Journal of Nuclear and Radiochemical Sciences, Vol. 9, No. 2, pp. 41-44, 2008

Relationship between Carbon-14 Concentrations in Tree-ring Cellulose and Atmospheric CO_2

Yoshimune Yamada,*[,a] Kaeko Yasuike,[a] and Kazuhisa Komura[b]

[a]*Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa-City 920-1181, Japan*
[b]*Low Level Radioactivity Laboratory, Kanazawa University, Tatsunokuchi-machi, Nomi-City 923-1224, Japan*

Received: June 19, 2008; In Final Form: Sptember 1, 2008

Concentrations of organically-bound ^{14}C in the tree-ring cellulose of a Japanese Cedar (*Cryptomeria japonica*) grown in a rural region of Kanazawa, Ishikawa prefecture, Japan (36.5°N, 136.7°E), were measured for the ring-years from 1989 to 1998 to study relationship between ^{14}C concentrations in tree-ring cellulose and atmospheric CO_2 in a narrow region. An interesting result in comparing our data of tree-ring cellulose with those of atmospheric CO_2 is that the ^{14}C concentration in tree-ring cellulose was close to the corresponding average from mid-June to early September of ^{14}C concentrations in atmospheric CO_2. Furthermore, the ^{14}C concentrations in tree-ring cellulose were found to be merely influenced by the drastic decrease of ^{14}C concentrations in atmospheric CO_2 in winter, which might be caused by air pollution from the Asian continent and additional local fossil fuel contribution. These results suggest that the ^{14}C concentration in tree-ring cellulose for a given growing year reflects the ^{14}C concentrations of atmospheric CO_2 during the warm summer months.

1. Introduction

Most of environmental ^{14}C (half life = 5730 y) originates from continuous production by cosmic rays in the upper atmosphere and from thermonuclear bomb tests carried out during the 1950s and early 1960s.[1-3]

It could be estimated that the ^{14}C records in a series of annual rings of trees reflect the variations in the levels of ^{14}C concentration in atmospheric CO_2 at the growth site of the tree.[4-16] Carbon necessary for synthesizing a variety of chemical compounds in tree rings is derived essentially from the CO_2 in the air by photosynthesis. Measurement of ^{14}C in the cellulose fraction of tree rings is a preferred method for the analysis of annual variations in ^{14}C concentrations, since organically-bound carbon in the cellulose undergoes no changes following the time of tree-ring formation. However, there has been little literature referring to the relationship between ^{14}C concentrations in tree-ring cellulose and atmospheric CO_2 in a narrow region up to date.[7-9]

In our previous paper,[17] temporal variation of ^{14}C concentrations in atmospheric CO_2 samples collected every 10 days was measured in the Ohkuwa area of Kanazawa, Ishikawa prefecture, Japan (36.5°N, 136.7°E), where local contamination from fossil-fuel combustion can be disregarded, during the period from April 1991 to December 2000 to estimate the background level of environmental ^{14}C and to clarify the influence of air containing a large amount of ^{14}C-free fossil fuel CO_2 transported across the Sea of Japan from the Asian continent on the levels of environmental ^{14}C. The Ohkuwa area is located in the lowlands about 40 m above sea level in a rural region southeast out of the center of the city. There are no factories releasing a large amount of ^{14}C-free fossil fuel CO_2 in the surrounding area. Thereafter, the same method was applied to the samples collected in the Takao area of Kanazawa (36.5°N, 136.6°E), which is located in an urban area near the center of the city, and then, levels of ^{14}C in atmospheric CO_2 in urban area were compared with background levels of ^{14}C in atmospheric CO_2 to estimate the local fossil fuel contribution to ^{14}C concentrations in atmospheric CO_2.[18]

In the present study, the concentration of organically-bound ^{14}C in the tree-ring cellulose of a Japanese Cedar (*Cryptomeria japonica*) grown at a site located about 1.6 km southeast of the sampling site of atmospheric CO_2 samples in the Ohkuwa area of Kanazawa was measured for the ring-years from 1989 to 1998 to study relationship between ^{14}C concentrations in tree-ring cellulose and atmospheric CO_2.

