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Atmospheric ^{14}C changes resulting from fossil fuel CO_2 release and cosmic ray flux variability

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A high-precision tree-ring record of the atmospheric ^{14}C levels between 1820 and 1954 is presented. Good agreement is obtained between measured and model calculated 19th and 20th century atmospheric $\Delta^{14}\text{C}$ levels when both fossil fuel CO_2 release and predicted natural variations in ^{14}C production are taken into account. The best fit is obtained by using a box-diffusion model with an oceanic eddy diffusion coefficient of $3\text{ cm}^2/\text{s}$, a CO_2 atmosphere-ocean gas exchange rate of $21\text{ moles m}^{-2}\text{ yr}^{-1}$ and biospheric residence time of 60 years.

For trees in the state of Washington the measured 1949–1951 atmospheric $\Delta^{14}\text{C}$ level was $20.0 \pm 1.2\%$ below the 1855–1864 level. Model calculations indicate that in 1950 industrial CO_2 emissions are responsible for at least 85% of the $\Delta^{14}\text{C}$ decline, whereas natural variability accounts for the remaining 15%.

1. Introduction

In recent years, carbon reservoir models have been used to describe quantitatively the past and future fate of fossil-fuel-produced carbon dioxide. The ultimate test of models of the global carbon cycle is the reproduction of observed data. One critical set of observations is derived from the atmospheric ^{14}C change related to the release of ^{14}C -free fossil fuel CO_2 . We measured, with high precision, tree-ring ^{14}C levels that record the ^{14}C content of Pacific marine air CO_2 between A.D. 1820 and 1954. We tried to reproduce the time change in $\Delta^{14}\text{C}$ observed in these data using a carbon exchange box-diffusion model that attempts to take the natural atmospheric ^{14}C production rate variability into account.

The first measurements of 19th and 20th century anthropogenic atmospheric ^{14}C dilution were made by Suess [1], who compared the ^{14}C levels of mid-19th century wood with those of the mid-20th century. After correction for ^{14}C decay in the older wood he concluded that the mid-20th cen-

tury reduction in atmospheric ^{14}C level was probably less than 1%. Later measurements have increased this estimate to the 2.3–3.0% range [2–6]. The reduction in atmospheric ^{14}C level can only be followed to 1952 because nuclear-bomb-produced ^{14}C was added subsequently. The reduction of ^{14}C levels between the mid-19th and 20th century has been named the Suess effect, and has been attributed to the atmospheric release of anthropogenic-produced CO_2 lacking ^{14}C . However, during this time interval the atmospheric levels of ^{14}C would have varied even without the influence of man. Atmospheric levels of ^{14}C measured over the last millennium vary several percent [7].

The cosmic-ray-induced ^{14}C production rates (Q) are influenced by the sun's modulation of magnetic properties of the solar wind, and by changes in earth geomagnetic field intensity. In the following discussion, we attempt to quantify the natural variation of Q during the 1850–1950 interval and calculate the relative effect that fossil fuel and natural variation in Q have on the atmospheric ^{14}C records. Previous calculations [8,9]

also attempted to account for the natural variability in Q when discussing fossil fuel dilution of the atmospheric ^{14}C levels. The present calculations use a new interpretation of cosmic ray flux modulation that yields a larger natural Q variability [7]. The high-precision ^{14}C data also allow a search for ^{14}C change in the permil range.

The incorporation of natural ^{14}C variability in carbon reservoir modeling is required to obtain a more accurate understanding of the atmospheric ^{14}C dilution due to fossil-fuel-produced CO_2 .

2. Site and chemical treatment

Important for the determination of a global 1860–1950 atmospheric $\Delta^{14}\text{C}$ change is the selection of the trees and the chemical treatment of the wood. Regional ^{14}C depression exceeding the global average in industrial areas is a possible complication. Also the “feedback” of nuclear bomb ^{14}C in mobile compounds to earlier formed rings may interfere with the assumption that each ring accurately records the atmospheric ^{14}C level of the year of its formation.

