

Temporal Variation of Carbon-14 Concentration in Tree-ring Cellulose for the Recent 50 Years

Yoshimune Yamada,^{*,a} Kaeko Yasuike,^a and Kazuhisa Komura^b

^aFaculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa-City 920-1181, Japan

^bLow Level Radioactivity Laboratory, Kanazawa University, Nomi-shi, Ishikawa 923-1224, Japan

Received: June 6, 2005; In Final Form: August 7, 2005

Concentration of organically-bound ^{14}C in the tree-ring cellulose of a pine tree grown in Shika-machi, Ishikawa prefecture, Japan (37.1°N , 136.5°E), was measured for the ring-years from 1949 to 1999 and compared with those in several trees from East Asia region reported by other researchers. The difference of $\Delta^{14}\text{C}$ values was found during the period of 1970–1981 between our data and those of other reports, in addition to the difference during the period of 1963–1967 caused by the so-called latitude dependence of the ^{14}C variations in the northern troposphere. These results suggest that the ^{14}C concentration in atmospheric CO_2 was considerably disturbed during the period of 1970–1981, especially in 1970, 1976, and 1978–1981, in the East Asia region. This phenomenon may be interpreted by the possibility of the several times of injections of ^{14}C originated from a series of Chinese thermonuclear bomb tests.

1. Introduction

Most of environmental ^{14}C originates from the continuous production by cosmic rays in the upper atmosphere and from thermonuclear bomb tests carried out during the 1950s and early 1960s¹⁻³ as well as the case of environmental tritium.⁴

The long-term variation in environmental ^{14}C concentration at the specific site is preserved in the ^{14}C records in a series of annual rings of the tree grown there.⁵⁻¹³ Measurement of ^{14}C in the cellulose fraction of tree rings is a preferred method for the analysis of annual variation of ^{14}C concentration, since organically-bound carbon in the cellulose undergoes no change following the time of tree-ring formation.

In the previous paper,⁹ the ^{14}C concentration in the tree ring cellulose of an 80-year-old pine tree grown in Tatsunokuchi-machi, Ishikawa prefecture, Japan (36.4°N , 136.5°E) (hereafter the Tatsunokuchi-sample) was reported for the period of 1941–1987. An interesting fact was that there was a difference in the amplitude of the ^{14}C concentrations between our result and those of other researchers during the period of 1963–1967, though the year of two peaks in our result coincided with those in the known ^{14}C concentration patterns in the tree rings.⁵⁻⁷ The difference may be interpreted by the so-called latitude dependence of the ^{14}C variations in the northern troposphere,¹⁻³ which was due to the ^{14}C released to the atmosphere at higher northern latitudes by a series of thermonuclear bomb tests carried out during the 1950s and early 1960s.

In the present work, the ^{14}C concentration in the tree-ring cellulose of a pine tree grown in Shika-machi, Ishikawa prefecture, Japan (37.1°N , 136.5°E) (hereafter the Shika-sample), was measured for the ring-years of 1949 to 1999, and the results were compared with those of the Tatsunokuchi-sample to study regional differences in environmental ^{14}C concentration. Shika-machi is located at little higher latitude than Tatsunokuchi-machi, as shown in Figure 1.

Furthermore, the annual variation of ^{14}C concentration obtained from the Shika-sample was compared with those of ^{14}C concentration in tree rings from East Asia region reported by other researchers.

