# The Variation of Radiocarbon-14 Content
# in the Atmosphere

**Kyung Rin Yang**

*Radiocarbon Dating Laboratory*
*Atomic Energy Research Institute, Seoul, Korea*
(Received Dec. 26, 1971)

**Abstract** The Carbon-14 content in surface air at Seoul, Korea, was measured from February 1970 to August 1971 and a Larix Leptolepis, Gordon tree (Ip-Gal Namu) grown at Kwang-Nung, Kyunggi-Do, Korea, having 37 growth rings, was assayed for $^{14}C$.

From the results of the surface air study, it was calculated that during the above period the inventory of excess $^{14}C$ in the atmosphere decreased with a half-time of 4.6 years. The overall yearly decrease was also checked. The tree-ring study showed that the tree's atmosphere was affected by $^{14}C$ from nuclear tests after 1956.

In one study, atmospheric $CO_2$ samples were collected bi-monthly by the absorption of $CO_2$ in alkaline hydroxide solution. In the other, 5 year annual growth rings were assayed for radiocarbon.

For the radioactivity measurement, carbon atoms in samples were converted to carbon atoms of benzene. The resulting benzene was taken as primary solvent for liquid scintillation counting.

## Introduction

The atmosphere, sea, and biosphere contained an estimated $2.2 \times 10^{30}$ atoms or 51 metric tons of $^{14}C$ before 1950. $^{14}C$ is produced by the nuclear reaction

$$^{14}N + {}^1n = {}^{14}C + {}^1H$$
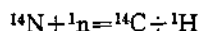
and disintegrates with a half-life of 5730 years.

In the formation of natural $^{14}C$, neutrons which interact with nitrogen atoms of the atmosphere are produced by the action of cosmic ray primaries in the upper atmosphere. By some unknown mechanism, $^{14}C$ atoms are oxidized to $^{14}CO_2$ which enters first the lower atmosphere and eventually the sea and biosphere.

The 315 ppm of ordinary $CO_2$ in the atmosphere dilutes this $^{14}CO_2$ by a factor of about $10^{12}$. Thus atmospheric $CO_2$ has always been radioactive to the extent of about $14\pm1$ disintegrations per minute per gram of carbon. Although fluctuations have occurred during the past several thousand years, variations have been only a few percent of the above value.

In the case of nuclear produced $^{14}C$, neutrons were generated by the nuclear explosions. As a result of nuclear testing, particularly of thermonuclear devices in the atmosphere, an additional $6 \times 10^{28}$ atoms of $^{14}C$, about 3% of the preatomic era amount, were added to the atmosphere, which then contained only about 2% of the total reservoir of natural $^{14}C$. About 60 %

of this excess $^{14}C$, $3.5 \times 10^{27}$ atoms, was produced in the 1961—1962 tests conducted by the USSR and the USA. In 1963, the $^{14}C$ content of tropospheric $CO_2$ at mid-latitudes of the northern hemisphere was double the natural level. The nuclear $^{14}C$ has been introduced into the northern hemisphere stratosphere mainly because the pathway for stratospheric air entering the troposphere is through the mid-latitude tropopause gap. This injection from the stratosphere occurs mostly in the spring of the year.

The non-uniform distribution of nuclear $^{14}C$ in the atmosphere, and its change with time, has given valuable insight into mixing processes in the troposphere and into the rate of air-sea exchange of $CO_2$. Since 1966 the whole troposphere has become fairly uniform in $^{14}C$, so that occasional sampling at only one place suffices to establish the prevailing levels. The decrease of atmospheric $^{14}C$ is due to uptake by the terrestrial biosphere, and to exchange of $CO_2$ between the atmosphere and the surface of the sea. Of these two sinks the latter is undoubtedly the more important. An estimated 82% of atmospheric $CO_2$ goes into the sea and only 18% goes into the terrestrial bisophere.

That part of the biosphere which is utilized for food by animals, including man, quickly returns most of its carbon to the atmosphere by metabolic processes. Only a portion of the terrestrial biosphere is relatively fixed in long-lived trees, or as slowly-decaying humus.

As anticipated, this large increment of $^{14}C$ has proved to be a valuable tracer for gainig insight into a number of geochemical processes, and it shows prcmise of bcing useful in a number of others. Results of $^{14}C$ measurements in atmospheric $CO_2$ at 37° 38, North Latitude during the period of February 1970 to August 1971 and the $^{14}C$ contents of tree rings grown during 1932—1968 at 37° 44' North Latitude will follow.