2. Experimental

2.1. Cellulose samples of tree rings. The trunk of a 54-year-old Japanese Cedar (*Cryptomeria japonica*), 0.48 m in diameter, and 0.7 m in length, was cut at the position of 0.5–1.2 m above the ground surface on October 18, 1998, and was analyzed in the present study. The tree was grown at a site on the top of a small hill in the Tachi area of Kanazawa, Ishikawa prefecture, Japan (36.5°N, 136.7°E), as shown in Figure 1. The growing site of the tree in the Tachi area was located about 1.6 km southeast of the sampling site of atmospheric CO_2 in the previous study, which was in a rice field of 1 km^2 in the Ohkuwa area.[17] There are no factories releasing large amounts of ^{14}C-free fossil fuel CO_2 in the surrounding area.

Each cellulose fraction corresponding to the 1989–1998 ring-years was isolated from wood chips according to the same method that was applied to a 67-year-old pine tree (Japanese Black Pine; *Pinus thunbergii*) grown in Shika-machi, Ishikawa prefecture, Japan (37.0°N, 136.8°E) in our previous study.[15]

2.2. Combustion of cellulose samples. The cellulose fraction of 100 g corresponding to a single year was gently burned to obtain the combustion water for tritium measurement and CO_2 for ^{14}C measurement.[15,19] The carbon dioxide gas was collected as a dry-ice form, and the resulting dry-ice was immediately converted to calcium carbonate. Approximately 280 g of dried $CaCO_3$ obtained from 100 g of cellulose was stored in an airtight vessel.

2.3. Benzene synthesis for the preparation of ^{14}C counting sources. The original CO_2 was regenerated by adding a solution of perchloric acid dropwise to 40 g of the stored

*Corresponding author. E-mail: yo-yamada@hokuriku-u.ac.jp, FAX: +81-76-229-2781

Published on Web 12/05/2008

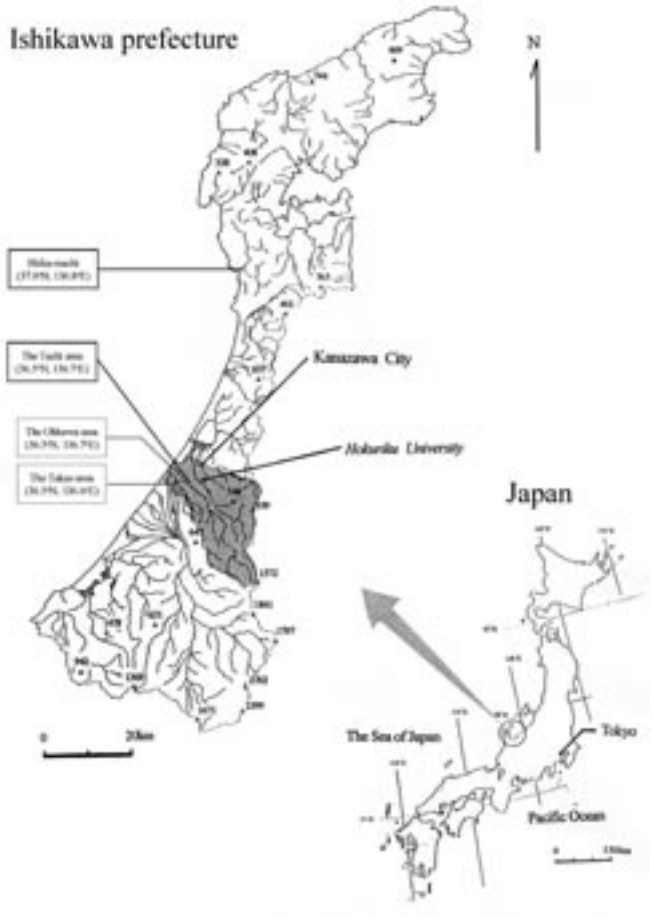

Figure 1. Sampling sites of the tree and the atmospheric CO_2 samples for ^{14}C measurement, Kanazawa, Ishikawa prefecture, Japan (36.5°N, 136.7°E).
Fine lines in the figure represent rivers in Ishikawa prefecture, Japan.