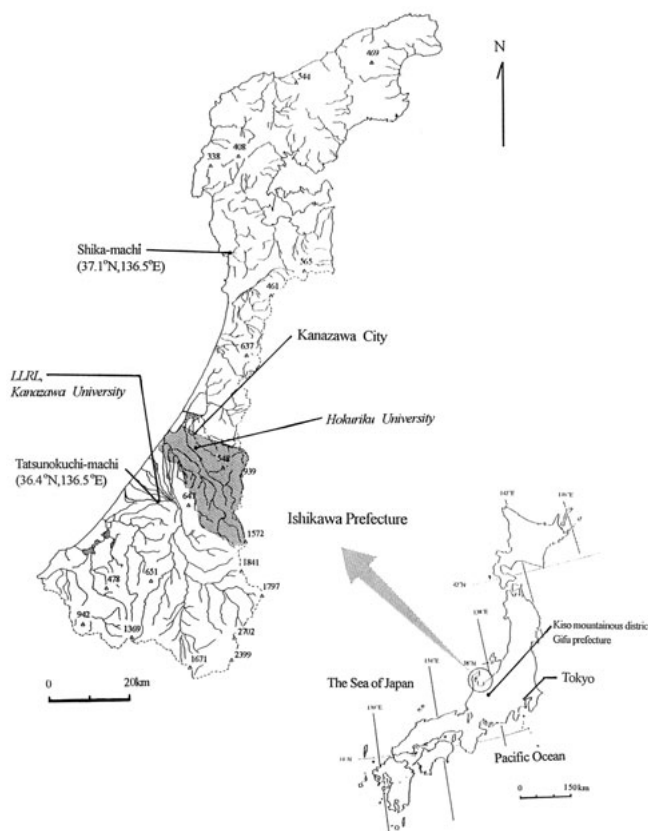


Figure 1. Sampling sites of the pine trees for ^{14}C measurement, Shika-machi, Ishikawa prefecture, Japan (37.1°N , 136.5°E) and Tatsunokuchi-machi, Ishikawa prefecture, Japan (36.4°N , 136.5°E). Fine lines in the figure represent rivers in Ishikawa prefecture, Japan.

2. Experimental

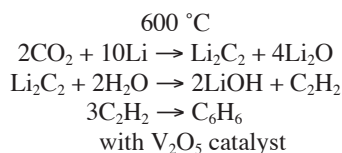
Cellulose samples of tree rings. The trunk of a 67-year-old pine tree (Japanese Black Pine; *Pinus thunbergii*), 0.5 m in diameter, and 1.2 m in length, was cut at the position of 0.5–1.7 m above the ground surface on August 10, 1999, and was analyzed in the present work. The pine tree is the same tree used for tritium measurement in the annual growth rings by the present authors, previously.¹⁴

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

All of the tree-ring layers had a thickness of more than 1.5 mm, which was enough to separate without cross-contamination from subsequent years. Each cellulose fraction corresponding to the 1949–1999 ring-years was isolated from wood chips according to the same method without pre-treatment by the steam explosion of wood chips¹⁵ which was applied to the Tatsunokuchi-machi tree (Japanese Red Pine; *Pinus densiflora*).

Combustion of cellulose samples. The cellulose fraction of 100 g corresponding to a single year was gently burned to obtain the combustion water and CO₂ by the method described previously.^{9, 14} The combustion water was condensed in two dry-ice traps connected in tandem. The carbon dioxide gas was collected as dry-ice form by an EtOH trap cooled with liquid nitrogen located behind the dry-ice traps. The resulting dry-ice was immediately converted to calcium carbonate according to the following procedure. A stream of CO₂ generated from the dry-ice was trapped by bubbling in a 7M NH₄OH solution, and the absorbed CO₂ was precipitated quantitatively as CaCO₃ by adding an excess of CaCl₂ to the solution followed by heating. Approximately 280 g of dried CaCO₃ obtained from 100 g of cellulose was stored in an airtight vessel.

Benzene synthesis for the preparation of ¹⁴C counting sources. The original CO₂ was regenerated by adding a solution of perchloric acid dropwise to the 40 g of stored CaCO₃. It was then converted to benzene in vacuum through the following reactions.



The counting source for 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 ¹⁴C.

Measurement of ¹⁴C. The ¹⁴C 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 × 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 Δ¹⁴C, defined in the previous paper.⁹ Isotopic fluctuation of a sample was corrected using the δ¹³C value of –26.4 ‰, which was the average of the δ¹³C values determined for several tree-ring samples with the Finnigan MAT Stable Isotope Ratio Mass Spectrometer, MAT 252.

3. Results and Discussion

Concentration of organically-bound ¹⁴C in the Shika-sample (37.1°N, 136.5°E) was measured for the ring-years of 1949 to 1999 and compared with those of the Tatsunokuchi-sample (36.4°N, 136.5°E)⁹ for the 1941–1987 period to investigate the regional differences of environmental ¹⁴C concentration.

The Shika-sample was grown in a small pine forest at the seaside of Shika-machi situated on a lowland plain area about 20 m above sea level and lies along the coast of the Sea of Japan; high mountains are not present in the surroundings. On the other hand, Tatsunokuchi-sample was grown at a site halfway down a hill of about 50 m above sea level near the rim of the high mountain region of 1500–2000 m, located about 70 km south of Shika-machi. The two sets of sampling sites are shown in Figure 1.