## Experimental

### Sample collection and pretreatment

**Atmospheric carbon dioxide** Atmospheric $CO_2$ samples were collected bimonthly on the roof of the Atomic Energy Research Institute main building in a north east suburb of Seoul (37° 38' N Lat., 127° 06' E Long) from February 1970 bi-monthly. $CO_2$ was absorbed into the exposed 0.5 N NaOH solution in a tray of 900cm² surface area for five days. To the above solution, hot saturated $CaCl_2$ solution was added, thus precipitating $CaCO_3$. The precipitates were then washed several times with distilled water.

**Tree rings** A Larix Leptolepis' Gordon grown at Kwang-Nung, Korea (37° 44' N Lat. 127° 12' E Long) was obtained from the Forest Experimental Station, Seoul, Korea. This tree, having 37 growth rings was cut in April 1968. The rings were separated into 5 year annual growth portions for the $^{14}C$ assay. The wood samples were treated with HCl and NaOH, and the wood was converted to charcoal before burning. $CO_2$ was collected in liquid nitrogen toaps and then allowed to sublime.

The liberted $CO_2$ was absorbed in concentrated $NH_4OH$ solution, then precipitated as $CaCO_3$ as in the atmospheric $CO_2$ collection method.

### Chemical steps in benzene synthesis

For low level $^{14}C$ measurement, a liquid sample scintillation counting sample was benzene, so the carbon atoms of the sample were converted to the carbon atoms of benzene. The benzene synthesis included the following four chemical steps. A schematic diagram of the benzene synthesis is shown in *Fig.* 1.

1). Carbon dioxide production; $CaCO_3 + 2HCl \rightarrow CO_2 + CaCl_2 + H_2O$

The $CaCO_3$ was placed in a 2000 m$l$

A : $H_2O$ Freeze Trap                         I : Lithium Reaction Chamber

{B : $P_2O_5$ & Ascarite Purification Column  J : Combustion Flask

C{D : $CO_2$ & $C_2H_2$ Freeze Traps          ◯ : Pressure Vacuum Gauge

E : Transfer Freeze Trap                       ◯ : Stopcocks

F,G : Gas Storage Tanks                         △ : Heater

H : Catalyst Column                             ◖ : Ball & Socket Joint
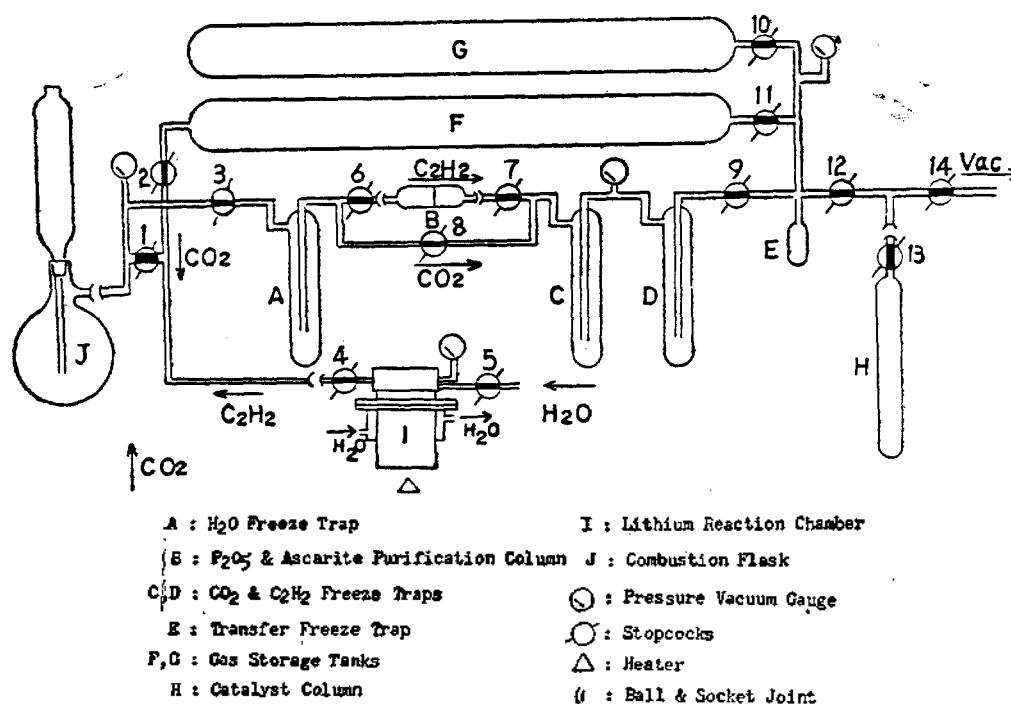
*Fig.* 1. Schematic diagram of benzene synthesis apparatus

