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DATING RECENT PEAT DEPOSITS

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Abstract: Dating recent peat deposits (i.e., past ~ 300 yrs of peat accumulation) has emerged as an important yet challenging task for estimating rates of organic matter accumulation and atmospheric pollutant deposition in peatlands. Due to their ombrotrophic nature and the tendency for *Sphagnum*-derived peat to have high cation exchange capacity, peatlands are ideal archives of atmospheric pollution. However, efforts to establish depth-age relationships in peats are complicated by the difficulty of dating deposits reliably. Assumptions underlying the techniques available for dating peat deposits often are poorly understood and generally untested. We outline the approaches used to establish depth-age relationships in peat chronologies, including brief descriptions of the theory, assumptions, methodology, and logistics of each technique. We include both continuous dating methods (i.e., methods based on ^{14}C, ^{210}Pb, constant bulk density, acid-insoluble ash, moss increment, pollen density) and chrono-stratigraphic markers (i.e., fallout isotopes from the Chernobyl accident and nuclear weapons testing, pollen stratigraphies, isothermal remanence magnetism, charcoal particles, spherical carbonaceous particles, PAHs, PCBs, DDT, toxaphene) that can be measured in peat and correlated temporally with known historical events. We also describe the relatively new radiocarbon application of wiggle matching and use hypothetical data to highlight the potential of this developing technique for dating recent peat. Until the uncertainty associated with each of these dating approaches is clarified, we recommend employing multiple techniques to allow for corroboration between different methods.

Key Words: dating, bogs, peat, ^{14}C, wiggle matching, ^{210}Pb, bulk density, ash, pollen, isothermal remnance magnetism, fire, soot balls, PAHs, PCBs, DDT, Toxaphene, ^{241}Am, ^{137}Cs, ^{207}Bi

INTRODUCTION

Peatlands have a wide geographic distribution but are located mostly at northern latitudes where they cover major portions of Alaska, Canada, Russia, the Baltic Republics, and Fennoscandia (Gore 1983, Lappalainen 1996). Peat accumulates when the rate of net primary production at the surface exceeds losses from decomposition, leaching, and/or disturbance throughout the peat column, resulting in a vertically and/or laterally aggrading deposit of organic matter. Low rates of decomposition are thought to control the accumulation of peat more than high net primary productivity (cf. Clymo 1965, 1984, 1992, Vitt 1990, Trumbore and Harden 1997, Frolking et al. 1998). De-

composition in peatlands may be retarded by high acidity, low oxygen supply at depth, low nutrient availability, and/or poor substrate quality for microbial activity (cf. Yavitt and Lang 1990, Johnson and Damman 1991, Valentine et al. 1994, Maltby and Proctor 1996, Bridgham et al. 1998).

Peat deposits are highly organic (often > 95 % organic matter on a dry mass basis), especially in ombrotrophic bogs, which receive water and inorganic nutrient inputs solely from atmospheric deposition. *Sphagnum*-derived peat in bogs and poor fens has a high cation exchange capacity, which has been attributed to high concentrations of unesterified polyuronic acids in *Sphagnum* cell walls (Spearing 1972). Through cation exchange, positively charged ions sorb strongly to the negatively charged functional groups on peat (Rapaport and Eisenreich 1986, Livett 1988, Clymo et al. 1990, Cole et al. 1990, Wieder 1990, Vile et al. 1999). This may immobilize cations that are deposited via dry or wet deposition or via surface/ground water flow (fens only) in the peat column.

Peatlands can serve as ideal archives of atmospherically deposited cations/particulates due to cation exchange and the ombrotrophic nature of bogs (Clymo et al. 1990). Since the inception of the Industrial Revolution (~ 1850 A.D.), increasing pollution in the northern hemisphere has led to contamination of both terrestrial and aquatic ecosystems. Peatlands serve as archives for atmospheric chemical deposition and may provide useful records of the spatial and temporal patterns and magnitude of this deposition (e.g., Norton 1987, Schell 1986, 1987, Rapaport and Eisenreich 1988, Schell et al. 1989, 1997, Brännvall et al. 1997, Espi et al. 1997, Farmer et al. 1997, Norton et al. 1997, Shotyk et al. 1997a,b, Weiss et al. 1997, Vile et al. 2000).

Peatlands contain 1/3 of the world's soil carbon pool, storing an estimated 397–455 Pg (10^{15} g) of C (Gorham 1991, Zoltai and Martikainen 1996, Moore et al. 1998) as organic matter. Currently, peatlands are thought to function simultaneously as a net sink for atmospheric CO_2, sequestering approximately 76 Tg (10^{12} g) of C yr^{-1} from the atmosphere, and as a substantial source of CH_4 (Gorham 1991, 1994, 1995, Wahlen 1993). Global warming, which will be most pronounced at northern latitudes (Raisanen 1997), likely will affect the mass balance of C near peat surfaces where peat temperature fluctuates with air temperature. Therefore, it is important to focus research efforts on C cycling of recently accumulated peat. It certainly is possible to estimate directly both net primary production and decomposition rates in peatlands. Methodological limitations, however, combined with typically large spatial and temporal variability lead to substantial errors in extrapolating from direct measurements to annual C budgets in near-surface peat. An alternative approach to estimating the short-term C sink capacity of a peatland takes advantage of the longer-term records stored in vertically accumulating peat, which allow for the quantitative estimation of recent net rates of organic matter accumulation (e.g., Belyea and Warner 1994a,b, Wieder et al. 1994, Oldfield et al. 1995, Clymo et al. 1998, Turetsky et al. 2000, Wieder 2001).

Because of ongoing decomposition and compaction within a peat deposit, depth generally is not linearly related to age (Clymo 1984, Clymo et al. 1990). Accurate dating of a peat profile is essential to construct chronologies from which rates of historical contaminant loading or organic matter accumulation can be calculated. Many commonly used dating methods take advantage of the ombrotrophic nature of some peatlands. These methods rely on the deposition of atmospherically-derived constituents as a basis for absolute dating, using a constant rate of supply approach (e.g., ^{210}Pb, acid-insoluble ash, pollen density), or provide chrono-stratigraphic markers recording historical changes in atmospheric loadings (e.g., ^{137}Cs, ^{241}Am or ^{207}Bi from nuclear weapons testing and/or the Chernobyl accident, pollen, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), pesticides). These dating approaches rely on the assumption of post-depositional immobility of atmospherically derived constituents mainly through cation exchange (cf. Shotyk et al. 1997b, Vile et al. 1999). Large, non-polar compounds (such as PCBs and PAHs) also bind strongly to the organic peat matrix (Rapaport and Eisenreich 1988, Sanders et al. 1995). Such strong binding limits mobility of certain atmospherically-deposited materials within peat.

No single tool for dating recent peat deposits has emerged as the most reliable (cf. Belyea and Warner 1994a). Many studies either use a single method or corroborate dates using several methods. Most independent dating methods can provide continuous chronologies that are useful in revealing fluctuations in peat accumulation over time. Chrono-stratigraphic markers record only single points in time but can provide helpful corroborations with other methods. In light of the increasing interest in both the role of peatlands in global C cycling and in the use of peatlands as archives of past atmospheric deposition of pollutants, we review currently available methods for dating recent peat deposits (defined here as the past 300 years of peat accumulation). Some methods, such as radiocarbon and ^{210}Pb dating, have been extremely popular tools in peatlands. Less commonly used methods have less literature on their use in peat.

For each method, we identify background information necessary to understand the theories behind each

technique, methodology commonly used, an evaluation of key literature, and any practical considerations including the assumptions, advantages, and limitations of each approach. In addition, to provide information on wiggle matching, a relatively recent application of radiocarbon dating, we outline its potential use in dating recent peat using a hypothetical data set.

ABSOLUTE OR CONTINUOUS DATING METHODS

Radiocarbon (^{14}C) Dating

Radiocarbon (^{14}C) was the first cosmogenic isotope detected (Rubin and Kamen 1941). The principles and application of radiocarbon dating were developed in the 1940s (Arnold and Libby 1949, Libby 1955). Radiocarbon dating has applications for dating materials up to approximately 50,000 years in age (see Taylor et al. 1992, Taylor 2000). For the principles and practice of radiocarbon dating in depth, see Olsson (1986), Taylor (1987, 1997), Délibrias (1989), Duplessy and Arnold (1989), Aitken (1990), Bowman (1990), Pilcher (1991), Kromer and Münnich (1992), Gove (1992), Cook et al. (1996), and the specialist literature, especially the journal *Radiocarbon* (also see Björck and Wohlfarth (2001) for a review of ^{14}C dating of lake sediments and similar materials). An excellent general resource may also be found at: http://www.c14dating.com/. Although much development in radiocarbon focuses on the more distant past (e.g., Hughen et al. 2000, van der Plicht 2000), we highlight in this review the potential for high-resolution dating of recent peat (here regarded as the last $\sim$ 300 yrs).

Carbon-14 exists in minute concentrations, at about one out of every 10^{12} carbon atoms, most of which are the stable isotopes ^{12}C (99% abundance) and ^{13}C (1% abundance). A radioactive (unstable) isotope, radiocarbon is produced in the upper atmosphere (the stratosphere) when thermal neutrons (produced by cosmic rays) react with ^{14}N atoms (Masarik and Beer 1999). Since the arrival of cosmic rays is modulated by solar winds, ^{14}C production offers a solar variation proxy (e.g., Stuiver and Braziunas 1993, Bard et al. 1997, 2000). The resulting ^{14}C is oxidized to $^{14}CO_2$, which mixes into the lower atmosphere (the troposphere), and is quickly homogenized within the overall atmospheric CO_2 reservoir. From there, ^{14}C (as $^{14}CO_2$) can be fixed into stable plant matter via photosynthesis and, hence, also enters the food web. Animal tissues contain ^{14}C: ^{12}C ratios proportional to ingested plant material. Upon the death of an animal or plant, uptake of fresh ^{14}C ceases. The amount of ^{14}C in the organic matter then begins to decrease as the ^{14}C undergoes radioactive beta particle (β^-) decay. $^{14}CO_2$ can also enter the chemical pathways of terrestrial and marine carbonates and so allows the ^{14}C dating of inorganic carbon samples. However, in this review, we consider only the dating of organic carbon samples.

The basis for ^{14}C dating is the basic radioactive property of the isotope: in an isolated sample, abundance decreases by 1% every 83 years, such that after 5730 years (the half-life) only half the original number of atoms remain. As conceived by Libby, this decay process allowed radiocarbon to be used in determining ages for organic materials. The time elapsed since the death of an animal or plant is calculated using Equation 1:

$$^{14}C \text{ age (years)} = \ln\frac{A_0}{A} \times \frac{T_{1/2}}{\ln 2} \quad (1)$$

In Equation 1, A is the sample's current ^{14}C specific activity (in disintegrations per gram of C), A_0 is the AD1950 ''modern'' reference ^{14}C specific activity, and $T_{1/2}$ is the half life. The value of A_0 is determined from a standard, either AD1850 wood or SRM 4990 oxalic-acid (now available as SRM 4990-C) supplied by NIST (National Institute of Standards and Technology, formerly the U.S. National Bureau of Standards, Goh 1991a, Arnold 1995). The currently accepted half life of ^{14}C is 5730 $\pm$ 40 years (Godwin 1962). However, during the development of radiocarbon dating, a half life of 5568 $\pm$ 30 years (Engelkemeir et al. 1949—referred to now as the ''Libby half life'') was used in Equation 1 to determine age. This results in a 2.9% error from the ''true'' radiocarbon age (Arnold 1995). However, because of the preponderance of ^{14}C dates published using the Libby half-life, this value has long been used as a convention in all radiocarbon dating. Radiocarbon dates are reported in radiocarbon years before present (''years BP''), where the present is defined as AD1950. For the established conventions on reporting ^{14}C dates, see Stuiver and Polach (1977).

In conventional ^{14}C-dating, measurement of beta particle emissions is used to estimate ^{14}C activity either by gas proportional counting or liquid scintillation spectrometry. A relatively large amount of sample (typically 5–10 grams for dry peat) is needed with the conventional technique, as only a small proportion of ^{14}C disintegrations actually can be counted (Hedges 1981, Hedges and Gowlett 1986). Counting time is typically up to a week. With older material, it becomes difficult to separate the radioactive disintegration of ^{14}C from background radiation. As a result, background signals contribute increasingly to error with progressively older samples (Hedges 1981). Since the late 1970s, the use of accelerator mass spectrometry (AMS) to quantify carbon isotopes directly by atomic mass separation has become increasingly popular in

Table 1. Summary of the various dating methods commonly applied to recent (post-Industrial Revolution) peat profiles. Methods are either absolute (providing ages independent of other methods) or relative (providing age information relative to an independent absolute dating technique). Methods also are either continuous (providing a series of age information throughout some portion of the peat profile) or provide age information for a single event or period in time.

Method	Type of Dating	Key Assumptions and Requirements	Cost
^{14}C	Absolute, single event	Rapid ^{14}C mixing in biosphere; no ^{14}C exchange after death	Moderate to high
Wiggle-matching (^{14}C)	Absolute, potentially continuous	Same as above	High
^{210}Pb	Absolute, continuous	Model specific (see text)	Moderate to high
Acid Insoluble Ash	Relative, continuous	Constant AIA inputs; immobility	Low
Moss increment	Relative, continuous	Increments record annual growth	Low
Constant bulk density or nitrogen accumulation	Relative, continuous	Constant peat accumulation rates; no stratigraphic changes in bulk density or chemistry	Low
Pine dendrochronology	Relative, continuous	Constant peat accumulation rates; requires the presence of tree cover and dendrochronology records	Low to moderate
Pollen density	Relative, continuous	Constant pollen deposition and pollen immobility; requires independently derived date	Low
Pollen stratigraphy	Relative, single event	Pollen immobility; known ages of historical land-use or vegetation/species changes	Low
Magnetic records	Relative, usually single event	Particle immobility and little dissolution with depth; requires historical information on deposition of magnetic particles	Low to moderate
Fallout isotopes	Relative, single event	Radionuclide immobility	Moderate to high
Organic compounds	Relative, single event	Compound immobility; known dates of historical records of use	Moderate to high
Spherical particles	Relative, usually single event	Particle immobility; known ages of historical fuel combustion	Low

radiocarbon dating (cf. Libby 1979, Hedges 1981, Polach 1984, Hedges and Gowlett 1986, Duplessy and Arnold 1989, Gove 1992, Taylor 1997, Taylor 2000). For an example of the current state of the art from one of the major facility suppliers, see Gottdang et al. (2001). The AMS technique uses sample sizes approximately 1/1000 of the mass required for conventional beta counting, depending on sample type (Elmore and Phillips 1987, Goh 1991a). AMS dating of peat requires less than 1 gram of dry material (and the technique can date samples of less than a milligram of carbon). Measurement time is less than 1 hour. Because AMS measures ^{14}C concentration rather than activity, background radiation does not affect the results. However, the age range of ^{14}C dates by AMS is limited instead by carbon contamination inherent to the instrument itself (Vogel et al. 1987, Kirner et al. 1995).

A list of university and commercial laboratories (to the end of 1999) employing either conventional or AMS techniques is available at http://www.radiocarbon.org/Info/lablist.html; for laboratories with www links, see http://www.radiocarbon.org/Info/index.html.

