

UNEXPECTED PROBLEMS IN AMS ¹⁴C DATING OF FEN PEAT

Minna Väliranta^{1,2} • Markku Oinonen³ • Heikki Seppä⁴ • Sanna Korkonen¹ • Sari Juutinen⁵ • Eeva-Stiina Tuittila⁶

ABSTRACT. Four fen peat sequences in northern Finland were dated by the accelerator mass spectrometry (AMS) radiocarbon method in order to study past peatland dynamics and carbon accumulation patterns. Initially, plant macrofossils were used for dating. However, the dates were severely disordered, with marked inversions in all sequences. In one 140-cm peat core, for example, all ages fell within a ~1000-yr time window. Following these unreliable results, a few bulk peat samples were dated to help assess if any of the plant macrofossil-derived dates were reliable. Bulk dates did not help to solve the problem. This study evaluates the possible sources of error but is unable to single out one clear cause. It is probable that many factors related to the fen environment, such as flooding and root intrusion, may have contributed to the errors. Peat plant macrofossils and bulk peat samples are considered to be reliable dating materials, but the examples given herein highlight the difficulties that can be associated with AMS dating of peat samples.

INTRODUCTION

Robust chronological control is a key concept in paleoecological research. Macroscopic plant remains and bulk peat samples are considered to be reliable materials for radiocarbon dating (e.g. Kilian et al. 1995; Shore et al. 1995; Nilsson et al. 2001; Blaauw et al. 2004; Head et al. 2007). However, in a series of several datings outliers may occur. Based on international ¹⁴C intercomparison studies, it has been estimated that 1 date out of 20 may be an outlier, and this can be integrated into the calibration procedures as an *a priori* assumption (Bronk Ramsey 2009b). The deviating dates are commonly omitted when constructing age-depth models without much further consideration. However, this does not necessarily serve the scientific community; failures might be an important key to understanding how to circumvent problems related to the use of ¹⁴C methodology (Glaser et al. 2012). This article presents a case from the Finnish Lapland where unexpected dating problems were repeatedly encountered. The studied fen slopes gradually to a lake, and it has two basins, here named A-basin and B-basin. A small stream flows through the basins and near this channel the fen surface is particularly wet throughout the year. In addition, the fen is annually flooded during May to early June. The peatland lies on sandy fluvio-glacial terrain and is probably affected by groundwater. The fen is covered by rich vegetation with sedges as a major vascular plant component. Four peat sections were dated from A-basin to investigate peat initiation and development history. In addition, three bottom peat samples from B-basin were dated using plant material.

Despite several attempts using plant remains, bulk peat and finally palynological correlation with pollen stratigraphy from the adjacent lake, fully consistent and reliable ¹⁴C chronologies were not achieved. Furthermore, B-basin basal peat samples appeared partly problematic. This article assesses the possible sources of error. Different factors are discussed related to fen environments in particular, such as flooding and root intrusion, which may have contributed to the errors (Glaser et al. 2012). Peat plant macrofossils and bulk peat samples are considered to be reliable dating materials, but the encountered adversities presented here highlight the difficulties that can be associated with accelerator mass spectrometry (AMS) dating of peat samples.

1. Department of Environmental Sciences, P.O. Box 65, FI-00014 University of Helsinki, Finland.

2. Corresponding author. Email: minna.valiranta@helsinki.fi.

3. Finnish Museum of Natural History - LUOMUS, Laboratory of Chronology, P.O. Box 64, FI-00014 University of Helsinki, Finland.

4. Department of Geosciences and Geography, P.O. Box 64, University of Helsinki, FI-00014 Helsinki, Finland.

5. Peatland Ecology Group, Department of Forest Sciences, P.O. Box 27, University of Helsinki, FI-00014 Helsinki, Finland.

6. School of Forest Sciences, P.O. Box 111, University of Eastern Finland, FI-80101 Joensuu, Finland.

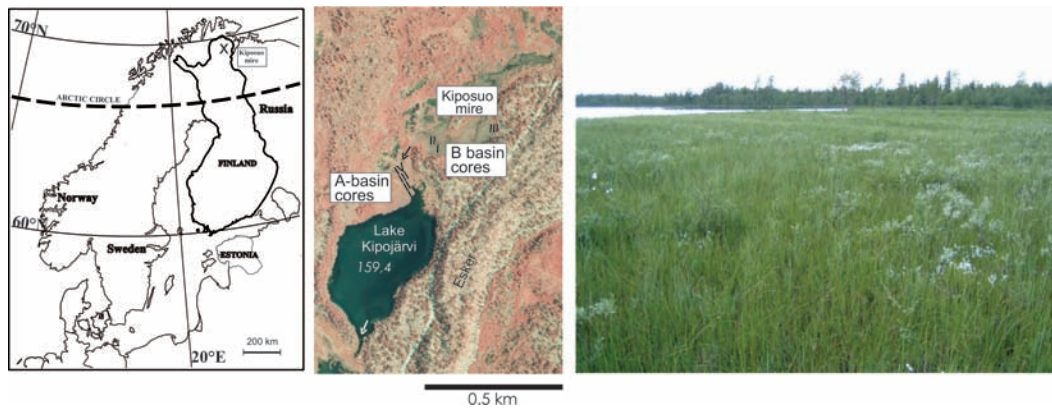


Figure 1 Study site in eastern Finnish Lapland. Four peat cores were collected from A-basin and these were dated and studied for fossil plant composition, loss on ignition, and bulk density. Only basal peat layers were dated from the B-basin peat cores. The photograph on the right illustrates the study site type.