combustion generator flask in a closed benzene synthesis train and the system was evacuated. $CO_2$, produced by adding 1 : 1 HCl to $CaCO_3$, was collected in liquid nitrogen traps. $CO_2$ was kept in storage tanks before reaction with lithium metal.

2). Carbide formation: $2CO_2 + 10Li \rightarrow Li_2C_2 + 4Li_2O$

A 50% excess of lithium was spread over the bottom of the chamber. The chamber was evacuated and the system sealed for 10 minutes to check for leaks. Evacuation was then continued while heat was applied to the chamber to melt the lithium. Evacuation was terminated, and $CO_2$ was reacted with the molten lithium to form lithium carbide. The reaction was quantitative, requiring approximately 30 minutes for 10 liters of $CO_2$ to react.

3). Acetylene production; $Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH$

Hydrolysis consisted of allowing distilled water, to flow slowly onto the carbide. Acetylene, accompanied by a large amount of hydrogen, was preferentially collected in liquid nitrogen traps, after passage through powdered phosphorous pentoxide and an ascarite purification column. Hydrogen was removed through evacuation. The acetylene was either expanded into storage tanks or sent directly to the catalyst.

4). Benzene production; $3C_2H_2 \rightarrow C_6H_6$

The catalyst was prepared by incorporating vanadium oxide onto the surface of pelletized activated alumina of 1/8″ diameter having a surface area of at least $200m^2/g$. Activation of the catalyst was accomplished by drying at 300°C for 4 hrs. under vacuum. The cyclization of acetylene to benzene was accomplished by allowing acetylene gas to come in contact with the vanadium catalyst. A slight exothermic

reaction followed, with a notable darkening of the catalyst. Careful control of acetylene gas flow rate was unnecessary, and 100 grams of catalyst was ample for the synthesis of 5cc of benzene in yields approaching 90%. On completion of the acetylene to benzene conversion, benzene was removed from the catalyst by heating at 100°C under vacuum of —30 inches Hg. Benzene was collected in an isopropyl alcohol-day ice trap. Sample purity was checked by infrared spectra obtained from a Beckman IR-4 using a NaCl cell with 200$\mu$ light path. The range of wave numbers scanned for each analysis was from 1000 to 4000.

### Radioactivity measurement

The sample-derived benzene was used as part of the counting solution, and spectrograde benzene containing the necessary amount of dissolved solutes was added. $^{14}C$ radioactivity was counted at 0.018 Mev—0.156 Mev, using a Beckman Model Ls-100 liquid scintillation counting system. The 10cc glass-metal counting vial, made of potassium free glass, was supported by a pure aluminium bar for geometry control. Three cc of sample-derived benzene and 1cc of spectrograde benzene phosphor cocktail were used for the $^{14}C$ measurement. The resulting counting solution contained 0.3% PPO and 0.025% POPOP. For the background measurement 3cc of spectrograde benzene was taken instead of the sample-derived benzene. The detection efficiency and background of the counting system were ca. 45—48%, and ca. 8—9 cpm, respectively. Radioactivity was calculated using the following equations. Gross sample activity; $G$ (dpm)

$$G \pm \sigma_G = \frac{G_C}{E_G} \pm \frac{\sigma_{G_C}}{E_G} \quad\cdots\cdots\cdots\cdots(1)$$

$\sigma_G$; Standard deviation of gross sample activity

$G_C$; Gross sample count rate

$\sigma_{G_C}$; Standard deviation of gross sample count rate

$E_G$; Detection efficiency of gross sample count

Bactground activity; $B$ (dpm)

$$B \pm \sigma_B = \frac{B_C}{E_B} \pm \frac{\sigma_{B_C}}{E_B} \quad\cdots\cdots\cdots\cdots(2)$$

