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Lead-isotope ratio measurements on hummock and hollow peat from Detour Lake area, Ontario

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Abstract: Lead-isotope ratios determined for peat from a hummock and hollow sequence in a peatland near Detour Lake in northeastern Ontario are variable (^{206}Pb/^{207}Pb of 1.14 to 1.27 in peat and 1.17 to 1.19 in till) and indicate input of Pb from different sources. Although the Pb-isotope ratios show a pattern of systematic decrease during the last 100 years (^{206}Pb/^{207}Pb from 1.21 to 1.14), there is not a corresponding pattern of systematic change in Pb abundances. The Pb-isotope data, along with the Pb and Sc abundance data, from the hummock samples are best explained by Pb inputs from anthropogenic activities. Highest Pb-isotope ratios (^{206}Pb/^{207}Pb of 1.269) are found in hollow peat formed during the xerothermic period, 6500 to 4000 BP, a time when warmer and drier conditions affected most environmental systems.

Résumé : Dans une tourbière située près du lac Detour (nord-est de l'Ontario), l'analyse isotopique du plomb effectuée sur la tourbe d'une séquence en creux et bosses révèle des rapports isotopiques variables (^{206}Pb/^{207}Pb de 1,14 à 1,27 dans la tourbe et de 1,17 à 1,19 dans le till) et des contributions de plomb de différentes sources. Bien que les rapports isotopiques du plomb présentent une diminution systématique au cours des 100 dernières années (^{206}Pb/^{207}Pb de 1,21 à 1,14), aucun changement systématique semblable n'est observé dans l'abondance de cet élément. Dans des échantillons prélevés au sein d'une bosse (monticule) de la tourbière, les données sur les isotopes du plomb, ainsi que celles sur l'abondance du plomb et du scandium s'expliquent le mieux par l'existence d'apports de plomb résultant d'activités humaines. Les rapports isotopiques du plomb les plus élevés (^{206}Pb/^{207}Pb de 1,269) ont été mesurés dans la tourbe formée au cours de la période xérothermique comprise entre 6 500 et 4 000 ans BP, alors que les systèmes environnementaux étaient soumis à des conditions plus chaudes et plus sèches.

INTRODUCTION

The isotopic composition of Pb has enormous potential for tracing the sources and migration patterns of heavy metals in surficial materials. Because Pb can be retained over considerable periods of time in the natural environment and environmental processes do not fractionate Pb-isotope ratios, Pb-isotope signatures can be used to fingerprint Pb derived from different sources. Lead-isotope ratios have been used to monitor the sources of heavy metals in lake sediments (Graney et al., 1995), glacial till (Bell and Franklin, 1993; Bell and Murton, 1995), soil (Erel et al., 1994), lichens (Carignan and Gariepy, 1995), and anthropogenic fluxes into the atmosphere (Rosman et al., 1993; Hong et al., 1994; Hurst et al., 1996).

Lead-isotope measurements on peat samples from bogs have also been used to evaluate the sources of airborne heavy metals into the natural environment (Kettles and Bell, 1996; Shotyk et al., 1996, 1998; Mackenzie et al., 1998; Dunlap et al., 1999; Renberg et al., 2000; Weiss et al., 2002; Martinez Cortizas et al., 2002). Peatlands are repositories of atmospherically derived metals from both natural and anthropogenic sources. Those forming under weakly to strongly minerotrophic conditions in the fens are nourished to varying degrees by mineralized groundwater and surface waters, as well as airborne inputs, whereas those accumulating in ombrotrophic conditions in bogs are nourished only by atmospheric fallout (Zoltai, 1988).

Until recently, most Pb-isotope studies in peat have concentrated on peat bogs in relatively densely populated and long industrialized parts of the world (e.g. Europe). In these areas, peat has clearly documented a continuous record of atmospheric fallout, including the increase in element abundances, such as Pb and Cd, brought about by anthropogenic effects. The aim of the present study is to evaluate the Pb-isotope signatures of peat from different stratigraphic levels in a bog situated in a remote area in northeastern Ontario, and to compare these to Pb-isotope signatures of European peat and those determined for a bog in New Brunswick. Peat deposits located in remote areas have a greater potential for evaluating anthropogenic inputs into the environment, since they can be used to monitor background levels of metals away from point sources of heavy-metal pollution.

The study bog is located near Detour Lake in northeastern Ontario (Fig. 1, inset). Unlike the bogs in Europe, there was no industrialization in the nearby regions until around the beginning of the 20th century. The nearest major point sources of industrial pollution are four base-metal smelters: at Rouyn-Noranda, 225 km to the south (since 1927); at Timmins, 200 km to the southwest (since around 1970); at Sudbury, 410 km to the southeast (since 1887); and at Cobalt, 275 km to the south (since 1954). The Detour Lake bog lies along the only road in the area, which leads to a small gold mine with a small blast furnace (since 1983), 15 km to the northeast.

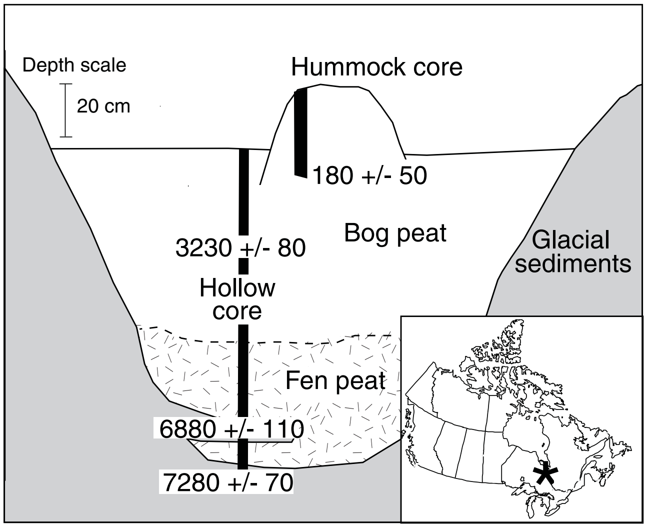


Figure 1. *Location and schematic cross-section of Detour Lake bog. Vertical exaggeration approximately 500X. Locations of hummock and hollow cores indicated by solid vertical lines.*

