate basis makes it possible to construct a time/depth scale.

As it is more convenient to measure the content of the α-emitting daughter, Po-210, an equilibrium between Pb-210 and Po-210 must be required. The decay of Pb-210,

β-radiation	←	Pb-210	half-life =	22.26 y
		↓		
β-radiation	←	Bi-210	half-life =	5 d
		↓		
α-radiation	←	Po-210	half-life =	138 d
		↓		
		Pb-206	stable	

shows that the equilibrium between Pb-210 and Po-210 is established very quickly. Francis et al. (1970) have shown that Pb-210 and Po-210 are in radioactive equilibrium at the time of deposition from the atmosphere.

Dating of hollow peat column II

As the Pb-210 dating procedure is a relative dating, it is necessary to use a known age-fix-point in order to obtain absolute dates. In the present study the surface of the peat column was fixed at the year 1978 as the sampling was carried out after the vegetative growth had stopped in mid-September this year.

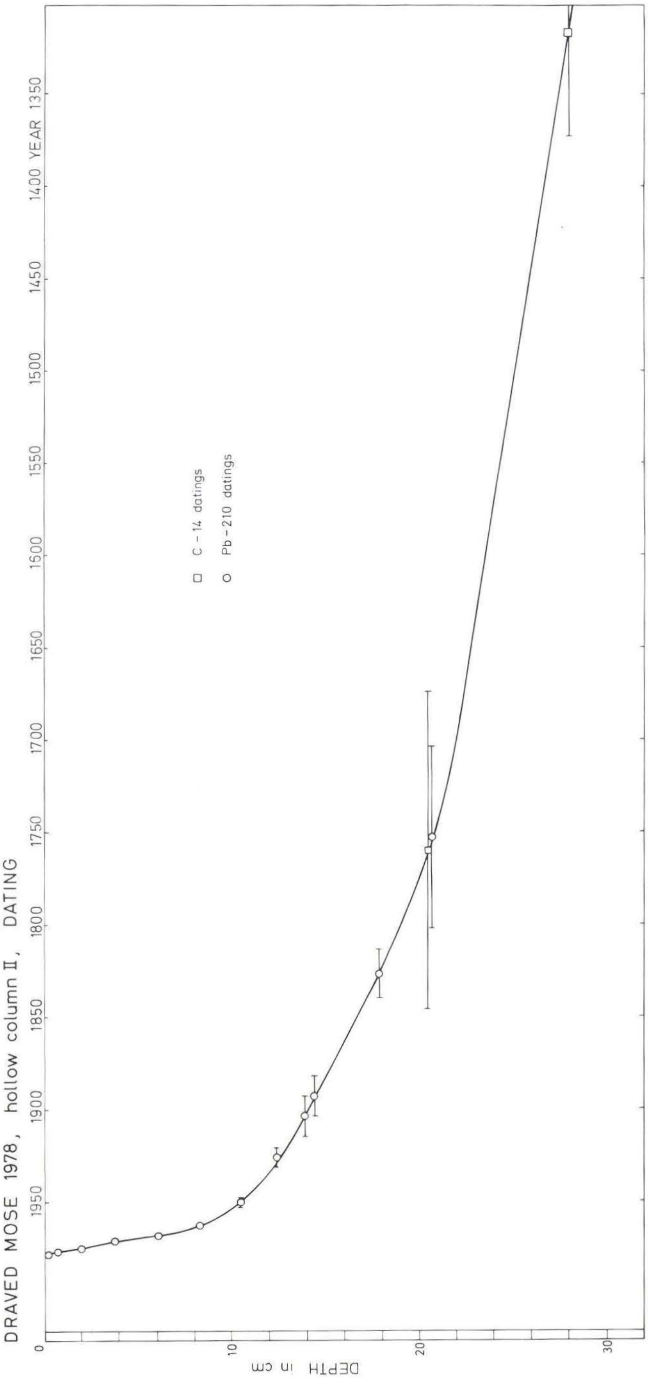


Fig. 8. Age profile in hollow column II. Horizontal bars ±SD.