$\sigma_B$; Standard deviation of background activity

$B_C$; Background count rate

$\sigma_{B_C}$; Standard deviation of background count rate

$E_B$; Detection efficiency of background count

Net sample activity; $A$ (dpm)

$$A \pm \sigma = G - B \pm \sqrt{\sigma_G^2 + \sigma_B^2} \quad\cdots\cdots\cdots(3)$$

$\sigma$; Combined standard deviation of $G$ and $B$

$^{14}C$ activity per gram carbon; $S$ (dpm)

$$S = \frac{A}{C} \pm \frac{\sigma}{C} \quad\cdots\cdots\cdots\cdots\cdots(4)$$

$C$; Grams of carbon in sample counted

### Results and Discussion

As noted in the introduction, $^{14}C$ in the atmosphere was fairly constant for several thousand years. Since the end of World War II, however, the explosion of nuclear devices introduced more $^{14}C$ into atmosphere. As a result, the $^{14}C$ concentration was increased, and there appeared pronounced seasonal fluctuations in $^{14}C$ levels in the northern hemisphere and strong north-south gradients. These latter developed in 1963 but declined to nearly zero by 1967.

Both are a consequence of the seasonally varying pattern of injection of excess $^{14}C$ from the stratosphere into the troposphere, and of the meridional mixing of the troposphere. The bulk of the excess $^{14}C$ enters the tropopause gap

in the northern hemisphere during the spring and early summer. During this period meridional mixing is the weakest. The levels of excess $^{14}C$ in tropospheric air weie therefore highest at mid-latitude in the northern hemisphere, and they reached their maximum by late summer.
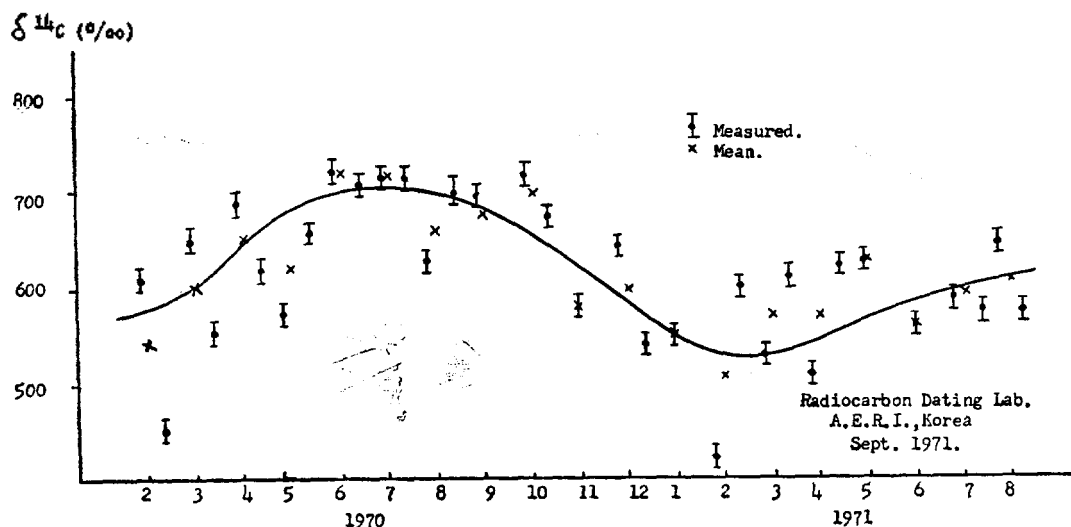


*Fig.* 2. Carbon-14 content in surface air Seoul, Korea. $-37°38'$ N. Lat.

*Table* 1. Radiocarbon content in surface air Seoul, Korea. $-37°38'$ N. Lat.