Wood of two Douglas firs from the Olympic Peninsula ($47^\circ46'\text{N}$, $124^\circ06'\text{W}$) was used for this study. The site is 15 miles from the ocean, and predominant onshore winds bring in air that has been transported over the Pacific Ocean. Tree A grew from 1815 to 1972, whereas tree C grew from 1914 to 1975. The heartwood-sapwood boundaries of trees A and C were, respectively, near the 1930 and 1957 rings. At the start of nuclear bomb testing, the heartwood-sapwood boundaries are estimated to have been near 1895 for the A tree, and near 1939 for the C tree. In both cases we assume a constant sapwood thickness when estimating this earlier heartwood-sapwood boundary.

Alpha cellulose was extracted from the wood of the C tree. Wood samples of the A tree were all treated at 60°C with 2% NaOH and HCl solutions to remove resins, sugars, and a portion of the lignin (the so-called De Vries method). This treatment may not remove all components that were added after the year of growth [10]. The influence of incomplete removal of these late additions on the ^{14}C ratio was studied by comparing the ^{14}C

activities of wood treated by the De Vries method with the ^{14}C activities of alpha cellulose derived from the same wood. The largest differences in ^{14}C activity of sample pairs were found in rings that were transformed into heartwood after 1952 when nuclear bomb ^{14}C was added to the atmosphere. Here the “De Vries” wood of four sample pairs of the C tree (1942, 1945, 1948, and 1951) was an average of $3.8 \pm 1.4\%$ higher in ^{14}C activity. Similarly, De Vries wood of the A tree of the years 1918–1930 was an average of $6.3 \pm 0.8\%$ higher in ^{14}C activity than alpha cellulose from the C tree. Clearly, the De Vries method does not remove all material incorporated during the later stage of heartwood formation. However, an increase of about 50% in atmospheric ^{14}C level due to bomb testing during heartwood formation resulted in a hundred times smaller ^{14}C contamination of De Vries-treated wood. Pre-bomb variations in ^{14}C level are in the percent range only, and the calculated contamination is a few tenths of a permil. This agrees with the measurements of 8 sample pairs of the C tree (1918, 1921, 1924, 1927, 1930, 1933, 1936, and 1939), for which De Vries-treated wood on average differs only $0.7 \pm 0.8\%$ in ^{14}C activity from alpha cellulose. The ^{14}C level of De Vries-treated wood of the A tree formed prior to 1895 should therefore repre-

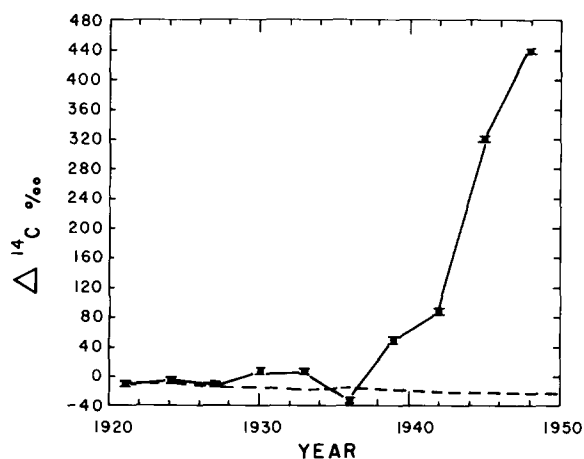


Fig. 1. $\Delta^{14}\text{C}$ values of organic materials extracted from tree rings with petroleum ether. The extractives from 1940 and following years contain nuclear bomb ^{14}C from the post 1952-era. The dashed line represents cellulose $\Delta^{14}\text{C}$ values.

sent the actual atmospheric ^{14}C level.