LEAD ISOTOPES

Lead in any mineral is a mixture of four isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. Three of these, ^{206}Pb, ^{207}Pb, and ^{208}Pb, change throughout geological time since they are the daughter products of the radioactive parents ^{238}U, ^{235}U, and ^{232}Th, respectively. The fourth isotope, ^{204}Pb, is invariant and does not change with time. Although Pb isotopes will not be discussed in detail in this paper (*see* Faure (1986) for a more detailed account), the following three points are relevant to our study:

1. If Pb is derived from a sole source with a uniform Pb-isotope composition, the Pb-isotope composition is independent of the total amount of Pb derived from the source.
2. The Pb-isotope composition of Pb derived from two or more distinct sources with different Pb-isotope ratios, will lie between the Pb-isotope ratios of the end members.
3. The isotopic composition of Pb (and other heavy isotopes) cannot be modified by biological uptake or the formation of secondary mineral phases in surficial materials (Erel et al., 1994).

PREVIOUS WORK ON DETOUR LAKE BOG

The bog location (lat. 49°59.58′N, long. 79°53.97′W) is shown in Figure 1 (*see* inset), along with a simplified cross-section of the peatland. The bog developed in a region dominated by drumlins, where peatlands are a minor component of the boreal forest landscape. The bog is underlain by calcareous silty till derived primarily from Paleozoic carbonate bedrock in the Hudson and James Bay regions (Dredge and Cowan, 1989) and metasedimentary rocks of the Canadian Shield (Ontario Geological Survey, 1991; Fig. 1).

In 1993, two cores, each 130 cm in length, were collected in close proximity from peat, along with the underlying glacial till, in a hollow (flat part of the bog) of the Detour Lake bog using a stainless steel macaulay corer (4.5 cm diameter). Another core, 35 cm long, was hand cut from an approximately 25 cm high hummock (mound of *Sphagnum* peat), located less than 1 m from the hollow coring site. All cores were wrapped in plastic film, placed in plastic containers, and refrigerated. In the laboratory, the hummock core was subsampled at 0.5 cm depth intervals, and the hollow cores at 10 cm intervals, using a stainless-steel electric knife.

Peat from one hollow core was dated at selected intervals and analyzed for macrofossils and pollen, and to determine its long-term history (Kettles et al., 2000; Fig. 2). Peat from the hummock core was dated using both radiocarbon and ^{210}Pb methods (Kettles et al., 2000; Turner and Kettles, 2000), and the hollow core was dated by radiocarbon methods. The bulk density was measured and the ash content determined from loss-on-ignition (500°C) data on subsamples from the hummock and hollow cores (Kettles et al., 2000; Fig 2).

Other subsamples from the hummock core and the second hollow core were analyzed for selected trace, minor, and major elements using inductively couple plasma–atomic emission spectroscopy (ICP-AES) methods after an aqua-regia partial extraction (Kettles et al., 2000). Scandium was analyzed using instrumental neutron activation analysis (INAA). The five duplicate splits analyzed after the aqua-regia extraction had Pb and Cd levels below or just at the detection limits, and low Cu and Zn levels (most <10 ppm). Laboratory duplicate data were plotted using Thompson-Howarth plots (Thompson and Howarth, 1978) and precision was estimated at 15% for Ca, 25% for Mg, 35% for Cu, and 40% for Zn. At 10 times the detection limit (0.1 ppm), the uncertainty for Sc was less than 5% of the reported values. The bulk density, ash content, and abundances are plotted as a function of depth in Figures 2 and 3.

Using radiocarbon dating methods, wood at the base of peat in the hollow core (118 cm) was dated at 7280 ± 70 BP (Beta-70113, AMS); peat between 92 and 100 cm at 6880 ± 110 BP (GSC-5694, conventional); and peat between 30 and 40 cm at 3230 ± 80 BP (Beta-79045, conventional). The assemblage of mosses and sedges, the presence of *Typha latifolia* (cattail) seeds, and the relatively high levels of Ca, Cu, Mg, and Zn in peat indicate minerotrophic to mesotrophic conditions between depths of 120.5 and 70 cm (Kettles et al., 2000). The sedimentary layer that occurs at depths of 100 to 116 cm, above the peat base, probably represents infilling, as there is no other evidence for a glacial readvance in the Quaternary record for this region (Dredge and Cowan, 1989; Vincent, 1989; Thorleifson et al., 1993), and no major change in drainage is reflected in the macrofossil record.

Above a depth of 70 cm, the hollow sequence is characterized by an increase in *Picea mariana* pollen, only a few seeds of *Carex*, a marked decrease in *Larix* pollen, and a prevalence of bryophyte remains, dominated by *Sphagnum magellanicum,* all indicating an evolution to ombrotrophic conditions, which are reached by a depth of about 40 cm. The change to ombrotrophic conditions in the hollow is also marked by a gradual decrease in Ca and Mg and low levels of Cd, Cu, and Zn. Peat that formed in the hollow sequence above 20 cm and in the hummock has markedly higher levels of Cd, Pb, and Zn compared to peat from depths of 20 to 40 cm, although each accumulated in an ombrotrophic environment.

In the hummock, peat collected between depths of 33 and 35 cm was dated at 180 ± 50 BP (GSC-5764, conventional), whereas ^{210}Pb determinations on 25 subsamples between the surface and a depth of 22.5 cm suggest that the peat above 22.5 cm formed in the 100 years prior to 1993.

LABORATORY METHODS

Subsamples were collected at selected intervals along the hummock core and one of the hollow cores, and analyzed for their Pb-isotope composition. Dried peat samples weighing 100 mg were digested using HNO_3 and HF. Samples were fluxed overnight, the residue taken into solution using 2.5 N HCl, and the Pb separated using a two-column extraction procedure. Lead isotopes were determined using a Finnigan-MAT 261 multicollector mass spectrometer operated in the static mode. Samples were loaded onto a rhenium filament with orthophosphoric acid and silica gel. The NBS 982 Pb standard was also measured with each magazine load of samples. Our precision is considered to be less than 0.1% of the reported ratios, based on analyses of the NBS standard over a period of at least ten years. An average fractionation factor of 0.1% per amu was applied to all of the isotope-ratio measurements. Duplicate analyses (Table 1) agree to better than 0.3 % of the reported values for the ^{206}Pb/^{204} Pb ratios. The Pb-isotope signatures of three samples that were also analyzed after leaching with 2.5 N HCl are similar to those obtained using HNO_3 and HF, suggesting either that most of the Pb in peat is contained only in an easily leachable form or that the Pb-isotope compositions in both the easily leachable and less labile fractions are similar.