Table 2. List of C-14 datings.

Location	No. Level b.s.	C-14 date before year 1950	Calendar year A.D.
Hummock	K3126 13.0-15.0 cm	330 ± 65	
		210 ± 65	
	average	270 ± 50	1605 ± 70
Hollow column I	K3127 27.0-29.0 cm	710 ± 70	
		690 ± 70	
	average	700 ± 50	1315 ± 70
Hollow column II	K 3122 19.8-21.2 cm	80 ± 110	
		170 ± 120	
	average	120 ± 75	1765 ± 90

Increased decomposition of the peat with depth and hence decreasing annual content of matrix apparently caused a higher concentration of Pb-210 in the lower part of the dating profile. As the background radiation is low (0.15 dpm (g DM)$^{-1}$), it was possible to obtain datings back to A.D. 1752 ±48 y, corresponding to 20.7 cm. This equalizes about 10 times the half-life of Pb-210.

To justify this extreme Pb-210 dating, two C-14 datings were carried out on material from 20.5 cm depth giving an average dating of A.D. 1765 ± 90 y (table 2). This mean dating is in agreement with the Pb-210 dating (fig. 8).

The applicability of the Pb-210 dating in hollow peat has been compared to datings obtained from other accumulation systems. As an ombrotrophic peat bog receives atmospheric input only, supported Pb-210 is extremely low. In contrast rather high values of supported Pb-210 are found in systems receiving considerable amounts of allochthonous material (Christensen et al. 1978; Benninger 1978). The latter author found in Long Island Sound that about 20% derived from non-atmospheric deposition (including redeposition of sediments). This caused that trustworthy datings could only be obtained 3-5 half-lives back (~100 years). Investigations in Blelham Tarn showed a disagreement between the C-14 datings and the corresponding Pb-210 datings (Pennington et al. 1976). The youngest C-14 datings obtained showed an increased age probably caused by release of organic carbon from agriculture in the watershed, (Pennington et al. 1976). The C-14 datings in Draved Mose seem reliable as no support of C-14 from a hydrological catchment area is present.

Increment rates in hollow column II

Increment rates have been calculated for each 1 cm layer to 20 cm below the surface based on the Pb-210 dates. The mean increment rate in the layer 20.5-28.0 cm (A.D. 1765-1315) is based on C-14 dates only (fig. 7).

The annual increment of the uppermost material was 7.6 mm y^{-1} and is considered to represent the annual vertical gross deposition of organic matter from the *Sphagnum* vegetation. In accordance with this, Hansen (1966) estimated an increment of *Sphagnum cuspidatum* in Draved Mose by measuring the annual internodal growth of *Drosera intermedia* at 6-14 mm y^{-1} (n=4).

Judging from the increment values a considerable compaction takes place in the uppermost part of the aerobic zone, at 0-4 cm. At 4-6 cm depth the increment values are high (7.2 mm y^{-1}) due to lower degree of humification (fig. 6). The layer at 6-8 cm differs from the previous layer by a higher degree of humification and the increment values are approx. 50% smaller. Below 8 cm the increment values decrease gradually, and from 20.5 to 28.0 cm the mean annual increment is 0.2 mm y^{-1}, or only about 3% of the original thickness of one year's deposit.

Calculation of lead deposition

Lead deposition was calculated from measurements of lead concentration, bulk density, and dating in hollow column II representing the period A.D. 1978-1580. Some premises have to be considered:

(1). The physical environments and the micro climate must have been constant during the entire period used for the calculations.

(2). Pb-210-lead must be fixed in the peat similar to C-14-carbon.

Regarding item 1, Draved Mose belongs to the oceanic type of plateau ombrotrophic peat bogs, and hence no arboreal vegetation has been present (fig. 2). Further, the formation of the hummock-hollow structure was completed more than 600 years ago at the sampling site (p. 52). Hence it is concluded that the microtopography and the vegetation has been extremely constant during this period.