$CaCO_3$. It was then converted to benzene in a vacuum by the method described previously.[15]

The counting source for a liquid scintillation spectrometer was prepared by adding a toluene based butyl-PBD scintillation solution to 3.5–4.0 g of synthesized benzene to a total volume of 20 mL. The synthesized benzene prepared from NIST oxalic acid (SRM 4990C) was used as a standard reference of ^{14}C.

2.4. Measurement of ^{14}C. The ^{14}C activity was measured by a low background liquid scintillation counter, Aloka LB-1, under temperature-stabilized conditions at 12 °C at least for 100 min x 40 times. The counting background of the 20 mL low potassium glass vial was 2.64 cpm at a rate of 58% efficiency. The results are presented as $\Delta^{14}C$, as defined in our previous paper.[10] Isotopic fluctuation of a sample was corrected using the $\delta^{13}C$ value determined by a Finnigan-MAT Delta^{PLUS} Stable Isotope Ratio Mass Spectrometer.

3. Results and Discussion

The concentration of organically-bound ^{14}C in the tree-ring cellulose of a Japanese Cedar grown in a rural region of Kanazawa, Ishikawa prefecture, Japan (36.5°N, 136.7°E), was measured for the ring-years from 1989 to 1998 to study relationship between ^{14}C concentrations in tree-ring cellulose and atmospheric CO_2. The growing site of the tree was located about 1.6 km southeast of the sampling site of atmospheric CO_2 samples in the Ohkuwa area, in which temporal variation of ^{14}C concentrations in the atmospheric CO_2 samples collected every 10 days was measured during the period from April 1991 to December 2000.[17]

TABLE 1: Carbon-14 concentration in tree-ring cellulose of a Japanese Cedar (*Cryptomeria japonica*) in Kanazawa, Ishikwa prefecture, Japan (36.5 °N,136.7 °E)

Year	$\Delta^{14}C^{*}$ (‰)	$\delta^{13}C$ (‰)
1998	101.0 ± 4.6	-24.36
1997	107.5 ± 4.8	-24.07
1996	113.3 ± 4.6	-23.68
1995	123.6 ± 4.8	-23.65
1994	138.7 ± 4.4	-23.46
1993	138.4 ± 6.0	-23.39
1992	154.1 ± 4.5	-22.96
1991	140.5 ± 4.3	-23.13
1990	159.4 ± 4.8	-23.93
1989	171.1 ± 5.2	-23.77

*The error denotes a counting error of 1σ.
All samples were measured using a low background liquid scintillation counter, Aloka LB-1.

The results of measurement for the tree expressed as the $\Delta^{14}C$ value are given in Table 1. The $\Delta^{14}C$ values in the table, after corrections for isotopic fluctuation using $\delta^{13}C$ and radioactive decay of ^{14}C, were reproducible at ±10‰ or less, as described previously.[10]

The relationship between the $\Delta^{14}C$ and the ring year of the Japanese Cedar for the ring-years from 1991 to 1995 is illustrated by bar graphs in Figure 2. The temporal variation of $\Delta^{14}C$ values in atmospheric CO_2 every 10 days is also illustrated in the figure. In addition, annual averages and averages from mid-June to early September of the $\Delta^{14}C$ values in atmospheric CO_2 are plotted in the figure, respectively.

The most important result in this study is that the $\Delta^{14}C$ value in tree-ring cellulose of the Japanese Cedar demonstrated elevated levels higher than the corresponding annual average of $\Delta^{14}C$ values in atmospheric CO_2. Furthermore, the $\Delta^{14}C$ value in tree-ring cellulose was close to the corresponding average between mid-June and early September of the $\Delta^{14}C$ values in atmospheric CO_2, although a significant difference appeared in 1994.

In the previous paper,[17] it was revealed that the $\Delta^{14}C$ values in atmospheric CO_2 in the Ohkuwa area, where local contamination from fossil-fuel combustion can be disregarded, decreased gradually by about 5‰ each year from 1991 to 2000, with a pronounced seasonal cycle which began to increase from spring and reached the maximum in late July or early August, followed by a decrease to the minimum from December to February. The appearance of the extreme decrease of the $\Delta^{14}C$ value in winter seemed to be caused by the influence of air containing a large amount of ^{14}C-free fossil fuel CO_2 transported across the Sea of Japan from the Asian continent. Furthermore, it was also revealed that the monthly mean levels of ^{14}C concentration in the Takao area demonstrated 10–50‰ lower concentrations than the background levels only in the winter season.[18] This additional decrease seemed to be caused by the local fossil fuel contribution by heating in the winter season in the Takao area, which is located in an urban region near the center of Kanazawa.