Ash remaining from the 500°C burning of five hummock samples from depths of 2, 9, 10, 11, 17, and 57 cm, and two hollow samples from 34 and 95 cm, was mounted on aluminium scanning electron microscope (SEM) stubs using double-sided carbon tape. Scanning electron microscope microbeam images and x-ray spot detection chemistry were generated using a Cambridge S-360 SEM connected to an energy dispersive X-ray spectroscopy beam (Oxford-Link eXL11 EDS). Digital, tagged image file format (TIFF), back-scattered electron images were captured at various magnifications.

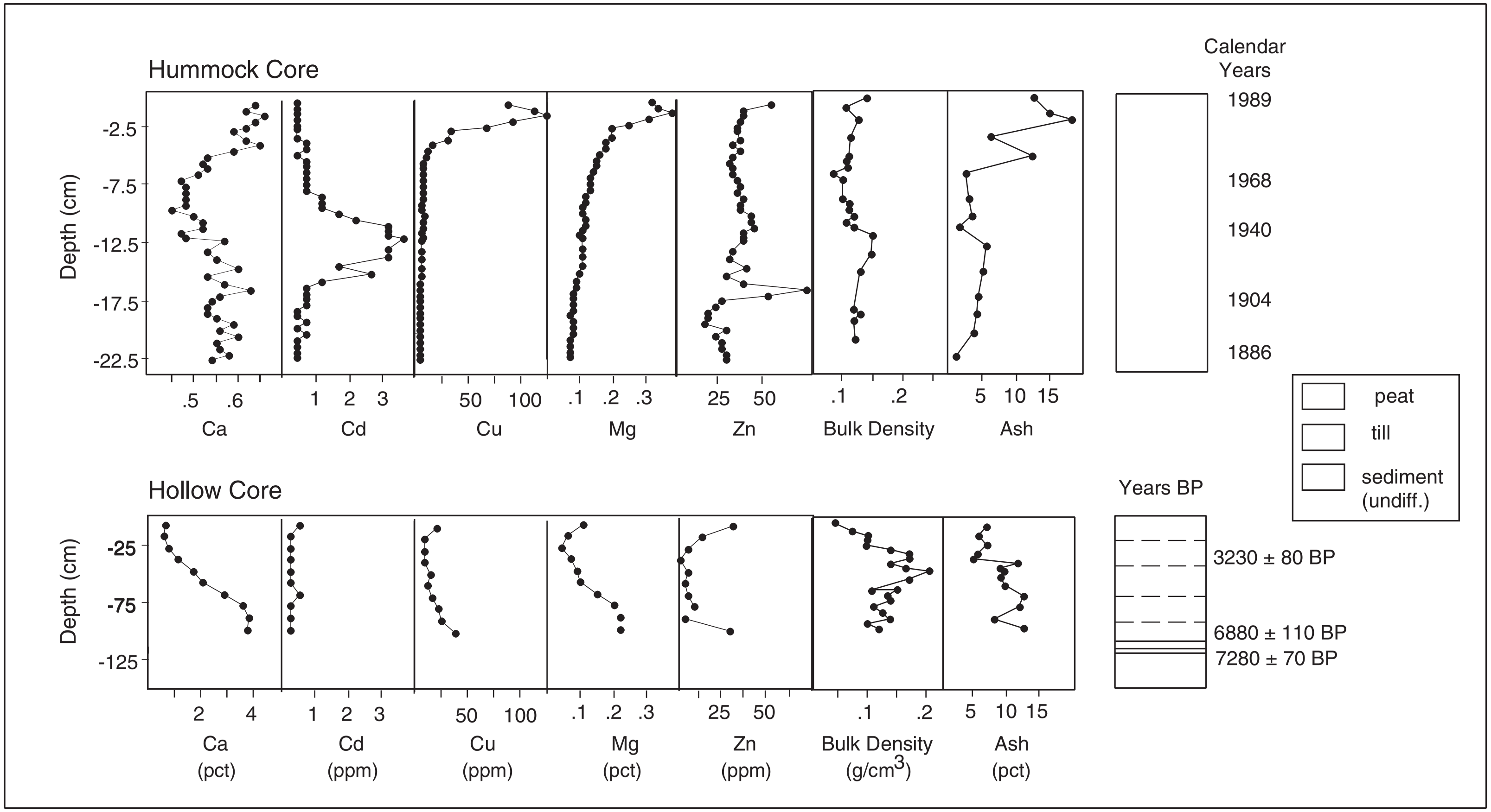


Figure 2. *Plot of distribution of selected trace elements in peat from the hummock and hollow cores, and peat ages (*after *Kettles et al., 2000; Turner and Kettles, 2000).*

