TOO OLD AMS RADIOCARBON DATES OBTAINED FROM MOSS REMAINS FROM LAKE KWIECKO BOTTOM SEDIMENTS (N POLAND)

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Abstract: The paper presents the results of the AMS radiocarbon dating of moss macrofossils which seem to be too old in the context of palynological data. The lack of agreement between the obtained results of radiocarbon dating and pollen analysis has been discussed. Some possible causes of the discrepancies between the results of radiocarbon dating and palynological dating have been given.

Keywords: AMS radiocarbon dating, old carbon effect, moss remains, Holocene

1. INTRODUCTION

Radiocarbon dating based on the $^{14}$C isotope is a tool that is frequently used to determine the age and duration of changes taking place in the palaeoenvironment. The remains of terrestrial plants are reliable material for radiocarbon dating, but they are not always present in sediment. Dating the remains of aquatic plants often gives highly skewed results, as does dating the remains of terrestrial plants which are capable of photosynthesis under conditions of episodic flooding, and thus of incorporating into their tissues atoms of carbon dissolved in the surrounding environment.

The introduction of modern accelerator technique (AMS) has made it possible both to date samples which are much smaller than those used in conventional methods and to date new kinds of material which are not available in larger quantities. Dating pollen grains isolated from sediment is particularly important in reconstructing changes taking place in the flora (Brown et al., 1989). This method is most useful in those situations in which sediments contain no macroremains of land plants.

Correlating the radiocarbon age obtained from a profile together with palynological data concerning changes taking place in the flora with data available for other profiles taken from adjacent areas whose dates do not appear dubious allows the former to be critically verified.

This paper presents the results of the radiocarbon dating of moss macrofossils and pollen concentrates. The lack of agreement between the obtained results of radiocarbon dating and pollen analysis has been discussed, and the age of the investigated sediment has been determined by confronting the palynological data with those taken from other, already dated pollen profiles. Some possible causes of the discrepancies between the results of radiocarbon dating and palynological dating have been given.

2. STUDY SITE

Lake Kwiecko (54° 01’ 30” N, 16° 42’ 00”E) lies in the Bytowskie Lake District which is a part of the West Pomeranian Lake District, Northern Poland (Fig. 1) within the stadial moraines of Late Glacial time (Kondracki, 2002). Lake Kwiecko is located at an elevation of 80 m a.s.l. and its surface area is approximately 127 ha. The lake basin occupies a depression formed in calcareous glaciofluvial gravels. The basement of the Quaternary sediments is composed mainly of Tertiary marine green glauconite sands, sandy loams, silts and Miocene clays, sands and brown coals.
3. MATERIALS AND METHODS

Fossil material

A core over 22 m deep was taken using a Więckowski sampler (Więckowski, 1970). Sediment of a gyttja carbonate nature contained distinctly laminated material at a depth of 19.29-21.06 m, and sandy clay at the bottom. There was mossy peat at the depth of 22.08-22.27 m in the profile, with mainly Drepanoclados aduncus, as well as Calliergon stramineum and Scorpidium scorpioideae. The proportions of organic carbon and carbonates were assessed in the profile (Dean, 1974), and palynological investigations were carried out.

Palynology

Samples for palynological analysis were taken from segments of the core at 5-10 cm intervals. Samples with Lycopodium tablets were prepared for palynological analysis using the modified Erdtmann’s acetylsis method (Stockmarr, 1971; Berglund and Ralska-Jasiewiczowa, 1986). In each of the samples, 800 grains of tree and shrub pollen were analyzed, together with accompanying grains of herbaceous plants, and spores.

The results of pollen analyses were presented in the form of diagrams made using the POLAPL program (Walansus and Nalepka, 1999). The relative percentages of taxa were determined in relation to the total sum (AP+NAP), excluding the pollen and spores of local plants.

Radiocarbon dating

AMS radiocarbon dating was carried out in the Poznań Radiocarbon Laboratory for two types of material, namely the macroremains of the mosses Drepanoclados aduncus and Calliergon stramineum, present only in the bottom part of the profile, and grains of pollen isolated according to the method described by Nakagawa et al. (1998). Calibration of the dates was performed with the help of CALIB Radiocarbon Calibration Program version 5.0.2 (Stuiver and Reimer, 1993; Reimer et al., 2004).