However, the present data for the tree demonstrated that the air pollution from the Asian continent and additional local fossil fuel contribution in winter merely affected the $\Delta^{14}C$ values in tree-ring cellulose. The unexpected result mentioned above suggests that the tree-ring cellulose was scarcely synthesized in winter, since the carbon necessary for synthesizing cellulose seems to be supplied essentially by photosynthesis from the

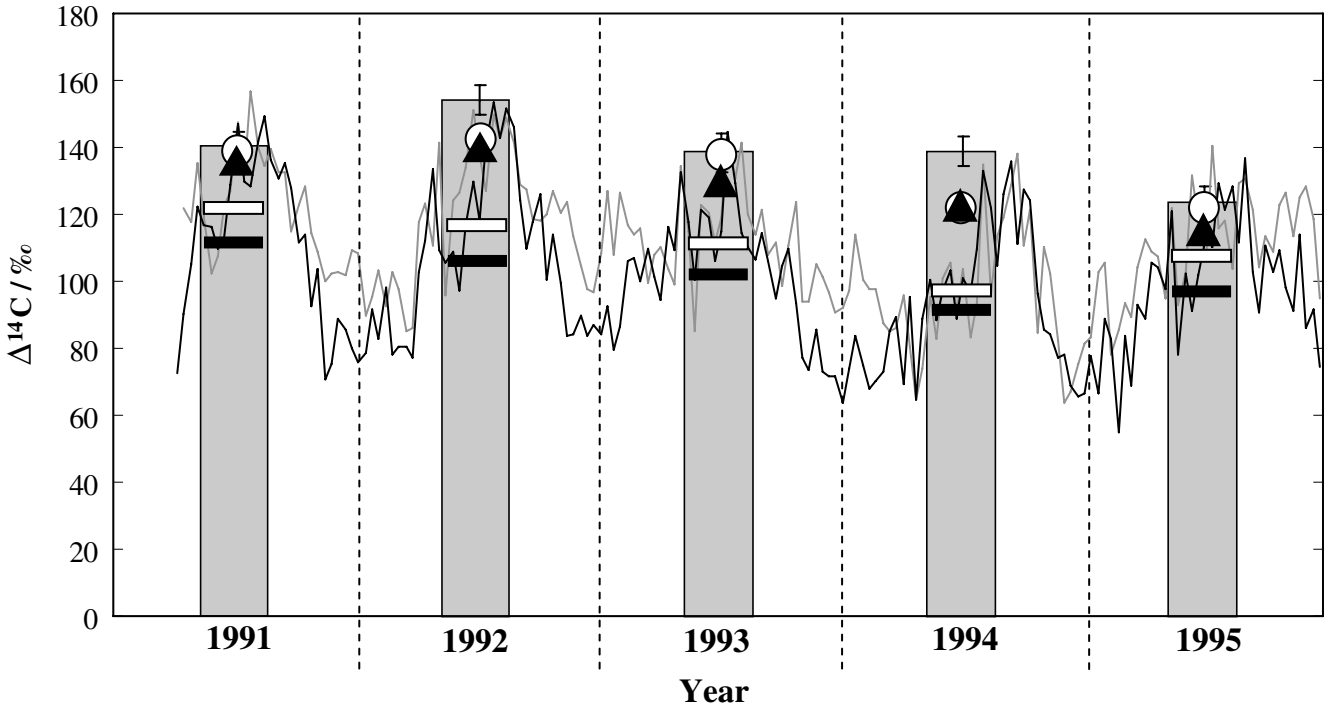

Figure 2. Relationship between $\Delta^{14}C$ values in tree-ring cellulose and atmospheric CO_2 in Kanazawa, Ishikawa prefecture, Japan.
The bar graph (dark gray): Japanese Cedar (*Cryptomeria japonica*) in the Tachi area (36.5°N, 136.7°E) in this study.
Gray line: The atmospheric CO_2 in the Ohkuwa area (36.5°N, 136.7°E).[17]
Black line: The atmospheric CO_2 in the Takao area (36.5°N, 136.6°E).[18]
Annual average of the atmospheric CO_2: ▭ The Ohkuwa area, ▬ The Takao area.
The average from mid-June to early September for atmospheric CO_2: ◯ The Ohkuwa area, ▲ The Takao area.