The Δ¹⁴C values measured for the Shika-sample are given in Table 1. The Δ¹⁴C values in the table were reproducible at ±10 ‰ or less, as described in the previous paper.⁹

TABLE 1: Carbon-14 Concentration in Tree-ring Cellulose of a Pine Tree in Shika-machi, Ishikwa Prefecture, Japan (37.1°N, 136.5°E)

Year	Δ ¹⁴ C* / ‰	Total counting time/min
1999	107.0 ± 4.6	4000
1998	116.7 ± 4.6	4000
1997	115.7 ± 5.4	4000
1996	121.4 ± 5.8	5000
1995	124.3 ± 4.2	5000
1994	132.2 ± 3.2	10000
1993	137.7 ± 3.0	11000
1992	159.0 ± 4.3	5000
1991	134.3 ± 4.3	8000
1990	166.6 ± 4.4	5000
1989	176.7 ± 4.4	5000
1988	187.1 ± 4.4	5000
1987	175.9 ± 4.8	4000
1986	195.9 ± 3.5	8000
1985	222.7 ± 4.8	5000
1984	224.6 ± 5.5	4000
1983	242.4 ± 5.3	4000
1982	275.7 ± 5.4	4000
1981	259.3 ± 5.2	4000
1980	307.2 ± 6.2	4000
1979	293.2 ± 6.1	4000
1978	313.1 ± 5.3	8000
1977	358.1 ± 4.8	5000
1976	351.0 ± 4.8	5000
1975	393.1 ± 5.5	6000
1974	402.1 ± 5.5	4000
1973	434.2 ± 5.5	4000
1972	483.2 ± 5.2	5000
1971	480.5 ± 3.7	10000
1970	499.4 ± 3.1	14000
1969	538.7 ± 3.8	10000
1968	573.6 ± 6.1	4000
1967	654.2 ± 6.5	4000
1966	691.9 ± 6.8	4000
1965	760.7 ± 6.4	4000
1964	814.0 ± 6.7	4000
1963	726.9 ± 6.5	4000
1962	327.2 ± 4.4	8000
1961	218.0 ± 3.6	8000
1960	215.7 ± 4.9	4000
1959	233.0 ± 5.1	4000
1958	128.1 ± 2.8	12000
1957	235.9 ± 3.7	8000
1956	38.0 ± 4.6	4000
1955	–2.6 ± 4.4	4000
1954	–17.6 ± 4.3	4000
1953	–28.7 ± 4.6	4000
1952	–42.3 ± 2.8	9000
1951	–35.9 ± 3.8	5000
1950	–33.9 ± 3.6	4000
1949	–44.4 ± 4.3	4000

*The error denotes a counting error of 1σ.

All samples were measured using a low background liquid scintillation counter, Aloka LB-1.

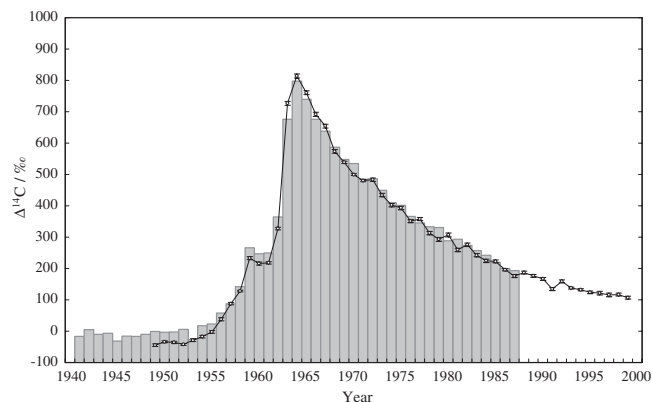


Figure 2. Annual variation of the $\Delta^{14}\text{C}$ values of the Shika-sample and Tatsunokuchi-sample.