Modern material

In order to determine whether Drepanoclados aduncus is capable of photosynthesis when submersed, the photosynthetic activity (changes in oxygen concentration and pH) of a live specimen of Drepanoclados aduncus was measured using the method described by Bain and Proctor (1980), Allen and Spence (1981) and MacDonald et al. (1987). Leaves cut into pieces were placed inside a reaction chamber filled with 0.2 mM NaHCO3 solution as the source of carbonate ions, with an initial pH of 7.1. The electrode of a pH-meter was placed in the chamber and also Clark’s oxygen electrode measuring the amount of evolved oxygen. The reaction mixture was illuminated with light from a source with an effective emitter temperature of 2650ºK. Measurements were made by the equipment developed for real-time simultaneous measurements of pH using pH-meter Oakton Series pH510 (USA) and oxygen concentration changes in aqueous samples using Clark Electrode HansaTech (UK).

4. RESULTS AND DISCUSSION

Palynology

The profile spans a continuous record of local changes which took place in the Holocene in the vegetation of the vicinity of Lake Kwiecko. Pollen analysis of the lake’s bottom sediments made it possible to determine that sedimentation in its basin had started at the beginning of the Preboreal, when pine-birch forests with a small proportion of Ulmus (Fig. 2) dominated there. The high proportion of tree pollen, up to a maximum of 99%, is evidence of the whole area having been forested. During the boreal period, Corylus became an important element of the pine-birch forests. The Atlantic is characterized by a reduction in the proportion of Pinus and the spread of Ulmus, Quercus, Tilia and Alnus. Hedera helix and Viscum, indicators of a warm climate, were present. At the beginning of the sub-boreal period, the proportion of Ulmus declined, Corylus, Quercus, and Alnus dominating instead. New taxa of trees spread, namely Fagus and Carpinus. During the sub-Atlantic the proportion of Fagus and Carpinus increased. At the top of this chronzone the area becomes much more open and herbaceous plants spread, these including palynological indicators of human activity. The course of pollen curves does not show a possible break in sedimentation at any point in the profile.

A similar palynological picture of vegetation transformation at the beginning of the Holocene is known from other pollen diagrams whose chronology has been examined in detail and from isopollen maps for Poland.
The results of radiocarbon dating obtained for moss remains (16,270±230, 16,420±100 and 16,490±170 14C BP) (Table 1) are undoubtedly aged and are not supported by the palynological data. Pollen grains of *Ulmus*, *Quercus*, and *Alnus* are present in the Preboreal identified in the pollen diagram from Lake Kwiecko, much as in analogous chronozones identified in a pollen diagram from Lake Gacno Wielkie (Hjelmroos-Ericsson 1981), 70 km from Lake Kwiecko, and from Lake Gościan (Ralska-Jasiewiczowa et al., 1998) 250 km away (Fig. 1).

On the basis of AMS radiocarbon dating, the section discussed should be associated with the upper Plenivis- tulan. The pollen spectra recorded in sediments of this period suggest the existence of sparse pioneer vegetation of the steppe tundra type with occasional trees, which is associated with conditions of climate that are not conducive to the development of richer communities (Mamakowa, 2003; Balwierz, 2003). Before the encroachment of the glacier the climate varied along a north-south axis, from high arctic in the north, midarctic in central Poland, to subarctic-boreal in the southern part of the country. Whereas in the southern part of Poland forest tundra communities of the park type with *Larix*, *Pinus cembra* and *Betula* (Mamakowa and Starkel, 1977) may have persisted, localities from Central Poland (such as Maliniec II; Tobolski, 1991) indicate the dominance of open tundra communities with a NAP pollen component of above 90%.