As for item 2 several measurements have confirmed that lead is fixed to the hollow peat layer in which the lead is precipitated. Experiments on peat sorption capacity of heavy metals have shown an extremely high degree of fixation ability (unpublished data; Rühling and Tyler 1970). This is in agreement with the adjoining datings of C-14 and Pb-210 about A.D. 1750. According to the chemical state of lead in the peat profile (table 1), less than 2 ‰ of the total lead content is present in the semi-mobile fraction indicating that none or only a minor part of the lead is translocated vertically.

As the calculation of lead deposition rates is based on Pb-210 datings, no time depending disagreements seem possible.

Integration over time and depth using a variable discrete time step is chosen to minimize the uncertainty of the calculations. As the annual increment decreased by a factor 35 from the top to the bottom of the column (fig.7), the time steps used were 50 years during 1600-1700, 20 years during 1700-1900, 10 years during 1900-1950, and 5 years after A.D. 1950 (fig. 9).

The lead deposition during the period A.D. 1600-1800 seems to have been rather constant, about 0.5 mg Pb $m^{-2}y^{-1}$. During A.D. 1800-1900 the deposition rate increased and reached a value of 5 mg Pb $m^{-2}y^{-1}$ around the turn of the 20 th century after which a rapid elevation in lead deposition took place. From A.D. 1900 to A.D. 1950 the rate more than doubled and reached a level of about 15 mg Pb $m^{-2}y^{-1}$. An enormous escalation took place during the sixties, to approx. 60 mg Pb $m^{-2}y^{-1}$, and the deposition seems to have stagnated or even decreased through the seventies to a level less than 50 mg Pb $m^{-2}y^{-1}$.

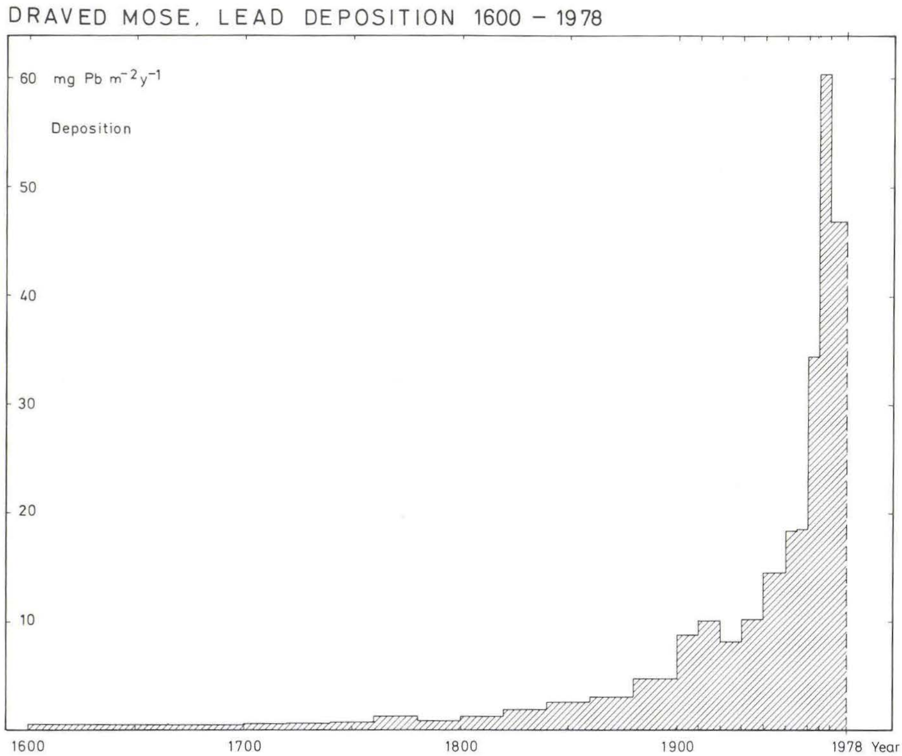


Fig. 9. Lead deposition in hollow column II, Draved Mose A.D. 1600-1978.