STUDY SITE

The study site Kiposuo (unofficial name) is a subarctic fen located in the eastern Lapland of Finland (69°18'N, 27°32'E, 159.4 m above sea level). It lies on fluvio-glacial terrain and is bordered by an esker to the east and Lake Kipojärvi to the south. Kiposuo is a minerotrophic fen supporting a rich and diverse bryophyte community, including *Scorpidium* spp., *Paludella squarrosa*, *Warnstorfia* spp., *Sphagnum subsecundum*, accompanied by an abundant sedge cover (e.g. *Carex limosa*, *C. lasiocarpa*, *C. chondrorrhiza*) and herbs such as *Menyanthes trifoliata* and *Comarum palustre* (syn. *Potentilla palustris*). Higher strings are covered by dwarf shrubs, such as *Betula nana*, *Salix* spp., and *Rubus chamaemorus*. The studied mire consists of two basins (A-basin and B-basin) (Figure 1), which are separated by a mineral sill, currently overlain by peat. A small (~1 m width) and shallow (~0.5 m) brook runs through the mire. The surface peat near the brook is especially wet. Strong spring floods inundate the fen annually.

METHODS

In order to study Holocene peatland dynamics, four cores were collected in summer 2005 from A-basin: 0–284 cm (A-I), 0–284 cm (A-II), 0–140 cm (A-III), and 0–150 cm (A-IV) (Figure 2). A-III and A-IV are underlain by mineral soil, while limnic sediments, deposited in kettle holes, underlay A-I and A-II. The actual thickness of A-II was 600 cm but limnic sediments below 284 cm were excluded from this study. All peat was sedge-brown moss-dominated fen peat (Juutinen et al. 2013). Cores A-I to -IV formed a transect from the Lake Kipojärvi shore to the adjacent mineral soil. Initially, all A-basin cores were dated using mixed plant remains (Table 1).

Following somewhat doubtful results, additional bulk peat samples were dated to attain information on which plant macrofossil-derived dates were trustworthy. One additional sample was dated from A-I and A-IV and two samples from A-II and A-III. All A-basin radiocarbon analyses were performed at the Finnish Museum of Natural History (LUOMUS) (formerly Dating Laboratory; lab code Hela-) in 2007–2010.

From B-basin (Figure 1), only the bottom peat was dated from the three peat cores. Cores B-I and B-II were underlain by limnic sediments and B-III by mineral soil. Selected plant material was submitted for dating to Poznań Radiocarbon laboratory (lab code Poz-). In the case of B-I, two separate

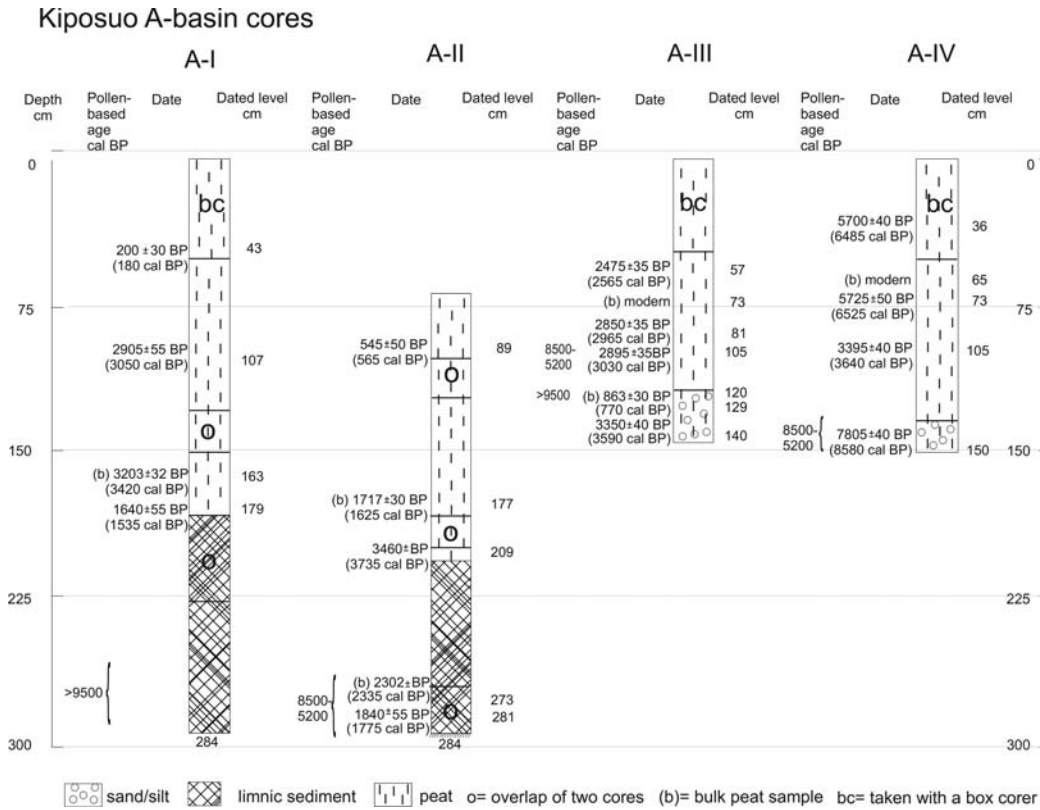


Figure 2 Kiposuo A-basin peat core I-IV stratigraphies and ¹⁴C dates BP. Calibrated ¹⁴C dates (cal BP) are given in parentheses. Pollen-based age estimations are expressed as cal BP. Variations in pollen proportions of certain key taxa: *Pinus*, *Betula*, and *Sphagnum* were used to estimate basal peat ages.

samples derived from the same 2-cm peat slice were submitted for dating. The samples contained (a) *Scorpidium* spp. bryophyte remains and (b) *Menyanthes trifoliata* and *Carex* spp. seeds.