Palynological data spanning the period during which the ice sheet receded, from the Smerek locality in the Bieszczady Mountains in southern Poland (Ralska-Jasiewiczowa, 1980) indicate the existence of a refuge of open forest with *Larix* and *Pinus cembra*. Meanwhile, pollen analysis carried out for two localities from central Poland (namely Lublinek-station 1, dated at 17,100±200 14C BP and Lublinek-station b dated at 16,200±200 14C BP) points to the existence of very poor, discontinuous sedge and moss communities of a pioneer type (Balwierz, 2003). In this context the section of the profile from Lake Kwiecko dated at around 16,000 years 14C BP, with a
high proportion of trees (AP min. 92%-99.5%) such as Pinus (min. 55% - max 75%) and Betula (min. 40%, max 65%) as well as Corylus (max 20%) does not contribute in terms of its pollen composition to the picture presented here of the vegetation present in the upper Plenivistulian.

Neither should this section of the palynological profile from Kwiecko under discussion be associated with the late Vistulian. Despite an improvement in climate, the forest communities were not as unbroken as can be inferred from the diagram from Lake Kwiecko, where the component of herbaceous vegetation varies from 0.5% to a maximum of 8% in the Preboreal. To compare, in the pollen diagram from Lake Mukrz the proportions of NAP grains in the sediment from Lake Kwiecko, which were not recorded at other sites of the latter part of the late glacial (Miotk-Szpiganowicz et al., 2003). A characteristic feature of open communities of the Late Glacial is a generally high proportion of heliophytes such as Helianthemum, Artemisia or Chenopodiaceae. In the discussed section of the profile from lake Kwiecko no Helianthemum pollen grains were recorded; the Artemisia curve remains at a level of 1%, much as sediments from Lake Kwiecko that the conditions of climate were relatively favorable during the sedimentation of the section under discussion may be proved by the fact of recording Typha latifolia grains in the sediment from Lake Kwiecko, which required the mean July temperature to be no lower than 13-15°C, and Myriophyllum verticillatum – average July temperature required is 10-13°C (Isarin and Bohncke 1999; Weber and Nooden, 1974), as well as the presence of high percentages of Tetraedron minimum (Ralska-Jasiewiczowa et al., 2003).

Loss on ignition

The content of carbonates and organic carbon obtained during analysis indicates its variability throughout the profile. However, their concentration was found to be highest, reaching 40%, at the bottom of the profile which is associated with the Preboreal, from where the moss remains subjected to the AMS radiocarbon dating method were taken.

Radiocarbon dating

In the whole profile from Lake Kwiecko, 15 AMS radiocarbon dates were made. Within the section associated with the Preboreal, 8 samples were dated: three of moss remains (Drepanocladus aduncus, Calliergon stramineum and one unidentified moss fragment), three samples of pollen concentrates, and two of unidentified plant remains.

The dated moss remains taken from the same level (22.23-22.25 m) gave results of 16,490±170, 16,420±100 and 16,270±230 ¹⁴C BP Poz-264, Poz-211, Poz-304). In accordance with the palynological dating adopted, the beginning of sedimentation at the bottom of Lake Kwiecko should be associated with the beginning of the Holocene, i.e. with a date of around 10,000 ¹⁴C BP. Accordingly, the ¹⁴C results obtained should be considered to be too old over 6000 years. Grains of pollen isolated from layers found 10 cm and 60 cm above the bottom of the rock layer gave a date of 12,050±380 and 11,900±200 ¹⁴C BP (Poz-2308, Poz-2307), while the plant remains from a depth of 21.31 m and 21.23 m gave dates of 10,220±50 and 9480±50 ¹⁴C BP, respectively. Here the age differences between the expected and obtained dates are smaller (Fig. 3).

Contemporary material

The two species of moss identified at the bottom of the rock layers, Drepanocladus aduncus and Calliergon stramineum, have similar requirements in terms of habitat. They often occur at localities in which there is a high

Table 1. Results of AMS radiocarbon dating of various types of material from Lake Kwiecko sediments, (pe = pollen extract, wood = terrestrial plant wood fragment, Call = Calliergon stramineum leaves, mo = mosses fragments, Drep = Drepanocladus aduncus leaves).