The processes of transport, uptake, respiration of $^{14}CO_2$ in plants, and also subsequent laboratory processing, all tend to discriminate against the heavier isotopes of carbon (a process called fractionation), i.e. ^{14}C and ^{13}C compared to ^{12}C. The outcome is that the proportion of ^{14}C to total C in plant tissue can be lower than in the atmosphere (in effect the ^{14}C is apparently 'old'). This fractionation effect, or excess of progressively ^{12}C to ^{13}C to ^{14}C, varies slightly among different plant species (Stuiver and Polach 1977, Burleigh et al. 1984, Kerby and Raven 1985, see also Table 1 in http://depts.washington.edu/qil/calib/calib.html). Fractionation must be corrected by measuring ^{13}C concentration to estimate the appropriate atmospheric ^{14}C level for a sample. Carbon-13 is a stable isotope and, at about 1% concentration, can be satisfactorily measured with a routine mass spectrometer. Fractionation is proportional to atomic mass; therefore, the depletion found for ^{13}C is merely doubled to derive the depletion for ^{14}C. This correction is then applied to the value determined for the ^{14}C in the sample (Wigley and Muller 1981). Carbon-13 abundances are calculated relative to an agreed standard: Pee Dee Belemnite (PDB). The typical $\delta^{13}C$ for wood is c.-25 ‰; all ^{14}C isotopic fractionation corrections are normalized to this value. Such $\delta^{13}C$ correction has been routine in most laboratories for several decades, and ^{14}C ages supplied to the user will have been corrected (e.g., Ralph and Michael 1974, Arnold 1995). Where pos-

sible in peat/sediment studies, selection of samples whose $^{14}CO_2$ is derived from the atmosphere (e.g., plant macrofossils) is usually preferable.

Various other processes can also affect the C available for analysis in an organic sample and lead to distortions between the date obtained and the real date for the target event of interest. The generic label 'contamination' is usually applied to such issues. Hedges (1992) provides a useful general review of sample treatment strategies for radiocarbon samples. With reference to peat, we note the following:

(i) Particularly in permafrost systems, frost heaving can disturb peat chronologies and bury surface peat with underlying, older deposits (Brown 1969; but see Vorren and Vorren 1976).

(ii) Peat samples may be contaminated by younger carbon through root penetration, infiltration of dissolved modern organic carbon (humics), or bacterial action on stored samples, leading to underestimates of bulk peat age (Geyh et al. 1974, Matthewes 1985, Goh 1991a, Hammond et al. 1991, Olsson 1991, Törnqvist et al. 1992, Punning et al. 1993, Charman et al. 1994, Killian et al. 1995, Oldfield et al. 1997). Standard laboratory pretreatments (NaOH) aim to remove such mobile material. Dating 'bulk' samples can remain troublesome if materials are heterogeneous in age. In this case, dating only the NaOH insoluble fraction can bias data towards old and reworked material. In other situations, dating the NaOH-soluble fraction may lead to more correct ages (Olsson 1986, Gulliksen et al. 1998). However, the best strategy generally is to date specific macrofossil remains.

(iii) Bulk samples may be subject to other local reservoir effects. For example, hard-water sources in lake deposits may have a significant reservoir component (Barkenow et al. 1998). MacDonald et al. (1987) found that aquatic moss samples gave older than expected ages because of uptake of ^{14}C-deficient carbon from an unknown source. The presence of tough decay-resistant plant remains (such as heather) or the in-wash of soil materials containing old carbon are other apparent sources of a reservoir effect (Edwards and Rowntree 1980). This especially can be a problem in recent times, as the proportion of soil in-wash has increased in many areas from late prehistoric through modern times. Thawing permafrost can also be a factor releasing old reservoirs of organic matter in close proximity to plant uptake (Damon et al. 1996).

(iv) Organic matter fractions, such as humic acid, humin, and fulvic acid, in soils and peats have been shown to differ substantially in radiocarbon content (Scharpenseel 1971, Scharpenseel and Schiffmann 1977, Stout et al. 1981, Hammond et al. 1991, Shore et al. 1995). Physical removal of roots and/or chemical pre-treatment of samples are recommended to minimize sample contamination by adsorption or exchange with non-contemporaneous carbon (Goh 1991b). Where peat samples represent time intervals significantly longer than the 10-year measurement segments of the ^{14}C calibration (see text on calibration below), it is appropriate to employ a smoothed calibration curve more suitable for the time window represented in the peat (Mook 1983). However, AMS dating permits the dating of specific macrofossils from intensively sampled peat sequences and is likely to overcome this problem.

Minor variations in ^{14}C levels at different times and places on the Earth is another complication for ^{14}C dating. Excluding modern fossil fuel CO_2 contributions (about 50% of the modern observed variation), the production and flux of ^{14}C naturally varies slightly by time of year on a c.1–4 ‰ range (winter-spring low, summer peak). This can be relevant if seasonally specific materials are dated (sub-annual growth samples) or at times of rapidly and significantly changing ^{14}C levels (i.e., changing solar irradiance: Kromer et al. 2001, Manning et al. 2001). The atmospheric ^{14}C content at earth surface level varies slightly depending on both latitude and altitude (Levin et al. 1989, 1992, Levin and Kromer 1997a, Levin and Hesshaimer 2000). Thus, while mid-northern latitude North America and Eurasia near sea-level generally have similar ^{14}C levels within a c.1 ‰ range (Braziunas et al. 1995), areas further north or south have generally increasing but temporally varying offsets (Stuiver and Braziunas 1998, Stuiver et al. 1998a). More significant is the inter-hemisphere offset (the current standard recommendation is that southern hemisphere ages be reduced by 41 ± 14 ^{14}C years: McCormac et al. 2002); however, this varies through time and has become smaller since the mid-19th century (Kromer et al. 1998, McCormac et al. 1998, Stuiver et al. 1998b). For very recent samples, it can be largely ignored. For equatorial or near-equatorial locations, the relevance of which hemispheric trend samples follow will vary according to movements in the Intertropical Convergence Zone (Hua et al. 2002).

Calibration. Libby's earliest models for radiocarbon dating assumed that (i) the ratio of ^{14}C:^{12}C has been constant worldwide over time; (ii) radiocarbon is rapidly mixed following production throughout the biosphere; and (iii) measured ^{14}C is from the organism being studied (i.e., no exchange occurs between the environment and the organism after death). As measurement precision improved, discrepancies between known ages and measured ^{14}C ages led to much investigation (Libby 1963). As early as the 1950s, dendrochronological analysis (tree rings of known age) was used to document continuous variations in ^{14}C

concentrations in the atmospheric C reservoir over time (de Vries 1958; see later, e.g., Suess 1965, Damon et al. 1974). High-precision radiocarbon measurements in the 1970s and 1980s verified that this was real variation rather than a measurement or laboratory artifact (Pearson et al. 1977, de Jong et al. 1979, Stuiver 1982, Pearson et al. 1983). Such variations occur both as a result of natural changes in ^{14}C production rate due to solar variability, geomagnetic field intensity (Damon et al. 1978, Stuiver et al. 1991, Stuiver and Braziunas 1993, 1998, van Geel et al. 1998), and anthropogenic activities such as ^{14}C dilution in the atmosphere through fossil fuel combustion (von Gunten 1995) or ^{14}C enrichment of the atmosphere with nuclear weapons testing in the 1950s and 1960s (Matthews 1985, Goh 1991b).

Sets of absolutely time-resolved, high-precision ^{14}C measurements have been internationally adopted, first in 1986 (Pearson 1986, 1987, Stuiver and Pearson 1986), and then again in 1998 (an INTCAL04 revision is in preparation: Reimer et al. 2002 and Paula Reimer, pers. comm.) (Stuiver et al. 1998a), and these are now routinely employed to 'calibrate' measured ^{14}C ages on samples of unknown age to determine true calendar ages. A southern hemisphere calibration data set (SHCal02) also exists for the period 1955AD to 950AD (McCormac et al. 1998, 2002). The current (1998) standard relationship between ^{14}C age and calendar (tree-ring) age is shown in Figure 1A (data from Stuiver et al. 1998a). This calibration curve derives from measurements on 10-year blocks of wood (thus providing a 10-year average curve; various statistical models are adopted to interpolate between the data points for analysis or to generate smoothed curves best fitting the data pattern versus specific data points. e.g., Dekling and van der Plicht 1993, Knox and McFadgen 2001). Additionally, a few partial calibration datasets built from higher resolution data exist, in particular a 1-year curve for AD1511–1955 (Stuiver et al. 1998b) (Figure 1B). These data show short-term variation around the long-term trend determined from the standard 10-year timeframe measurements.

Several computer programs (most notably CALIB—available at http://www.calib.org; OxCal—available at http://www.rlaha.ox.ac.uk/orau/index.htm; and BCal—available at http://bcal.shef.ac.uk/) are available to carry out the calibration process (for these and other computer calibration programs, see Stuiver and Reimer 1986, 1993, van der Plicht 1993, Bronk Ramsey 1995, Puchegger et al. 2000, Weninger and Jöris 2001, Jones and Nicholls 2002). OxCal and BCal (and related: Bwigg) provide comprehensive statistical packages for the analysis of radiocarbon dates using Bayesian approaches and represent the current 'state of the art' (see Buck et al. 1991, 1992, 1994, 1996, 1999, Bronk Ramsey 1994, 2001, Christen and Litton 1995, Christen 2003).

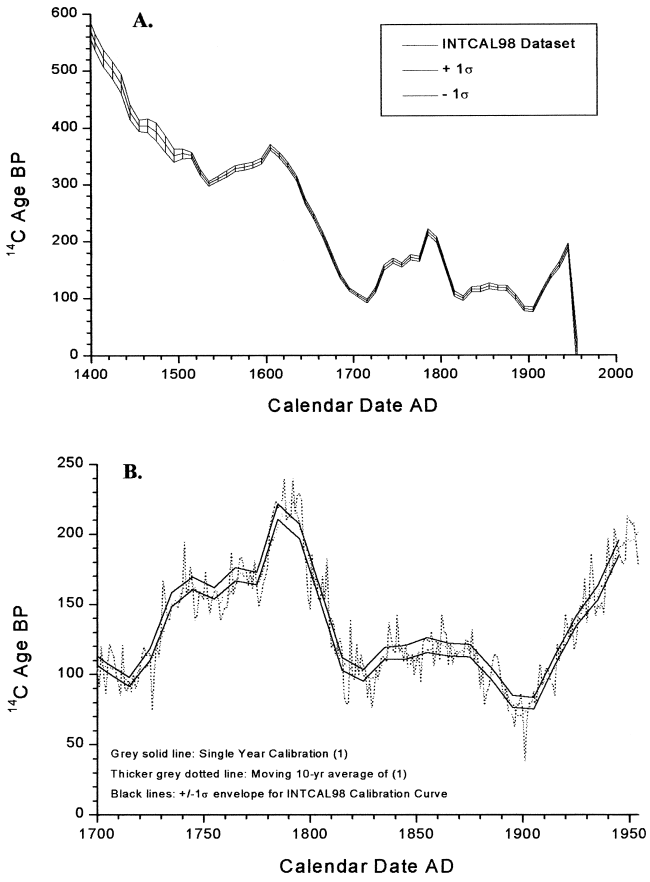

Figure 1. A. Last six centuries of the INTCAL98 ^{14}C calibration curve (Stuiver et al. 1998a). This curve consists of measurements on consecutive 10-year sections of wood. The grey lines show the $\pm$ 1σ envelope for the INTCAL98 dataset. B. Comparison of the 1-year calibration dataset (AD1511–1955; Stuiver et al. 1998b) against the standard 10-year timeframe INTCAL98 dataset (AD1700–1955; Stuiver et al. 1998a). Note that a 10-year moving average of the 1-year dataset is largely consistent with the INTCAL98 curve.

Wiggle Matching. A common misconception is that ^{14}C dating stops at AD1950—due to atmospheric thermonuclear bomb activity distorting natural ^{14}C levels. It is merely a little more difficult and non-standard. Although no internationally agreed-upon curve exists for ^{14}C levels since 1954, there are extensive data available for both hemispheres (see at http://cdiac.esd.ornl.gov/trends/co2/contents.htm). A recent paper by Goodsite et al. (2001) provides a detailed post-bomb calibration curve and analytical assessment for the northernmost northern hemisphere and demonstrates the ability to achieve dates for peat accurate to within 1 to 2 years. Meanwhile, in the southern hemisphere, a study by Hua et al. (2003) using tree-

rings from northern New South Wales, Australia has likewise demonstrated the application of annual resolution radiocarbon dating for the period 1952–1978. In theory, given use of ^{7}Be to determine the current 0–1 year present peat horizon, a 1–2 year dating accuracy/precision via careful and detailed ^{14}C analysis should be possible for stratigraphic sequences over the last five decades. Goodsite et al. (2001) conclude that such ^{14}C dating offers far better accuracy and precision than any other dating technique for recent contexts (in this case, recent is defined as the post-bomb spike).

A time-ordered (from oldest to most recent) series of ^{14}C ages should resemble the time-series of ^{14}C ages represented by the ^{14}C calibration curves. By comparison of such time-resolved datasets, it is possible to derive highly precise calendar ages for each individual constituent ^{14}C determination, potentially with resolution close to that of the underlying calibration dataset. This technique has come to be called 'wiggle-matching.'

Although first employed four decades ago (e.g., Ferguson et al. 1966, Neustupný 1973), wiggle-matching is a relatively new application of radiocarbon dating. It can significantly improve the precision of age chronologies and may be used for dating recent peat. This technique capitalizes on the irregularities or 'wiggles' in ^{14}C calibration curves (see Figure 1) due to changes in atmospheric ^{14}C concentrations over time. Wiggle-matching involves superimposing sequences of ^{14}C dates onto the individual irregularities in the tree-ring calibration curve.

Two distinct forms of wiggle-matching exist. The first, usually relevant to dendrochronological samples, takes a fixed calendar-year sequence (e.g., a 200-growth rings = 200-calendar years piece of wood), dates a series of blocks of these rings at fixed intervals (e.g., 10 samples of 10 rings each, spaced either 10 or 20 years apart, from the 200-year sample), and then matches this series against the ^{14}C calibration curve. Given the choice of similar dated sections (e.g., 10-year blocks) and inter-sample intervals (e.g., units of 10-years), the unknown sample should be compatible with the calibration curve, and a satisfactory match is likely where no significant laboratory offset/error interferes. For some examples of fixed-sequence wiggle-matching, see Ferguson et al. (1966), Clark and Renfrew (1972), Pearson (1986), van der Plicht et al. (1995), Manning et al. (2001). The second form of wiggle-matching, relevant to peat sequences (and archaeology), is variable or flexible sequence wiggle-matching. Here, the order of the samples is known, but the intervals between the samples are either not known, or known only in approximate terms (e.g., from estimates from sedimentation rates or peat-growth rates), and so are flexible within the series.