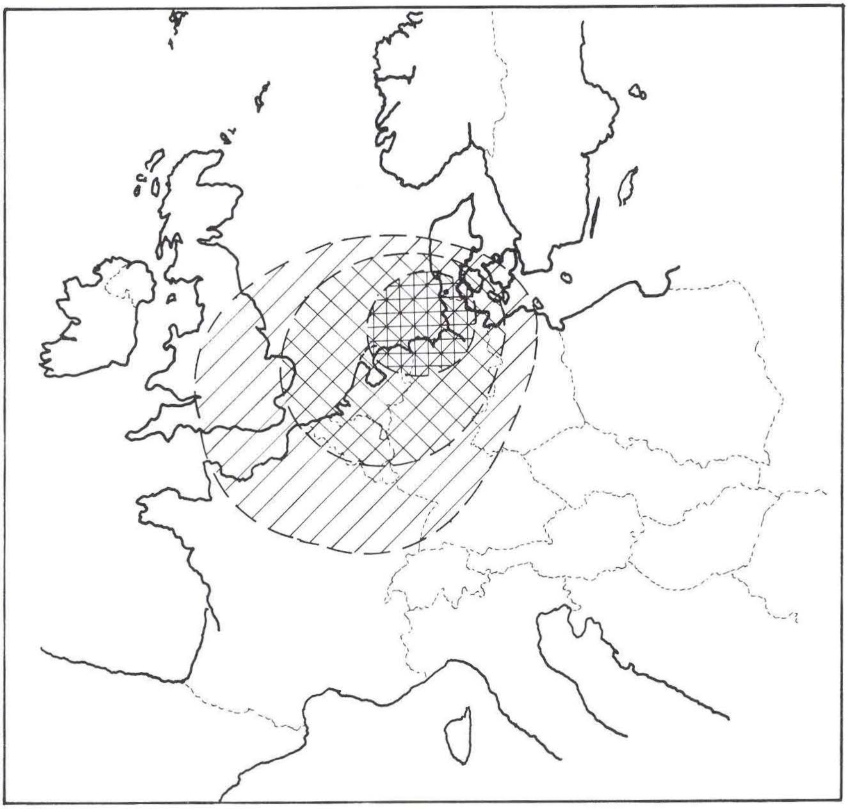


Fig. 10. Emission areas for airborne lead found in Draved Mose. Calculations are based on the seasonal variation of wind direction, wind frequency and lead deposition. Intensity of shading corresponds to the deposition probability in Draved Mose.

The vicinity of Draved Mose has not changed radically during the last centuries except for an intensified farmland use giving an increased deposition of soil dust during the last century. As shown by Aaby and Jacobsen (1979) the annual input of soil dust does not influence the measured lead deposition values markedly. The localization only 20 km from the North Sea and far from main roads and industrial areas means that mainly regional changes in air pollution have affected the development in lead deposition in Draved Mose.

The most frequent wind direction in the area is southwest. Based on seasonal variations of wind direction, wind frequency, and lead deposition (Hovmand 1977), a map of emission areas was calculated (fig. 10). Investigations of airborne transport of mildew conidia (Hermansen et al. 1974; Hermansen and Stix 1974) seem to confirm the calculated emission areas. Western Germany, The Nether-

