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Cosmogenic ^{10}Be as a potential dating tool in peat

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Abstract Because ombrotrophic peat bogs receive inputs of water, nutrients, pollutants, and xerobiotic materials solely from the atmosphere, and accumulate organic matter vertically, dated peat cores can provide a historical record of deposition. We propose a novel method for accurately determining dates of peat, based on cosmogenic ^{10}Be. In a laboratory study, we document limited post-depositional mobility of atmospherically-deposited Be, a requisite for ^{10}Be dating. We provide an example of how the ^{210}Pb-dated upper portion of a peat core can be used to back-calculate a site-specific ^{10}Be deposition rate, which can then be used to estimate dates for peat throughout a core, and also discuss limitations to the application of cosmogenic ^{10}Be to the dating of peat deposits.

Keywords ^{10}Be · Beryllium · Dating · Peat · *Sphagnum*

Introduction

Since the Industrial Revolution, industrial expansion and manufacturing in the northern hemisphere has resulted in large scale loading of contaminants to the environment. Records of atmospheric contamination often can be stored in undisturbed sediments, thus providing powerful tools with which to assess the magnitude and history, both regionally and globally, of contaminant deposition. *Sphagnum*-dominated bogs are ideal for geochemical monitoring of atmospheric constituents since they are ombrotrophic, deriving their water, nutrients, pollutants, and xenobiotic materials solely from the atmosphere (Turetsky et al. 2004; Wieder et al. 2009). *Sphagnum* mosses grow apically from densely packed capitula composed of immature stems, while dying at the base (Clymo 1984). Peat accumulates when the rate of net primary production exceeds that of decomposition to such an extent that a vertically aggrading deposit of organic matter results. Therefore, moving downward throughout a peat profile, concentrations of contaminants that remain immobile in peat after deposition, reflect atmospheric loadings through time.

Deeper peat is older than shallower peat, but because of ongoing decomposition within a peat deposit, depth is not linearly related to age (Clymo et al. 1990). Relatively young layers of a peat deposit can be dated accurately using the ^{210}Pb approach. However, two factors limit the use of ^{210}Pb to dates no older than about 150 years. First, ^{210}Pb has a half-life of 22.6 years, such that peat that was at the surface of a deposit 150 years ago (6.6 half-lives) has only 1% of the ^{210}Pb activity of peat at the surface. Second, because ^{210}Pb activities decrease with depth, counting errors associated with peat from individual

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samples within a peat core increase with depth. In calculating dates based on ^{210}Pb, uncertainties are based on counting errors associated with each depth interval, and these errors are propagated from the surface downward (date uncertainties associated with a given depth incorporate the uncertainties of all of the depth intervals above). Thus, uncertainties associated with each date estimate increase with depth (cf. Turetsky et al. 2004).

Traditional ^{14}C dating is a reliable technique for dating individual peat samples that are older than about 300 years. For more recently deposited peat, ^{14}C activities in contiguous peat samples within a core from the surface downward have been used to estimate dates using the wiggle-matching approach. Wiggle-matching is costly and does not always provide unambiguous dates (cf. Turetsky et al. 2004).

Here we propose a novel dating method based on applying the constant rate of supply model commonly used in ^{210}Pb dating (Appleby and Oldfield 1978) to the vertical distributions of atmospherically deposited ^{10}Be in peat cores. The cosmogenic nuclide ^{10}Be ($t_{1/2} = 1.387 \pm 0.012 \times 10^6$ year; Korschinek et al. 2010) is produced in the stratosphere and troposphere mostly through nitrogen and oxygen spallation by cosmic radiation (Lal and Peters 1967). Within 1–2 years after production, ^{10}Be becomes scavenged by atmospheric aerosols or particulates and is removed from the atmosphere mainly through precipitation (Raisbeck et al. 1981; McHargue and Damon 1991). The proposed novel dating method invokes two assumptions: that the deposited ^{10}Be is immobile in peat, and that the site-specific rate of ^{10}Be deposition to the surface of a particular peat deposit, averaged over several years, is constant. We show that atmospherically deposited Be is quite immobile in peat. We also provide an example of how the ^{210}Pb-dated portion of a peat core can be used to back-calculate a site-specific ^{10}Be deposition rate, and then use that deposition rate to estimate dates for peat.