When it became clear that the A-basin ¹⁴C dates were inconsistent, a few pollen samples from the basal part of every core were analyzed to evaluate the ¹⁴C-derived chronologies. A dated Holocene pollen stratigraphy is available from the adjacent Lake Kipojärvi (Siitonen et al. 2011; Väiliranta et al. 2011) and this was used for pollen-stratigraphic and chronological comparisons. The synchronization was based on the pollen proportions of *Betula*, *Pinus*, and *Sphagnum*. The relative proportions of *Betula* vs. *Pinus* were used to define the maximum age of the peat sample. A prominent increase in *Pinus* pollen in the area has been dated to 9500 cal BP [before present, where the present is AD 1950 (Stuiver and Polach 1977)] (Seppä 1996; Mäkelä 1998; Siitonen et al. 2011; Väiliranta et al. 2011). The minimum age estimation was based on the values of *Sphagnum* spores. In the Lake Kipojärvi sequence, the rise of the proportion of *Sphagnum* spores begins after ~5200 cal BP (Siitonen et al. 2011; Väiliranta et al. 2011).

Samples at the LUOMUS laboratory were treated with a typical acid-alkali-acid (AAA) pretreatment procedure. The samples were washed with 2% hydrochloric acid (HCl) at 80°C to remove possible carbonate contaminants. After neutralization, organic acids were removed from the samples by performing a hot (80°C) wash in 2% sodium hydroxide (NaOH) twice. The samples were

Table 1 Results of ¹⁴C analyses of Kiposuo peat cores. Dating samples were selected and identified by M Väiliranta.

Lab nr	Core code	Depth (cm)	Dated material	Standard	Sample C mass (mg)	δ ¹³ C (‰)	¹⁴ C age (BP)	95% hpd range and the median (cal BP)
Basin A								
Hela-1964	I	42–43	<i>Betula</i> leaf remains	normal	0.600	-31.5	200 ± 30	-2–303, 180
Hela-1965	I	106–107	<i>Carex</i> seeds, <i>Menyanthes trifoliata</i> seed, <i>Equisetum</i> remains, <i>Betula</i> leaf remains	small	0.500	-24.9	2905 ± 55	2877–3215, 3050
Hela-2309	I re-date	162–163	bulk peat		1.600	-25.7	3203 ± 32	3365–3474, 3420
Hela-1966	I	178–179	<i>Carex</i> seed, <i>Betula</i> bark and leaf remains	small	0.100	-30.1	1640 ± 55	1406–1693, 1535
Hela-1967	II	88–89	<i>Betula</i> leaf remains, <i>B. nana</i> catkin scale	small	0.500	-29.7	545 ± 50	507–650, 565
Hela-2310	II re-date	176–177	bulk peat		1.800	-24.1	1717 ± 30	1551–1702, 1625
Hela-1968	II	208–209	<i>Menyanthes trifoliata</i> seeds, <i>Pinus</i> bark, <i>Betula</i> leaf remains	small	0.100	-25.2	3460 ± 55	3584–3863, 3735
Hela-2311	II re-date	272–273	bulk limnic		1.200	-26.7	2302 ± 30	2182–2355, 2335
Hela-1969	II	280–281	<i>Vaccinium</i> sp. leaf, <i>Betula</i> bark, <i>Menyanthes trifoliata</i> seed	small	0.500	-28.8	1840 ± 55	1619–1894, 1775
Hela-1971	III	56–57	Wood, <i>Betula</i> remains, <i>Salix</i> leaf remains, <i>Salix</i> bud, <i>Carex</i> seeds	normal	1.000	-29.2	2475 ± 35	2365–2715, 2565
Hela-2312	III re-date	72–73	bulk peat		2.000	-28.9	modern	
Hela-1972	III	80–81	Mixed <i>Betula</i> remains	small	0.700	-30.7	2850 ± 35	2868–3071, 2965
Hela-1973	III	104–105	Mixed <i>Betula</i> remains <i>Pinus sylvestris</i> bark and needle remains	normal	0.800	-28.3	2895 ± 35	2896–3197, 3030
Hela-2313	III re-date	128–129	bulk peat		1.300	-28.9	863 ± 30	694–902, 770
Hela-1974	III	139–140	Mixed <i>Betula</i> remains, <i>Equisetum</i> remains	small	0.300	-28.3	3350 ± 40	3477–3688, 3590
Hela-1975	IV	35–36	Wood	normal	1.000	-29.7	5700 ± 40	6404–6630, 6485
Hela-2314	IV re-date	64–65	bulk peat		1.800	-27.9	modern	
Hela-1976	IV	72–73	<i>Sphagnum</i> stems	small	0.300	-26.9	5725 ± 50	6408–6639, 6525
Hela-1977	IV	104–105	Mixed <i>Betula</i> remains, <i>Menyanthes trifoliata</i> seeds	small	0.400	-28.0	3395 ± 40	3487–3821, 3640
Hela-1978	IV	149–150	Mixed <i>Betula</i> remains, <i>Carex</i> seeds	small	0.500	-26.3	7805 ± 40	8455–8692, 8580
Basin B								
Poz-18418	I (sample a)	322–323	Bryophytes (<i>Scorpidium</i> spp.)		2.222	-28.8	5340 ± 40	5997–6270, 6120
Poz-18419	I (sample b)	322–323	<i>Menyanthes trifoliata</i> seeds and <i>Carex</i> seeds		0.951	-31.8	7570 ± 50	8211–8454, 8385
Poz-20664	I re-date (sample a)	320–321	Bryophytes (<i>Warnstorfia</i> spp.)		1.265	-29.6	7840 ± 40	8542–8766, 8620
Poz-20684	I re-date (sample b)	320–321	<i>Menyanthes trifoliata</i> seeds, <i>Carex</i> seeds, <i>Betula</i> seed		1.531	-24.6	7800 ± 40	8453–8646, 8575
Poz-18417	II	165–166	<i>Carex</i> seeds, <i>Comarum palustre</i> seeds		1.913	-29.6	8830 ± 50	9698–10 156, 9900
Poz-18416	III	155–156	Bryophytes (<i>Pelludella squarrosa</i>), <i>Carex</i> seeds, <i>Betula</i> seeds and bud		0.913	-33.5	8350 ± 50	9149–9485, 9370

again neutralized and washed with 2% HCl at 80°C. AAA washings were continued until no visual change was noticed in the solution. The samples were neutralized with distilled water and dried at 90°C overnight. Pretreated samples were mixed with a stoichiometric excess of copper oxide (CuO) and packed into glass ampoules, which were pumped into a vacuum and torch-sealed. The packed samples were combusted overnight at 520°C. The released carbon dioxide (CO₂) was collected and purified with liquid nitrogen (N₂) and ethanol traps at -196 and -85°C, respectively. After purifying and measuring the sample δ¹³C value with a isotope ratio mass spectrometer (IRMS) (Finnigan MAT Delta-E), the CO₂ samples were converted to graphite targets in the presence of zinc powder and iron catalyst (Slota et al. 1986). AMS measurements were performed at the Uppsala Tandem Laboratory.