The bar graph: Tatsunokuchi-sample
○: Shika-sample

The annual variation of $\Delta^{14}\text{C}$ values of the Shika- and the Tatsunokuchi-sample are plotted as a function of the ring-year in Figure 2. Temporal variation of organically-bound ^{14}C concentration in the Shika-sample showed essentially similar variations to that of the Tatsunokuchi-sample. The $\Delta^{14}\text{C}$ value of both the Shika- and the Tatsunokuchi-sample began to increase from 1954 to a small broad peak of 250 ‰ in 1959–1961, followed by a rapid increase to the highest value of approximately 800 ‰ in 1964. After the maximum, it diminished gradually year by year during past two or three decades. However, it demonstrated a small difference in the amplitude of the $\Delta^{14}\text{C}$ value during the period of 1949–1967, 1970, and 1978–1981. After 1982, significant difference was not observed between the two sets of samples. These differences suggest that the ^{14}C concentration in atmospheric CO_2 fluctuated even in the narrow region only by about 70 km of distance for the period before 1982. It is assumed that the ^{14}C records in a series of annual rings of the tree reflect the variation of annual average levels of ^{14}C concentration in atmospheric CO_2 at the growth site of the tree, since the carbon necessary for synthesizing cellulose is derived essentially by photosynthesis from the CO_2 in the air.

In Figure 3, the annual variation of $\Delta^{14}\text{C}$ values obtained from the Shika-sample is compared with those of $\Delta^{14}\text{C}$ values in tree rings from East Asia region reported by other researchers, for a spruce from Dailing, China (47°N, 129°E),⁷ for red pines from Mt. Chiak (37°23'N, 128°3'E and 37°20'N, 128°4'E) and Mt. Kyeryong (36°20'N, 127°13'E), Korea,¹³ and for Japanese cypress from Kiso mountainous district, Gifu prefecture, Japan (35.6°N, 137.5°E).⁶

An interesting result in comparing our data with those of other researchers is that there existed significant difference in the amplitude of the $\Delta^{14}\text{C}$ value during the period of 1963–1967. The disagreement of the $\Delta^{14}\text{C}$ value among trees during the period of 1963–1967 can be interpreted by the so-called latitude dependence of the ^{14}C variations in the northern troposphere,^{6–7} which was due to the ^{14}C released to the atmosphere at higher northern latitudes by a series of thermonuclear detonations carried out during the early 1960s.

The most important result in this work is that the difference of $\Delta^{14}\text{C}$ values was found during the period of 1970–1981 between our data and those of other reports. The spruce from Dailing, China, located in higher latitude than Shika-machi, showed higher $\Delta^{14}\text{C}$ values than our pine tree. The red pines from Mt. Chiak and Mt. Kyeryong, Korea, located at almost the same latitude of Shika-machi, showed slightly lower $\Delta^{14}\text{C}$ values than our pine tree. On the contrary, the $\Delta^{14}\text{C}$ values of Japanese cypress from Kiso mountainous district, Gifu prefecture, Japan, coincided with those of our pine tree, except for the period of 1976 and 1980–1981.

On the basis of these results, it was found that the ^{14}C concen-

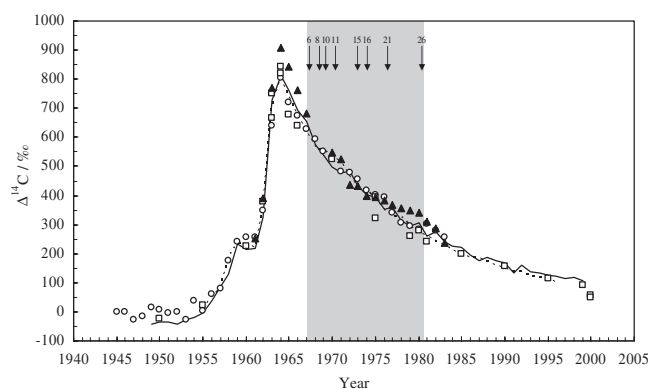


Figure 3. Comparison of annual variation of $\Delta^{14}\text{C}$ values in tree rings from different sites. Arrows and numerals at the top of the figure represent the number and time of year of the Chinese thermonuclear bomb test.