| Sample No. | Date | dpm/g-C | Sample No. | Date | dpm/g-C |
|---|---|---|---|---|---|
| AERIK-31 | Feb. 2—Feb. 7 '70 | 22.9±1.0 | AERIK-48 | Oct. 25—Oct. 31 '70 | 23.7±1.0 |
| AERIK-32 | Feb. 23—Feb. 28 '70 | 20.5±0.9 | AERIK-49 | Nov. 25—Nov. 30 '70 | 22.3±1.0 |
| AERIK-33 | Mar. 10—Mar. 15 '70 | 23.3±1.0 | AERIK-50 | Dec. 10—Dec. 15 '70 | 23.3±1.0 |
| AERIK-34 | Mar. 25—Mar. 30 '70 | 21.9±0.9 | AERIK-51 | Dec. 24—Dec. 30 '70 | 21.7±1.0 |
| AERIK-35 | Apr. 11—Apr. 16 '70 | 23.8±1.0 | AERIR-54 | Jan. 10—Jan. 16 '71 | 21.9±1.0 |
| AERIK-36 | Apr. 25—Apr. 30 '70 | 22.8±1.0 | AERIK-55 | Feb. 10—Feb. 15 '71 | 20.0±1.1 |
| AERIK-37 | May 11—May 16 '70 | 22.3±1.0 | AERIK-56 | Feb. 25—Mar. 3 '71 | 22.6±1.0 |
| AERIK-38 | May 25—May 30 '70 | 23.4±1.0 | AERIK-57 | Mar. 15—Mar. 22 '71 | 21.6±1.0 |
| AERIK-39 | June 10—June 15 '70 | 24.3±1.0 | AERIK-58 | Mar. 25—Mar. 31 '71 | 22.8±1.0 |
| AERIK-40 | June 25—June 30 '70 | 24.1±1.0 | AERIK-59 | Apr. 6—Apr. 16 '71 | 21.2±1.0 |
| AERIK-41 | July 10—July 15 '70 | 24.2±1.1 | AERIK-60 | Apr. 20—May 3 '71 | 23.0±1.0 |
| AERIK-42 | July 25—July 30 '70 | 24.2±1.0 | AERIK-61 | May 25—May 30 '71 | 23.0±1.0 |
| AERIK-43 | Aug. 8—Aug. 14 '70 | 23.0±1.1 | AERIK-62 | June 25—June 30 '71 | 22.3±1.0 |
| AERIK-44 | Aug. 25—Aug. 31 '70 | 23.9±1.1 | AERIK-63 | July 15—July 20 '71 | 22.4±1.0 |
| AERIK-45 | Sept. 10—Sept. 16 '70 | 24.0±1.1 | AERIK-64 | July 26—July 30 '71 | 22.3±1.0 |
| AFRIK-46 | Sept. 25—Sept. 30 '70 | 23.3±1.0 | AERIK-55 | Aug. 16—Aug. 22 '71 | 23.6±1.0 |
| AERIK-47 | Oct. 10—Oct. 15 '70 | 24.2±1.1 | AERIK-66 | Aug. 25—Aug. 29 '71 | 22.2±1.0 |

Counting errors; one sigma.
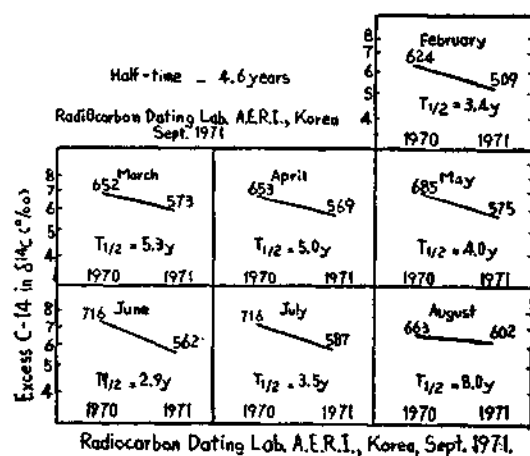
*Fig.* 3. Half-time of ¹⁴C in surface air Seoul, Korea, —37° 38′ N. Lat.

Meridional mixing, which occurs mostly in the fall and winter months, sends the bulk of this injected ¹⁴C southward and into the southern hemisphere troposphere. Thus, each year, from September through February, the levels of ¹⁴C declined at more southerly latitudes the levels of ¹⁴C rose, until by about mid-1966 the entire troposphere became fairly homogeneous in ¹⁴C concentration.

The retults of atmospheric ¹⁴C measurements are given in *Table* 1. ¹⁴C concentrations were calcualted in units of dpm/g. c. *Fig.* 2 shows the levels of excess ¹⁴C in units of per mill above the natural level of 14. 1 dpm/g. c. It was found that 70 to 100% of additional ¹⁴C in 1963—1964 declined to about 50 to 60% within 6—7 years. It has been estimated that this 70 to 100% of additional ¹⁴C will decrease to about 3% by the year of 2040. Seasonal variation of ¹⁴C concentration in the atmosphere was observed and its decline was confirmed. According to Hagemann et. al., in the northern hemisphere from 1963 to 1964 there was a half-time decline of 1.7 years, and from 1964 to 1965 a half-time of 2.3 years.