<table>
<thead>
<tr>
<th>Sample name / material / depth</th>
<th>Laboratory code</th>
<th>Radiocarbon age (yr BP)</th>
<th>Cal age BP Conf. intervals</th>
<th>Remark of the Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Kwiecko/pe/175cm</td>
<td>Poz-2298</td>
<td>1780±30</td>
<td>1619-1674</td>
<td>1567-1739</td>
</tr>
<tr>
<td>Lake Kwiecko/pe/365cm</td>
<td>Poz-2299</td>
<td>1940±30</td>
<td>1865-1926</td>
<td>1822-1949</td>
</tr>
<tr>
<td>Lake Kwiecko/pe/555cm</td>
<td>Poz-2300</td>
<td>2840±35</td>
<td>2919-2996</td>
<td>2863-3064</td>
</tr>
<tr>
<td>Lake Kwiecko/pe/805cm</td>
<td>Poz-2301</td>
<td>3810±30</td>
<td>4151-4240</td>
<td>4137-4295</td>
</tr>
<tr>
<td>Lake Kwiecko/pe/1255cm</td>
<td>Poz-2303</td>
<td>5630±40</td>
<td>6393-6452</td>
<td>6314-6487</td>
</tr>
<tr>
<td>Lake Kwiecko/pe/1465cm</td>
<td>Poz-2297</td>
<td>6010±40</td>
<td>6791-6897</td>
<td>6745-6948</td>
</tr>
<tr>
<td>Lake Kwiecko/pe/1930cm</td>
<td>Poz-2304</td>
<td>7860±120</td>
<td>8543-8787</td>
<td>8429-8997</td>
</tr>
<tr>
<td>Lake Kwiecko/pe/2096cm</td>
<td>Poz-2305</td>
<td>9500±90</td>
<td>10654-10832</td>
<td>10561-11143</td>
</tr>
<tr>
<td>Lake Kwiecko/wood/2123cm</td>
<td>Poz-203</td>
<td>9480±50</td>
<td>10654-10787</td>
<td>10582-10833</td>
</tr>
<tr>
<td>Lake Kwiecko/wood/2135cm</td>
<td>Poz-206</td>
<td>10220±50</td>
<td>11953-12050</td>
<td>11751-12130</td>
</tr>
<tr>
<td>Lake Kwiecko/pe/2185cm</td>
<td>Poz-2307</td>
<td>11900±200</td>
<td>13535-13979</td>
<td>13293-14203</td>
</tr>
<tr>
<td>Lake Kwiecko/pe/2215cm</td>
<td>Poz-2308</td>
<td>12050±380</td>
<td>13458-14491</td>
<td>13210-15099</td>
</tr>
<tr>
<td>Lake Kwiecko/Coll/2223-2225cm</td>
<td>Poz-304</td>
<td>16270±230</td>
<td>19168-19580</td>
<td>18997-19870</td>
</tr>
<tr>
<td>Lake Kwiecko/mo/2223-2225cm</td>
<td>Poz-211</td>
<td>16420±100</td>
<td>19466-19588</td>
<td>19411-19844</td>
</tr>
<tr>
<td>Lake Kwiecko/Drep/2223-2225cm</td>
<td>Poz-264</td>
<td>16490±170</td>
<td>19495-19816</td>
<td>19307-19998</td>
</tr>
</tbody>
</table>

CONF. INTERVALS: 68.3% (1 SIGMA) 95.4% (2 SIGMA)
level of ground moisture. Calliergon stramineum is most frequently recorded in areas of springs and wet meadows while Drepanocladus aduncus is also found in fens, wet meadows, muds, and the edges of lakes, ponds, and watercourses (Szafran, 1961). They are often present in an environment characterized by very high CaCO₃ content (Vitt et al., 1993).

Photosynthetic activity was measured using a fresh specimen of Drepanocladus aduncus collected in the field and immersed in the aqueous reaction mixture. These measurements showed both the pH of the bathing solution to rise above ca. 1 unit, and the release of oxygen (Fig. 4), thus clearly demonstrating high photosynthetic activity of the moss. However, these results show also that source of carbon for sugar synthesis in Drepanocladus aduncus is not bicarbonate but mostly carbon dioxide (Bain and Proctor, 1980; Mott and Jackson, 1982; MacDonald et al., 1987). If the HCO₃⁻ ion were being used to produce sugar photosynthetically, the result would be an accumulation of (H₃O⁺) ions and acidification of the environment as evidenced by a fall in the pH of the solution.