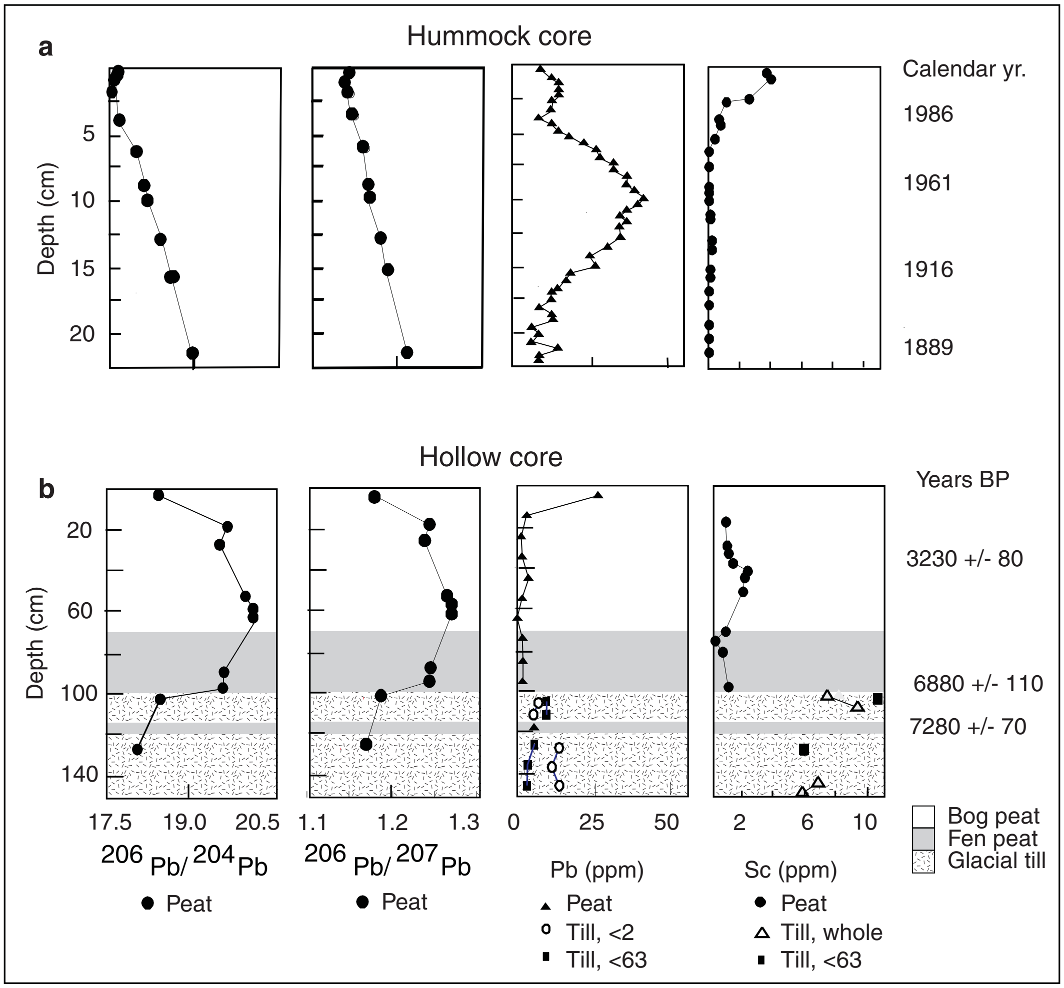


Figure 3. *Plot of ^{206}Pb/^{204}Pb, ^{206}Pb/^{207}Pb, and Pb and Sc abundances as a function of depth for* ***a)*** *the hummock core, and* ***b)*** *the hollow core. Calendar years based on ^{210}Pb dates (Turner and Kettles, 2000). Abundance of Pb determined on the <2 and <63 µm fractions and that of Sc on the <63 µm fraction.*

RESULTS

Lead-isotope data from both the hollow and the hummock core samples are given in Table 1. The ^{206}Pb/^{204}Pb ratios range from 17.54 to 20.08, the ^{207}Pb/^{204}Pb ratios from 15.36 to 15.82, and the ^{208}Pb/^{204}Pb ratios from 37.25 to 40.17. The ^{206}Pb/^{207}Pb ratios lie between 1.14 and 1.27.

In the top 22.5 cm of the hummock core, the ^{206}Pb/^{204}Pb ratios increase systematically from 17.58 at the surface to 18.96 cm, corresponding to a time interval of about 100 years BP (Fig. 3a). In the hollow core (Fig. 3b), Pb-isotope ratios increase from 18.33 at the surface to 19.59 at about 18 cm. Levels continue to increase to 20.08 at a depth of 62 cm, then decrease to lower values until a value of 18.08 is reached in the till sample collected at a depth of 127.5 cm. The profile is mimicked by the ^{206}Pb/^{207}Pb ratios.

The data are plotted on Pb-isotope ratio diagrams in Figure 4a and 4b. The data define two and possibly three groups, one corresponding to the hummock, the uppermost sample in the hollow, and the till (lowest ratios), and the other corresponding to depths of greater than 20 cm in the hollow core (higher Pb-isotope ratios). Both diagrams show a positive, linear correlation between the two Pb-isotope ratios.

In the hummock samples, iron-oxide particles of irregular and/or spherical shape were observed in the 2, 9, 10, 11, and 17 cm samples (e.g. Fig. 5), and Si spheres were noted in the 9, 10 and 17 cm samples. These particles and spheres range in diameter from about 0.002 to 0.025 mm, and they were found to contain metals in three hummock samples: Cu was found in a 0.025 mm iron-oxide particle in the 2 cm sample; Zn was found in a 0.002 mm iron-oxide sphere in the 11 cm sample (Fig. 5); and Cu and Zn were found in a 0.002 mm Si-rich

Table 1. Pb isotope data and radiocarbon dates for Detour Lake bog.

Core	Segment (cm)	Material	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{206}Pb/^{207}Pb	^{14}C Date
Hummock	0.0-1.0	peat	17.58	15.38	37.37	1.143	
Hummock	0.0-1.0 L	peat	17.74	15.46	37.63	1.147	
Hummock	2.0-2.5	peat	17.58	15.43	37.44	1.139	
Hummock	2.0-2.5D	peat	17.54	15.37	37.25	1.141	
Hummock	2.0-2.5L	peat	17.59	15.36	37.24	1.145	
Hummock	3.5-4.0	peat	17.67	15.40	37.34	1.147	
Hummock	3.5-4.0L	peat	17.77	15.41	37.43	1.153	
Hummock	6.0-6.5	peat	17.96	15.46	37.57	1.162	
Hummock	8.6-9.1	peat	18.09	15.50	37.75	1.167	
Hummock	9.6-10.1	peat	18.16	15.54	37.89	1.169	
Hummock	12.6-13.2	peat	18.38	15.58	38.15	1.180	
Hummock	15.4-15.9	peat	18.55	15.62	38.36	1.188	
Hummock	15.4-15.9D	peat	18.61	15.70	38.61	1.185	
Hummock	15.4-15.9L	peat	18.56	15.62	38.37	1.188	
Hummock	20.5-21.5	peat	18.96	15.66	38.77	1.211	
Hummock	33-35	peat					180 +/- 50 BP
Hollow	0-8	peat	18.33	15.58	38.10	1.177	
Hollow	16-20	peat	19.59	15.75	39.65	1.244	
Hollow	24-28	peat	19.46	15.73	39.60	1.237	
Hollow	30-40	peat					3230 +/-80 BP
Hollow	50-54.5	peat	19.93	15.78	39.97	1.263	
Hollow	54.5-59.5	peat	20.06	15.81	40.15	1.269	
Hollow	59.5-64	peat	20.08	15.82	40.17	1.269	
Hollow	93-99	peat	19.55	15.73	39.75	1.243	
Hollow	92-100	peat					6880 +/- 110 BP
Hollow	100-103	till	18.43	15.54	38.37	1.186	
Hollow	118	wood					7280 +/- 70 BP
Hollow	125-130	till	18.08	15.46	37.77	1.169	