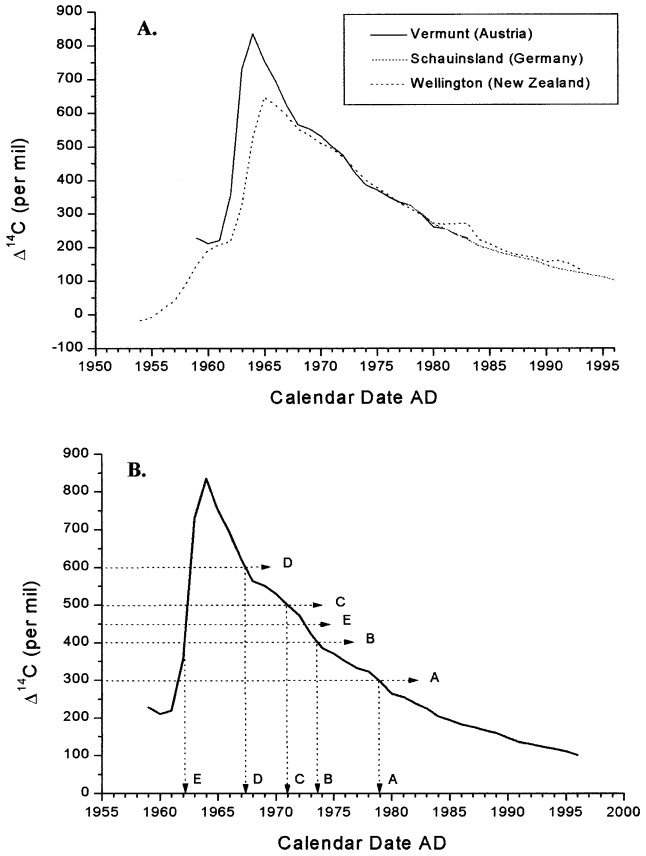

Figure 2. A. Annual weighted average values for atmospheric ^{14}C from Vermunt (Levin et al. 1994) and Schauinsland (Levin and Kromer 1997b) in the northern hemisphere, and Wellington (Manning and Melhuish 1994) in the southern hemisphere. 1 σ errors range from approximately 2 to 4 per mil (data not shown). B. Hypothetical calibration of a stratigraphic (known order) series of modern ^{14}C samples against the northern hemisphere data is shown in A (sample A collected at the peat surface while sample E was located at the base of a peat core). Errors are ignored in this example. The stratigraphic order allows resolution of the otherwise problematic apparent age inversion for sample E. The detailed ^{14}C record allows its precise dating at the start of the sequence.

Within the sequence constraints, the issue then is whether the sequence can plausibly be pushed or pulled so as to best match the calibration curve's record of past atmospheric ^{14}C levels. If the sequence covers a time of dramatic change in ^{14}C levels, then this can almost be considered a graphical exercise of matching the shape in the data to the shape of the calibration curve (e.g., van Geel and Mook 1989, Mauquoy et al. 2002; see Figure 2). At other times, there may be differing possibilities with varying probabilities, and the analysis of the overall sequence is necessary to try to resolve the likely best placement. For some examples of work using variable/flexible sequence wiggle-matching, see Clymo et al. (1990),

Manning and Weninger (1992), Tolonen et al. (1993), Day and Mellars (1994), Christen and Litton (1995), Kilian et al. (1995, 2000), Oldfield et al. (1997), and Gulliksen et al. (1998). In general, variable/flexible wiggle-matching is more approximate than fixed-sequence analysis; analyses are susceptible to complications caused not only by measurement accuracy, but also stratigraphic interpretation or misinterpretation. For example, in palaeoenvironmental sequences, it is typically necessary to employ bulk sediments to obtain the required dense time-series data (e.g., Gulliksen et al. 1998). Such work should (i) include comparison of bulk material and macrofossils at several points in the sequence to test the reliability of the bulk sample data and (ii) only use samples from terrestrial or soft-water contexts.

Initial applications mainly employed simple least squares (chi-squared) fitting to determine the placement of a floating sequence versus the known sequence (the calibration curve)—a recent development uses Monte Carlo simulation to better derive overall dating uncertainties. Another approach is to use Bayesian statistics, where the relative likelihood of each year of fit is determined. Bayesian wiggle-matching is available through the OxCal and BCal software packages. As the recent paper of Bronk Ramsey et al. (2001) shows, all techniques achieve consistent results. The great advantages of the Bayesian approach are the ability to include additional prior knowledge beyond mere sequence into the analysis model (e.g., allowing for approximate intervals and a confidence range on these, or including a known historical datum), and to be able to quantify the errors involved.

To give an idea of the sort of analyses possible, we present a hypothetical case study using the OxCal 3.9 software. This situation involves a peat deposit that is 87 cm in depth and is thought to be a relatively recent sequence. The peat developed above an old soil surface that used to support some tree cover. The peat seems to have formed at a relatively consistent rate but shows signs of slightly greater compaction in the core with depth. Two cores were taken in AD1980; one was analyzed immediately and the other stored (frozen). A ^{14}C age of 110±50BP was obtained some years ago from a sample deep in the first core. The calibrated age at 1σ is AD1685–1731, 1809–1895, 1906–1925, 1948–1951. A date in either of the first two intervals is most likely, but covering over 200 years, the initial workers concluded the core was modern with little utility in further ^{14}C dating.

Now a new team wishes to examine the frozen core to achieve chronological resolution. A stump from a tree formerly growing on the old soil surface is recognized in the section exposed for study, and the team waits for a dendrochronological report. Microscope examination of the core also reveals traces of volcanic tephra at around 65 cm depth in the core; a sample has been sent away for analysis. The stored core is sampled at 1-cm resolution and 10 AMS dates are analyzed using macrofossils (*Sphagnum* branches and leaves) from the 1-cm slices (Figure 2, 3).

The team considers samples C-J using the Sequence function of OxCal (Figure 3). This already yields quite a refined resolution calendar chronology. Then, the team examines the two 'modern' results (A and B) and compares them with one of the available bomb ^{14}C curves (Figure 4). Each sample could calibrate in two places. However, as sample A is known to be more recent than sample B, sample A must lie around AD1980 (and it is known that the core was obtained in AD1980). We have no constraint on sample B; it could thus date either around AD1966 or AD1963. The team thus has a high-precision dating of the first 7 cm of the core. Given the apparent observation of fairly consistent accumulation, each cm of peat likely represents >2.2 years. Thus, the approximate likely time interval between the various samples could be estimated, and this information could be incorporated into the dating model. See Figure 5 where the gaps are estimated in round terms with a suitably cautious ±50% error allowance.

The results on the dendrochronological examination of the tree stump and the tephra analyses are now both available. The tree had bark preserved in one part of the radius, and after matching its growth curve to the regional master chronology, the last year of growth (death) has been assigned to AD1717. We can incorporate this *terminus post quem* into the dating model. Further, the tephra from depth 65 cm (between samples H and I) has been found to match closely the AD1783 Laki eruption products. We can also incorporate this information into the model (Figure 5). Two examples of the derived calibrated ranges for individual samples from Figure 5 are shown in Figure 6. Samples are now dated with a resolution of a couple of decades, even at a 95% confidence level. Dating of more samples through the core could further refine these age estimates towards decadal level or a better resolution. An assessment of Figure 5, or use of other dating methods, might allow refinement of the between-sample intervals employed (Figure 5), with additional revisions to a dating model.

In theory, wiggle-matching may provide much more concise peat ages than single radiocarbon dates (Kilian et al. 1995) and may establish depth-age relationships that can be accurately extrapolated to surface peat (Clymo et al. 1990, Oldfield et al. 1995). Recent work indicates that ^{14}C can offer more accurate and precise data for modern peats/sediments than other common radioisotope techniques such as ^{210}Pb (Goodsite et al.

A.

Sample	Depth (cm)	^{14}C Age
A	0	'modern' 265 ± 10 Δ ^{14}C per mil
B	7	'modern' 710 ± 10 Δ ^{14}C per mil
C	17	157 ± 30
D	28	77 ± 30
E	36	120 ± 30
F	49	115 ± 30
G	53	105 ± 30
H	61	205 ± 30
I	71	173 ± 30
J	79	152 ± 30

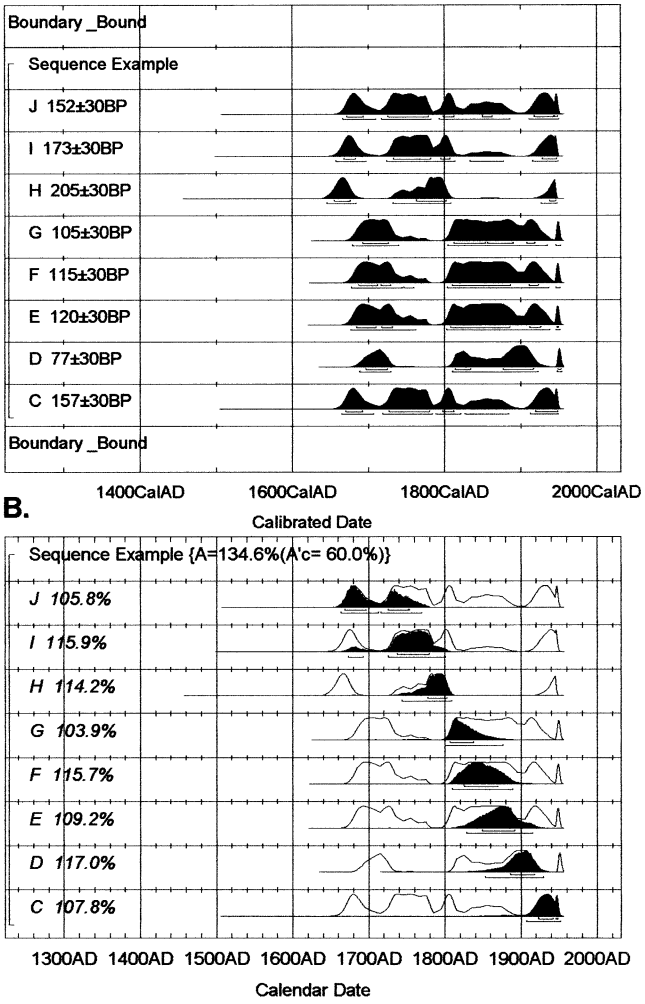

Figure 3. A. The 'normal' calibrated age ranges for the eight data points in a hypothetical case study using OxCal 3.9 (curve resolution set at 1). The upper and lower lines under each histogram indicate respectively the 1 σ and 2 σ calibrated age ranges. Note the multiple and differing calendar ranges possible for each sample, reflecting the wiggly nature of the calibration curve where several calendar years (even a century or more apart) have effectively the same ^{14}C age. This situation appears problematic for refined dating. B. Sequence analysis of the ordered series of data enables the calculation of possible fit ranges (the solid histograms) *within* the possible dating ranges for the individual samples taken in isolation (hollow histograms). This approach provides more refined dating precision. An agreement statistic of >c.60% indicates satisfactory agreement of data, model and calibration curve at 95% confidence level; therefore, the sequence analysis outlined here is satisfactory.

2001). Bomb-period ^{14}C calibration can be included in such analyses to enable accurate and precise dating to the present (see case study above; Goodsite et al. 2001). Surprisingly, few adequately (towards high-precision) dated ^{14}C series for peat or lake sediment sequences have been published (e.g., Oldfield et al. 1995, but see Clymo et al. 1990, Ilkonen 1995, Pilcher et al. 1996, Mäkilä 1997, Oldfield et al. 1997, van der Knaap and Ammann 1997, Gulliksen et al. 1998, Mauquoy et al. 2002). Much more work should now follow on modern peats.

C-14 dating (and in particular via AMS dating of selected macrofossils) of modern peat samples may offer accurate and precise decadal-scale or better age resolution over the last several hundred years and at near annual-scale for the very recent past. 'Wiggle-matched' ^{14}C dating is a suitable approach for the high-resolution dating of post-Industrial Revolution peats, enabling detailed stratigraphic information to yield tight chronological control. In all cases, however, proper sample preparation and attention to stratigraphic context are vital to enable accurate and precise dating.

^{210}Pb Dating

Based on the radioactive decay series of ^{238}U, ^{210}Pb-dating (Goldberg 1963, Appleby and Oldfield 1978) allows for radiometric dating of peat deposited over the past 150–200 years. Uranium-238 is a primordial nuclide, present since the earth first condensed into a solid mass some four billion years ago. Because of its long half-life (4.46×10^9 yr), about half of the original ^{238}U remains today. Widely dispersed in the earth's crust, ^{238}U is found in all sediments and continually is decaying to produce ^{210}Pb and other daughter isotopes. Within soil, ^{238}U decays to ^{226}Ra through a number of decay products, which subsequently decays to inert ^{222}Rn gas. Radon gas then decays through a series of short-lived isotopes to ^{210}Pb (half life of 22.3 yr). The total ^{210}Pb pool in soil, sediment, or peat has two components: 1) a supported ^{210}Pb component produced within the soil/sediment via radioactive decay of ^{222}Rn that never diffused to the atmosphere and 2) an unsupported ^{210}Pb component derived from ^{222}Rn that first diffused into the atmosphere and subsequently decayed to ^{210}Pb. Unsupported ^{210}Pb, removed from the atmosphere via wet deposition and dry fallout, is deposited onto the earth's surface. Mean global ^{210}Pb flux onto

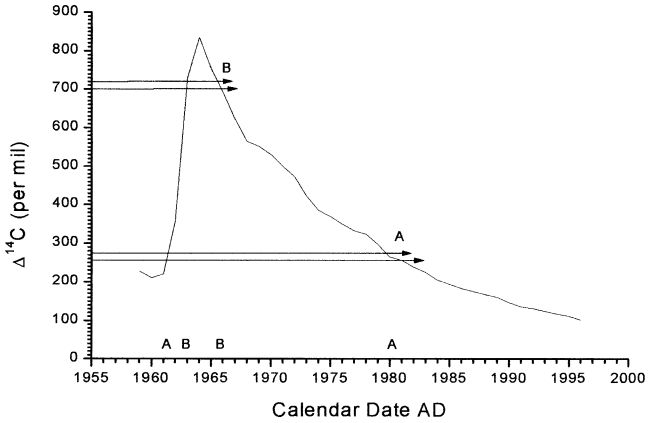

Figure 4. Comparison of the 'modern' ^{14}C ages for samples A and B from the hypothetical case study (Figure 3) with the bomb curve.

land surface has been estimated at 166 becquerels (Bq; equivalent to one disintegration per second) m^{-2} yr^{-1} (Krishnaswamy and Lal 1978) but varies among sites. Estimates of unsupported ^{210}Pb deposition to the earth's surface, calculated from the integrated ^{210}Pb inventory in peat deposits, have ranged from 95 to 329 Bq m^{-2} yr^{-1} (Schell 1986, Schell et al. 1986, Urban et al. 1990, Belyea and Warner 1994a, Appleby et al. 1997, Norton et al. 1997, Vile et al. 2000).

In general, activities of unsupported ^{210}Pb in undisturbed, vertically aggrading peats are greatest in young surface deposits and decrease in older, deeper material as a result of radioactive decay (Appleby and Oldfield 1983). By quantifying the unsupported ^{210}Pb inventory from the surface to a depth where unsupported ^{210}Pb is undetectable, it is possible to calculate the age-depth relations for a peat deposit. If sediment has accumulated at a constant linear rate over time (cm yr^{-1}), the unsupported ^{210}Pb activity will decline exponentially with the cumulative dry mass of sediment, yielding a log-linear relationship between unsupported ^{210}Pb activity and depth. In this situation, referred to as the constant flux-constant sedimentation rate (cf:cs) model, sediment accumulation rates can be determined from the mean slopes of regressing log (^{210}Pb concentration) on depth (cf. Appleby and Oldfield 1983, Schelske et al. 1988, Craft and Richardson 1998).