All BP ages were calibrated using OxCal (Bronk Ramsey 2009a) with the IntCal09 calibration data set (Reimer et al. 2009). To facilitate discussion and to enable comparison with palynological data, median values of the calendar year probability distributions rounded to the nearest 5 yr are presented. The 95% highest posterior density (hpd) ranges are given in Table 1.

The Fifth International Radiocarbon Intercomparison (VIRI; Scott et al. 2007) took place at the same time as our analyses. The overall performance of the laboratory could thus be determined by comparing the obtained VIRI results to the VIRI consensus values. Furthermore, in every set of 35 samples, reference samples of fossil graphite and known-age humic acid were included to control the instrument background and background induced by the combustion, CO₂ purification, and graphitization steps, respectively.

RESULTS

Initially, three levels were dated by plant macrofossils from A-I and A-II, and four levels from A-III and A-IV. In all four cores, the dates were seriously disordered (Figure 2). For example, all A-III dates fell inside a ~1000-yr time window, with a range of 2565 cal BP at 56–57 cm and 3590 cal BP at 139–140 cm. The bulk dates did not help in evaluating the correctness of the plant macrofossil-derived dates. For instance, two bulk dates from the depths 72–73 cm (A-III) and 64–65 cm (A-IV) yielded modern ages.

Palynological Correlation

All Kiposuo pollen samples (A-I to A-IV) contained either a few or no *Sphagnum* spores (Figure 3), indicating that all samples were deposited before 5200 cal BP. Palynological analysis suggested that the A-I bottom 284 cm (limnic) is of an early Holocene age (≥9500 cal BP) because the bottommost sample was dominated by *Betula* pollen and the rise in *Pinus* pollen proportion in the area occurs ~9500 cal BP (Figure 3; Siitonen et al. 2011; Väiliranta et al. 2011). The dated limnic sample at 284 cm in A-II was probably deposited between 8500 and 5200 cal BP because *Pinus* is the main tree pollen component, but the proportion of *Sphagnum* spores is very small. It is noteworthy that the sample A-II 284 cm does not represent the actual core bottom because underneath lies a ~3.5-m-thick limnic sediment layer. The palynological age estimation based on pollen stratigraphy of A-III suggests that peat accumulation had already started before 9500 cal BP, while in the equally long A-IV sequence, the pollen data suggest that peat accumulation started between 8500 and 5200 cal BP. The ¹⁴C dates support peat initiation around 8500 cal BP.

B-Basin Basal Ages

Unexpectedly, two B-basin samples from the same 2-cm peat slice yielded notably different ages: sample (a) with bryophyte remains was younger (6120 cal BP) than sample (b) with *Menyanthes* and *Carex* seeds (8385 cal BP). To repeat the procedure, two new samples, 2 cm above the previous

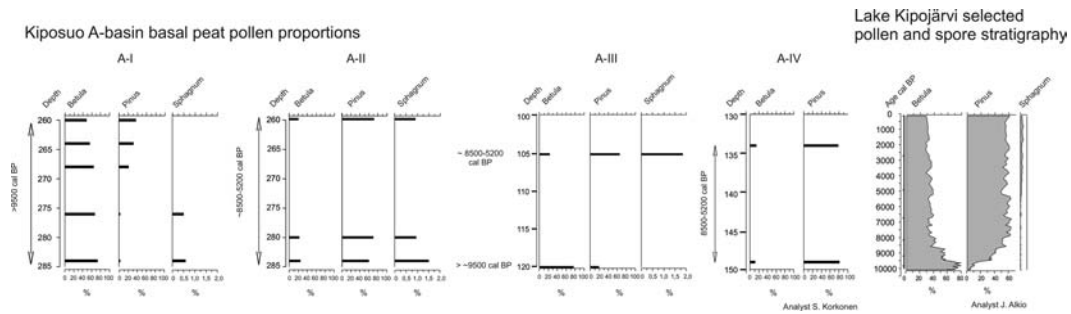


Figure 3 Pollen-based age estimations were derived by comparing proportions of *Pinus* and *Betula* pollen and *Sphagnum* spores of the bottom peat samples to dated pollen stratigraphy available from the adjacent Lake Kipojärvi and proportion values found from the literature. Note that the depth scales vary between the cores. Original pollen data were published in Siitonen et al. (2011) and Väiliranta et al. (2011).

samples, with comparable plant macrofossil composition (semiaquatic bryophytes and *Menyanthes/Carex/Betula* seeds, respectively), were submitted for redating. This time, both samples provided relatively similar ages: 8620 and 8575 cal BP, respectively, suggesting that the original age of 8385 cal BP derived from the *Menyanthes/Carex* remains was correct. After the redating, the three bottom ages were consistent, i.e. all cores had an early Holocene bottom age: B-I: 8385–8620 cal BP (320–322 cm); B-II: 9900 cal BP (165–166 cm); B-III 9370 cal BP (155–156 cm).