CO_2 in the air.

In comparing ^{14}C concentrations in tree rings with those of atmospheric CO_2, it is of importance that a subject when the cellulose in a certain part of tree ring was synthesized from the CO_2 in the air. There have been several literatures concerning this subject.[5,7-9]

Levin and Kromer[9] reported that the tree-ring data closely match the summer values of the air samples averaged over the months May to August by the analysis of individual tree rings (*Picea abies*) collected in the vicinity of Schauinsland station (48°N, 8°E) located close to the top of Schauinsland Mountain in the Black Forest, southern Germany, at an elevation of 1205 m asl.

Nakamura et al.[5] reported that early wood of each annual ring for a Kiso hinoki tree (*Chamaecyparis obtusa*, Japanese cypress) grown in a rural forest, Gifu prefecture, Japan, was formed from the beginning of May to the end of July by assuming an equal growth rate. They also reported that the variations in the $\Delta^{14}C$ values of the early wood of individual annual rings for the Kiso hinoki from 1958 to 1966 showed good agreement with those of atmospheric CO_2 in Spain from 1962 to 1963 and in Norway from 1963 to 1966. On the basis of these observations, they explained that the time-lag between the fixation of CO_2 by the tree through photosynthesis and the cellulose formation of the tree using the photosynthetic products seems to be negligible during the growing season of the tree. Similar results were reported by Olsson and Possnert[8] that the total growing time was normally from June to the end of August for an oak tree grown in a suburb of Uppsala in Sweden, and there was no clear evidence for any delay in ^{14}C activity between the atmospheric CO_2 in Abisko in northern Sweden and the cellulose fraction in the tree on a time scale of weeks. However, it should be noted that there have been conflicting reports concerning this subject. Grootes et al.[7] reported that $\Delta^{14}C$ values of tree ring cellulose seem to follow those of atmospheric CO_2 with a delay of 5 to 6 weeks.

It is apparent from these considerations that the ^{14}C concentration in tree-ring cellulose for a given growing year indicates the ^{14}C concentration of atmospheric CO_2 during the growing season of the tree. The difference of the indicated intervals of growth of tree rings within one month among several trees grown in distinct areas in the northern hemisphere seemed to be mainly caused by the climatic conditions, since the formation of boundaries of tree rings can be influenced easily by external factors, such as the climate of the place where the sample tree grew.[20]

The relationship between the $\Delta^{14}C$ and the ring year of the Japanese Cedar for the ring-years from 1991 to 1999 is illustrated by bar graphs in Figure 3 together with those of the pine tree (Japanese Black Pine; *Pinus thunbergii*) from Shika-machi (37.0°N, 136.8°E), Ishikawa prefecture, Japan, revealed in the previous paper.[15]

The comparison of $\Delta^{14}C$ values in tree-ring cellulose for the two sets of trees collected at different regions of Ishikawa prefecture indicated that annual variation of $\Delta^{14}C$ values in tree-ring cellulose of the Kanazawa-sample in this study had essentially similar variations to that of the Shika-sample and significant difference was not observed in the $\Delta^{14}C$ values between the two sets of samples.

From these results, it was found that there was no local variation of the ^{14}C concentration in atmospheric CO_2 between two different regions of Ishikawa prefecture, and that the $\Delta^{14}C$ values in tree-ring cellulose of the Shika-sample for a given growing year might reflect averages of the $\Delta^{14}C$ values of atmospheric CO_2 from mid-June to early September. It is noteworthy that significant difference of the $\Delta^{14}C$ value derived from the difference of species of tree was not observed between the Japanese Cedar and the Japanese Black Pine.