But the total atmospheric inventory of excess ¹⁴C declined with a half-time of 3.3 years during during 1963 to 1965. These data show that the rate of excess ¹⁴C disappearance in the atmosphere is slowed by decreasing ¹⁴C concentrations. In this work, the half-time decrease in the atmosphere during the period of 1970 to 1971 was observed, and results are given in *Fig.* 3. Higher values of the ¹⁴C concentrations in February 1970 and March 1970 were taken, because low atmospheric pressure significantly affects the ¹⁴C concentration. The meteorological data during the $CO_2$ collection period were as follows.

| Sampling date | Sea level pressure (mb) | Wind | ppt. (mm) | Snow (cm) | dpm/g. C |
|---|---|---|---|---|---|
| 2— 7 Feb. '70 | 1029. 2 | WNW | — | — | 22. 9 |
| 23—28 Feb. '70 | 1020. 1 | ENE | 2. 4 | — | 20. 5 |
| 10—15 Mar. '70 | 1023. 2 | WNW | 0. 1 | 0. 1 | 23. 3 |
| 25—30 Mar. '70 | 1021. 9 | WNW | — | — | 21. 9 |

Low atmospheric pressure prevents the vertical mixing of $CO_2$ in the atmosphere, resulting in higher concentration of fossil $CO_2$ in the surface air. This is known as the Suess effect. Wind direction does not seem to be play a part this abnormality. The ¹⁴C concentrations of May 1970 and 1971 were taken from *Fig.* 2. Because the values obtained from our ¹⁴C measurements showed an unusual increase of ¹⁴C during the above period, we felt that the samples collected were abnormal. The meteorological data during the sample collected were abnormal. The meteorological data during the sample collection period are shown.

| Sampling date | Sea Level Pressure (mb) | Wind | ppt. (mm) | Snow (cm) | dpm/g. c |
|---|---|---|---|---|---|
| 11—16 May '70 | 1011.8 | WNW | — | — | 22.3 |
| 25—30 May '70 | 1006.5 | WSW | 5.9 | — | 23.4 |
| 25—30 May '71 | 1007.5 | WSW | 0.1 | — | 23.0 |

*Table* 2   Radiocarbon concentration in Larix Leptolepis' Goldon tree rings

| | Grown 1932—1968 | 37° 38′ N. Lat. | |
|---|---|---|---|
| Sample No. | Age span | dpm/g. C | d$^{14}$C (‰) |
| AERIK-67 | 1932—1936 | 14.73±1.0 | 41.7 |
| AERIK-68 | 1937—1941 | 14.97±1.0 | 58.7 |
| AERIK-69 | 1942—1946 | 14.97±1.0 | 58.7 |
| AERIK-70 | 1947—1951 | 15.00±1.0 | 60.8 |
| AERIK-71 | 1952—1956 | 15.05±1.0 | 64.4 |
| AERIK-72 | 1957—1961 | 18.49±1.0 | 307.6 |
| AERIK-73 | 1962—1968 | 22.32±1.0 | 578.5 |

The most probable source of abnormality was an extremely low atmospheric pressure during the collection period. Wind direction also allowed for the possibility of movement of fossil $CO_2$ from the metropolitan area, which would have lowered the $^{14}$C concentration. But the latter effect would be less than the former, since the sampling site is not very high and the site is surrounded by hills. The other data given in *Fig.* 3 are average values of the measurements, except for the value of June 1971. This was from a single determination due to one sample being spoiled. The following equation was used for the half-time calculations.

$$\left( T_{1/2} = 0.693 \cdot \ln \frac{A_o}{A} \right)$$

$A_o$;   $^{14}$C activity in same month of 1970

$A$;   $^{14}$C activity in same month of 1971

$T_{1/2}$;   Half-time of $^{14}$C decrease

$t$;   one year, time elapsed

The results show that the atmospheric inventory of excess $^{14}$C in this area declined with a half-time of about 4.6 years during the period of 1970 to 1971. This value was found to be in the range estimated by Comar and Hagemann.