Abbreviations: L, partial leach; D, duplicate sample

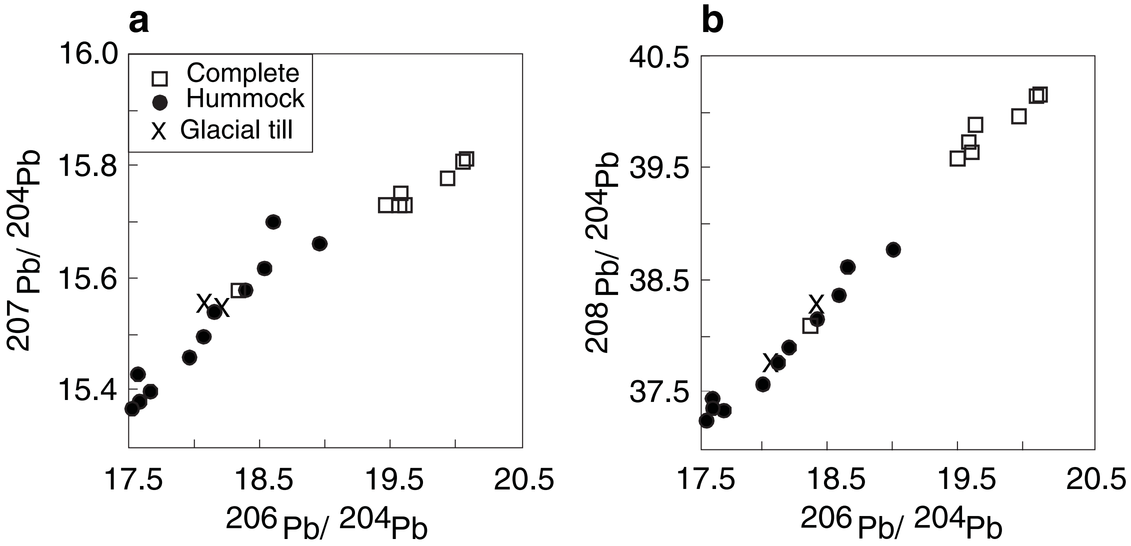


Figure 4. Plot of ***a)*** *^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb ratios, and* ***b)*** *^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb ratios. Peat data from complete core designated by open squares, and those from hummock core by solid circles. Crosses represent data from glacial till.*

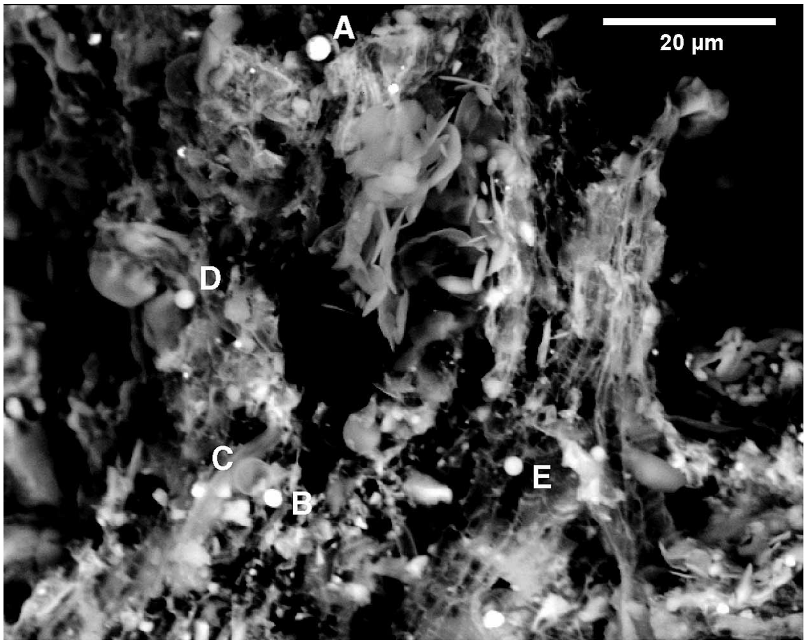


Figure 5.

Back-scattered electron image from the SEM analysis of ashed peat from a sample collected at a depth of 11 cm in the hummock. Chemical composition of the five spheres was determined using x-ray spot detection: A = Fe + O + Zn; B = Fe + O; C and D = Si; E = C (organic). Particles denoted A to D are similar to others interpreted as smelter dust in humus (Knight and Henderson, work in progress, 2002).

particle in the 17 cm sample. In the hollow samples, Zn and S was detected in a 0.015 mm, irregularly shaped fragment in the 95 cm sample.