4. Conclusion

The concentration of organically-bound ^{14}C in the tree-ring

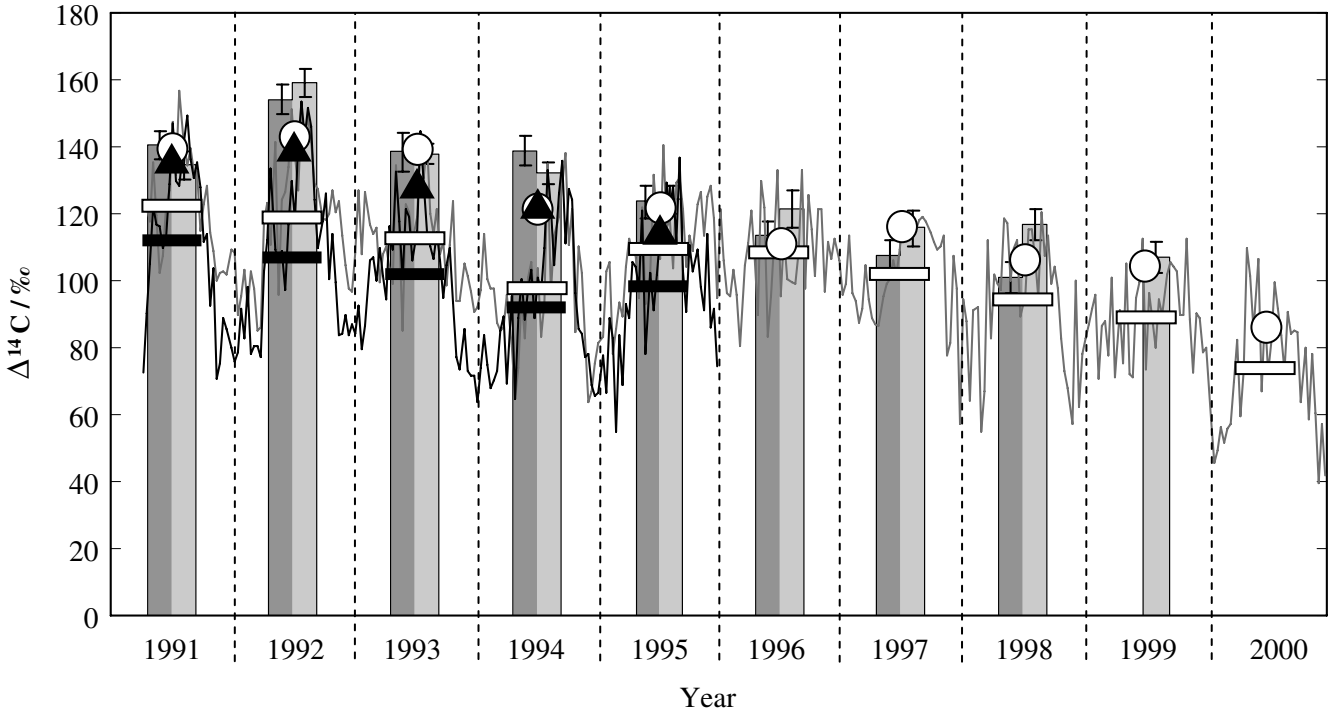

Figure 3. The relationship between the $\Delta^{14}C$ and the ring year of the Japanese Cedar (*Cryptomeria japonica*) for the ring-years from 1991 to 1999 together with those of the Japanese Black Pine (*Pinus thunbergii*) from Shika-machi (37.0°N, 136.8°E), Ishikawa prefecture, Japan.
The bar graph (dark gray): Japanese Cedar (*Cryptomeria japonica*) in the Tachi area of Kanazawa (36.5°N, 136.7°E) in this study.
The bar graph (light gray): Japanese Black Pine (*Pinus thunbergii*) in Shika-machi (37.0°N, 136.8°E).[15]
Gray line: The atmospheric CO_2 in the Ohkuwa area of Kanazawa (36.5°N, 136.7°E).[17]
Black line: The atmospheric CO_2 in the Takao area of Kanazawa (36.5°N, 136.6°E).[18]
Annual average of the atmospheric CO_2: ▭ The Ohkuwa area, ▬ The Takao area.
The average from mid-June to early September for atmospheric CO_2: ◯ The Ohkuwa area, ▲ The Takao area.

cellulose of a Japanese Cedar grown in a rural region of Kanazawa, Ishikawa prefecture, Japan (36.5°N, 136.7°E), was measured for the ring-years from 1989 to 1998 to study relationship between ^{14}C concentrations in tree-ring cellulose and atmospheric CO_2.

