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The application of radiocarbon techniques to environmental monitoring

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Abstract. The radiocarbon technique, commonly used in measurements of cosmogenic isotope abundances in order to solve problems of cosmic ray significance, may also be very useful for monitoring the global environment. We show how the abundance of fossil carbon in the atmosphere can be determined and present an example of environmental monitoring using fallen leaves which has been carried out in Japan during the past 4 years.

On comparing the radiocarbon content in various regions, high ^{14}C concentrations have been found for fallen leaves from mountain and country sites, while low concentrations have been observed for leaves from city regions, especially near roads with heavy traffic. The results indicate that the atmosphere of the mountain and country sites in Japan is still clean compared to the other sites but the CO_2 coming from fossil non-radioactive carbon significantly pollutes the atmosphere of the city sites. The decrease of δ^{14}C near heavy traffic sites in large cities is consistent with the increase of CO_2 concentration in the atmosphere assuming that almost all CO_2 in this region originates from fossil fuel. We have found that the CO_2 content of the atmosphere originating from the petrol combustion (mainly by cars) in central Tokyo is more than 8 % of that of natural origin.

1 Introduction

Natural radiocarbon (^{14}C) on the earth is produced by high-energy cosmic rays mainly in the upper atmosphere. Its content in the atmosphere should be in equilibrium involving production by cosmic rays and the exchange of carbon with other reservoirs such as the ocean and the biosphere. However, this equilibrium has been interfered with the anthropogenic production of excess radiocarbon and also dilution by non-radioactive (dead) carbon. The former was produced by atomic bomb tests in the atmosphere in the 1950s

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and early 1960s and also by nuclear power facilities. Utilization of label isotopes at medical and research institutions may also contribute. The latter originates from the increase of carbon dioxide containing dead carbon as a result of fossil fuel combustion. It is very important to investigate both effects from the environmental point of view.

Since the late 19th century, after the industrial revolution, the concentration of carbon dioxide containing dead carbon has been significantly increased and the content of radiocarbon has been diluted (Suess effect). In the 1950s and early 1960s, many atomic bomb tests were carried out until the test ban treaty was adopted in 1963. Soon after that, the content of ^{14}C in the atmosphere of the Northern Hemisphere was peaked and decreased slowly (time constant $\sim$ 16 years). Even in the 1990s, the effect of the bomb tests still remains and the excess of radiocarbon above the pre-bomb level is 10 % or more (Muraki et al., 1998; Krajcar-Bronic et al., 1998). Environmental measurements of atmospheric $^{14}CO_2$ concentration have been made at several stations in Europe, Canada, Far East of Asia, and so on. Some researchers directly measure the ^{14}C content in atmospheric CO_2 (Meijer et al., 1995; Nydal and Lovseth, 1996; Levin and Kromer, 1997; Kuc and Zimnoch, 1998) and the others measure mainly the content in plants (McNeely, 1994; Muraki et al., 1998; Krajcar-Bronic et al., 1998; Leung et al., 1995).

Variation of the local ^{14}C content is a good indication of fossil fuel consumption in the limited region. Some kinds of tree leaves are essentially yearly-growing material which incorporate carbon dioxide from the surrounding atmosphere. Since anthropogenic carbon dioxide is emitted from industrial facilities, traffic vehicles and human daily life and originates from fossil fuel, it does not include radiocarbon whose radioactive half-life is 5730 years. Environmental materials like tree leaves in large cities may have a smaller concentration of radiocarbon, compared with that of clean air as the global background. Thus the content of ^{14}C would reflect the concentration of the local environmental carbon dioxide.

We have measured the radiocarbon contents of fallen leaves collected from several sites in Japan over the past four years

as an environmental monitor. Radioactivity of ^{14}C β-decay was measured using a liquid scintillation counting system. In this paper, we briefly describe the apparatus used and report on the results of the measurements. The possibility of environment monitoring by measurement of radiocarbon is discussed.