DISCUSSION

Identifying the Most Reliable Dates

In order to determine the most reliable dates, it must be assumed that peat accumulation rates may have varied considerably within a small area. In Kiposuo, the peat thickness varied between 323 and 140 cm (Figure 2, Table 2). Pollen evidence suggests that peat initiation started on mineral ground at sites A-III and A-IV during the early Holocene. Accordingly, it is probable that the A-IV ^{14}C

Table 2 List of the most plausible ^{14}C date results.

Core	Depth (cm)	Age (cal BP median)	Pollen age (cal BP)
A-I	42–43	180	
A-I	106–107	3050	
A-I	162–163	3420	
A-I	260–284		>9500
A-II	88–89	565	
A-II	176–177	1625	
A-II	208–209	3735	
A-II	280–281		8500
A-III	56–57	2565	
A-III	80–81	2965	
A-III	139–140		>9500
A-IV	104–105	3640	
A-IV	149–150	8580	
A-IV	135–150		8500
B-I	165–166	9900	
B-II	322–323	8385	
B-III	155–156	9370	

bottom date of 8580 cal BP is reliable but that the A-III ^{14}C basal date of 3590 cal BP at 139–140 cm is too young, as is clearly the age 770 cal BP at 128–129 cm. Furthermore, all B-basin basal ^{14}C dates suggest an early Holocene initiation age (Table 1). This is consistent with previous studies from Lapland (Mäkilä and Moisanen 2007; Weckström et al. 2010) that have shown an early Holocene initiation of peat accumulation probably driven by regional climate and landscape factors (cf. Ruppel et al. 2013). However, the peat initiation process via pond infilling probably follows more individualistic pathways, i.e. bottom peat ages may indeed differ within short distances depending on the infilling rate and the depth of the depression. In any case, the two A-II ^{14}C bottom ages, 1775 cal BP at 280–281 cm and 2335 cal BP at 272–273 cm, must be too young (Figures 2 and 4).

It is tempting to think that the ages around 3000 cal BP that are clustered near peat depths 80–100 cm in A-I, III, and IV (Figures 2 and 4) are correct. This would mean relatively stable peat accumulation rates for the last ~3000 yr. This assumption is supported by a study from western Lapland where accumulation rates of four peat sequences stabilized and reached even levels after ~3000 cal BP (Mäkilä and Moisanen 2007). If the A-III ^{14}C ages 2965 cal BP at 80–81 cm and 2565 cal BP at 56–57 cm are correct, this suggests that the pollen-derived age at 105 cm might be closer to the minimum age 5200 cal BP rather than the maximum age 8500 cal BP. Moreover, the A-I topmost date of 180 cal BP at 42–43 cm and A-II date 565 cal BP at 88–89 cm may be correct. Nonetheless, in total, nine dates remain incompatible with the stratigraphy. The most reasonable dates are listed in Table 2.

Assessment of Laboratory Procedures

The graphite samples included in each of the sample sets provide a means to assess the instrumental errors at the Helsinki Museum AMS facility. During 2007–2012, the observed instrumental background corresponds to an average of $48,200 \pm 2100$ ^{14}C yr. The values for the sample sets containing the Kiposuo samples were within this range. Therefore, it can be concluded that the AMS was performing satisfactorily during the measurements.

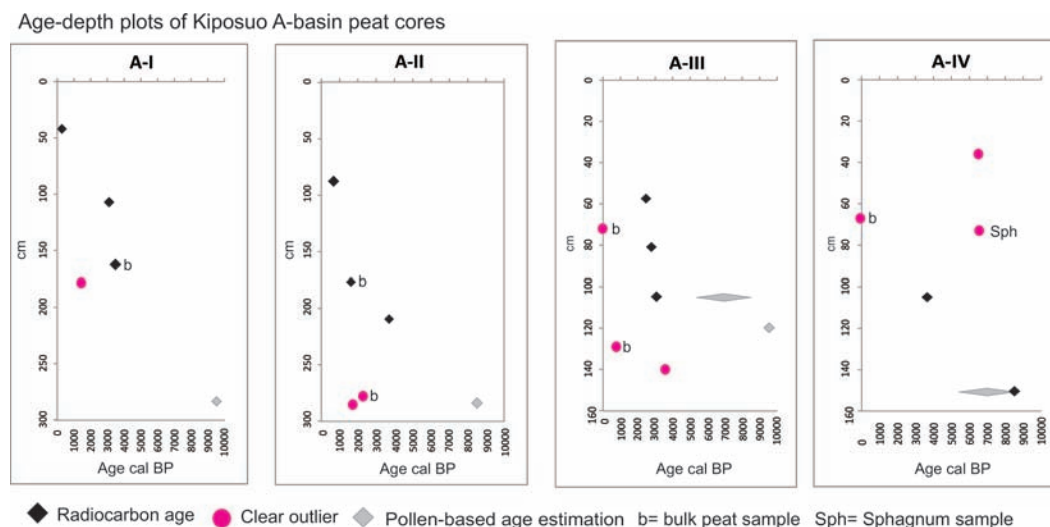


Figure 4 Age-depth plots of four Kiposuo A-basin peat cores. The probable outliers are marked with dots. Samples that were dated from bulk peat are indicated by “b” and the only sample where *Sphagnum* remains were used for dating is also indicated. The other samples contained mixed terrestrial remains, often mainly *Betula* (Table 1).

The combustion, CO₂ purification, and graphitization steps are potential contamination sources for ¹⁴C measurements mainly due to possible atmospheric leaks. Such potential problems should be observed in the ¹⁴C concentrations of the humic acid samples included within the sample sets. During 2007–2012, an average ¹⁴C age of 3379 ± 45 BP was deduced for these samples. This compares well to the consensus value for the material of 3360 ± 5 BP. The difference in the accuracy values falls within the obtained statistical precision. Moreover, for the humic acid samples, the values corresponding to the Kiposuo sample sets were within the observed average. Thus, there seems to be no reason to doubt the overall process quality for the combustion, CO₂ purification, or graphitization steps. Furthermore, examination of the vacuum line pressure readings indicates that no leaks were observed during the preparation of the Kiposuo samples.