As part of our alpha cellulose preparation, we remove extractives in petroleum ether. The extractives and the cellulose of pre-1939 rings of the C tree have about identical ^{14}C activities. Much higher ^{14}C levels are encountered in the extractives of the rings that were transformed to heartwood in our nuclear age (Fig. 1). For instance, the cellulose of the 1948 ring of the C tree has a $\Delta^{14}\text{C}$ activity of about -2% , but mobile compounds that were incorporated later in the heartwood of the rings have a $\Delta^{14}\text{C}$ activity of $+44\%$. The amount of carbon derived from the extractives was about one tenth of the cellulose carbon, and thus the 4% higher ^{14}C level of 1948 De Vries-treated wood can be attributed to a removal of extractives that is only about 90% complete.

3. Measurements

Tree-ring $\Delta^{14}\text{C}$ levels (the relative deviation in ^{14}C activity from the NBS oxalic acid standard

after correction for decay and isotope fractionation [11]) are given in Table 1 and Fig. 2 for the 1820–1954 interval. The lack of sufficient wood of the A tree required a combination of some rings for the 1890–1915 interval. The $\Delta^{14}\text{C}$ values of De Vries-treated wood of the A tree reported between 1895 and 1915 may also be a few permil too high due to the previously discussed “feedback” of nuclear bomb ^{14}C . These years will be remeasured.

The 20th century reduction in atmospheric ^{14}C level reported here is less than the change reported by Tans et al. [6] for trees from the Netherlands. The difference between those measurements and our three-year moving average is plotted in Fig. 3. Tans et al. used wood from three trees, of which only one yields a couple of 20th century $\Delta^{14}\text{C}$ values that agree with our data. The other two trees (triangle and plus signs in Fig. 3) have an increasing divergence with the Pacific Northwest data towards the present. This trend could be explained by a regional fossil fuel CO_2 contamination of the Dutch trees, resulting in more depleted values.