The $\Delta^{14}C$ values in tree-ring cellulose demonstrated elevated levels higher than the corresponding annul average of $\Delta^{14}C$ values in atmospheric CO_2, and was close to the corresponding average of the $\Delta^{14}C$ values in atmospheric CO_2 from mid-June to early September. Furthermore, the $\Delta^{14}C$ values in tree-ring cellulose was found to be merely influenced by the drastic decrease in $\Delta^{14}C$ values in atmospheric CO_2 in winter, which might be caused by the air pollution from the Asian continent. These observations suggest that a large part of the carbon necessary for synthesizing tree-ring cellulose seems to be derived from the atmospheric CO_2 during the growing season of the tree.

On the basis of these results, it is concluded that the $\Delta^{14}C$ values in tree-ring cellulose for a given growing year might reflect the average of $\Delta^{14}C$ values in atmospheric CO_2 from mid-June to early September.

Acknowledgments. The authors wish to express their thanks to Dr. Hikaru Amano, Japan Atomic Energy Agency, and Ms. Miwako Yamamichi, Japan Marine Science Foundation, for their helpful advice in our mass spectrometry analyses.

This study was supported in part by a Grant from the Ishikawa Prefectural Institute of Public Health and Environmental Science.

References

(1) E. M. Druffel and H. E. Suess, J. Geophys. Res. **88**, 1271 (1983).
(2) I. Levin, Radiocarbon **46**, 1261 (2004).
(3) Q. Hua and M. Barbetti, Radiocarbon **46**, 1273 (2004).
(4) W. F. Cain and H. E. Suess, J. Geophys. Res. **81**, 3688 (1976).
(5) T. Nakamura, N. Nakai, and S. Ohishi, Nucl. Instrum. Methods **B29**, 355 (1987).
(6) D. Kaimei, Q. Youneng, and C. Y. Fan, Radiocarbon **34**, 753 (1992).
(7) P.M. Grootes, G. W. Farwell, F. H. Schmidt, D. D. Leach, and M. Stuiver, Tellus **41B**, 134 (1989).
(8) I. U. Olsson and G. Possnert, Radiocarbon **34**, 757 (1992).
(9) I. Levin and B. Kromer, Radiocarbon **39**, 205 (1997).
(10) Y. Yamada, K. Yasuike, M. Itoh, N. Kiriyama, K. Komura, and K. Ueno, J. Radioanal. Nucl. Chem. **227**, 37 (1998).
(11) Y. Muraki, G. Kocharov, T. Nishiyama, Y. Naruse, T. Murata, K. Masuda, and Kh. A. Arslanov, Radiocarbon **40**, 177 (1998).
(12) I. Krajcar-Bronić, N. Horvatinčić, and B. Obelić, Radiocarbon **40**, 399 (1998).
(13) A. Z. Rakowski, S. Pawełczyk, and A. Pazdur, Radiocarbon **43**, 679 (2001).
(14) J. H. Park, J. C. Kim, M. K. Cheoun, I. C. Kim, M. Youn, Y. H. Liu, and E. S. Kim, Radiocarbon **44,** 559 (2002).
(15) Y. Yamada, K. Yasuike, and K. Komura, J. Nucl. Radiochem. Sci. **6**, 135 (2005).
(16) H. Kawamura, H. Kofuji, S. Gasa, M. Kamamoto, N. Sawafuji, and M. Mori, Radiocarbon **49,** 1045 (2007).
(17) K. Yasuike, Y. Yamada, and K. Komura, J. Radioanal. Nucl. Chem. **275**, 313 (2008).
(18) K. Yasuike, Y. Yamada, and K. Komura, J. Radioanal. Nucl. Chem. **277**, 389 (2008).
(19) Y. Yamada, K. Yasuike, and K. Komura, J. Radioanal. Nucl. Chem. **262**, 679 (2004).
(20) T. Fukuda, I. Mori, N. Terasima, and T. Kanda, Mokuzaigakkaisi **15**, 182 (1969). (In Japanese)