DISCUSSION

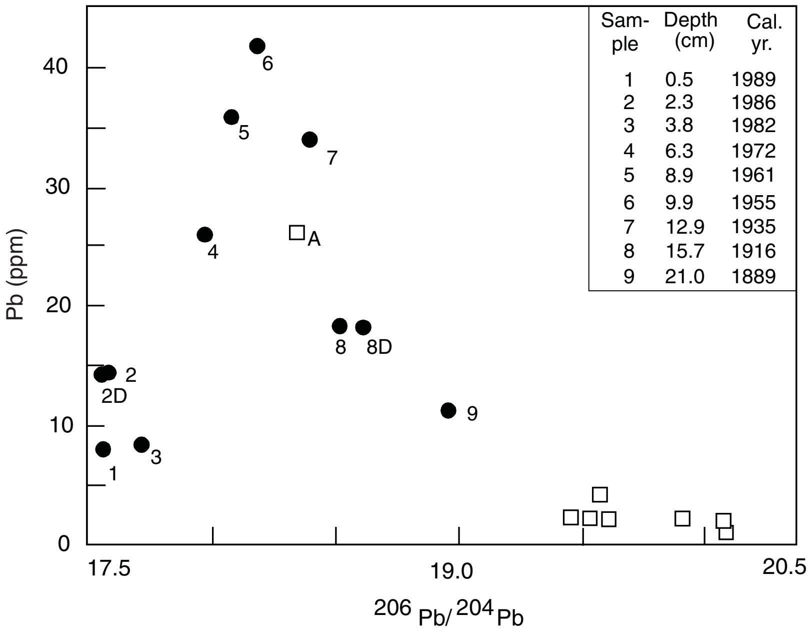
There is a wide range of $^{206}Pb/^{204}Pb$ ratios (17.75–20.08) and a variable pattern of change in the Detour Lake peat sequence that formed during the last 7000 years (Table 1; Fig. 4). The marked Pb-isotope heterogeneity shown by our data supports the finding of Shotyk et al. (1996) for samples from the Jura Mountain peat bog, indicating little vertical, downward migration of Pb. The Pb-isotope variation shown by the data lies well outside the limits of analytical uncertainty, and indicates inputs of Pb from different, isotopically distinct sources throughout the bog's history. That the isotope signatures are capable of being preserved for time intervals of less than a hundred years is shown by data from the hummock core.

In the hollow sequence, $^{206}Pb/^{204}Pb$ ratios for the basal peat that accumulated in a minerotrophic environment (depth >70 cm) are intermediate between those from the underlying till and those from the overlying peat that formed under weakly minerotrophic to ombrotrophic conditions. Peat samples from depths of between 54.5 and 65 cm have the most radiogenic Pb and have the highest content of *Pinus strobes* pollen, which normally characterizes a warmer climate, and charcoal, indicative of a higher incidence of forest fires (Kettles et al., 2000). These features suggest that Pb accumulation during these times reflected atmospheric inputs during the xerothermic or hypsithermal period (approximately 6500–4000 BP), a time of warmer, drier climatic conditions that affected most environmental systems (McAndrews et al., 1982; Payette, 1984; Ritchie, 1987). In peat that formed in the last 3200 years (depth <40 cm), the ratios decrease with decreasing depth. The $^{206}Pb/^{204}Pb$ ratio of the youngest peat sample from the hollow (depth <10 cm) lies within the range of ratios determined for peat from the hummock.

There is no relationship between Pb abundances and $^{206}Pb/^{204}Pb$ ratios in peat and the underlying glacial till (Fig. 3). In the hollow peat sequence, Pb concentrations are low in all samples collected below 10 cm and show little variation. This contrasts with the Pb-isotope composition that varies markedly over the interval 10 to 100 cm. In peat that accumulated in the hummock during the last 100 years, the isotope ratios decrease systematically with decreasing depth, whereas the total Pb abundances increase and then decrease with decreasing depth.

Figure 6 is a plot of Pb abundance against $^{206}Pb/^{204}Pb$ ratios for the Detour Lake peat samples. Marked on this are the stratigraphic sequence of the hummock peat samples indicated by numbers from 1 (youngest) to 9 (oldest). An interesting feature, and one that is not apparent from any of the other diagrams, is that the $^{206}Pb/^{204}Pb$ ratios for samples 1 to 6 from the hummock (formed between about 1990 and 1955) show a systematic increase with Pb content. For the older part of the succession (samples 7 to 9) that formed between about 1935 and 1890, the Pb-isotope ratios systematically increase, an increase that is accompanied by a decrease in Pb abundances.

In the hummock section, Pb levels are high in peat that formed as twentieth-century industrial activity in North America increased and as leaded gasoline was used (from 1923 until the early 1980s). However, when the distribution pattern of $^{206}Pb/^{204}Pb$ ratios for the hummock peat is compared to Pb and Cd abundances (*see* Fig. 2), interpretations of surface Pb enrichment become even more complicated. It seems unlikely that the isotopic composition of Pb pollutants from gasoline, only, would combine to have compositions needed to produce the regular, near-linear patterns of decrease



Sam-ple	Depth (cm)	Cal. yr.
1	0.5	1989
2	2.3	1986
3	3.8	1982
4	6.3	1972
5	8.9	1961
6	9.9	1955
7	12.9	1935
8	15.7	1916
9	21.0	1889

Figure 6.

Plot of Pb versus ^{206}Pb/^{204}Pb. Data from the hummock core are represented by solid circles, data from the hollow core by open squares. Numbers refer to stratigraphic sequence within the hummock core (1 is younger, 9 is oldest). Open square A is the uppermost of the hollow core samples. Sample 9 is the average of two determinations. D indicates duplicate analysis.

in ^{206}Pb/^{204}Pb and ^{206}Pb/^{207}Pb ratios with decreasing depth observed in the hummock. In addition, the relatively high levels of Cd associated with high levels of Pb in the same core are inconsistent with the composition of refined Pb products. The Pb that is used to manufacture tetraethyl Pb is reported as being 99.9% pure (A. Slater, Associated Octel Company, pers. comm., 1996). High levels of Cd coupled with Pb are more consistent with pollution from base-metal smelting activities. Some particles in the hummock samples detected using SEM analysis were similar to those in humus interpreted as smelter dust from near the Rouyn-Noranda smelter in Quebec (Knight and Henderson, work in progress, 2002).

Comparisons with signatures from European and eastern Canadian peat bogs

The continuous record of atmospheric Pb documented by Shotyk et al. (1996, 1998), from a peat bog in the Jura Mountains in Switzerland, covers a period of 12 370 years (Fig. 7). Using both Pb isotopes and Pb/Sc ratios, they documented ten major periods in the history of atmospheric Pb deposition and concluded that anthropogenic Pb sources have dominated atmospheric Pb emissions in Europe since 3000 BP. The Pb/Sc ratios were used by Shotyk et al. (1998), and also by Steinmann and Shotyk (1997), to establish pre-anthropogenic background values, and to evaluate the concentration of soil-derived, atmospheric aerosols.