Methods

Eighteen peat cores were collected using PVC pipe (10-cm diameter, 40-cm tall) from a boreal bog near Calling Lake, Alberta (55°55′ N, 113°40′ W). Surface vegetation in all cores consisted predominantly of *Sphagnum fuscum*. Vascular plants were avoided during core collection. Upon return to the laboratory at Villanova University, six cores were randomly assigned to one of three water table position treatments: high (3 cm below the peat surface), low (15 cm below the peat surface), and fluctuating (alternating between high and low, with water table position changed weekly). Cores were watered every other day, applying 50 ml of synthetic rain water (Table 1) using a squirt bottle. For each water table position treatment, 2 cores received only synthetic rain water (controls) and 4 cores received synthetic rain water with added Be. Additions of Be were made every other watering day over a 20 day period such that over the course of 40 days, 10 additions were made, adding a total of 4 mg of soluble Be to each core (2 mg of Be as $Be(NO_3)_2$; 2 mg of Be as BeO). After the last Be addition, all cores were watered every other day with synthetic rain water over an additional 36 day period, maintaining the appropriate water table position treatments for each core.

Our experimental design was similar to that used in a previous study of Pb mobility in peat (Vile et al. 1999), which also used an experimental rainfall intensity of 50 ml every 2 days (corresponding to a rainfall rate of 3.2 mm d^{-1}). Annual precipitation at Athabasca, Alberta is 503.7 mm (Canadian Climate Normals 1971–2000), with a distinct summer peak (55.5, 84.8, and 65 mm in June, July, and August, respectively). Although our experimental rainfall rate

Table 1 Recipe for stock (×1,000) synthetic rain water, simulating 1996 concentrations in wet deposition at Esther, Alberta (site #CAPM80812A, 51°40′ N, 110°12′ W; Jon Maybury, NatChem, pers. comm.): pH, 5.06; and in concentrations of μequiv. L^{-1}, Ca^{2+}, 8.5; Mg^{2+}, 3.2; Na^+, 0.9; K^+, 0.8; NH_4^+, 19.0; NO_3^-, 15.5, SO_4^-, 17.9; HCO_3^-, 6.9 (HCO_3^- estimated assuming that the calculated anion deficit is contributed entirely by HCO_3^-

	Quantity (1,000 ml dw q.s.)
$(NH_4)_2SO_4$	0.5967 g
NH_4HCO_3	0.5455 g
$Ca(NO_3)_2$	0.6974 g
$Mg(NO_3)_2{\cdot}2H_2O$	0.2950 g
$NaNO_3$	0.0765 g
KNO_3	0.0809 g
NH_4NO_3	0.1521 g
NH_4Cl	0.0588 g
H_2SO_4 (conc.)	244 μl

was similar to average July rainfall at Athabasca (2.7 mm d^{-1}), as in the Vile et al. (1999) study, we applied the 50 ml of simulated rainfall to cores over about 1 min, producing an exceptional rainfall intensity equivalent to 38 cm h^{-1}.

At the end of the study, cores were frozen solid and then sectioned into 2-cm depth increments using a band saw. Low and fluctuating water table cores were sectioned to a depth of 20 cm, while high water table cores were sectioned to a depth of 8 cm. Cores were oven-dried at 65°C and ground using a Tecator Cyclotec sample mill. Duplicate or triplicate subsamples (0.5 g each) from each depth interval were acid digested using HNO_3, HCl, and H_2O_2 (EPA 1999). Digest solutions were analyzed for Be concentrations by Phase Separation Science, Inc. (Baltimore, MD) using inductively coupled plasma emission spectrometry.

To examine the potential of ^{10}Be as a dating method, we used material from a peat core collected from an ombrotrophic bog near Patuanak, Saskatchewan that had already been dated using ^{210}Pb (Turetsky et al. 2007). Dried ground peat from each 3-cm depth increment in the top 48 cm of the peat column was analyzed for ^{10}Be using Accelerator Mass Spectrometry (AMS), and dates for peat from the 48–51, 54–57, and 60–63 depth intervals were determined by AMS ^{14}C analysis, all at Purdue University's PRIME Laboratory. Sample processing and analysis methodologies are described in Sharma et al. (2000).

Results and discussion

In all sections from the control cores (no Be additions), Be concentrations were below the limits of detection (5 μg Be l^{-1} in digest solutions; 0.5 μg Be g^{-1} dry peat). Overall, recovery of the added Be was about 80% of what was added to the cores (3.2 out of 4 mg); differences between added and recovered Be were significant only for the fluctuating water table treatment ($p = 0.044$, 0.066 and 0.054 for fluctuating, low and high water table treatments, respectively; Student's t tests). The vertical distribution of Be (Fig. 1) indicated limited mobility, with concentrations that were highest in the top 2 cm section and decreased markedly with depth. On average, 91, 85, and 99% of the recovered Be was