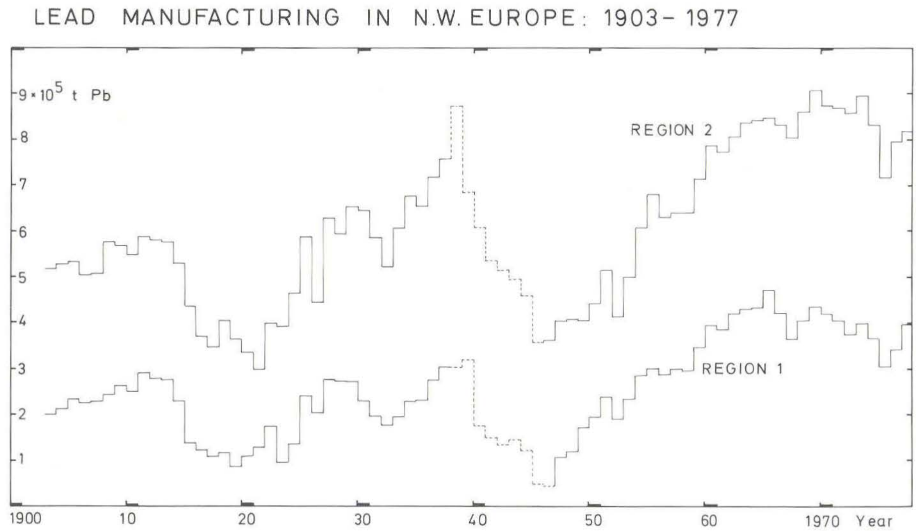


Fig. 11. Lead manufacture in selected areas of N-W Europe. Region I: Germany, Holland and Belgium. Region 2: Germany, Holland, Belgium, France and England.
Levels drawn with dotted line indicate calculated manufacture figures.

lands, Belgium, Northern France and Southwest England thus seem to be the most important source areas for airborne lead deposit at Draved Mose.

Consulting the metal statistics of N-W Europe detailed information on lead production, manufacture, and consumption has been available since the start of the 20th century (fig. 11). Primary and secondary smelters must be potential emittants. The lead manufacture industry has developed since A.D. 1700. During the 19th century the lead manufacturing was concentrated in industrial centres in Germany, Belgium, France and England. Consequently, a long-distance dispersal of air pollution was introduced, and a close relation between lead manufacture and emission must be expected.

As shown in fig. 9 and fig. 11 a nearly synchronous development of lead manufacture in Germany, France, Benelux and England and lead deposition in Draved Mose is found up to A.D. 1950. Even the decline in lead manufacture during the industrial depression during 1915-1925 seems to be reflected in the deposition rate.

Since 1950 the deposition rate increased enormously. This does not correspond to a parallel rise in the activity of lead manufacture, but may be explained by the introduction of tetraethyl-lead as an antiknocking agent in high octane petrol (fig. 12). Based on the curves in figs. 9 and 11 it is supposed that approx 70 % of the lead deposited on Draved Mose derives from alkyl-lead.

It has been pointed out that the use of coal and alkyl-lead petrol contributed by

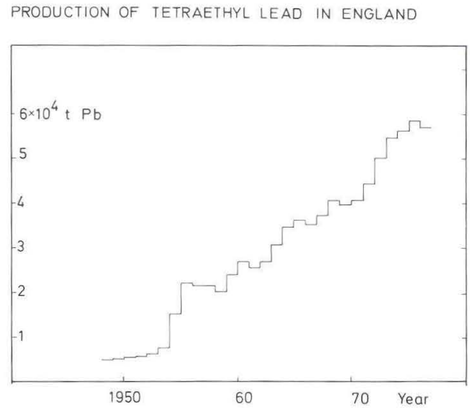


Fig. 12. The production of tetraethyl-lead (antiknocking agent) in England, 1948-1976.

the same amounts to lead emission (Jaworowski 1967). Coal burning contributes to lead emission, but neither statistic correlation between coal consumption and the measured increase in lead emission nor calculation of lead budgets in coal burning processes (Murozumi et al. 1969) would seem to support this suggestion of Jaworowski. Furthermore, airborne lead from coal burning is believed to be associated to »large-particle fractions« and consequently not dispersed over long distances.

An anthropogenic lead increase of 100 times the natural background deposition originating from earth-dust, vulcanic activity, and seaspray seems to agree with the results obtained from the inland ice of Greenland. Murozumi et al. (1969) found an elevation in lead concentration of two orders of magnitude from A.D. 1750 to A.D. 1965.

The absolute annual deposition of lead in Draved Mose is very high compared to measurements on bulk precipitation trapped in rain gauges. Hovmand (1973 and 1976) found values between 7 and 20 mg Pb $m^{-2}y^{-1}$ or 3-8 times lower than results obtained in this investigation (50-60 mg Pb $m^{-2}y^{-1}$).