In many cases, however, mass sedimentation rates over the past 150–200 yr have not been constant, yielding non-linear ^{210}Pb profiles (Appleby and Oldfield 1983). Currently, there are three models commonly used in situations of varying sedimentation rates: the constant rate of ^{210}Pb supply (CRS) model (cf. Goldberg 1963, Appleby and Oldfield 1978, 1983, Robbins 1978), the constant initial concentration (CIC) model (cf., Pennington et al. 1975, Appleby and Oldfield 1983), and the constant rate of supply minimum

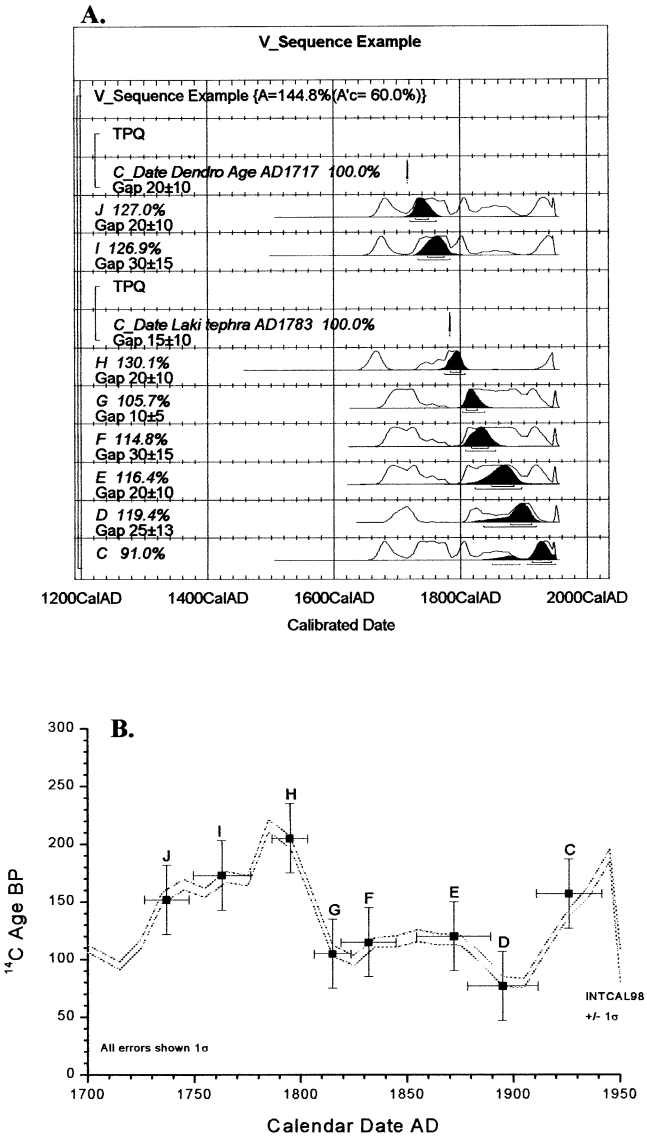

Figure 5. A. Sequence analysis of the pre-bomb data from the core incorporating the additional prior information now available. Solid histograms show calculated best fit ranges for samples C-J. B. 'Wiggle-match' for the same data given constraints integrated in dating model there at 1 σ confidence against the known atmospheric ^{14}C record from the INTCAL98 dataset (Stuiver et al. 1998a). Y axis shows the ^{14}C ages for the samples ± 1σ (see Figure 3); the X axis shows the best fit point (given constraints of the dating model—see Figure 6 for examples) and the total 1 σ range (non-symmetrical) within which this best fit point occurs.

variance (CRS-MV) model (Tobin and Schell 1988, Schell and Tobin 1994, Espi et al. 1997, Schell et al. 1997).

The CRS model assumes a constant supply of ^{210}Pb to the surface of a vertically aggrading soil, sediment, or peat deposit, and allows for accurate dating despite temporal variations in sedimentation/accumulation

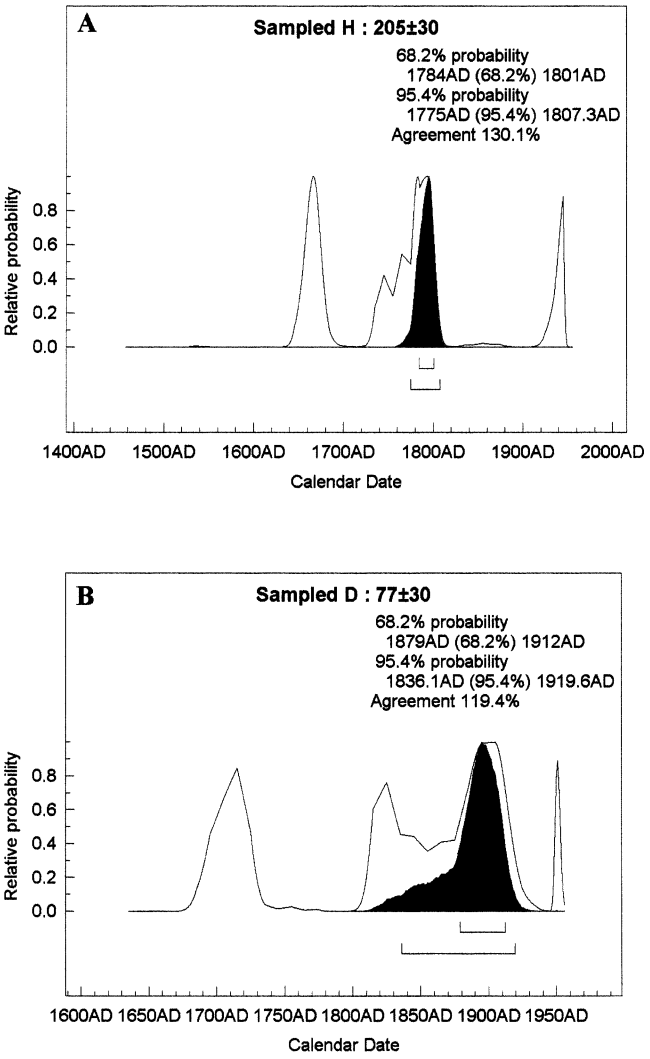

Figure 6. A. Best calibrated age estimate for sample H from the analysis in Figure 5A. B. Best calibrated age estimate for sample D from the analysis in Figure 5A.

rates. This model is suitable for dating peat cores, particularly in ombrotrophic peatlands that depend solely on the atmosphere for inputs of ^{210}Pb. According to this model, the age of each sediment layer is determined using the equation:

$$A = A_0 e^{-\lambda t} \quad (2)$$

where λ is the radioactive decay constant of ^{210}Pb (0.0307), A is the cumulative residual unsupported ^{210}Pb beneath a specified surface area to particular depth interval of age *t* within a core, and A_0 is the total residual unsupported ^{210}Pb in the entire peat core (Appleby and Oldfield 1978). The sedimentation rate (r) can be determined from the following equation:

$$r = \lambda\ (A/C) \quad (3)$$

where C is the total unsupported ^{210}Pb inventory, calculated by subtracting the supported amount from the total amount of ^{210}Pb for each depth interval through the peat core and summing across all depths. In addition, the ^{210}Pb supply rate (P) can be calculated by the equation:

$$P = \lambda\ A_0 \quad (4)$$

The CIC model, often used in dating lake sediments, assumes that 1) the amount of ^{210}Pb in sediments is proportionally related to the flux of sediment particles from the water column and 2) on a dry mass basis, sediments have the same initial unsupported ^{210}Pb concentration despite potential variation in sediment accumulation rates. With this approach, the unsupported ^{210}Pb concentration in a sediment layer (C) varies according to the following equation:

$$C = C_0 e^{-\lambda t} \quad (5)$$

where C_0 is the unsupported ^{210}Pb concentration at the sediment-water boundary (cf. Appleby and Oldfield 1983, Shukla and Joshi 1989).

The CRS-MV model is a modification of the CRS model in which least squares iterative techniques are used to fit the CRS model equations to the observed core data in such a way that the residual variance is minimized (Tobin and Schell 1988, Schell and Tobin 1994). The CRS-MV approach yields exactly linear vertical accumulation rates (fixed number of years per specified depth increment) throughout the datable portion of the core, which may be unrealistic for peat accumulation (cf. Schell et al. 1997).

To ^{210}Pb-date a peat deposit, a core typically is collected and sectioned into contiguous depth increments, each of which is weighed and processed for measurement of ^{210}Pb activity by either α, β, or γ spectrometry (Joshi 1989, Nevissi 1991, Moser 1993). For peat, the most commonly used approach for measuring ^{210}Pb activity involves acid digestion, often with added H_2O_2 to facilitate oxidation of organic matter, and typically with the addition of either ^{208}Po or ^{209}Po as a chemical yield tracer (e.g., Wieder et al. 1994, Norton et al. 1997, Schell et al. 1997, Craft and Richardson 1998, Vile et al. 2000). Subsequently, the solubilized Po isotopes are passively plated onto copper or silver disks for activity measurements using alpha spectrometry. Although ^{210}Pb is not an α emitter, it decays to stable ^{206}Pb via two daughter isotopes, ^{210}Bi (β^- emitter, half life ($T_{½}$)=5.01 d) and ^{210}Po (α emitter, $T_{½}$=138.4 d). Because of the short half-lives of ^{210}Bi and ^{210}Po, they rapidly reach secular equilibrium with the parent ^{210}Pb (Blais and Marshall 1988) within about 2 years. Hence, measurement α emissions from ^{210}Po decay can be used as an estimate of ^{210}Pb activity in peats. Disadvantages to the α spectrometry approach are the tedious digestion, the need to correct for extraction and

plating efficiency using ^{208}Po or ^{209}Po tracers, and the destructive nature of the method. Advantages, however, include the ability to digest large (several gram) subsamples of peat (concentrating the extracted Po isotopes onto a single copper or silver disk for counting), and the sensitivity of modern alpha detector systems with respect to the α emissions from ^{210}Po decay.

Pb-210 emits a weak γ ray (46.5 keV; one electron volt is equivalent to 1.602×10^{-19} joules), and its activity in a peat sample can be measured directly by gamma spectrometry (e.g., Appleby et al. 1986, 1988, 1990, 1997, Schelske et al. 1994, Farmer et al. 1997). Compared to α spectrometry, sample processing is minimal (samples are weighed into containers and placed directly into a gamma counting chamber). In addition, analysis of ^{210}Pb activity by gamma spectrometry is non-destructive. However, the weak energy of the emitted γ rays and the small fraction of decays emitting γ rays contribute to difficulties in quantifying ^{210}Pb activities, particularly in deeper samples where unsupported ^{210}Pb activities become diminishingly small.

In principle, ^{210}Pb activity in peat could be determined by β^- counting of digested solutions, although for peat samples, this has not been the method of choice. Pb-210 is a β^- emitter (0.063 MeV), but so is ^{210}Bi, a granddaughter of ^{210}Pb decay (β^- energy of 1.16 MeV). Pb-210 activity can be estimated by measuring β^- emissions, separating β^- emissions from ^{210}Pb and ^{210}Bi based on their respective energy spectra, or by chemical separation before measurement (e.g., Blais and Marshall 1988, Nevissi 1991, Ament and Lieser 1993, Sapozhnikov et al. 1993, Gogrewe et al. 1996).

Pb-210 dating constructs a continuous dating record extending back to generally no more than about 150 yr from the present (time of core collection). After 10 half-lives ($T_{1/2}$ = 22.3 yr) or about 223 yr, unsupported ^{210}Pb concentrations will be only 2^{-10} of their initial respective values, at which point detection against a background of supported ^{210}Pb technologically is not feasible. Because the temporal frequency of decay events is low, counts of disintegrations over time follow the Poisson distribution in which the variance (σ^2) is equal to the mean (total number of counts measured over the counting time, *N*), and hence the standard deviation of the total number of counts, σ, is equal to the square root of *N*. Thus, the counting error, ε, expressed as a proportion of the total accumulated counts is given as

$$\varepsilon = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}. \quad (6)$$

Counting error is high when the total accumulated number of counts is low (deeper in a profile) and decreases as the N increases (closer to the surface). In practice, errors are propagated from the surface downward (cf. Bevington 1969, Binford 1990). As a result, moving from section to section downward through a core, errors increase, to the point where the counting error (in years) may actually exceed the age of the section. Therefore, although it often is possible to calculate dates that are older than 5 half-lives of ^{210}Pb (111.5 yr), the error terms associated with these dates may be quite large.

Pb-210 dating assumes immobility of atmospherically deposited ^{210}Pb at the peat/sediment surface and subsequently within the peat profile over time (von Gunten 1995, Shotyk et al. 1997b, Vile et al. 1999). Several studies have invoked mobility of Pb in peat to explain vertical distributions of Pb in peat columns (Damman 1978, Clymo and Hayward 1982, Pakarinen et al. 1983, Pakarinen and Gorham 1983, Urban et al. 1990, Oldfield et al. 1995, Sanders et al. 1995). For example, Sanders et al. (1995) conclude that ^{210}Pb in peat may be impacted by decomposition, cation mobility, lateral water movement, and/or DOM concentrations. However, others have concluded that Pb remains immobile after deposition onto a peat surface (Figure 7; Benninger et al. 1975, Livett et al. 1979, Mitchell et al. 1992, Appleby et al. 1997, Farmer et al. 1997, MacKenzie et al. 1997, Vile et al. 1999) or have found good agreement between ^{210}Pb-dating in peat cores and other dating methods (El-Daoushy et al. 1982, Clymo et al. 1990, Cole et al. 1990, Belyea and Warner 1994a, Wieder et al. 1994, Vile et al. 1995, Appleby et al. 1997, MacKenzie et al. 1997, Shotyk et al. 1997a).

Pb-210 dating is a popular tool available for quantitatively dating peat accumulation over the past ~ 200 years. The chemistry involved in ^{210}Pb dating can be complicated and lengthy, and commercial analysis is expensive. The digestion procedure for α-counting requires fairly large sample sizes, about 3 g of dried material.

Pb-210 dating is one of the few independent dating methods that can yield a continuous chronology (Table 1). Once ^{210}Pb concentrations in sediment layers have been measured and the appropriate model has been utilized, however, there is no guarantee that the profile will be datable. Any past disturbance to the soil, sediment, or peat profile (bioturbation, treefall, trampling by animals) may preclude construction of a continuous chronology. Similar to other methods that build continuous chronologies, considerable effort can be expended in core collection, processing, and measurement of ^{210}Pb activities before it becomes evident that a core is undateable.