The average obtained graphite mass for the humic acid samples is 1.1 ± 0.5 mg. The observed statistical deviation allows us to monitor the process quality by investigating the humic acid ¹⁴C age as a function of graphite sample size. The linear fit does not deviate significantly from a constant trend and, particularly, the small-mass humus sample of 0.1 mg results in an age of 3379 ± 32 BP, consistent with the consensus value. Therefore, small graphite masses for AMS do not essentially affect the overall measurement accuracy within the procedure used. This is relevant, since some of the graphite masses of the Kiposuo samples were small (0.1–0.5 mg). For these samples, the oxalic acid II normalization standards were also selected to be correspondingly small (0.1–0.3 mg). However, the selection of a standard size affected the results by no more than ~50 ¹⁴C yr. Furthermore, of the samples A-I at 178–179 cm and A-II at 208–209 cm that had smallest masses, 0.1 mg (Table 1), A-I at 178–179 cm seemed to yield too young an age (1535 cal BP) but A-II at 208–209 cm returned too old an age (3735 cal BP). This all suggests that the origin of the contradictory results resides somewhere other than the sample size.

Sample pretreatment can be considered another potential source of uncertainty. During 2007–2009, the LUOMUS participated in the Fifth International Radiocarbon Intercomparison (VIRI) by performing a series of measurements on VIRI 3 samples (J-U). The sample materials included cellulose, charcoal, humic acid, shell, and wood. Since the whole process chain is included when treating the samples, the measurement series should provide an examination of the overall quality of the ¹⁴C measurements. When comparing the nine VIRI samples with Holocene ages, the correlation between the measured percent modern carbon (pMC) values with the VIRI consensus values was excellent ($R^2 = 0.9999$, Figure 5). In particular, the residual between the sets was on average –15 ¹⁴C yr. This is well below the typical statistical error of an individual ¹⁴C date, which is 30–70 ¹⁴C yr for the Holocene samples. Thus, the overall laboratory performance is deemed satisfactory.

Other Potential Sources of Errors

In all cases, the erroneous ¹⁴C ages were inconsistently distributed along the peat sequence. Some of the ages are clearly too young (i.e. A-I 1535 cal BP at 178–179 cm) and some ages are too old, such as A-IV 6485 cal BP at 35–36 cm. Furthermore, in two cases, A-III at 72–73 cm and A-IV at 64–65 cm, the analyses yielded values greater than modern values (130–150 pMC) for layers several tens of centimeters below the surface (Figure 2, Table 1). This inconsistent pattern suggests that there has been no systematic contamination by contaminants that are either too old or too young.

Sampling Procedures

Theoretically, human errors could explain the inconsistent results. For example, the A-basin cores might have been mislabeled or turned upside down during the fieldwork, packing, or slicing. However, this explanation can be dismissed. Each peat sequence was individually cored by a group of

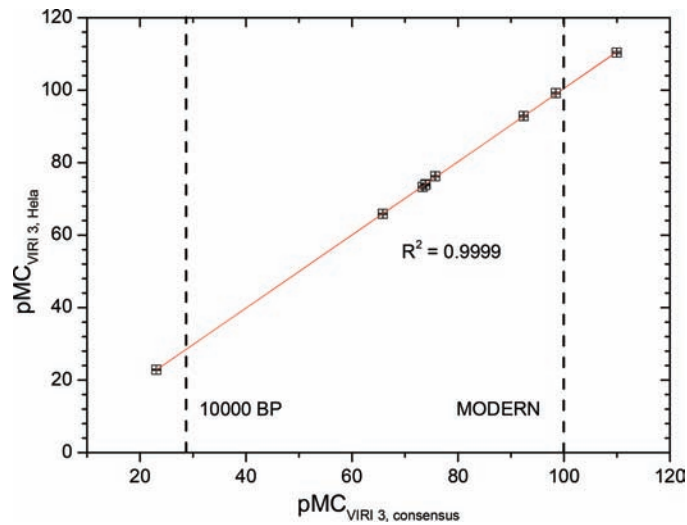


Figure 5 Comparison of the results of the VIRI measurements from 2008 in units of percent modern carbon (pMC).

three experienced scientists using a Russian peat corer with a 1-m-long cylinder. Peat cores were immediately wrapped and marked. Altogether, six cores were collected, starting from A-I. The sampling points formed a transect where the distance between the points was ~ 20 m. Surface (50 cm) peat sequences of A-I, -III, and -IV were collected separately with a box corer. The surface peat of A-II, -III, and -IV was very wet and, in the case of A-II, we were not able to collect a proper surface peat core. It is worth noting that the core stratigraphies differed considerably from each other. The bottom sequences of A-III and A-IV were collected by single coring, and the bottom sediment was sand/silt (Figure 2). Core A-I required two down corings and limnic sediments underlay the peat. A-II sediment thickness was 6 m and several corings were needed. Most of the sediment was limnogenic; the peat layer was only ~ 2 m thick (Figure 2). Other available data, such as high-resolution plant macrofossil records, loss on ignition (LOI), bulk density, and C/N ratio, show no indication of mixing or reversal orientation of the cores (Figure 6 and Juutinen et al. 2013). Moreover, the pollen data show typical regional Holocene proportion patterns.

Dated Material

It is not possible to find any consistency between the dated material and the dating outcome. All dated materials are generally considered as reliable material for ^{14}C dating (Nilsson et al. 2001), with one possible exception where a bulk limnic sediment sample was dated from A-II at 272–273 cm (cf. Donner et al. 1971; Olsson 1986). This particular date, 2335 cal BP, appears too young with respect to the pollen-derived age, while typical bulk lake sediment dates tend to be older than macrofossil-derived dates (Barnekow et al. 1998; Kultti et al. 2003; Väiliranta et al. 2006). Kiposuo dating samples mostly consisted of a mixture of terrestrial plant remains (Table 1), mostly birch remains: leaf pieces, bark, seeds, catkin scales. Only one sample, A-IV at 72–73 cm, consisted solely of *Sphagnum* remains. This sample yielded approximately the same age as the age derived from wood remain further up from level 35–36 cm from the same sequence (Figure 2).