Scandium was used as a geochemical indicator because it is widely dispersed in crustal rocks and is widely distributed in soil-derived aerosols. It is also detectable at very low abundance levels (0.1 ppm) and with high precision using INAA methods. Scandium values are shown along with Pb abundances for the Detour Lake hummock and hollow sequences in Figure 3. Comparing the Pb and Sc data from the hummock core, the abrupt increase in Pb concentration, which reaches a maximum at a depth of about 10 cm, does not correspond to any changes in Sc content, which remains relatively constant between 0.2 and 0.3 ppm. This suggests that the Pb increase with depth in the hummock section might be due to anthropogenic aerosols. In the hollow peat sequence, the increase in Sc content between depths of 40 and 60 cm is unaccompanied by corresponding changes in the Pb content, supporting a model that involves an increase in soil-derived atmospheric aerosols during the xerothermic period.

In Figure 7, a comparison is made between the Pb-isotope data from the Detour Lake peatland and the data from the Swiss bog. In general, ratios are higher in the Detour Lake hollow peat sequence than the pre-1900 peat samples from the Jura Mountain bog, and there is much more variation in ^{206}Pb/^{207}Pb ratios in peat from Detour Lake that is older than 3000 years. These differences most likely reflect the influence of mineralized groundwater on peat below 40 cm in the hollow sequence of the Detour Lake peatland. In those peat samples formed since 1890 in the Detour Lake hummock, there is a marked lowering of the Pb-isotope ratios from ^{206}Pb/^{207}Pb values of 1.18 to slightly more than 1.14. A similar trend of decrease is noted in samples collected from the Swiss bog peat that formed after the mid-1800s.

The ^{206}Pb/^{207}Pb values for the Detour Lake hummock also fall within the range of values determined for ombrotrophic peat from bogs in other parts of Europe and the United Kingdom. Peat in some Norwegian bogs formed since 1900 has ratios of 1.17, and peat formed after 1980 has values of 1.12 to 1.14 (Dunlap et al., 1999). In a study of the Scottish bogs, Mackenzie et al. (1998) determined that peat that formed around 1990 has ratios of 1.13, whereas peat from the early 1900s lies between 1.16 and 1.18. Ratios fell within the same range in another bog in Scotland in the 20 cm of peat that formed since the late 1800s. Values decreased from 1.168 at around 18 cm to 1.115 in the near-surface (Weiss et al., 2002)

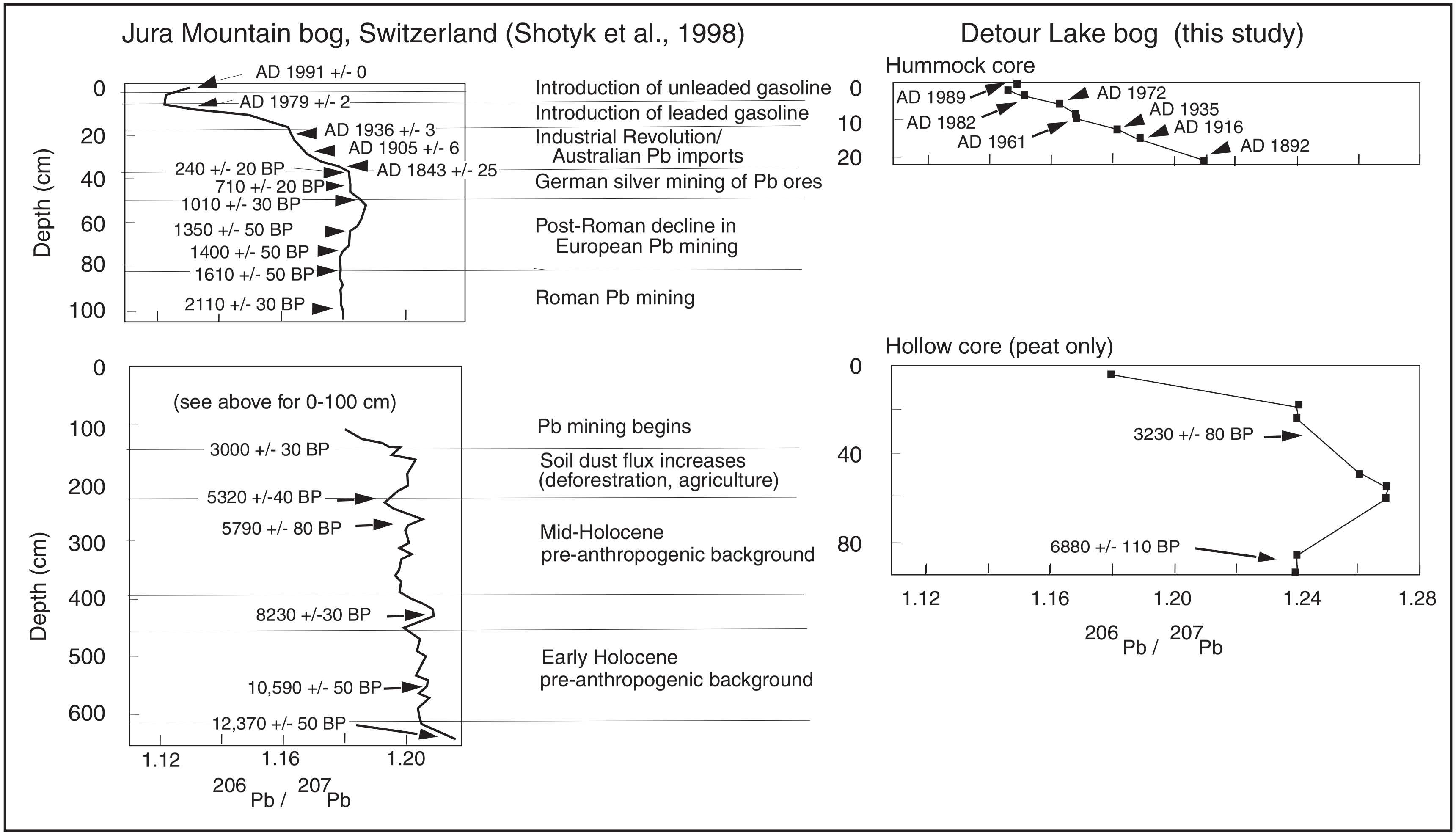


Figure 7. *Section through the Detour Lake bog and Jura Mountain bog, showing the* $^{206}Pb/^{207}Pb$ *ratios. Profiles through Jura Mountain bog excerpted with permission from Shotyk et al. (1998), © 1998 American Association for the Advancement of Science.*