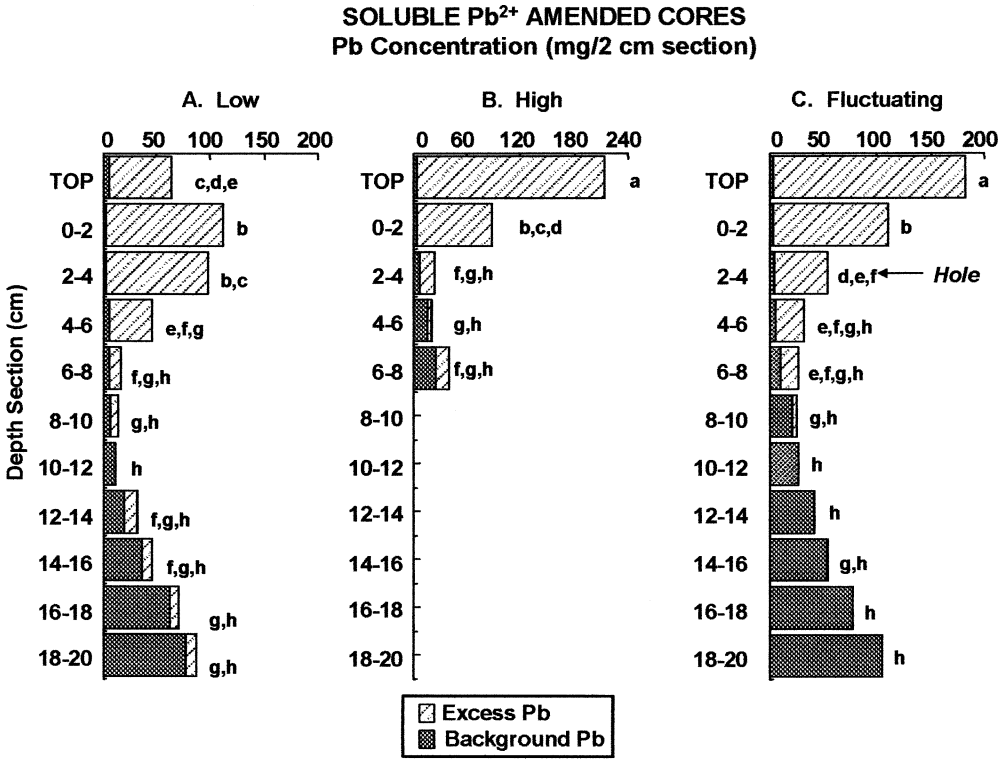

Figure 7. Mean excess lead concentrations versus depth in peat cores receiving soluble Pb additions under 3 water level treatments: A. low, B. high, and C. fluctuating water levels. Hatched bars represent excess Pb (means of 5 cores to which soluble Pb was added), while solid bars represent background Pb (means of 3 control cores). Means with the same letter superscripts do not differ significantly from one another. All of the excess Pb added to peat cores in this experiment was retained in the peat by binding to organic matter. Modified from Vile et al. (2000).

Acid-Insoluble Ash Dating

Acid-insoluble ash (AIA) consists mostly of refractory oxides and silicates that form the basic components of soil. AIA-dating (Urban et al. 1989) is based on the assumptions that 1) inputs of AIA to a bog remain constant over time and 2) after deposition, AIA remains immobile in the peat column.

Functionally, AIA is the acid-insoluble residue remaining after peat is subjected to combustion at 550 °C for 4 hr and the resulting ash dissolved in hot aqua regia (solution of 12 M HCl and 16 M HNO_3 in a 3: 1 v/v ratio). Input rates are determined from the amount of AIA in one year's growth of moss cover and serve as the basis for calculating the age at depth in a peat core. Alternatively, it should be possible to validate the amount of AIA in one year's moss growth by calibrating the AIA profile using an independent dating method.

AIA dating was corroborated by pollen and ^{210}Pb chronologies in northern Minnesota peatlands (Rapaport and Eisenreich 1986, 1988) but has been unsuccessful for dating peats older than 1930 in several U.S. and Czech temperate peatlands (Wieder et al. 1994, Vile et al. 1995). The AIA approach may be more useful in peatlands that are isolated from anthropogenic activities, where inputs of AIA are more likely to be constant over time. Major sources of AIA are fossil fuel combustion and the transportation of mineral soil particles from agriculture, other human activities, as well as episodic droughts (Wieder et al. 1994, Görres and Frenzel 1997, Hölzer and Hölzer 1998, Vile et al. 2000). These human activities violate the assumption of AIA dating by altering the deposition of refractory oxides and silicates. However, patterns of AIA deposition caused by these historical events potentially can be used as chrono-stratigraphic markers in peat.

AIA dating offers a low-cost, straightforward approach to building continuous chronologies in bogs. The assumption that AIA remains immobile in peat post-deposition has never been tested. Determining the amount of AIA in one year's growth of moss is a challenge, for example, given the difficulties of accurately estimating one year of *Sphagnum* growth (Clymo 1970). The chemistry involved in acid insoluble ash, however, is fairly straightforward and rapid. Small sample sizes are digested, about half a gram of dried sample per depth interval. As with ^{210}Pb-dating, any prior physical disturbance to the peat core may invalidate results.

Moss-Increment Dating

The shape and microstructure of individual moss plants have been correlated to the periodicity of annual growth increments and have been proposed as a dating method (Pakarinen and Tolonen 1977, Vitt and Pakarinen 1977). Potentially useful features include size and orientation of leaves, cyclic pigmentation, branching patterns and density, location of groups of gametangia, and changes in the growth direction of main shoots by pressure from snow cover (cf. Pakarinen and Tolonen 1977, Vitt and Pakarinen 1977, Pakarinen and Rinne 1979, El-Daoushy et al. 1982, Norton 1986, Eustis and Tolonen 1990, Jungner et al. 1995).

El-Daoushy et al. (1982) showed good agreement between moss-increment dating, ^{210}Pb dating, pollen markers (see section on pollen stratigraphy below), and radiocarbon dating in cores collected from Finnish peatlands (Figure 8). Norton (1986), however, found that ^{210}Pb dating in Maine peat provided ages consistently younger than the chronology constructed with moss-increment dating, while Eustis and Tolonen (1990) found good agreement between moss-increment ages and AIA dating for peat only to 10 cm in depth.

Moss-increment dating offers a low-cost approach to dating peat profiles. This method, however, is useful for only a few bryophyte taxa (i.e., *Dicranum majus*, *Hylocomium splendens*, *Meesia triquetra*, *Polytrichum spp*., *Sphagnum* spp.). Identification of annual markers may be subjective (Belyea and Warner 1994a) and becomes more difficult with depth (Eustis and Tolonen 1990), as ongoing decomposition and compaction alter moss macrostructure. Eustis and Tolonen (1990) concluded that moss-increment dating is practical only in hummocks when moss stems have not been horizontally compressed. Nonetheless, the presence of clear markers on several common moss species in bogs, poor fens, and rich fens makes this a valuable dating technique, at least for near-surface peat layers.

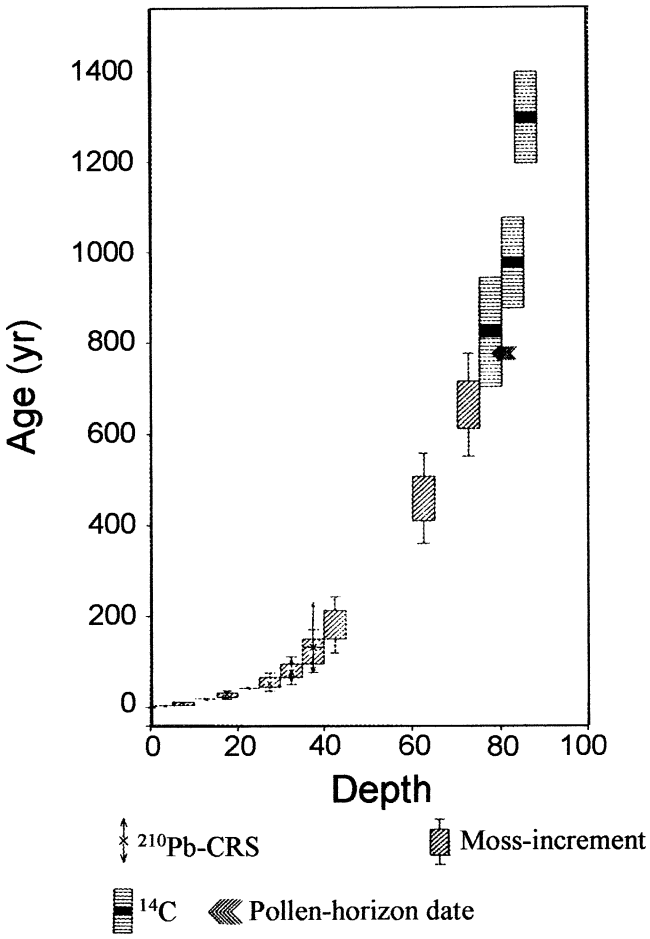

Figure 8. Age-depth profiles of peat layers from a *Sphagnum* hummock of a Finnish bog (Kunonniemensuo bog) showing good agreement between moss increment chronologies, ^{14}C dates, ^{210}Pb chronologies, and a pollen marker. Vertical bars represent $\pm$ 1σ of the ^{210}Pb ages or average error of the moss-increment years. Length of rectangles represents either the moss-increment age intervals or the uncertainties in the ^{14}C ages. Modified from El-Daoushy et al (1982). Reprinted by permission from Nature copyright 1982 Macmillan Magazine Ltd.

Constant Bulk-Density or Nitrogen Accumulation Dating

Bulk-density measurements of samples in a peat profile have been used to estimate peat age (Ilomets 1980, Punning et al. 1993, Belyea and Warner 1994a). This approach assumes a constant rate of peat accumulation over time, and provides rough estimates of peat age (Zoltai 1991, Belyea and Warner 1994a). Estimates are based upon an independently derived datum, usually established by radiocarbon dating. The mean volumetric peat accumulation rate is determined by measuring total peat mass beneath a specified surface area to the dated depth divided by the age of the datum. Ages of depth intervals in a peat core are calculated by multiplying the dry mass per volume of each depth interval by the age:cumulative dry mass ratio at the datum.

Based on radiocarbon dating of peat columns collected from 66 peatlands in western Canada, Zoltai (1991) found a significant linear relationship between peat cumulative dry mass and age (Figure 9). He concluded that mass measurements are useful indicators of age when absolute accuracy is not critical. Punning et al. (1993) used constant bulk density dating in association with pollen and radiocarbon dating. While the authors did not comment specifically on the usefulness of constant bulk density as a corroborative dating method, constant bulk density dates appeared to

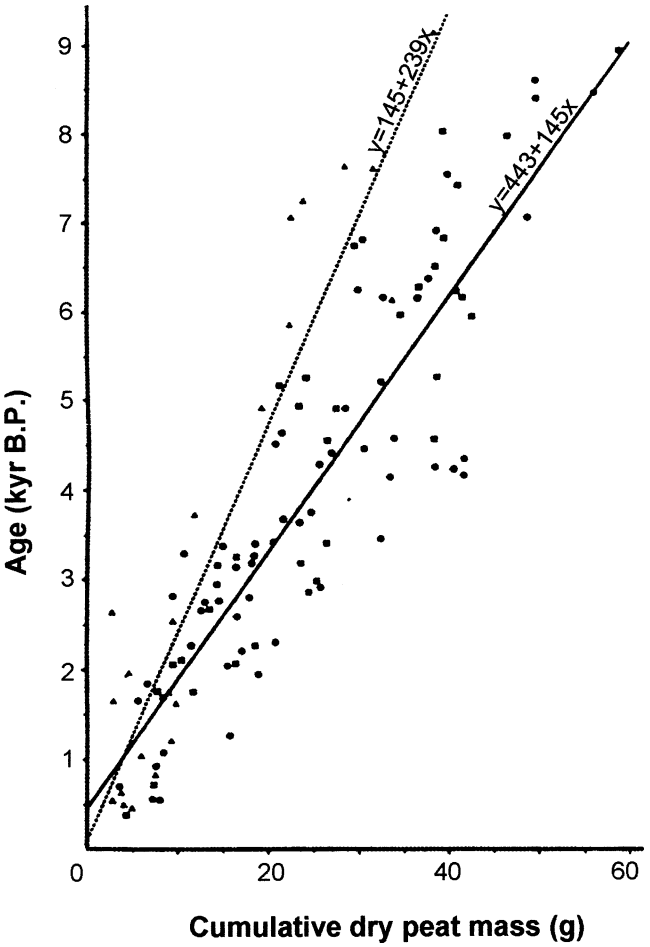

Figure 9. Age versus dry mass from Subarctic and Boreal peatlands in western Canada. The broken line with triangles represents Subarctic peat while the solid line with squares represents Boreal peat. Modified from Zoltai (1991).

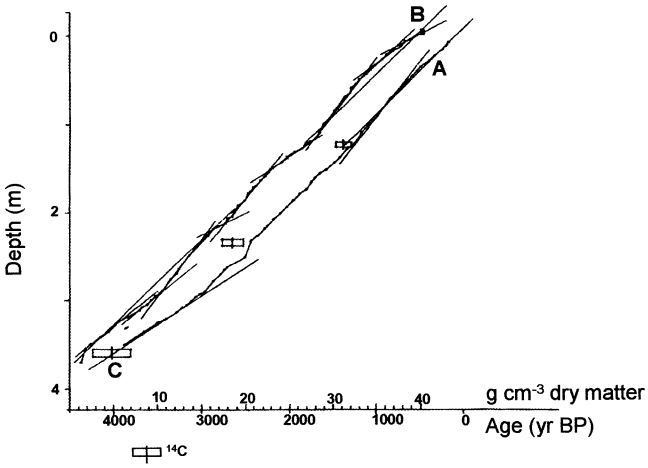

Figure 10. A. Depth versus the age of peat from a site in northeast Estonia derived from the constant peak bulk density method, B. Depth versus the cumulative curve of dry matter (g cm^{-3}), and C. changes in peat increment (mm yr^{-1}; based on A.). The constant bulk density curve shows fairly good agreement with radiocarbon dating. From Punning et al. (1993).

agree reasonably well with three radiocarbon dates within a peat core (Figure 10). These approaches, however, were appropriate at timescales of thousands of years and might not be useful for estimating ages in younger peat deposits or for quantifying ages at finer temporal scales.

Similarly, Malmer et al. (1997) used the mass balance of nitrogen and estimated N accumulation rates to establish time scales between radiocarbon dates. This method assumes that all nitrogen deposited on the surface of a bog is retained in organic matter over time.

These methods should not be applied to peat chronologies with stratigraphic changes that might indicate changes in bulk density or nutrient chemistry unless well-constrained by other dating methods. Accurate measurements of peat bulk density can be obtained with the use of coring techniques that cause minimal compaction in peats. Nitrogen concentrations require additional chemical measurements but are relatively inexpensive. Constant bulk density dating or nitrogen accumulation, therefore, can provide quick, rough estimates of peat age. The assumption of constant rates of peat accumulation above or between radiocarbon dates, however, is not realistic.

Pollen Density Dating

Von Post first applied pollen analysis to peat deposits in a study published in 1917 (in Jansonius and McGregor 1996). Today, fossil pollen analysis is a major tool used in paleoecology, paleoclimatogy, biostratigaphy, and archaeology. Many textbooks and reviews cover various aspects of palynology; for terrestrial Quaternary palynology, see especially McAndrews et al. (1973), Birks and Birks (1980), Berglund (1986), Prentice (1988), Faegri and Iversen (1989), Moore et al. (1991), MacDonald (1996), Jackson and Lyford (1999).

Quaternary palynologists generally assume that pollen in historical records was produced by plants with similar genotypic and phenotypic affinities to living species and that relationships between pollen-producing plants and environmental conditions in the past are similar to those of today (MacDonald 1996). Thus, palynologists often seek to understand modern pollen production and mechanisms influencing its subsequent transport and deposition. Generally, plants relying on wind pollination (anemophily) contribute to the largest component of pollen rain, much of which eventually is deposited into aquatic and wetland sediments (Jarzen and Nichols 1996). Pollen exines, consisting of a

complex polymer of carotenoids and carotenoid esters, are highly resistant to degradation and are preserved well in anaerobic sediments. Pollen grains can often be identified to genera and sometimes to species levels, allowing for the reconstruction of the vegetational history of a site or region. The transport of pollen to lake or wetland basins is dependent upon plant species, plant morphology, community/canopy structure, landscape position, and climate (Jarzen and Nichols 1996, MacDonald 1996).