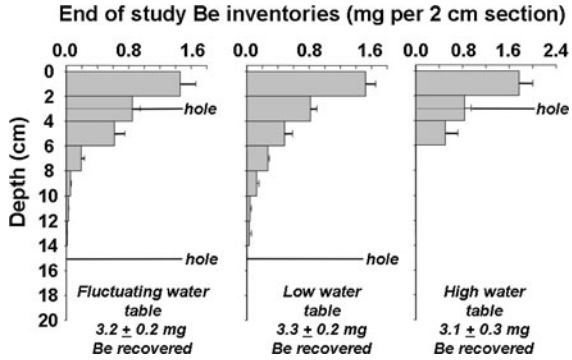

Fig. 1 Depth distributions of Be in treated peat cores at the end of the laboratory Be mobility experiment. Values for each bar and for total Be recovery are means ± standard errors ($n = 4$). Positions of the holes in the PVC pipes used to control water table position are shown

located within the top 6 cm of the cores in the fluctuating, low, and high water table treatments. The vertical distribution of Be at the end of the study mirrors that obtained for Pb in a similarly conducted laboratory assessment of Pb mobility in peat (Vile et al. 1999). As in the Vile et al. (1999) study, we suggest that the very high simulated rainfall intensity (equivalent to 38 cm h^{-1}) may have allowed downward penetration of added Be into the peat to an extent that is greater than would be expected in natural field rain events. We interpret the vertical distributions of added Be (Fig. 1) as supportive of limited post-depositional mobility of atmospherically deposited Be.

Inventories of ^{10}Be in mineral soils have been used as the basis for dating over thousands of years (e.g., Egli et al. 2010; Willenbring and von Blanckenburg 2010). In these applications, the ^{10}Be deposition rate must be either measured or more commonly estimated through models, and corrections must be made for the in situ cosmogenic production of ^{10}Be in quartz minerals in soil, losses of ^{10}Be from the soil via erosion, and radioactive decay of ^{10}Be. These corrections are not applicable to the potential use of ^{10}Be for dating of recently accumulated bog peat. Bog peat represents a vertically accumulating organic soil, separated from mineral soils and mineral-rich groundwater and/or surface water, and hence bog peat is devoid of quartz minerals. Except in severely disturbed situations, bog peat is not susceptible to erosional losses, and if ^{10}Be is to be used for dating deposits that have accumulated over centuries, the

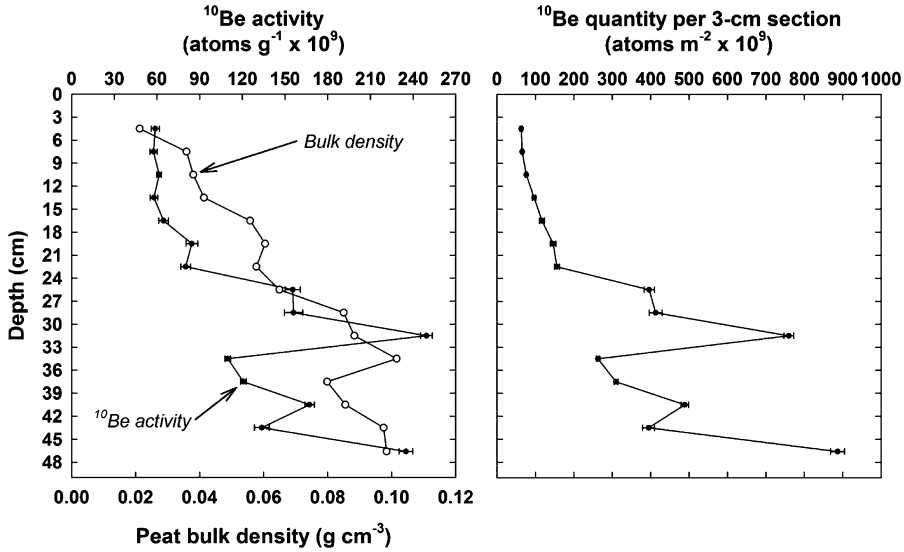

Fig. 2 Peat bulk density, ^{10}Be activity and ^{10}Be quantities as a function of depth; error bars associated with the ^{10}Be data indicate uncertainties

long half-life of ^{10}Be precludes the need to correct for radioactive decay.

We suggest that ^{210}Pb dating of peat can form the basis for estimating a site-specific atmospheric ^{10}Be deposition rate. We obtained ^{10}Be data for a core that we had previously ^{210}Pb-dated (Turetsky et al. 2007). For this core, both peat bulk densities and ^{10}Be activities generally increased with depth (Fig. 2), patterns that would be expected given ongoing decomposition of peat, a relatively constant rate of ^{10}Be deposition to the peat surface, and limited post-depositional ^{10}Be mobility. The 3–6 cm depth section of this core represented 4.62 ± 0.45 year of accumulation (based on ^{210}Pb dating), had a ^{10}Be concentration of 58.8 ± 2.8 × 10^9 atoms g^{-1}, and a bulk density of 0.036 g/cm^3, from which we calculated an atmospheric ^{10}Be deposition rate of 4.3 ± 0.5 atoms dm^{-1} s^{-1}. McHargue and Damon (1991) report a global range of atmospheric ^{10}Be deposition of 1.5–4.5 atoms dm^{-1} s^{-1}. Our value is higher than atmospheric ^{10}Be deposition for northern Alberta (55° N latitude) estimated through modelling efforts as about 2.5 atoms dm^{-1} s^{-1} (Field et al. 2006; Heikkilä et al. 2008). We used the section of peat immediately beneath the capitula of the *S. fuscum* canopy to estimate the ^{10}Be deposition rate because the apical portion of the *Sphagnum* plant, the capitulum, is the meristematic region that produces new cells; plant growth and hence vertical accumulation of the peat deposit occurs beneath the capitulum.