2 Methods

2.1 Leaf sample

Samples of leaves were collected from 17 sites in Japan, including mountain areas, country sites and city areas, for the past four years. The leaves from the mountain areas were collected at Agematsu (35°45'N, 137°34'E, 1300m above sea level) and Norikura (36°07'N, 137°08'E, 1450m asl). The leaves from the country site were sampled at Asahikawa (43°46'N, 142°25'E, 130m asl) in Hokkaido, Owase (34°04' N, 136°12'E, 30m) in Mie, Heijokyo (34°41' N, 135°49'E, 72m) in Nara and at Tokai (36°28'N, 140°33'E, 30m asl), Ibaraki. Tokai is a town where many nuclear power facilities

Table 1. List of sampling sites

ID	Location	Kind of tree[b]	Feature[c]
	Tokyo region		
T1	Toyotama	A	HT, big city
T2	Nozawa	A	HT, big city
T3	Zenpukuji	A	MT, suburbs
T4	Tanashi	B	MT, suburbs
T5	Shakujii	C	P, suburbs
	Nagoya region		
N1	City Hall	A	MT, big city
N2	Nagoya Port	A	MT, big city
N3	N.U.[a](Eng.)	D	MT, suburbs
N4	N.U.[a](STEL)	D	P, suburbs
N5	Ohdaka	D	P, suburbs
N6	Higashiyama	D	P, suburbs
S1	Kawagoe, Mie	A	TP, industrial
	Country site		
C1	Asahikawa	E	MT, local city
C2	Tokai,Ibaraki	H	NP, llcal town
C3	Heijokyo, Nara	D	P, local town
C4	Owase,Mie	A	local city
	Mountain site		
M1	Agematsu	I	NT
M2	Norikura	J	NT

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[b] A, *Zelkova serrata*; B, *Magnolia kobus*; C, *Carpinus tschonoskii*; D, *Quercus variabilis*; E, *Magnolia quinquepeta*; F, *Betula platyphylla*; G, *Aesculus turbinata*; H, *Castanea crenata*; I, *Betula ermanii*; J, *Quercus crispula*
[c] HT, heavy traffic; MT, moderate traffic; NT, no traffic; P, park; TP, thermal power station; NP, nuclear power facilities
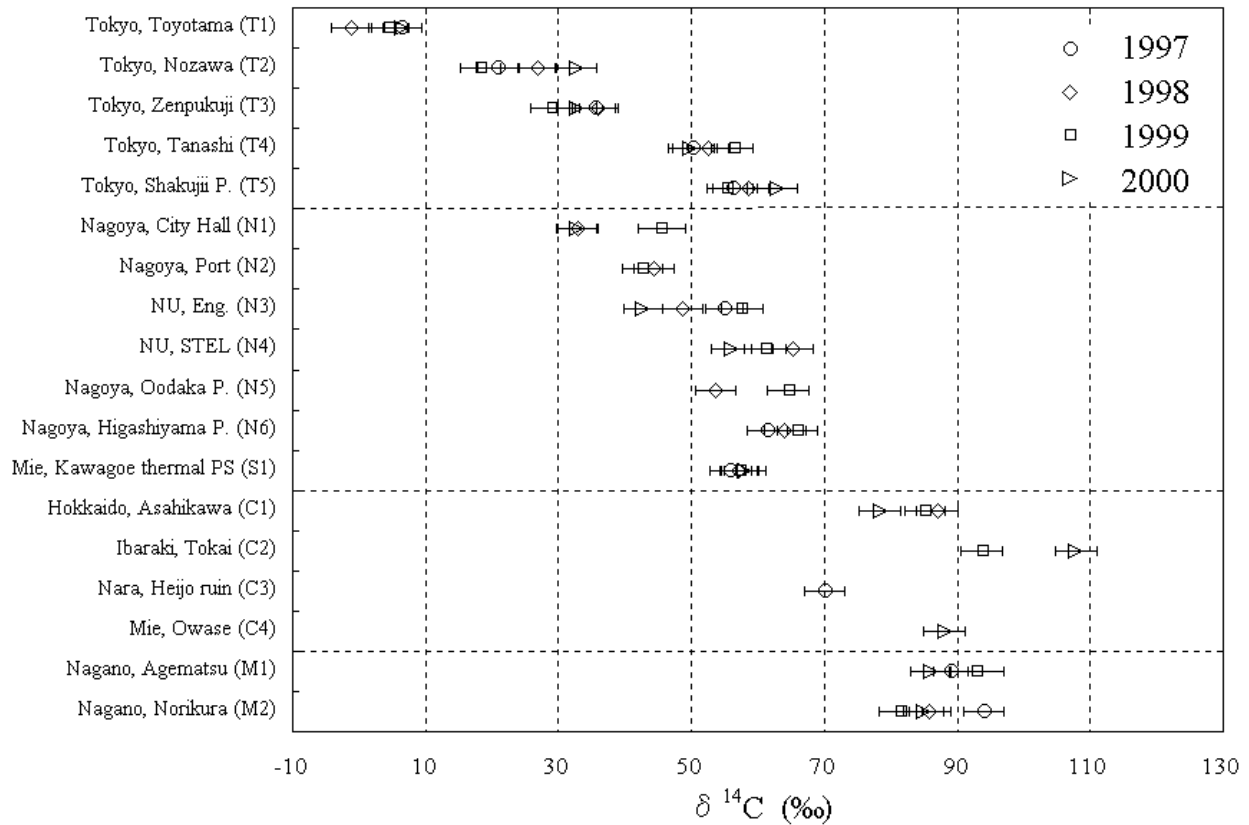
exist. The leaves from the city areas were gathered from Tokyo (35°N, 139°E, 20-60m asl) and Nagoya (35°N, 137°E, 0-70m asl) regions. All samples are yearly-fallen leaves of hardwoods such as *Zelkova serrata* and *Quercus variabilis*. Details are listed in Table 1.