The solid line: pine tree in this work (37.1°N, 136.5°E)

▲: spruce from Dailing, China (47°N, 129°E), by D. Kaimei et al.⁷

□: red pines from Mt. Chiak (37°23'N, 128°3'E and 37°20'N, 128°4'E) and Mt. Kyeryong (36°20'N, 127°13'E), Korea, by J. H. Park et al.¹³

○: Japanese cypress from Kiso mountainous district, Gifu prefecture, Japan (35.6°N, 137.5°E), by T. Nakamura et al.⁶

The dotted line: compiled atmospheric ^{14}C curve for the northern hemisphere temperate region by Q. Hua and M. Barbetti³

tration in atmospheric CO_2 was considerably disturbed during the period of 1970–1981, especially in 1970, 1976, and 1978–1981, in the East Asia region. However, for the period from 1970 onwards, it is known that there has not been much difference between locations in terms of the ^{14}C concentration in atmospheric CO_2 in the Northern Hemisphere, since the bomb ^{14}C reached a global equilibrium in the late 1960s.^{1–3} Compiled atmospheric ^{14}C curve for the northern hemisphere temperate region by Hua and Barbetti³ is shown by the dotted line in Figure 3. Their average yearly atmospheric $\Delta^{14}\text{C}$ values agreed well with our data except the period of 1970 and 1978–1981, whereas, they disagreed with the data of 1976–1982 rings of the spruce from Dailing, China. It was pointed out by Kaimei et al.⁷ that excessive ^{14}C in the 1976–1982 rings of the spruce from Dailing, China, was likely due to the effect of 1976 and 1980 Chinese bomb tests.

After the Partial Test Ban Treaty of 1963, nuclear tests in the atmosphere declined greatly, however, the People's of Republic of China continued atmospheric nuclear test until 1980. Bomb ^{14}C is produced in the nuclear reaction between thermal neutrons delivered in the explosion and nitrogen in the air. About 7 times larger amounts of thermal neutron are released by the thermonuclear explosion than by the atomic explosion. Thus, the time of year of the Chinese thermonuclear bomb tests are shown by arrows in Figure 3. The Chinese thermonuclear bomb tests were conducted 8 times, namely the 6th (June, 1967), 8th (December, 1968), 10th (September, 1969), 11th (October, 1970), 15th (June, 1973), 16th (June, 1974), 21st (November, 1976), and 26th (October, 1980).⁴

It is apparent from these considerations that the disturbance of the ^{14}C concentration in atmospheric CO_2 occurred during the period of 1970–1981 in the East Asia region may be interpreted by the possibility of the several times of injections of ^{14}C originated from a series of Chinese thermonuclear bomb tests. This assumption was supported by the fact that the $\Delta^{14}\text{C}$ values from three distinct sites in the East Asia region agreed well with each other after 1982, when the Chinese thermonuclear bomb tests were suspended.

Acknowledgments. The authors wish to express their thanks to Dr. Hikaru Amano and Dr. Mariko Andoh, Japan Atomic Energy Research Institute, for their helpful advice in

our mass spectrometer 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) Y. Katsuragi, K. Kawamura, and H. Inoue, *Pap. Met. Geophys.* **34**, 21 (1983).
- (5) W. F. Cain and H. E. Suess, *J. Geophys. Res.* **81**, 3688 (1976).
- (6) T. Nakamura, N. Nakai, M. Kimura, S. Ohishi, Y. Hattori, and Y. Kikata, *Chikyu Kagaku* **21**, 7 (1987) (in Japanese).
- (7) D. Kaimei, Q. Youneng, and C. Y. Fan, *Radiocarbon* **34**, 753 (1992).
- (8) I. U. Olsson and G. Possnert, *Radiocarbon* **34**, 757 (1992).
- (9) Y. Yamada, K. Yasuike, M. Itoh, N. Kiriya, K. Komura, and K. Ueno, *J. Radioanal. Nucl. Chem.* **227**, 37 (1998).
- (10) Y. Muraki, G. Kocharov, T. Nishiyama, Y. Naruse, T. Murata, K. Masuda, and Kh. A. Arslanov, *Radiocarbon* **40**, 177 (1998).
- (11) I. Krajcar-Bronić, N. Horvatinčić, and B. Obelić, *Radiocarbon* **40**, 399 (1998).
- (12) A. Z. Rakowski, S. Pawełczyk, and A. Pazdur, *Radiocarbon* **43**, 679 (2001).
- (13) 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).
- (14) Y. Yamada, K. Yasuike, and K. Komura, *J. Radioanal. Nucl. Chem.* **262**, 679 (2004).
- (15) Y. Yamada, M. Itoh, N. Kiriya, C. Nishimoto, K. Komura, and K. Ueno, *J. Radioanal. Nucl. Chem. Articles* **130**, 169 (1989).