Discussion

The results obtained show inconsistencies between palynological data and radiocarbon ages obtained from mosses. The palynological picture is typical of the beginning of the Holocene, while the results of moss radiocarbon dating are aged considerably.

Problems with moss radiocarbon dating have been known for many years. It has been demonstrated that their remains can produce ¹⁴C ages which are older than those for terrestrial macrofossils from the same or younger stratigraphic level. Some interesting results obtained by MacDonald et al. (1987) showed that radiocar-

bon dating of living samples of Drepanocladus crassicoptatus collected in 1996 and 1985 provided radiocarbon ages significantly older than modern and contained less than 85% of modern ¹⁴C. This result suggests that the living plants had access to ¹⁴C-deficient carbon which they were able to assimilate during photosynthesis, so that the aforementioned is not simply the result of post-mortem processes.

As was demonstrated in our study of the moss Drepanocladus aduncus, it has photosynthetic activity while submerged in the water but cannot incorporate HCO₃⁻ ions. The main source of carbon for photosynthesis reactions is CO₂, but it is well known that in water CO₂ can be generated from HCO₃⁻, particularly when depletion of CO₂ is observed. Bain and Proctor (1980) suggested that mosses can draw upon the reservoir of CO₂ in HCO₃⁻ if pH remains below the free-CO₂ compensation point. CO₂ can be also generated from HCO₃⁻ in the groundwater as it enters the lake if the pH of the HCO₃⁻-rich groundwater is higher than that of the lake. It is also known that HCO₃⁻ ions can arise in water both as a result of the interaction of atmospheric CO₂ with water and as an effect of water contact with carbonate rocks in accordance with the following equilibrium:

\[ \text{Ca(HCO}_3\text{)}_2 = \text{Ca}^{2+} + 2\text{HCO}_3^- \]  

Ca(HCO₃)₂ is dissolved in water and may release CO₂ which can be used in photosynthesis:

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{CO}_2^{\uparrow} \]

and:

\[ \text{HCO}_3^- + \text{H}_3\text{O}^+ = \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \]

and:

\[ \text{H}_2\text{CO}_3 = \text{H}_2\text{O} + \text{CO}_2^{\uparrow} \]
If the limestone rocks contain 14C-deficient carbon, the CO2 released from these rocks will likewise be deficient in 14C. If the CO2 which contains 13C-deficient carbon is assimilated by plants and incorporated in sugar synthesis in their cells, the 13C/14C equilibrium in the plant tissues will be significantly disturbed. The release of the CO2 from 14C-deficient HCO3 is the main reason for the presence of 14C-deficient carbon in Lake Kwiekko.

The high level of carbonates probably also affected the results of dating pollen concentrates isolated from the sediment. Carbonates are readily deposited on the porous surfaces of pollen, if present in their vicinity in large amounts (Kilian et al., 2002). Perhaps the same phenomenon is also responsible for the aged results obtained for wood fragments (Poz-206, Poz-203) and had an additional effect on the results of dating moss remains. Another difficulty which must have affected the results of dating pollen concentrates taken from the bottom layer of the profile was that of obtaining suitably clean samples. They contained non-pollen contaminants such as the microfragments of unidentified plant tissues, possibly including those of mosses.

5. CONCLUSION

This paper presents the results of pollen analysis for the bottom sediments of Lake Kwiekko, the results of AMS radiocarbon dating, carbonate content in sediment, and also results that demonstrate the photosynthetic activity of Drepanoclados aduncus under conditions of being submerged in solution. The palynological data obtained clearly indicate the beginning of the Holocene as the period during which the accumulation of sediments begins in the lake. The proportion of CaCO3 in the sediment was high, reaching 40% at the bottom of the profile. The results of AMS radiocarbon dating of moss remains seem to be over 6000 years too old in relation to the palynological chronology. The most likely reason for such old dates having been obtained is the incorporation into the moss tissues of carbon atoms from dissolved old carbonates during the photosynthesis that took place during their periodic flooding. Doubtless, the possible carbonate deposition on the surface of the dated material could also have affected the dating, as could the presence of other molecules. While radiocarbon dating is without doubt one of the most important tools in palaeoecological research, the results obtained must be subject to critical evaluation and correlation with data obtained using other research methods.

REFERENCES