The leaves were chemically treated and converted to benzene, which is a solvent of liquid scintillator, by a method described previously (Muraki et al., 2001).

2.2 ^{14}C counting

A liquid scintillation counting system was constructed in our laboratory and was used for the ^{14}C measurement of leaf samples. The design of the system is based on a previous system (Muraki et al., 1998) but the temperature control and the radiation and electromagnetic shieldings have been improved. The details of the system is described elsewhere (Muraki et al., 2001). The spectra of the scintillation intensity were recorded in a computer through a CAMAC ADC system. We select an ADC channel region such that the deviation of the count rate for standard benzene was minimized.

The sample vials made of Teflon (body) and pure copper (cap) were supplied by Wallac Co. The light collecting efficiency of individual vials was measured using the same ^{14}C standard benzene. The standard deviation of the efficiency for 5 vials used in this work was 0.28 %.

The background count rate (B) was 3.7 cpm and the count rate for the modern standard (0.7459 of new NBS Standard activity) was 101 cpm in the selected stable counting channel region for 15 ml of benzene in a 20 ml Teflon vial. Then the counting efficiency (E) of the system is 60 % and the Figure of Merit ($= E^2/B$) is 970.

In our measurements, the ^{14}C-enriched benzene was used as a standard, which was prepared at the Geological Institute of the Academy of Sciences, Russia and calibrated at St. Petersburg University (Arslanov et al., 1993) (hereafter called the Russian Standard). The δ^{14}C values of samples were calculated by using the ratio of the activity of the Russian Standard and that of the modern standard, which is 5.0128 ± 0.0107 (Arslanov et al., 1993), as follows:

$$\delta^{14}\text{C(permil)} = 1000(A_\text{s} - A_\text{abs})/A_\text{abs}, \qquad (1)$$

$$A_\text{abs} = \exp((y - 1950)/\tau)A_\text{R}/5.0128, \qquad (2)$$

where A_s is the measured massic activity of the sample, A_abs the massic activity of the international standard in the year 1950 AD, A_R the measured activity of the Russian standard, $\tau (= 5730/\ln 2 = 8267\text{yr})$ the lifetime of ^{14}C and y the year when the sample was measured. The typical counting scheme is as follows: First, the activity of the Russian Standard is measured for 22 hrs, then the background is measured for 22 hrs using industrially produced dead benzene of spectral grade (Dojin Chemical Co., Japan). After that, two measurements of 15 ml samples of benzene produced from leaves are measured for 22hrs each. This scheme is repeated. The typical statistical error of the measurement was about 0.3 %. For smaller quantities, such as 10 ml, which result from

Fig. 1. Radiocarbon content in tree leaves in Japan.

small quantities of the original leaves, the counting time was prolonged appropriately to assure almost the same statistical accuracy. The calculation of the radiocarbon activity was carried out using the count rate of the sample together with the average count rates of the two nearest measurements of the Russian Standard and the dead benzene.