By dividing the total quantity of ^{10}Be in each core section (atoms m^{-2}), by our calculated ^{10}Be deposition rate (13.71 ± 1.48 × 10^9 atoms m^{-2} a^{-1}), we calculated the number of years of peat accumulation represented by each section, propagating the uncertainty of these values with increasing depth. This approach applies the constant rate of supply model used for ^{210}Pb dating (Appleby and Oldfield 1978) to ^{10}Be deposition and accumulation in the peat profile.

Our ^{10}Be dates are in good agreement with our ^{210}Pb dates (Fig. 3), especially in the top 24 cm of the peat core. Visual extrapolation of both the ^{210}Pb and the ^{10}Be date curves suggests good agreement with the AMS ^{14}C dates of deeper core sections, but we note that the uncertainties associated with the AMS ^{14}C dates are large.

An unresolved issue with respect to the potential use of ^{10}Be as a way of dating peat is that ^{10}Be production in the atmosphere and deposition to the earth's surface are known to vary over different time scales. Ice core data have shown that from the Maunder Minimum (1645–1715) to the present, ^{10}Be deposition has decreased (by an estimated 25% at 55° N latitude), as a consequence of increasing solar activity and to a lesser extent changing climate (Heikkilä et al. 2008). When our ^{10}Be dates were recalculated assuming that in 1715 ^{10}Be deposition was 25% higher than at present and has declined linearly since 1715, the ^{10}Be dates for a given depth were younger, such that a slightly better agreement with the ^{210}Pb dates was obtained (Fig. 3).

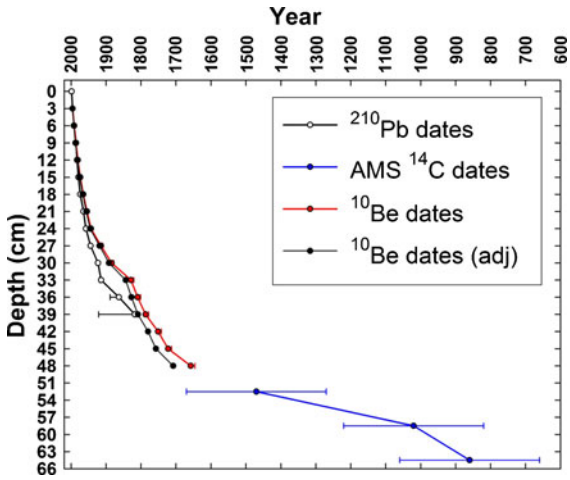

Fig. 3 Dating results from a single peat core from a peat bog neat Patuanak, Saskatchewan, Canada. ^{210}Pb dates have been published (Turetsky et al. 2007), AMS ^{14}C dates (and uncertainties) and ^{10}Be activities were determined at the Purdue University PRIME Laboratory (Sharma et al. 2000); uncertainties are shown by bars extending to the left for ^{210}Pb dates and to the right for ^{10}Be dates; bars often are obscured by the plotted points. See text for the approach to calculating ^{10}Be dates; ^{10}Be dates (adj) show results from calculation of dates assuming that at the end of the Maunder Minimum (AD 1715), ^{10}Be deposition was 25% higher than it is today and has been declining linearly since 1715

There is evidence that ^{10}Be production in the atmosphere and subsequent deposition not only are linked to 11-year solar activity cycles (cf. McHargue and Damon 1991; Beer 2000), but also have varied considerably throughout the Holocene (Vonmoos et al. 2006). Our goals in this contribution have been to demonstrate limited post-depositional mobility of ^{10}Be in *S. fuscum*-derived bog peat and to suggest that ^{10}Be may have potential for the dating of vertically accumulating *Sphagnum* bog peat deposits, using ^{210}Pb dating to estimate current ^{10}Be deposition rates at a specific site. Given that ^{10}Be production and subsequent deposition exhibit temporal variation on scales ranging from decades to millennia, modifications to the constant rate of supply model used to calculate dates may be needed, appropriate to the time scale over which the dating is carried out.

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