Rates of peat accumulation have been estimated with the abundance of pollen grains in a sequence (e.g., Conway 1947, Dickinson 1975, Middledorp 1982, 1986, Rowell and Turner 1985, Punning et al. 1993). This method depends upon an independently derived date (Belyea and Warner 1994a) and assumes that the pollen deposition rate has been constant during the period covered (Turner and Peglar 1988). Concentrations of pollen are expressed cumulatively beneath a specified surface area of peat and can be used to estimate age if the average rate of pollen accumulation in peat within a given time interval is known (Middledorp 1986). Changes in pollen concentration within the peat profile are interpreted accordingly as indicating variation in peat accumulation (Irwin 1989).

Depth-age chronologies based on radiocarbon dating in peat have corresponded well to relationships between depth and cumulative arboreal pollen (Middledorp 1982, Rowell and Turner 1985, Punning et al. 1993). Tolonen (1985b) applied pollen density dating to a peat chronology in southwest Finland using a mean accumulation rate of 1.3×10^4 pollen grains cm^{-2} yr^{-1} and estimated that 16 cm of vertical net peat accumulation represented 65 $\pm$ 15 yr. Punning et al. (1993) advocated the use of pollen density dating in peat if no major changes in the development or hydrology of the peatland have occurred.

Assumptions underlying this technique, including the immobility and constant deposition of pollen grains over time, have been investigated. Boyd (1986) found that moss morphology played an important role in the entrapment of pollen grains. Irwin (1989) reported higher concentrations of pollen in an ericaceous hummock than a *Sphagnum*-dominant hollow in the acrotelm of the same peatland, and concluded that hummocks trap pollen more efficiently than hollows. Pollen grains have been shown to move with water through peat under experimental flow regimes (Clymo and Mackay 1987). In a field setting, however, Rowley and Rowley (1956) found that downward movement of pollen was limited to less compacted *Sphagnum* peat. They concluded that pollen migration is differential with taxa and occurs only at the time of deposition. Nonetheless, spatial variability in pollen trapping may contribute an element of error to pollen density dating.

Jacobson and Bradshaw (1981) reported high variability in pollen accumulation rates in peat. Source area varies for pollen taxa. Even well-dispersed pollen such as pine (*Pinus)* may show variability in local deposition (Bennet 1986, Grimm 1988). Pollen spectra can reflect vegetation on different spatial scales, including local and long-distance components (cf. Janssens 1973). Pollen density dating may not be a suitable choice for dating small peat deposits with limited source areas, as single events such as treefall may have large effects on their pollen rain (Turner and Peglar 1988).

Pollen density dating is an inexpensive option, although time consuming. Preparation of samples for pollen analysis typically involves boiling in potassium hydroxide, concentrated hydrofluoric acid, and a mixture of sulfuric acid and acetic anhydride (acetolysis; Faegri and Iversen 1975; see also Berglund and Ralska-Jasiewiczowa 1986, Moore et al. 1991, and Wood et al. 1996 for useful descriptions of pollen methodology). Most organic material is destroyed by the latter solution, leaving pollen exines and resistant organic components in solution. Samples then are stained and mounted for slide preparation and microscopy (Jacobson 1988). Before chemical treatment, tablets containing known amounts of exotic pollen (i.e., *Eucalyptus* pollen or *Lycopodium* spores) can be added to each sample to help determine the pollen concentrations (Benninghoff 1962, Stockmarr 1971, Thompson 1980, Maher 1981, Ogden 1986). Pollen grains can be identified from published keys and reference material (cf. McAndrews et al. 1973, Birks and Birks 1980, Moore et al. 1991). Pollen density dating is a valid option for a dating tool where vegetation has not been altered significantly in the past few hundred years.

Pine Dendrochronology

Several studies have dated the accumulation of recently deposited moss-derived peat using pine dendrochronology (Ohlson and Dahlberg 1991, Koff et al. 1998, Schultze et al. 2002). This method can only be used in bogs or other treed peatlands, where the position of *Pinus* hypocotyls is expected to remain constant in relation to surrounding moss layers. Over time, mosses grow and essentially 'bury' tree stems. Therefore, the accumulation of moss layers above the hypocotyls can be dated in relation to the age of pine trees. This method assumes a constant rate of peat accumulation above the hypocotyl. Schulze et al. (2002) plotted the total accumulation of peat (in kg m^{-2}) as a function of tree age along a pine chronosequence in a Siberian bog to estimate annual rates of peat accu-

mulation. They concluded that the dendrochronology method was useful because of its applicability to large spatial scales but that it may overestimate carbon storage in relation to other methods.

CHRONO-STRATIGRAPHIC OR SINGLE EVENT MARKERS

Pollen Stratigraphy

Regional or local changes in pollen abundance or species composition may serve as reliable time markers in peat (Lee and Tallis 1973, Cole et al. 1990, Belyea and Warner 1994a, Wieder et al. 1994, Sanders et al. 1995, Vile et al. 1995, Appleby et al. 1997). The pollen record can provide insights into major changes in terrestrial vegetation caused by disease, land use, and introduction of cultivars/exotics (Brush et al. 1982). Increases in the abundance of ragweed (*Ambrosia*) pollen long have been associated with the widespread settlement and agricultural disturbance by Europeans in North America (Truman 1937, Bazzaz 1974, Brugam 1978, Kemp et al. 1978, van Zant et al. 1979, Engstrom and Swain 1986). Other pollen types such as plantain (*Plantago*), sorrel (*Rumex*), and rye (*Secale*) have been used as indicators for European cultivation (cf. McAndrews 1966, Davis 1967, Janssens 1967, Davis et al. 1971, Webb 1973, Brugam 1978, van Zant et al. 1979). Decreases in arboreal pollen may reflect forest clearance associated with agriculture. Because the timing of westward colonization is well-documented in North America, increases in the abundance of pollen types associated with disturbance or agriculture in a peat profile can provide a clear time marker for a particular region.

Agricultural development occurred much earlier in Europe than North America; therefore, pollen markers may not be as useful for dating recent European peats. Tolonen (1985b) found an increase in rye (*Secale*) pollen in a peat deposit in southwest Finland with the onset of rye cultivation in the area around 1600–1800 B.P. As early as 200 A.D., forest clearance and slash and burn cultivation in southern Finland were evident in pollen records from both lake and peat cores through increases in rye, flax, hemp, and hops pollen (Huttunen 1980). Dupont (1986) investigated the human influence on the palynology of a bog in The Netherlands and found that anthropogenic indicator pollen (including Cerealia, *Spergula*, *Urtica*, Chenopodiaceae, and *Artemisia*) peaked as early as 2250 B.P., and the first anthropogenic indicator pollen appeared at 1900 B.P. during the Roman Iron Age.

The decline of the American chestnut (*Castanea dentata* (Marsh.) Borkh.) pollen due to the spread of the chestnut blight has been used as a marker in North American peats (Wieder et al. 1994). The decline of American chestnuts began in New England in 1912 and spread southward through the Appalachian Mountains (Anderson 1974, Allison et al. 1986). Declining concentrations of *Ulmus* pollen due to Dutch Elm disease has been a useful regional marker in North American and European peats (Cole et al. 1990, Sanders et al. 1995).

Pollen markers have proven to be useful in corroboration with ^{210}Pb based chronologies (cf. Cole et al. 1990, Wieder et al. 1994, Vile et al. 1995, Appleby et al. 1997). Hemp was grown in the Jura Mountain region of Switzerland until 1930, providing a marker that was consistent with ^{210}Pb dating of peat cores in the region (Appleby et al. 1997). Pollen signals reflecting regional changes in land use, land cover, and agricultural practices in the Czech Republic also have been useful in corroborating ^{210}Pb dates in peats (Vile et al. 1995).

Dates associated with changes in land use or disease as reflected in the pollen record will vary regionally. Identifying historical events with the use of pollen may be useful in providing chrono-stratigraphic markers in peats, although pollen markers cannot provide a continuous chronology, especially for high resolution dating in near-surface peat. Nonetheless, pollen can be used to build chronologies that span long time periods, as long as the age of historical events recorded by pollen can be determined (i.e., from historical records, ^{14}C-dating, etc.). As with pollen density dating, the use of pollen markers relies upon the assumption of negligible post-depositional movement.

Constructing complete pollen profiles for entire peat cores is time-consuming (see section above for pollen methodologies). Screening for changes in the abundance of key pollen taxa (such as *Ambrosia*, *Castanea*, or *Cannabis* in the examples given above), however, can provide good corroboration of alternative dating techniques.

Magnetic Records

Fuel combustion, including metal smelting, iron and steel manufacturing, and coal combustion, converts iron impurities into ferro- and antiferro magnetic iron oxides, mainly magnetite and haematite, that are released to the atmosphere and subsequently deposited onto the earth's surface (Chaddha and Seehra 1983, Thompson and Oldfield 1986). Pure organic matter possesses weak magnetism (typically diamagnetic or paramagnetic); therefore, assessing the magnetic properties of a peat chronology can provide useful information on the timing and nature of regional fuel combustion. Because the concentrations of magnetic minerals in peatlands will be low except under conditions

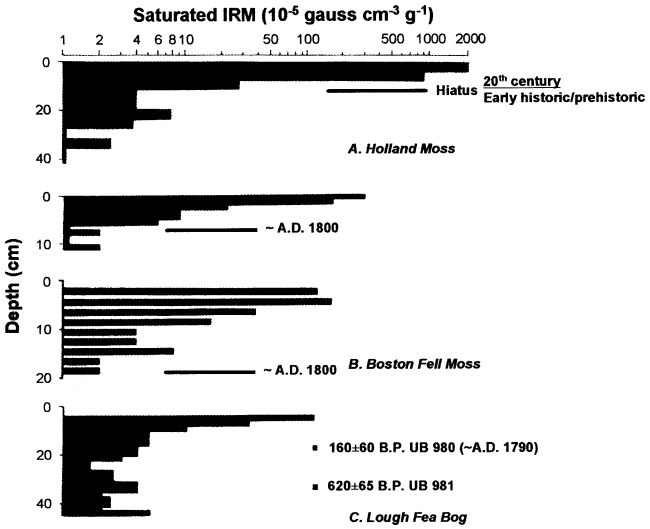

Figure 11. Variations in saturated isothermal remanent magnetization (SIRM) with depth in ombrotrophic peat profiles from bogs in the UK. All samples were measured after saturation in an applied field of 10^4 oersteds. Enriched magnetic particles in near surface peat could be used to date the onset of fuel combustion. Modified from Oldfield et al. (1978).

of extreme pollution, the characterization of magnetic records in peat chronologies is limited to sensitive techniques (Thompson and Oldfield 1986). Saturation isothermal remanent magnetization (SIRM) refers to the maximum remanence (or magnetization remaining in the absence of an external magnetic field) attainable by the application and subsequent removal of a strong magnetic field under laboratory conditions (Thompson and Oldfield 1986). Magnetic susceptibility, a measure of the ease with which a sample can be magnetized in laboratory conditions, also has been applied to peat deposits. In natural materials, SIRM and susceptibility mainly reflect magnetite content and are useful proxies for magnetite concentrations. In parts of the world where the history of regional industrial activity is well-documented, patterns of SIRM or susceptibility may serve as a useful time marker in peats (Oldfield et al. 1978, Beckwith et al. 1986, Schell 1987, Livett 1988, Sanders et al. 1995, Vile et al. 1995, 2000). Magnetic records also have been used in establishing fire histories (Rummery et al. 1979).

Oldfield et al. (1978) combined radiocarbon dating, pollen analysis, and SIRM measurements in ombrotrophic peatlands in Britain and N. Ireland and found increased levels of magnetic material in near-surface peat compared to prehistoric peat. Their sites differed in proximity to industrial sources; however, they concluded that even their remote location (Lough Fea Bog in N. Ireland) showed increased magnetism dominated by magnetite in surface layers (Figure 11; Oldfield et al. 1978, Thompson and Oldfield 1986). Similarly, elevated SIRM was reported in sub-surface peat samples from Cumbria (Oldfield et al. 1979). Rapaport and Eisenreich (1986) concluded that magnetic dating overestimated rates of peat accumulation compared to acid insoluble ash dating and dichloro-diphenyl-trichloroethane (DDT) inputs. Relationships between depth and magnetic susceptibility in Czech peatlands did not reveal clear trends towards increasing magnetic activity in surface peat (Vile et al. 2000).

Tehnological advances over the past few decades in magnetic susceptibility and remanence measurements have led to increases in sensitivity and decreases in the cost of analyses. The bulk of environmental magnetic measurements are made on susceptibility bridges and fluxgate magnetometers (Thompson and Oldfield 1986). The ease of sample preparation, rapidity of analysis, and non-destructive nature of the methods are advantages to reconstructing magnetic records as chrono-stratigraphic markers.

However, the immobility of magnetic particulates in peat profiles has not been tested, although post-depositional immobility remains a major assumption of this method. Williams (1992) concluded that magnetic records in peat stratigraphies will be influenced by the dissolution of magnetite in reducing, water-saturated peat layers. Oldfield et al. (1979) reported higher concentrations of magnetic particles in peatland hummocks compared to hollows. This pattern was interpreted as a result of differential uptake, where hollows or pools received particles mainly through precipitation while hummocks scavenged particles through horizontal eddy diffusion (Thompson and Oldfield 1986). This trend also could be attributed to Eh-controlled dissolution of magnetic oxides (Williams 1992). While the importance of regional or global deposition of magnetic particles has not been investigated in peat deposits, magnetic records based on anthropogenic activities probably are most useful in populated or industrial areas, as they rely on measuring the byproducts of fossil fuel combustion and interpreting historical patterns of deposition.

Hydrophobic Organic Compounds: PAHs, PCBs, DDT, and Toxaphene

Large, non-polar, hydrophobic organic compounds, such as polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs), bind strongly to the organic matter matrix in peat (Rapaport and Eisenreich 1988, Sanders et al. 1995). When such compounds have a known recent history of use and are deposited onto bog surfaces from the atmosphere, they may serve as time markers.

PCBs. PCBs have been used globally since their first manufacture in 1929 (Bracewell et al. 1993). PCB use in the U.S. decreased dramatically following a 1971 voluntary ban on non-contained use. The manufacturing, importation, and most non-electrical uses of PCBs in Canada were banned in 1977 (Environment Canada 1991). The sole manufacturer of PCBs in the United Kingdom limited their sale after 1971 for specified 'open' uses (Jones et al. 1992). PCB use decreased in 1973 following an Organization for Economic Cooperation and Development (OECD) control decision in 1973. Nevertheless, PCB production in some European countries exceeded 15,000 tonnes in 1980 (Yrjänheikki et al. 1987). Atmospheric transport and deposition are major modes of global distribution of PCBs and other organochlorine compounds (Simonich and Hikes 1995, Bignert et al. 1998, Wania 1999, Wania and Mackay 1999).