The counting system was tested with IAEA intercomparison samples. The measured values of radiocarbon activity for the samples C-2 through C-6 agreed well with the consensus values (Rozanski et al., 1992) within the errors. Details are described elswhere (Muraki et al., 2001). The long term stability was checked by measurements of the time variation of the count rates of the Russian Standard. The standard deviation of 36 measurements for 15 ml benzene over 5 months was about 0.27 %.

3 Results and discussion

The values of $\delta^{14}C$ (in permil) for a period of 1997 to 2000 are plotted in Fig.1. The radiocarbon contents are not corrected for the isotope fractionation. Stuiver and Polach (1977) recommended an average value of $\delta^{13}C$ for tree leaves of -27 permil relative to that of the PDB standard with an error of 2 permil. Then, we used the value of $\delta^{14}C$ for $\Delta^{14}C$, assuming that the $\delta^{13}C$ values of the leaves are -25 permil for simplification.

Comparing the $\delta^{14}C$ values in various areas, high ^{14}C concentrations (80-100 permil in $\delta^{14}C$) are found for leaves collected at mountain areas in Nagano and those at country sites, while low concentrations (0-40 permil) are observed for leaves from the cities, especially near roads with heavy traffic. This result indicates that the ^{14}C in the atmospheric carbon dioxide in city sites is significantly diluted by dead carbon from fossil fuels.

The excess of ^{14}C for leaves from Agematsu and Norikura mountain areas was around 90 permil in 1997-2000. The $\Delta^{14}C$ value at Schauinsland in Central Europe was 104 permil in 1996, which was almost the same as those in the clean sites (Levin and Kromer, 1997). Comparing the present values of the Japanese mountain sites with those in the Central Europe, it is supposed that the atmosphere of the mountain sites in Japan is also clean locally. This value of $\delta^{14}C$ is still higher than that of pre-bomb period and ^{14}C produced by nuclear bomb tests in the 1960s is still observed (Muraki et al., 1998).

The $\delta^{14}C$ values in big cities such as Tokyo and Nagoya show much scatter, probably depending on the amount of local traffic. At sites with very heavy traffic, the $\delta^{14}C$ value is quite low, indicating high concentration of fossil carbon

dioxide. Assuming the additional CO_2 comes only from fossil fuel consumption, we can eastimate the fraction a of CO_2 originated from fossil fuel to the total amount of CO_2 and the concentration of CO_2 at the local site, from the following equations:

$$a = (1 - A/A_{\text{clean}}), \tag{3}$$

$$C = C_{\text{clean}}(1 + a/(1 - a)), \tag{4}$$

where A and A_{clean} are the radiocarbon activity at the local site and that of the present clean air, for which we use the value of Agematsu in the mountain area. Using the value 370 ppm as the CO_2 concentration of clean air (Keeling et al., 1995; Levin et al., 1995; TMRIEP, 2000), the concentration of CO_2 in Tokyo area is calculated to be 390 to 400 ppm. In the worst place (the location T1) the calculated CO_2 concentration is 402 ppm and 8 % of atmospheric CO_2 is originated from fossil fuel. If we know the exact CO_2 concentration on the site, the fraction of fossil fuel-originated CO_2 in all carbon dioxide can be derived. Some data show the CO_2 concentration to be 394 ppm in the Tokyo area. This is consistent with the above estimate. We conclude that almost all excess carbon dioxide comes from the fossil fuel. In other city sites, the $\delta^{14}C$ value is not so low, indicating that the increase in the concentration of carbon dioxide is moderate.

The $\delta^{14}C$ value in Tokai is higher than that in other similar sites and even that in the mountain regions. This area is a concentration of nuclear power facilities, which possibly emit a certain amount of ^{14}C, although the fractional increase is very small.