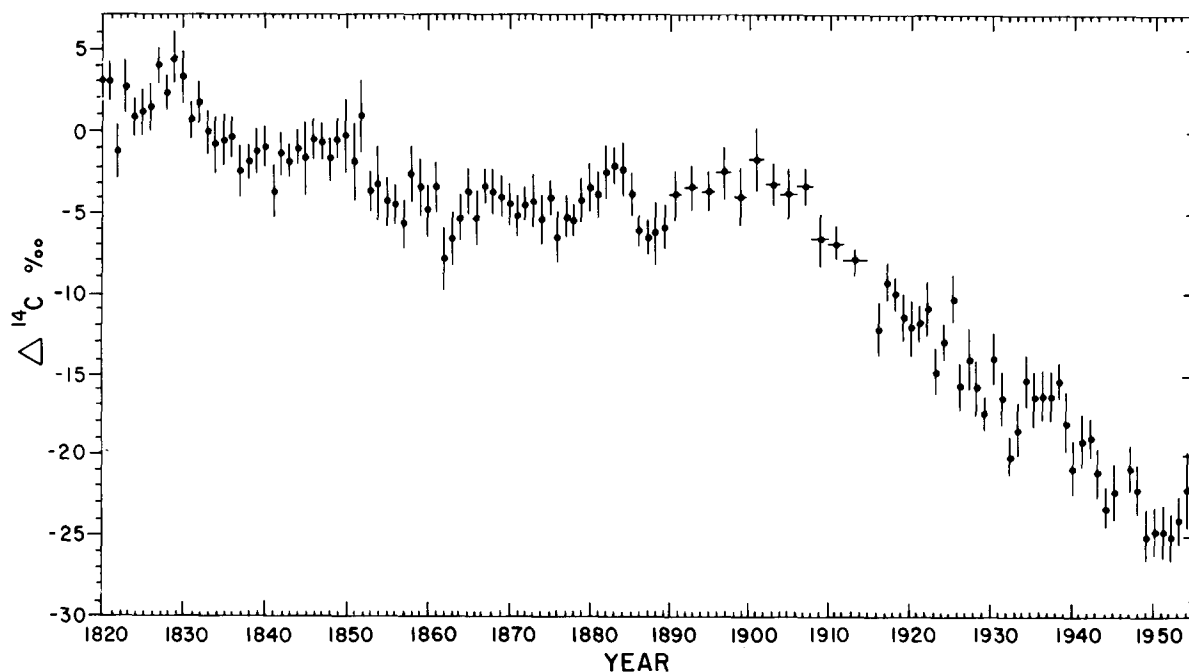


Fig. 2. Atmospheric $\Delta^{14}\text{C}$ levels, derived from tree rings, between 1820 and 1954. Single-year determinations are given, except for the 1890–1915 interval (Table 1). The vertical bar denotes one standard deviation. $\Delta^{14}\text{C}$ levels of the 1895–1915 interval probably give an upper limit only (see text).