As mentioned by Hovmand (1976) the rain collectors disregard deposition due to impaction and from aerosols. Flyger et al. (1976) found that lead from petrol engine exhaustion is associated with particles less than 0.5 μm. Consequently, airborne exhaustion particles are non-sedimentary. The most important deposition mechanisms are considered to be rain-out, drop nucleation, and filtration.

Groet (1976) has measured deposition rates as high as 43 mg Pb $m^{-2}y^{-1}$ in woodland areas by analysing the lead content in *Leucobryum* carpets. He found accordingly a very high regional deposition level, corresponding to the present investigation.

Discussion and conclusion

Ombrotrophic peat bogs have obvious advantages as recorders of past and present deposition rates. It is possible to select sites which have had an extremely stable biotic and physical environment during extended periods. Influx of allochthonous organic matter and bioturbation are insignificant. Finally, the deposited material can be dated with high accuracy.

The hollow areas are preferable to hummock areas because of less complexity in the hydrology, the biological structure, and the chemical processes. The water table is generally located close to the hollow surface and the peat is saturated most of the year. Accordingly, the »wash-down« or »rain-down« effect is much smaller than in hummock areas. The structure of the vegetation may influence the deposition efficiency; in hollows the dense structured *Sphagnum* carpet favours the immediate retention of the precipitate.

The hummocks are dominated partly by vascular plants with roots penetrating the aerobic zone to a depth of 20-25 cm and partly by *Sphagnum* species which derive their nutrients from the uppermost 2-3 cm. In contrast, a *Sphagnum* vegetation dominates the hollow areas, and the sparse vascular plants have superficial roots only. Secondary chemical changes caused by selective uptake from peat layers of different ages may be of some importance in hummock peat whereas these changes are negligible in hollow peat because the upper peat layers represent a short time span only.

Small organic particles (< 1 μm) may be translocated in peat and function as carriers of chemical compounds. Hollow peat is only moderately disintegrated having a small particulate fraction <1 μm, and the »wash-down« effect is supposed to be insignificant. The disintegration and formation of humus particles are more intensive in the hummock peat, and some translocation of elements may appear.

The lead deposition rates obtained from hollow column II have been compared with data from another hollow on the bog (Aaby and Jacobsen 1979). The mean deposition rate in hollow column II (47 mg Pb $m^{-2}y^{-1}$; A.D. 1970-1978) is within the variation found in *Sphagnum magellanicum* patches growing on hummocks in 1973 (41 ± 10 mg Pb $m^{-2}y^{-1}$; n=9). The cumulative lead content (A.D. 1605-1978) from hummock I and hollow II is 2000 mg Pb m^{-2} and 2200 mg Pb m^{-2}, respectively. Aaby and Jacobsen (1979) reported a corresponding lead content (A.D. 1530-1973) of 3200 mg Pb m^{-2} and 2200 mg Pb m^{-2}. These results indicate no general difference in deposition efficiency in hummock and hollow areas.

Thus, it is concluded that the annual deposition values from hollow column II are representative of the bog and may be considered the general background deposition rate in southwest Denmark and Schleswig, at least in areas of similar topo-climatic conditions (e.g. pastures, meadows and moorlands).

It is essential for the interpretation of the lead profile that a time/depth scale is established, and that the concentrations are corrected for changes in bulk density. Sillanpää (1972) concluded based on concentration curves only, cit. »The concentration of trace elements (including Pb) in the surface of the peat soils can be explained as a result of elementlifting activity of the most recent generations of plant«; but the results might as well be explained by the supply of lead from the atmosphere, as pointed out by Pakarinen and Tolonen (1977). These authors in turn claim that a concentration maximum found below the surface is indicative of leaching. This might, however, be a consequence of changes in bulk density and increment rates as demonstrated in this study (see figs. 7 and 9).

The lead profile from a hollow column sampled in Store Mosse, Småland, Sweden (Damman 1978) resembles the lead profile from Draved Mose. Unfortunately, Damman has not dated the material and thus, the two profiles cannot be compared further. Based on the concentration profile and budget considerations, Damman states that the lead has been removed almost completely from the anaerobic zone. However, the data reported might as well be explained by recent increased atmospheric input of lead. In addition, the leaching mechanism claimed to be active seems to be unrealistic.