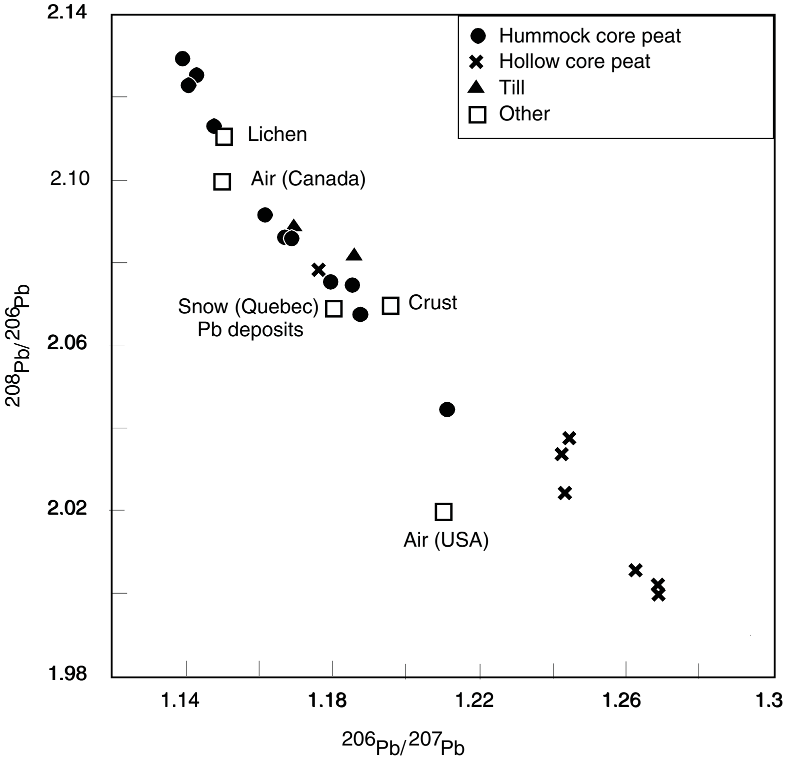


Figure 8.

Plot of ^{208}Pb/^{206}Pb versus ^{206}Pb/^{207}Pb. Also shown are some average values for Canadian Pb deposits, Canadian and American aerosols, average crustal values, and snow from four sites and lichen from three sites east of James Bay, Quebec.

and, similar to the Detour Lake hummock, the pattern of decrease was systematic. In addition, peat formed in a bog in Spain since the introduction of leaded gasoline has a ratio of 1.157, also within the range that characterizes the Detour Lake hummock (Martinez Cortizas et al., 2002).

The ^{206}Pb/^{207}Pb ratios measured in peat that formed since 1907 in the New Brunswick bog (1.177–1.199; Weiss et al., 2002) are similar to those found in peat below a depth of 9 cm in the Detour Lake hummock. However, there is a variable pattern of change in ratios in the New Brunswick peat, compared to a systematic pattern in the Detour Lake hummock. Lead in peat that formed in pre-industrial time in eastern Canada, with ratios of around 1.161, was less radiogenic than peat formed at depth under minerotrophic conditions in the Detour Lake bog.

Comparisons with atmospheric and other non-peat signatures

The isotopic findings from this study are summarized in Figure 8, in which ^{208}Pb/^{206}Pb ratios are plotted against ^{206}Pb/^{207}Pb ratios. The linear trend shown by all of our data is compared with the average estimates for continental crust (Stacey and Kramers, 1975), Canadian atmospheric Pb (Sturges and Barrie, 1987; Carignan and Gariepy, 1995), United States aerosols (Rosman et al., 1994), lichen and snow from east of James Bay (Carignan and Gariepy, 1995; Simonetti et al., 2000), and Canadian ores (Sangster et al., 2000). The youngest sample from the Detour Lake peatland has a ^{206}Pb/^{207}Pb ratio that is lower than any of the ratios from Greenland snow (Rosman et al., 1994; time period 1968–1988, weighted average ^{206}Pb/^{207}Pb of 1.16–1.18), the tropospheric Pb input over the western North Atlantic (1.19 to 1.20; Veron et al., 1992), and the anthropogenic component in sediments from the Great Lakes region (1.18–1.20; Sturges and Barrie, 1987). A sample of Pb-bearing ore from Noranda, one of the closest smelters to Detour Lake, is nonradiogenic (0.92) compared to Detour Lake peat samples (Sturges and Barrie, 1987). Snow-pack samples from 1994 and epiphytic lichens collected in 1994 at similar latitudes but east of Detour Lake, in northern Quebec, have ratios that fall within the range of those from the hummock samples but are higher than those of the surface hummock samples.

CONCLUSIONS

The large isotope variations shown by the Pb contained within the Detour Lake peat bog conclusively show that the Pb could not have been derived from a source with a single, uniform isotopic composition. During the past 7000 or more years, sources were tapped that provided Pb of quite different isotopic signatures. Lead in the lower parts of the peatland is much more radiogenic than that found in the younger peat. This pattern, we think, reflects the influence of minerotrophic groundwater and surface water, and changes in the patterns of natural soil dust deposition effected by the episode of warmer and drier climate that existed from at least 6500 to almost 4000 BP in northern Ontario. On the basis of the total Pb, Pb-isotope ratio, and Sc data, we attribute the high Pb abundances in the hummock peat to inputs from anthropogenic sources. Surface Pb-isotope ratios for the hummock peat samples are similar to those obtained for peat that formed in bogs in Europe and New Brunswick and since 1900.

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