The $^{14}$C content of a tree ring provides an accurate indication of atmospheric $^{14}$C only if the $^{14}$C content of the tree ring is not influenced by local conditions. Climatic factors may also control the fractionation of the carbon isotopes, but a correction can be made by measuring the $^{13}$C/$^{12}$C isotopic ratio. The results obtained by tree ring measurements indicate that the influence of climatic factors was smaller than the standard deviation of 3 to 5 per mill involved in the analysis. Since 1958, when the existence of fluctuations in the $^{14}$C content of tree rings was first demonstrated, the De Vries oscillations have been studied extensively.[11] We tried in this tree-ring study to investigate when nuclear $^{14}$C was inroduced into the tree's atmosphere. $^{14}$C activity of the sample and per mill deviation above N.B.S. standard value of 14.1±1.0 dpm/g. C of each age span are listed in *Table* 2.

No corrections were made for the $^{13}$C/$^{12}$C

ratio or for the radioactive decay, because 37 years are negligible when compared with the $^{14}C$ half-time of 5730 years. Climatic factors also were not cosidered. The fission yields of atmospheric explosions up to 1962, and the $^{14}C$ content in tree rings are given in *Fig.* 4. In this tree-ring study, each sample contained successive five year growth spans from 1932 to 1968. Although the exact date when the atmosphere of this area was contaminated by nuclear $^{14}C$ cannot be determined from the above results, it can be shown that the contamination occurred since 1956. According to the U. N. Reports on the effects of atomic radiation, tropospheric inventory of artificial $^{14}C$ were as follows.[12]

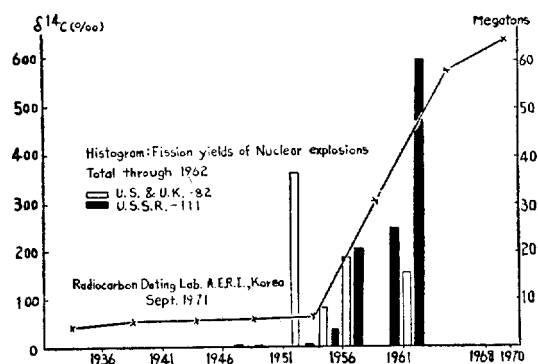| Year | $\delta^{14}C(‰)$ | year | $\delta^{14}C(‰)$ |
|------|------|------|------|
| 1956 | 80 | 1960 | 210 |
| 1957 | 120 | 1961 | 240 |
| 1958 | 180 | 1962 | 280 |
| 1959 | 210 | | |



*Fig.* 4. Radiocarbon content in Larix Leptolepis goldon Kwang-Nung, Korea. —37° 44' N. Lat.

According to the U. S. A. E. C. report [10], 51. 8 megatons of nuclear explosions took place before 1956. However the excess $^{14}C$ value of the 1952 —1956 period was only 64 $\delta^{14}C$ (‰). This

value was lower than the 1956 value of 80 $\delta^{14}C$ (‰) reported by the U. S. A. E. C. Furthermore, the $^{14}C$ content of four tree-ring samples from 1932 to 1951 was very low and relatively constant, as shown in *Fig.* 4. These results show that the tree was not affected by nuclear $^{14}C$ until 1956.

The $^{14}C$ contents of two samples, from 1956 to 1961, and then 1962 to 1968, were 308 and 579 $\delta^{14}C$ (‰) respectively. From these values, it is clear that the tree's atmosphere was contaminated by nuclear $^{14}C$ after 1956.

### Acknowledgement

### Reference

1. Libby, W. F., Radiocarbon Dating, Univ. Chicago Press, 2nd Ed. (1955).

2. Suess, H. E., *Science* 122, 415, (1955).

3. Craig, H., 9, 1, (1957).

4. Fairhall, A. and J. Young, Advances in Chemistry, ACS, 401, (1957).

5. Noakes, J. E., Kim, S. M., and Akers, L. K., *Geochim Acta* 31, 1094, (1967).

6. Tamer, M. A. and Bibron, R., *Nucleonics* 21, 90, (1963).

7. Fairhall, A. W., Progress Report, AT (45—1) —2091, Rlo-2091—3, (1969).

8. Leger, C., and Tamers, M. A., *Appl. Rad. Isotopes* 15, 697, (1964).

9. Fairhall, A. W., Progress Report, AT (45—1) —2091. RLO-2091-6, (1970).

10. Comar, C. L., Fallout from Nuclear Tests, USAEC, (1967).

11. Suess, H. E., *Science* 120, 5, (1954).

12. Report of the United Nations Scientfic Committee on the Effect of Atomic Radiation Supplement, No. 14, (A/5814), 27. (1964).