Based on the lead concentrations in surface moss samples (including *Sphagnum*) from different parts of N-W Eruope, a regional deposition pattern has been established (Rühling and Tyler 1971; Hvatum 1972; Pakarinen and Tolonen 1977). The concentration level in Draved Mose is in accordance with this pattern. In addition, the lead deposition rates obtained from Draved Mose have been compared with Danish data from bulk precipitation, sampled at rural stations in the period 1973-1976 (Hovmand 1977). The reported deposition rates (7.0-21 mg Pb $m^{-2}y^{-1}$) are much smaller than the mean value (47 mg Pb $m^{-2}y^{-1}$) in the same period found in the present study. As the fixation of lead in hollow *Sphagnum* tissue is evidenced, translocation can be neglected, and the high values found in the bog are attributed to natural deposition conditions. In general it is difficult to simulate deposition rates when sampling atmospheric bulk precipitation.

In the neighbouring forest, Draved Skov, Rasmussen (1977) has shown a raise in lead concentration in epiphytic mosses of 65% during the period 1951-75. As indicated by the author a development of the sampling area has taken place and accordingly, the deposition conditions have changed. An increase in lead concentration of an epiphytic moss (*Pterogonium gracile*) from Slotved Skov, N. Jutland, exceeded 150% during the period 1944 to 1976 (Johnsen and Rasmussen 1977), which is in fairly good agreement with the present investigation.

In defiance of very constant sampling areas in epiphytic and epigeic vegetation, differences and changes in exposure and environment make time-dependent comparisons less suitable than an accumulating ombrotrophic system.

Conclusively, ombrotrophic peat bogs must be categorized as optimal recording areas for most airborne depositive materials. Furthermore, the regional deposition of long-distance dispersed lead on natural surfaces has increased by a factor 20-40 due to lead manufacture and by a factor 60-80 due to consumption of alkyllead petrol.

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Dansk sammendrag

En forbedret Pb-210 dateringsmetode er blevet afprøvet på materiale fra Draved Mose i Sønderjylland. Dateringsproceduren bygger på, at et konstant nedfald af Pb-210-bly, der er en af datterradionucliderne fra U-238, har aflejret sig i mosens tørv. Derved er det muligt at bestemme tørvelagenes alder 7-10 halveringstider tilbage (150-200 år). Dette muliggør, at man kan fortsætte en kontinuert tids-dybde-skala ved hjælp af C-14-metoden tilbage til mosens dannelsestidspunkt (ca. 8000 f.Kr.).

En nøjagtig aldersbestemmelse af de yngste aflejringer i et ombrotroft system åbner hidtidig ukendte perspektiver for en beskrivelse af industrialiseringens udvikling op til i dag.

I nærværende arbejde er blynedfaldet over den sydvestlige del af Danmark gennem de sidste 600 år blevet beskrevet i detaljer. Fra 1300 e.Kr. til op i 1700-tallet var det årlige nedfald gennemsnitlig 0,5 mg Pb m^{-2}, hovedsagelig stammende fra jord- og havstøv. Herefter skete der en langsom stigning til starten af det 20. århundrede, hvorefter blynedfladet steg kraftigt, dog med fluktuationer svarende til svingninger i blyforarbejdningen i Nordvesteuropa. Efter 1945 har man målt en ekstrem stigning i det årlige blynedfald med en foreløbig top i 1965-1970 på omkring 55 mg Pb m^{-2}. Denne stigning i efterkrigstiden, som ikke afspejler en større forarbejdning af bly eller anvendelse af kul, må tilskrives anvendelsen af tetraethyl-bly som superbensinadditiv. Skønsmæssigt må benzinblyet udgøre ca. 70% af det totale blynedfald, mens bly kommende direkte fra industri andrager ca. 30%.

Endvidere er den kontinuerte aldersbestemmelse blevet anvendt til en detaljeret beskrivelse af pålejringshastighederne.

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