Extended storage of the wet macrofossil samples may have a marked rejuvenating effect on the ^{14}C ages if the samples are contaminated by fungi or microorganisms during the preparation and identification, even when the samples are kept in a dark and cool storage (Wohlfarth et al. 1998). Kiposuo

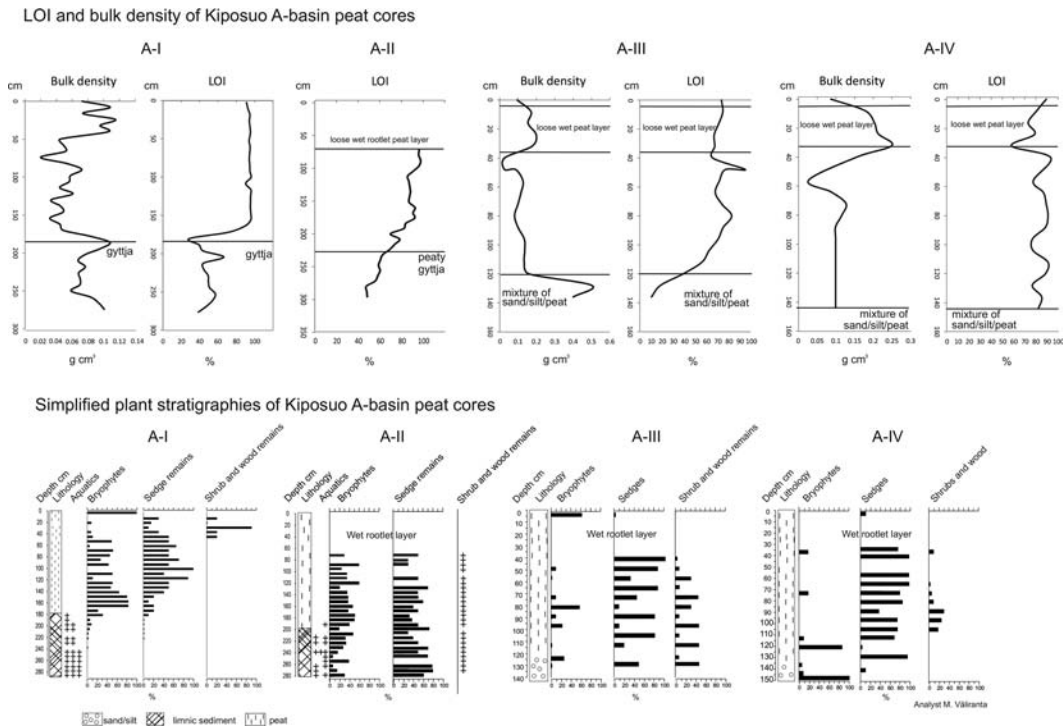


Figure 6 Additional data available from the Kiposuo A-basin peat cores. Loss-on-ignition (LOI) and plant macrofossil compositions were analyzed from cores A-I to A-IV, bulk density was measured from A-I, -III, and -IV. These data, showing for instance lower LOI values at the bottom, a clear vegetation succession from wet to dry in A-I, and a corresponding loose, wet layer near the surface in A-II-IV, illustrate that the doubtful ages are not a result of disorientation of peat cores during or after the coring.

peat samples were stored in cold and dark place before and after the subsampling. The macrofossils picked out for dating were stored in purified water with a drop of 10% HCl. After adding 10% HCl, the pH of the plant-water solution was as low as 1, which should effectively prevent the growth of microorganisms.

Different Peat Fractions

Identified plant macrofossil remains were used for ^{14}C dating and bulk peat was used for complementary dating. The main concern in using bulk-peat samples for AMS dating is related to the fact that peat contains different fractions (e.g. fulvic and humic acids), which often, if dated separately, provide divergent ^{14}C ages (Shore et al. 1995). Subsequent redistribution of these different fine fractions by vertical water movements in the peat column may result in spurious ^{14}C ages (van der Plicht 2012). The AAA pretreatment protocol should remove the mobile fulvic and humic contaminants. Should these substances nevertheless be present, a vertical downward transport of dissolved organic carbon through the peat column might, in principle, explain the small ^{14}C age difference between the samples A-I at 106–107 cm (3050 cal BP) derived from plant remains and A-I at 162–163 cm (3420 cal BP) derived from bulk peat. However, the vertical movement of humic acid does not explain the inconsistencies with the dates obtained from the plant macrofossils.

Minerogenic Load from the Surroundings

Different laboratory procedures may result in deviating ages for bulk peat samples (Nilsson et al. 2001), particularly if fluvial processes have resulted in input of minerogenic material (Törnqvist et al. 1992). In Kiposuo, one bulk peat sample, A-III at 128–129 cm, had a particularly low C%, i.e. 3.6%, and the sample age 770 cal BP appears too young. During the annual spring flooding, Kiposuo probably receives a minerogenic load from the adjacent sandy terrains. Because the VIRI inter-comparison did not contain sand- or silt-rich bulk peat samples, this possible source of uncertainty was not covered by our quality protocols, leaving it as a potential source of the inconsistencies (cf. McGeehin et al. 2001, 2004). However, this again fails to explain the errors associated with the plant macrofossil datings.