In this way, measurements of radiocarbon contents can give us the average CO_2 concentration and possibly the emission of artificial ^{14}C. In order to confirm the precise relation between $\delta^{14}C$ value and the true CO_2 concentration, it is necessary to measure the CO_2 concentration directly in the sampling sites for several months. However, direct measurements of carbon dioxide or other pollutant molecules are difficult. The present method of measuring $\delta^{14}C$ values in leaves is a rather easy way to estimate the concentration of carbon dioxide. The measurement of $\delta^{13}C$ is very helpful in determining the origin of carbon dioxide. Our preliminary measurements of $\delta^{13}C$ of several samples showed values of -26 to -31 permil, which are smaller than the value assumed in the present work. Measurements of $\delta^{13}C$ values of all samples are necessary for a more definitive discussion.

4 Conclusions

The measurements of $\delta^{14}C$ contents in fallen leaves clearly indicate an excess of CO_2 concentration in city regions, while there exists locally clean air in country sites as well as the mountain areas in Japan. The continuous measurement of tree leaves will tell us how the content of atmospheric radiocarbon changes and how our environment will change. This method provides a good environmental monitor and the measurements should be continued further.

References

Arslanov, Kh. A., Tertychnaya, T. V. and Chernov, S. B., Problems and methods of dating low-activity samples by liquid scintillation counting, Radiocarbon, 35, 393-398, 1993.

Keeling, C. D., Whorf, T. P., Wahlen, M. and van der Plicht, J., Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980, Nature, 375,666–669, 1995.

Krajcar-Bronic, I., Horvatincic, N. and Obelic, B., Two decades of environmental isotope records in Croatia: reconstruction of the past and prediction of future levels, Radiocarbon, 40, 399–416, 1998.

Kuc, T. and Zimnoch, M., Changes of the CO_2 sources and sinks in a polluted urban area (southern Poland) over the last decade, derived from the carbon isotope composition, Radiocarbon, 40, 417–423, 1998.

Leung, P. L., Stokes, M. J., Qiu, S. H. and Cai, L. Z., A survey of environmental ^{14}C levels in Hong Kong, Radiocarbon, 37, 505–508, 1995.

Levin, I., Graul, R. and Trivett, N. B. A., Long-term observations atmospheric CO2 and carbon isotopes at continental sites in Germany, Tellus, 47B, 23–34, 1995.

Levin, I. and Kromer, B., Twenty years of atmospheric 14CO2 observations at Schauinsland station, Germany, Radiocarbon, 39, 205–218, 1997.

McNeely, R., Long-term environmental monitoring of 14C levels in the Ottawa region, Environment International, 20, 675–679, 1994.

Meijer, H. A. J., van der Plicht, J., Gislefoss J. S. and Nydal, R., Comparing long-term atmospheric ^{14}C and ^3H records near Groningen, the Netherlands with Fruholmen, Norway and Izana, Canary Islands ^{14}C stations, Radiocarbon, 37, 39–50, 1995.

Muraki, Y., Kocharov, G., Nishiyama, T., Naruse, Y., Murata, T., Masuda, K. and Arslanov, Kh. A., The new Nagoya radiocarbon laboratory, Radiocarbon, 40, 177–182, 1998.

Muraki, Y., Masuda, K., Arslanov, Kh. A., Toyoizumi, H., Kato, M., Naruse, Y., Murata, T. and Nishiyama, T., Measurement of radiocarbon contents in leaves from some Japanese sites, Radiocarbon, in press, 2001.

Nydal, R. and Lovseth, K., Carbin-14 measurements in atmospheric CO_2 from Northern and Southern Hemisphere sites, 1962-1993, NDP-057 Oak Ridge National laboratory, 1996.

Rozanski, K., Stichler, W., Gonfiantini, R., Scott, E. M., Beukens, R. P., Kromer, B., and van der Plicht, J., The IAEA ^{14}C intercomparison exercise 1990, Radiocarbon, 34, 506–519, 1992.

Stuiver, M. and Polach, H. A., Discussion: reporting of ^{14}C data, Radiocarbon, 19, 355–363, 1977.

TMRIEP, Annual report of the Tokyo Metropolitan Research Institute for Environmental Protection, 2000.