Rapaport and Eisenreich (1988) used acid-insoluble ash dating and DDT (dichloro-diphenyl-trichloroethane; see below) inputs to determine that PCB concentrations in several eastern North American bogs followed closely the patterns of historical use in the United States, with maximum PCB inputs between 1967 and 1970. PCB concentrations began increasing around 1932 in an English peat chronology based on ^{210}Pb and ^{241}Am data (Sanders et al. 1994). Maximum concentrations of PCBs occurred at a depth corresponding to the early to mid-1960s, consistent with patterns of PCB production in the United Kingdom, which peaked in the late 1960s (Figure 12; Sanders et al. 1994, 1995). Himberg and Pakarinen (1994) estimated that atmospheric deposition of PCBs from 1976 to 1986 ranged from 13 to 63 $\mu g\ m^{-2}\ yr^{-1}$ from moss samples collected from two ombrotrophic bogs in southern Finland. They concluded that PCB concentrations in moss samples decreased consistently within this time period.

In both U.K. and U.S. peatlands, significant amounts of PCBs have been measured prior to the production periods. This may be the result of immediate downward percolation of PCBs with rainfall (Rapaport and Eisenreich 1988, Sanders et al. 1995). Movement of PCBs in peat has not been tested directly; however, field data suggest that PCB immobility may not be a completely reliable assumption.

PAHs. PAHs are the products of incomplete combustion and include many carcinogenic and/or mutagenic compounds (Jones et al. 1992). Fossil fuel combustion has been the major source of PAHs over the past century (Environment Canada 1991). Several studies have documented recent decreases in PAH loading to lake and peat sediments, most likely associated with decreases in heavy industry and the establishment of clean air regulations (Cranwell and Koul 1989, Sanders et al. 1993, 1995). PAH loadings to an English bog increased around the beginning of the Industrial Revolution and peaked in the early 1930s (Sanders et al. 1995). Correlations between PAH or hydrocarbon derived particulates and magnetic properties of sediments suggest that hydrocarbons can dominate ferromagnetic influx to peat and lake sediments (Williams 1992, Morris et al. 1994).

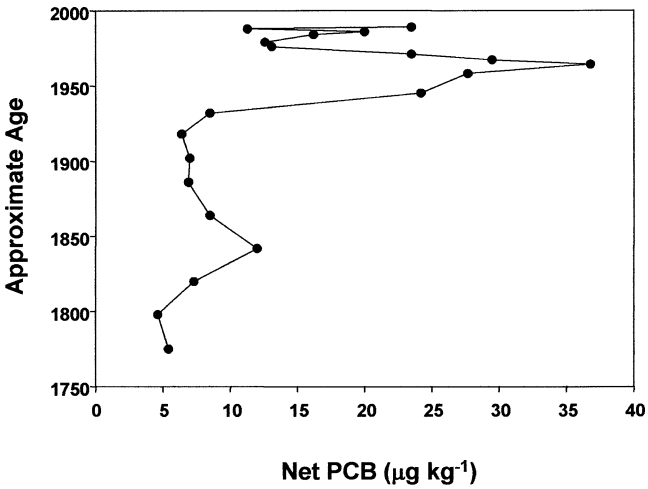

Figure 12. Net PCB concentrations (sum of 25 congeners) versus depth in a UK peat core. PCB concentrations peak at 17 cm (dated at ~1964 using a ^{210}Pb profile constrained by the ^{241}Am peak at 1963/1964 shown in Figure 14). Increasing PCB concentrations near the surface may be due to upward outgassing or transport by vegetation. Generally, these data agree with historical PCB production in the UK, which peaked in the mid- to late- 1960s. From Sanders et al. (1995) with permission from Elsevier Science.

DDT. DDT production began during World War II, and consumption in the United States peaked in 1960 (United States Environmental Protection Agency 1975). In 1972, the United States Environmental Protection Agency issued a ban on all but minor uses of DDT, limiting its use to nearly zero. Its use was severely restricted in Canada in the early 1970s, but it was not banned until 1991 (Environment Canada 1991). DDT remains an important insecticide globally, and small amounts continue to reach North America through long-range transport (Rapaport and Eisenreich 1988). The replacement choice for DDT after the U.S. ban was polychlorinated camphene (toxaphene), whose use peaked between 1975 and 1978 (Rapaport and Eisenreich 1986, 1988). The history of DDT and toxaphene production clearly is reflected in their concentrations in dated peat cores collected from bogs throughout the eastern U.S. and Canada (Rapaport and Eisenreich 1988).

Hydrophobic contaminants such as PCBs and PAHs

can be determined in organic solvent extracts using gas chromotography, high performance liquid chromatography, or gas chromatography-mass spectrometry. Various extraction and purification methods have been developed (cf. Wickström and Tolonen 1987, Wershaw et al. 1987, Sander et al. 1992, Foreman et al. 1994, Morris et al. 1994, Sanders et al. 1995, Van Metre et al. 1997). During analysis, individual congeners in samples are identified and quantified against known, calibrated standards.

PCBs, PAHs, DDT, and toxaphene all have the potential to serve as clear time-equivalent stratigraphic markers in peat. Each contaminant has well-known temporal patterns of use and release to the environment and can be measured quantitatively in peat samples even at low concentrations. Potential long-range transport of these chemicals also may produce historical markers in remote peatlands. However, constructing historical patterns of contaminant use may be difficult with larger scale distribution compared to local or regional deposition. Drawbacks to the use of these contaminants as dating tools in peats are the high cost and complexity of their analyses.

Spherical Particles

Spherical particles, often referred to as soot balls, soot spheres, or cenospheres, are a by-product of oil and coal combustion and have served as the basis for dating recent lake sediments (cf. Tolonen et al. 1975, Wik et al. 1986, Rose et al. 1995, Wik and Renberg 1996; Figure 13). The surface morphology and structure of carbonaceous particles can reveal information about the nature and history of fuel-use (Griffin and Goldberg 1979, 1981, Kothari and Wahlen 1984). In general, the combustion of fossil fuels is associated with the presence of spherical particles in sediments and peats (Kothari and Wahlen 1984). Clark and Patterson (1984) reported that the majority of spherical particles were 5–25 μm in diameter. Carbonaceous particles formed through oil combustion show convoluted, layered structures, whereas the surfaces of coal and wood carbons are homogeneous (Griffin and Goldberg 1979, 1981). Oil combustion tends to form spherical particles, while a mixture of spherical and elongate particles are generated by coal combustion. Particles formed via burning of wood and vegetation often show remnant cellular structures and tend to be elongate (length to width ratios > 3; Griffin and Goldberg 1979, 1981).

Carbonaceous particles can be quantified via light microscopy, with sample preparation usually involving oxidation of organic matter with H_2O_2 prior to counting or analysis of elemental carbon. Particle morphology can be examined through scanning electron microscopy (see Griffin and Goldberg 1979, Kothari and Wahlen 1984, Rose 1990).

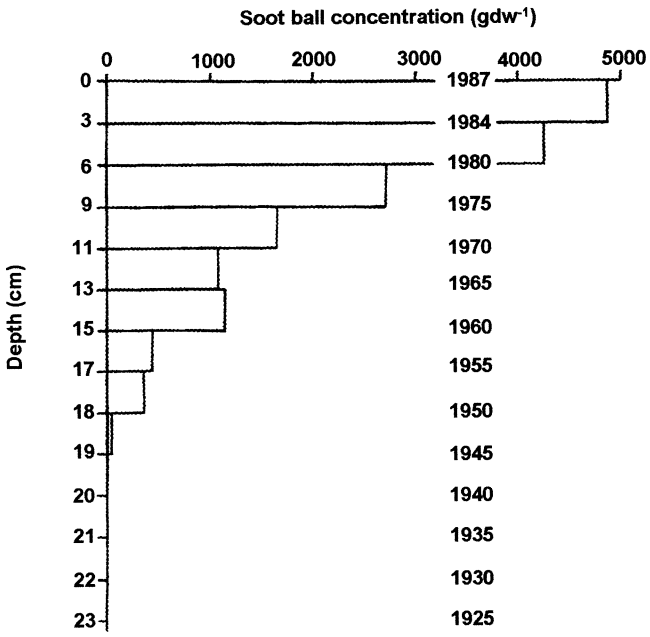

Figure 13. Concentrations of carbonaceous particles or soot balls (g dw^{-1}) versus depth and age in a varved sediment of Lake Laukunlampi. Soot ball chronologies in Finnish lakes agreed well with historical coal and oil consumption in the region. Dating by soot balls corroborated well with ^{210}Pb dating and varves in Bothnian Bay sediment, but ^{210}Pb ages were older than those derived from soot balls in more acidic lakes. Fom Tolonen et al. (1990).

Increases in the abundance of carbonaceous particles in lake and marine sediments have been compared with historical records of fossil fuel combustion to provide useful chrono-stratigraphic markers. Griffin and Goldberg (1979, 1981) reported increases in the abundance of spherical carbonaceous particles in Lake Michigan sediments around 1930, with shifts from elongate particles from wood consumption to a greater abundance of spherical coal particles. The first evidence of oil combustion appeared around the late 1940s. Similarly, increasing numbers of spherical particles deposited after 1900 were analyzed in intertidal sediments in New York (Clark and Patterson 1984). To our knowledge, however, there are few studies in which the profiles of carbonaceous particles in peat deposits have been linked directly to a known historical record of fossil fuel use. Tolonen (1985b) reported an exponential increase in carbonaceous particles in the upper 16 cm of a peat profile in SW Finland. Increases in spherical particles in Estonian peat were correlated to the development of the oil industry in the late 1950s (Punning and Alliksaar 1997, Koff et al. 1998). Focusing on a longer time scale, Gilbertson et al. (1997) linked patterns of soot concentration with

depth in a peat core collected from a bog in Sheffield, U.K. to regional manufacturing of iron and steel throughout the 19th and 20th centuries.

Quantification and evaluation of spherical carbonaceous particles are easy to combine with pollen analysis. Counting carbonaceous particles may be time-consuming but inexpensive. As with magnetic susceptibility measurements, this technique will identify only a general time period corresponding to regional combustion of fossil fuels. However, long distance transport of carbonaceous particles may interfere with interpretations of regional fuel use, as spherical particles have even been found in arctic systems (Rosen et al. 1981). Irregular shaped particles, formed by wood, coal, and oil combustion, also could complicate measurements of spherical particles.

Charcoal Particles

Charcoal from the incomplete combustion of plant tissue preserves well and can be used as a proxy of past fires (Patterson et al. 1987). Charcoal production is related to the intensity of fire as well as the nature of the material being burnt. Wind and water movements are the primary dispersal modes for charcoal, although most charcoal is deposited soon after production (Patterson et al. 1987). Charcoal layers within a peat core can be used as a dating tool when correlated to fire events of known age. Approaches may include analysis of historical records of regional fire activity, use of dendrochronological techniques, or corroboration of charcoal concentrations in nearby annually laminated (varved) lake sediments (cf. Gajewski et al. 1985, Tolonen 1985a, Alm et al. 1993, Pitkanen and Huttenen 1999, Pitkanen et al. 1999).

While charcoal has been used frequently to determine fire histories in peats, it rarely has been used as a dating tool, likely due to the difficulties in defining local versus regional signals in charcoal data. Alm et al. (1993) were able to assign dates to two charcoal layers in the upper portions of a peat deposit in central Finland using dendrochronologically-dated fire scars on Scots pine (*Pinus sylvestris*) stumps. Evidence of increased numbers of charcoal layers in peat deposits as a result of slash-and-burn cultivation may be a useful historical marker (cf. Tolonen 1985b).

Macroscopic charcoal or ash layers can be identified visually within intact cores or from sieve washing of samples (cf. Clark 1982, Tolonen 1985b,c, Patterson et al. 1987, Foster and Zebryk 1993, Efremova and Efremov 1994). Quantitative methods for charcoal analysis, however, including microscopy and elemental carbon analysis, are more time-consuming (Patterson et al. 1987). Individual particles, total area, or size classes of charcoal fragments can be counted under a light microscope in pollen slides, sediment sections, or sieved samples (cf. Waddington 1969, Tallis 1975, Cwynar 1978, Tolonen 1978, Tolonen 1985b, Patterson et al. 1987, Sarmaja-Korjonen 1991, Tinner and Hu 2003). Chemical analysis of charcoal involves nitric acid digestion followed by ignition at around 500 °C for several hours to determine mineral content (Tallis 1975, Robinson 1984). Data can be expressed as total charcoal content per unit sediment, influx of charcoal per unit area per year, charcoal percentage of the pollen sum, or ratio of charcoal to total pollen (Waddington 1969, Patterson et al. 1987). Winkler (1985) subtracted dry weight following ignition (500 °C for 3 hr) from the dry weight after digestion in nitric acid to yield charcoal percentages.

Robinson (1984) concluded that visual estimates by sieving provided qualitative measures of charcoal abundance but missed small particles that passed through sieves. The microscopic method (total area of charcoal particles) was considered more precise and reliable than chemical digestions (digested in sodium hydroxide and nitric acid, and combusted at 500 °C for 5 hr). Winkler (1985) found correlation between microscopic charcoal and results obtained from a digestion method. Tinner and Hu (2003) found that preparation techniques can influence charcoal size and size-class distributions in lake sediments and concluded that measurements of charcoal area in pollen slides may by unnecessary.

Because most charcoal analyses have been performed in corroboration with pollen analysis, microscopy has been used more commonly than elemental analysis. Breakage of large charcoal particles is thought to be a potential complication to investigations of charcoal abundance by microscopy (Patterson et al. 1987). However, no difference between the total number of charcoal particles and the total area of charcoal in size classes ranging from 25 to 3200 μm^2 was found in a Finnish peat once ratios of charcoal to arboreal pollen were used to correct for higher concentrations of particles with increasing bulk density (Sarmaja-Korjonen 1991).

The use of charcoal as a dating tool assumes minimal post-depositional movement of charcoal and ash particles in the peat matrix. This assumption may be more serious for charcoal analysis than for pollen dating, as fire events must be identified over short time periods. Clearly, undisturbed peat must be used to identify individual fires. Microscopic charcoal (5–80 μm diameter) might be more influenced by regional charcoal sources than local sources, complicating the use of charcoal records for constructing local fire histories (Clark 1988). Tolonen (1983) also cautioned that fire history information in peat may not be useful because 1) only local fires leave detectable horizons and

2) fire activity may be particularly heterogeneous in peatlands. Large abundances of charcoal particles not associated with burned peat within a core may be interpreted as reflecting charcoal deposition outside the local basin (Tolonen 1985b). Charcoal analyses may also be complicated by the presence of spherical carbonaceous particles generated through fossil fuel combustion. These carbonaceous particles may interfere with identification of charcoal particles.

Fallout Isotopes: ^{137}Cs, ^{241}Am, ^{207}Bi

Aboveground nuclear weapons testing in the late 1950s and early 1960s, along with the Chernobyl accident in 1986, left discrete radioactive markers in environments that favor post-depositional immobility (Walling and He 1993, von Gunten 1995). Fallout isotopes, including ^{137}Cs ($T_{½}$ = 30.2 yr), ^{241}Am ($T_{½}$ = 432.2 yr), and ^{207}Bi ($T_{½}$ = 31.55 yr), may be useful geochronological tools in peat deposits. Each of these isotopes is a gamma emitter, although their detection in peat cores may be limited by low activities.