Roots of the Vascular Plants

Roots of plants growing on a mire surface penetrate downwards in a peat column where they, if not removed, distort the age signal of the bulk peat sample (Shore et al. 1995; Head et al. 2007). Sedge roots can extend up to 2 m below the surface (Saarinen 1996). Because sedges are the most important vascular plant group growing on fens, the rejuvenation effect caused by modern roots has to be taken into account, especially if the peat accumulation rate is slow (Head et al. 2007). Rejuvenation may occur despite the fact that the main proportion of sedge roots in fens remain in the uppermost peat layers where the mineralization processes take place: a mixture of 25% of modern roots in 1000-yr-old peat would yield a modern ^{14}C sample age. The bulk peat-derived “modern” ages in A-III at 72–73 cm and in A-IV at 64–65 cm could, in theory, be caused by roots mixed in peat samples. Roots of plants growing during the second half of the 20th century have an average ^{14}C content of ~140 pMC. ^{14}C concentrations of 137.2 and 144.4 pMC in the bulk peat samples from A-III 72–73 cm and A-IV 64–65 cm, respectively, were closer to that value than 90 pMC, which is a typical ^{14}C concentration of plant material that grew 1000 yr ago, and can be regarded as a possible age for a peat layer at depth of 60–70 cm. However, to obtain such high ^{14}C concentrations, the dated sample should almost solely consist of intruded roots. Naturally, this explanation for the bulk samples does not explain the dates that are either too young or too old in the plant macrofossil samples.

Age comparison of different peat components, bulk peat and plants, can show a very complicated pattern. In two fen sites studied by Nilsson et al. (2001), bulk peat dates (without hydrolysis) were always a few hundred years younger than the dates derived from bryophytes from the same level, suggesting contamination by roots. However, ages derived solely from *Carex* roots were actually closer to the bryophyte-derived dates than bulk peat ages, while some of the bulk peat dates were older than the dates derived from *Carex* roots (Nilsson et al. 2001). In any case, the error between bulk peat and selected plant macrofossils was in the order of hundreds of years, rather than thousands.

Methanotrophy Dynamics and CO_2 Recycling

One of the samples, A-IV at 72–73 cm, contained only *Sphagnum* stems (Table 1). *Sphagnum* mosses are considered as reliable material for ^{14}C dating (Nilsson et al. 2001), but recent results have shown that communities of methanotrophic microbes within *Sphagnum* hyaline cells oxidize methane (CH_4) (Raghoebarsing et al. 2005; Larmola et al. 2010), which may cause a systematic bias in the radiocarbon dating. It is estimated that 10–30% of the carbon incorporated in mosses potentially originates from CO_2 derived from CH_4 oxidation (Larmola et al. 2010). If CH_4 is produced from the decomposition of the older organic matter, this mechanism yields ^{14}C ages that are too old. Putkinen et al. (2009) detected CH_4 production in deep peat samples in Kiposuo originating from 220 cm below the surface. Therefore, it is possible that old carbon circulated via methanotrophy may partly explain the old age of the *Sphagnum* sample and possibly also that of the moss-dominated bulk peat

samples. However, it is hardly likely that the *Sphagnum* age of 6525 cal BP at 72–73 cm would be solely due to methanotrophy, since this would require unrealistically old CH₄ ages and/or a very strong role for methanotrophy. Furthermore, the δ¹³C values of the *Sphagnum* sample (−26.9‰) and the other samples (−24.1 to −31.5‰) do not indicate significant methanotrophic contribution (cf. Pancost et al. 2000). Recycled CO₂ has been proposed to supply up to ~20% of the carbon to the *Sphagnum fuscum* growing on peat hummocks (Tolonen et al. 1993). Peatland carbon cycling is a complex process. Recent detailed δ¹³C and ¹⁴C analyses of peatland surface waters revealed diverging ages for CO₂ and CH₄ and suggested multiple carbon transportation pathways and sources from different peat depths (Billet et al. 2013). Thus, the cycling of different C species and origin of the CO₂ used by plants deserve further attention in the future as a part of the ¹⁴C dating quality control.

Environmental Factors

Surface dates that are too old (too-low ¹⁴C concentrations) are difficult to explain other than from mixing of peat layers, for instance, due to frost action. The mechanism could also work in the other direction by transporting younger material to deeper peat layers. However, the severe cryoturbation characteristics of permafrost environments can be ruled out; Kiposuo is located south of the discontinuous permafrost zone. Theoretically, normal frost action could possibly explain the high but still natural ¹⁴C concentrations observed in A-III at 72–73 cm. However, previous peatland studies from northern peatlands that have been studied with multiple cores and relatively large amounts of dates (e.g. Mäkilä and Moisanen 2007; van Bellen et al. 2011) have not reported any systematic problems in chronologies. Furthermore, the other available data from the Kiposuo peat cores (Figure 6 and Juutinen et al. 2013) do not show any indication that mixing of the peat occurred. In Kiposuo, surface peat erosion can also be excluded as the mire surface is densely vegetated and the surface remains wet throughout the year. Kiposuo is bordered by a lake and a stream runs through it. Severe spring floods and temporal inundations by the adjacent Lake Kipojärvi probably transport plant material horizontally and possibly vertically as well through the surface peat layers. In Kiposuo, the surface peat layer is very loose and water-saturated, allowing particle movement.

CONCLUSIONS

This article highlighted the major inconsistencies in the AMS ¹⁴C dating of the plant macrofossil and bulk peat samples from the Kiposuo mire, but cannot point out any single exhaustive explanation for the encountered dating inconsistencies. The study site represents a subarctic fen that is intersected by a stream and is located near a lake. The fen experiences not only annual spring flooding but the surface is also occasionally inundated outside the spring months. Based on fossil plant composition analyses, the surface has always been as wet in the past as it is currently. This permits the movement of plant remains in both vertical and horizontal directions. Some of the characteristics of fen environments, namely minerogenic loading and root intrusions, may have a considerable rejuvenating effect on fen peat when the peat accumulation rates are low. The comparable dating problems have not been widely reported in previous fen studies, but it is possible that the sources of inaccuracy and inconsistency reported here may have been overlooked in the AMS dating of peat samples that have generally been regarded as more reliable material than lake sediment samples.

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