^{137}Cs. Cs-137 is the predominant nuclide present in inventories from the Chernobyl accident and nuclear weapons testing. Worldwide deposition of ^{137}Cs from Chernobyl fallout reached 89,000 TBq (Colgan et al. 1993). Cs-137 does not appear to remain immobile in acidic peat and is affected by diffusion and advection through pore water as well as biological uptake by vegetation (Schell 1986, Schell et al. 1989, Urban et al. 1990, Mitchell et al. 1992, Colgan et al. 1993, Gerdol et al. 1994, Oldfield et al. 1995, Appleby et al. 1997, Kim et al. 1997, MacKenzie et al. 1997, Cohen et al. 1999). MacKenzie et al. (1997) reported a lower degree of ^{137}Cs mobility in peats with high mineral content due to the importance of clay minerals to ^{137}Cs exchange (Shand et al. 1994, Hird et al. 1996, Livens et al. 1996). Eight years after the Chernobyl accident, runoff coefficients of fallout ^{137}Cs from peatlands were about one order of magnitude greater than coefficients from soils with larger mineral contents (Kudelsky et al. 1996). Cs-137 losses from an Irish peatland were 63% from nuclear weapons testing and 47% from Chernobyl fallout compared to inventories from nearby mineral soils (Colgan et al. 1993).

Concentrations of ^{134}Cs ($T_{1/2}$=2.08 yr) remaining in soils and peats as a result of the Chernobyl accident can be quantified to separate the relative concentrations of ^{137}Cs into Chernobyl and nuclear weapons fallout components. Chernobyl fallout is isolated using measured ^{137}Cs:^{134}Cs activity ratios of sample, taking into account radioactive decay since deposition, as well as known ratios of fallout immediately following the Chernobyl accident (cf. McGee et al. 1992, Mitchell et al. 1992, Colgan et al. 1993, Gerdol et al. 1994, Mackenzie et al. 1997).

^{241}Am. Am-241 is produced via radioactive decay of ^{241}Pu (Colgan et al. 1993). Although the potential for post-depositional mobility of ^{241}Am remains largely untested, this nuclide appears to be less mobile within peat profiles than ^{137}Cs and hence may be a more useful chrono-stratigraphic marker (Clymo et al. 1990, Appleby et al. 1991, 1997, Oldfield et al. 1995, Sanders et al. 1995, Shotyk et al. 1997b, Smith et al. 1997). Mitchell et al. (1992), however, did find evidence for the mobility of ^{241}Am in peat, suggesting that this isotope may not be a useful dating tool.

^{207}Bi. Bi-207 has not been well-tested as a geochronological tool. However, peaks in the concentrations of ^{207}Bi in a salt marsh were found at similar depths in different locations, suggesting post-depositional immobility (Kim et al. 1997). Peaks in ^{207}Bi were found at depths corresponding both to the mid-1960s based on ^{210}Pb-dated chronologies in lake sediments (Joshi and McNeely 1988) and to peak fallout of ^{137}Cs in soil and vegetation samples (Aarkrog et al. 1984). Interference by ^{134}Cs may provide difficulties in detecting ^{207}Bi via gamma spectroscopy but should become less of a problem in samples older than about 20 years due to the short half life of ^{134}Cs (Kim et al. 1997).

Radiogenic fallout from the Chernobyl accident will become a more useful stratigraphic marker in the future, especially in central and eastern Europe, as it ingrows and is progressively buried deeper in peat chronologies (Schell et al. 1997). The low activities of nuclear fallout in peats may necessitate the use of large sample sizes and long counting times. As many have found evidence for ^{137}Cs mobility in soils and peats, we do not recommend its use as a dating method in peatlands. Moreover, Sanders et al. (1995) warn that classic radioisotopic methods often are inconsistent and unreliable to use alone or as corroborative tools (Figure 14). However, we feel that an investigation into the mobility of ^{207}Bi in peat would be worthwhile.

Other Dating Tools

Other chronostratigraphic markers may prove to be useful in dating recent peats. Deposition of heavy metals such as Pb, Cu, Zn, and V with mining, smelting, or other anthropogenic activities has not been used specifically as a dating tool but has been linked to historical patterns of use (cf. Farmer et al. 1997, Görres and Frenzel 1997, West et al. 1997, Shotyk et al. 1998, Vile et al. 2000) and could, therefore, serve as a stratigraphic marker in peat deposits. Lead in particular can be related to regional patterns of lead-based petrol additives and subsequent un-

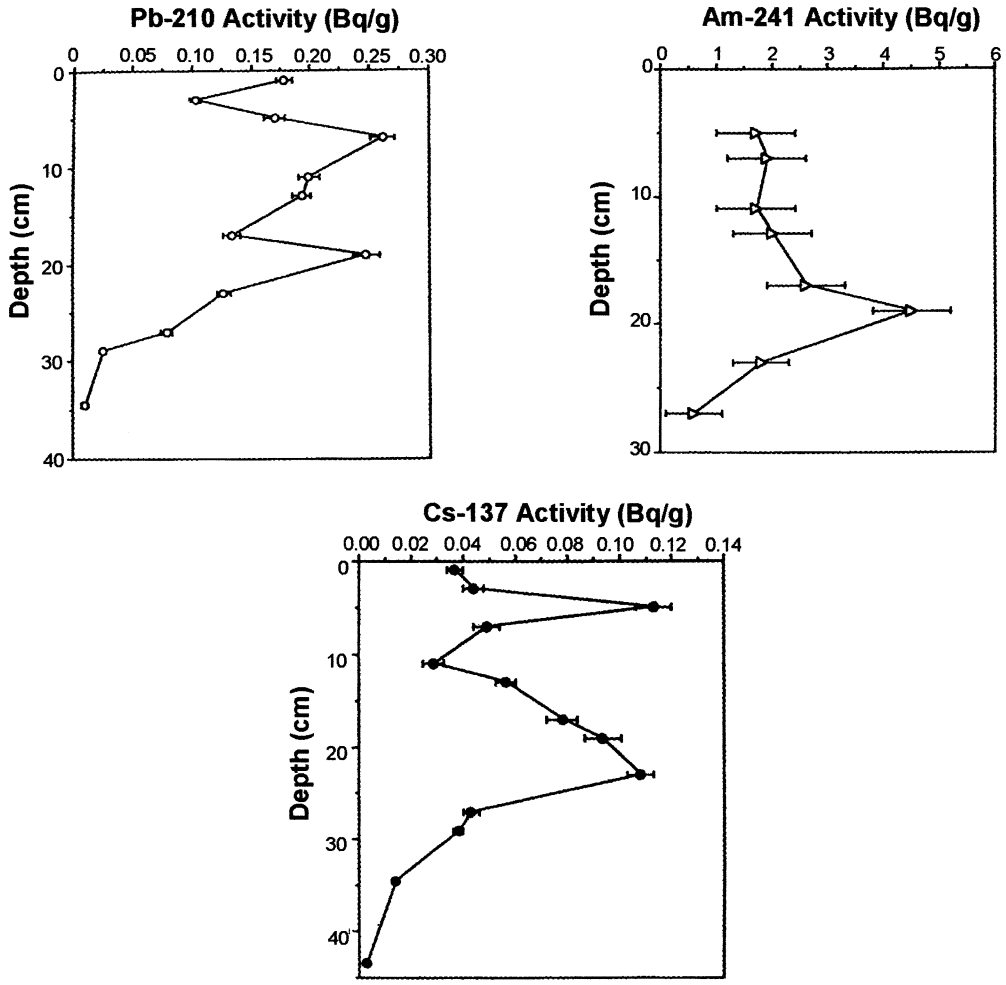

Figure 14. Depth versus radioisotope activities in a UK peat core. A. ^{210}Pb activities do not show a monotonic log-linear distribution, B. ^{241}Am activities show a relatively tight peak at 19 cm beneath the surface, which may correspond to the onset of nuclear weapons testing in the early 1960s, and C. ^{137}Cs activities show two maxima at 5 and 23 cm beneath the peat surface, which may correspond to Chernobyl- and nuclear weapons- derived ^{137}Cs. The latter maxima occurs 4 cm lower than the ^{241}Am bomb spike, suggesting that at least one radioisotope experienced downwards mobility. Modified from Sanders et al. (1995).

leaded gasoline use. Stable isotope abundances of Pb are useful in identifying the geochemical origins and fuel source of Pb deposition (Farmer et al. 1997). Shotyk et al. (1998) used ^{206}Pb/^{207}Pb and Pb enrichment factors to differentiate background from anthropogenic fluxes.

Tephrochronologies have been developed in peatlands situated in Great Britain, Canada, and New Zealand (cf. Dugmore et al. 1995, Dugmore et al. 1996, Pilcher and Hall 1996, Pilcher et al. 1996). This approach, however, mostly has been useful in dating peats on the order of thousands of years. Tephrochronology depends upon correlating layers of tephra to historical records of volcanic eruptions. Volcanic ash, the smallest tephra fragments, can travel up to thousands of kilometers downwind from a volcano. Tephra can be identified visually, microscopically, or chemically by electron microprobe analysis. The White River volcanic ash layer (originating from Mount Churchill 1200 years ago) has been used to estimate apparent rates of peat accumulation in the Northwest Territories, Canada (Harris and Schmidt 1994, Robinson and Moore 1999). Recent volcanic activity also could be used to determine rates of peat accumulation in some localities (i.e., the 1973 eruption of Heimaey, Iceland; 1980 eruption of Mount St. Helen's, Washington; 1991 eruption of Mt. Pinatubo; 1994 eruption of the Kliuchevskoi volcano, Russia or the 1994 eruption of Merapi, Indonesia). Tephra layers from some of these recent eruptions will become more valuable as stratigraphic markers as the ash progressively is buried within a peat deposit.

CONCLUSIONS

A variety of dating techniques exists for recently deposited peat, including radiometric methods, such as ^{14}C and ^{210}Pb-dating, and chrono-stratigraphic markers, such as fallout from atmospheric bomb testing and the Chernobyl accident. Each dating technique has its own set of assumptions, many of which have received little attention (Table 1). A number of dating tools rely upon the assumption of particle immobility within a peat profile. To our knowledge, however, only lead and pollen mobility in peat have been addressed experimentally. ^{210}Pb was found to be immobile in peat (Vile et al. 1999), while mixed results have been obtained for pollen grains (Rowley and Rowley 195, Clymo and Mackay 1987). Field evidence supports the mobility of ^{137}Cs fallout in peat. We therefore recommend against its use as a dating tool in organic soils. More investigation into the behaviors of ^{241}Am and ^{207}Bi is needed before these isotopes can be trusted as radiogenic markers. Movement of PCBs downward in peat columns has been noted; however, measurements of these contaminants still have been correlated to historical patterns of use (Rapaport and Eisenreich 1988, Sanders et al. 1995). Caution should be exercised in using PCB congeners as dating markers in peat.

It is important to consider carefully all assumptions underlying dating methods (Table 1). Both pollen density dating and acid insoluble ash dating assume constant rates of deposition over time. Constant bulk density dating depends upon the assumption that peat accumulation changes little with time (Punning et al. 1993). Clearly, these assumptions will not be valid in some peat-accumulating systems and may lead to erroneous dates. Many of the potential stratigraphic markers outlined here (i.e., spherical carbonaceous particles, magnetic susceptibility, PCBs, PAHs, DDT) depend upon changes in particulate deposition caused by anthropogenic activity. However, as noted above, such changes in particle deposition may preclude the use of acid insoluble ash dating. Thus, the nature of peatland development, proximity to industrial activity, and its position on the landscape should be taken into consideration when choosing a dating method.

Radiocarbon dating is by far the most commonly used dating tool in peats. It is an expensive method, however, and analyzing more than a few samples may not be feasible for all studies. Precise radiocarbon dates for modern samples would be valuable in corroboration with other techniques. Wiggle matching of ^{14}C dates allows radiocarbon dating to be extended to surface peat. This method is extremely promising but expensive and requires further development for common application to peat deposits.

Methods based on ^{210}Pb, acid insoluble ash, moss increments, constant bulk density, and pollen density provide continuous chronologies in recent peats (Table 1). As peat accumulation fluctuates with short-term environmental changes, continuous age chronologies will be more highly resolved than interpolation between independently derived dates. Within these continuous methods, we feel that ^{210}Pb dating and pollen density dating hold the most promise as reliable techniques. While constant bulk density dating may provide rough depth-age relationships (Zoltai 1991, Belyea and Warner 1994), this method will overestimate peat age, as it does not consider decomposition throughout the column. Moss increment dating appears useful, particularly in hummock topographies (Eustis and Tolonen 1990, Belyea and Warner 1994); however its application to dating peat may be limited as it covers only a short age range and few plant taxa.

Stratigraphic markers also can be used to construct age chronologies in peat and are useful for calibrating independent dates. Changes in pollen abundance associated with settlement, agriculture, or disease are used commonly in North American and European peats and seem to be reliable options as stratigraphic markers. While correlating charcoal abundance to regional or local fire activity is feasible, we feel that the difficulty in identifying single fires of known age will preclude the use of charcoal as a common dating tool. As mentioned previously, stratigraphic markers based on spherical carbonaceous particles, magnetic susceptibility, PCBs, PAHs, and DDT all depend upon knowledge of regional anthropogenic activity. Combining a number of these markers to build an age chronology in peat will save time with background research into contaminant use and fossil fuel combustion.

As noted throughout the text, many dating methods in peat rely upon the ombrotrophic nature of bogs to record atmospheric deposition (i.e., ^{210}Pb, pollen density, acid insoluble ash, magnetic susceptibility, carbonaceous particles, PCBs, PAHs, DDT) and the great potential for cation exchange in *Sphagnum* peat (i.e., ^{210}Pb, PCBs, PAHs, DDT). Violation of assumptions may occur if these methods are applied to minerotrophic sites. While underlying assumptions should be carefully considered for every site, radiocarbon dating, wiggle-matching, moss increment dating, constant bulk density dating, pollen markers, and charcoal abundance should be applicable to all peat accumulating systems regardless of hydrologic controls.

Because of uncertainties associated with dating peat deposits, the use of two or more dating methods seems prudent. The nature of corroborations to date, however, has been piecemeal in recent peats. No single study has undertaken a comprehensive assessment of all available dating/corroboration methods. The most

ambitious study to date in this regard was that of Belyea and Warner (1994a), who used ^{210}Pb, ^{14}C, and constant peat bulk density in two hummock and two hollow/depression peat cores. As well, they dated the hummock cores using moss-increment dating and the two hollow cores using pollen density dating. No two methods appeared to agree consistently. Pb-210 dates were young relative to other methods in one hummock and one hollow core. Cole et al. (1990), however, found good corroboration between ^{210}Pb dating, pollen markers, and radiocarbon dating in bog hummock cores. Oldfield et al. (1995) concluded that the best age chronologies in peat can be derived from pollen markers, ^{241}Am fallout, and ^{210}Pb dating. They recommended constraining the ^{210}Pb profile with the chronostratigraphic markers if the independent methods do not agree.

Given the diverse nature of dating tools outlined here, certain methods will be better suited for individual sites. We recommend careful consideration of peatland characteristics, including the ombrotrophic status, size of the wetland (i.e., catchment size for pollen, charcoal, etc.), and developmental history of the site itself (i.e., potential changes in bulk density), as well as surrounding regions that could affect pollen rain. We also advocate evaluating the assumptions underlying each method available for dating recently accumulated peat. Studies investigating these assumptions using experimental approaches would add to our confidence in these dating methods. Until the uncertainty underlying these methods is resolved, however, we recommend the use of two or more dating tools in building age chronologies in recent peat. The choice of appropriate methodologies should be dictated by individual objectives. Single-event markers may be adequate for many studies. However, studies investigating temporal change in peat stratigraphies will require a continuous method with independent validation. In all cases, corroboration of age/depth relationships derived from multiple methods, such as a continuous dating method with one or more markers or independent methods, seems ideal.

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