TABLE 1

Tree-ring-derived atmospheric $\Delta^{14}\text{C}$ values

| Year of growth | $\Delta^{14}\text{C}$ (‰) | Year of growth | $\Delta^{14}\text{C}$ (‰) | Year of growth | $\Delta^{14}\text{C}$ (‰) |
|----------------|---------------------------|----------------|---------------------------|----------------|---------------------------|
| 1820 | 2.9 ± 1.2 | 1861 | -2.6 ± 1.7 | 1916 | -12.5 ± 1.8 |
| 1821 | 2.9 ± 1.3 | 1862 | -8.0 ± 2.0 | 1917 | -9.6 ± 1.3 |
| 1822 | -1.3 ± 1.7 | 1863 | -6.8 ± 1.7 | 1918 | -10.9 ± 1.0 |
| 1823 | 2.5 ± 1.7 | 1864 | -5.5 ± 1.6 | 1919 | -11.7 ± 1.7 |
| 1824 | 0.7 ± 1.2 | 1865 | -3.9 ± 1.5 | 1920 | -12.3 ± 1.8 |
| 1825 | 1.0 ± 1.6 | 1866 | -5.5 ± 1.8 | 1921 | -10.6 ± 1.8 |
| 1826 | 1.3 ± 1.6 | 1867 | -3.4 ± 1.1 | 1922 | -11.2 ± 1.9 |
| 1827 | 3.8 ± 1.2 | 1868 | -3.9 ± 1.3 | 1923 | -15.0 ± 1.6 |
| 1828 | 2.1 ± 1.0 | 1869 | -4.2 ± 1.3 | 1924 | -10.6 ± 1.8 |
| 1829 | 4.3 ± 1.7 | 1870 | -4.7 ± 1.4 | 1925 | -10.6 ± 1.6 |
| 1830 | 3.1 ± 1.6 | 1871 | -5.4 ± 1.4 | 1926 | -15.9 ± 1.6 |
| 1831 | 0.6 ± 1.2 | 1872 | -4.7 ± 1.2 | 1927 | -14.3 ± 2.1 |
| 1832 | 1.6 ± 1.4 | 1873 | -4.5 ± 1.7 | 1928 | -16.0 ± 1.8 |
| 1833 | -0.2 ± 1.4 | 1874 | -5.6 ± 1.7 | 1929 | -17.6 ± 1.2 |
| 1834 | -0.9 ± 1.9 | 1875 | -4.3 ± 1.2 | 1930 | -14.2 ± 1.7 |
| 1835 | -0.7 ± 1.7 | 1876 | -6.7 ± 1.7 | 1931 | -16.6 ± 1.8 |
| 1836 | -0.5 ± 1.2 | 1877 | -5.5 ± 1.5 | 1932 | -20.2 ± 1.3 |
| 1837 | -2.6 ± 1.6 | 1878 | -5.8 ± 1.1 | 1933 | -18.5 ± 1.8 |
| 1838 | -2.0 ± 1.0 | 1879 | -4.4 ± 1.5 | 1934 | -15.5 ± 1.8 |
| 1839 | -1.4 ± 1.4 | 1880 | -3.7 ± 1.6 | 1935 | -16.6 ± 1.9 |
| 1840 | -1.2 ± 1.4 | 1881 | -4.1 ± 1.6 | 1936 | -16.4 ± 1.7 |
| 1841 | -3.9 ± 1.7 | 1882 | -2.7 ± 1.7 | 1937 | -16.5 ± 1.7 |
| 1842 | -1.6 ± 1.4 | 1883 | -2.3 ± 1.2 | 1938 | -15.6 ± 1.2 |
| 1843 | -2.0 ± 1.1 | 1884 | -2.6 ± 1.7 | 1939 | -18.1 ± 1.9 |
| 1844 | -1.2 ± 1.2 | 1885 | -4.0 ± 1.4 | 1940 | -21.0 ± 2.0 |
| 1845 | -1.8 ± 2.4 | 1886 | -6.3 ± 1.1 | 1941 | -19.2 ± 1.9 |
| 1846 | -0.7 ± 1.3 | 1887 | -6.7 ± 1.2 | 1942 | -19.1 ± 1.3 |
| 1847 | -0.9 ± 1.3 | 1888 | -6.5 ± 2.1 | 1943 | -23.3 ± 1.2 |
| 1848 | -1.9 ± 1.4 | 1889 | -6.1 ± 1.4 | 1944 | -21.3 ± 1.4 |
| 1849 | -0.7 ± 1.4 | 1890–1891 | -4.1 ± 1.6 | 1945 | -22.3 ± 1.8 |
| 1850 | -0.5 ± 2.4 | 1892–1893 | -3.7 ± 1.4 | 1946 | – |
| 1851 | -2.1 ± 2.4 | 1894–1895 | -3.9 ± 1.2 | 1947 | -20.9 ± 1.6 |
| 1852 | 0.7 ± 2.3 | 1896–1897 | -2.7 ± 1.7 * | 1948 | -22.1 ± 1.7 |
| 1853 | -3.9 ± 1.3 | 1898–1899 | -4.2 ± 1.9 * | 1949 | -25.0 ± 1.7 |
| 1854 | -3.5 ± 2.4 | 1900–1901 | -1.9 ± 2.0 * | 1950 | -24.8 ± 1.7 |
| 1855 | -4.6 ± 1.6 | 1902–1903 | -3.5 ± 1.4 * | 1951 | -24.8 ± 1.7 |
| 1856 | -4.8 ± 1.3 | 1904–1905 | -4.1 ± 1.6 * | 1952 | -25.1 ± 1.7 |
| 1857 | -5.8 ± 1.6 | 1906–1907 | -3.6 ± 1.2 * | 1953 | -24.0 ± 1.6 |
| 1858 | -2.8 ± 1.9 | 1908–1909 | -6.9 ± 1.7 * | 1954 | -22.2 ± 2.5 |
| 1859 | -3.6 ± 1.8 | 1910–1911 | -7.2 ± 1.1 * | | |
| 1860 | -5.0 ± 1.7 | 1912–1914 | -8.3 ± 0.9 * | | |

The $\Delta^{14}\text{C}$ values are the relative deviations of the measured ^{14}C activity from 95% of the activity of the NBS oxalic acid standard, after normalization to a $\delta^{13}\text{C}_{\text{PDB}} = -25\text{‰}$ and after correction for ^{14}C decay [11] ($T_{1/2} = 5730$ years). Two different Douglas firs, A and C, were used. Tree A covers the 1820–1914 interval; tree C, the years 1916–1954. $\Delta^{14}\text{C}$ values for the 1895–1914 period (*) may be a few permil too high due to the incorporation of nuclear bomb ^{14}C (see text). Alpha cellulose was used for tree C, and De Vries-treated wood for tree A (see text): The 1915 ring was too small for ^{14}C analysis.

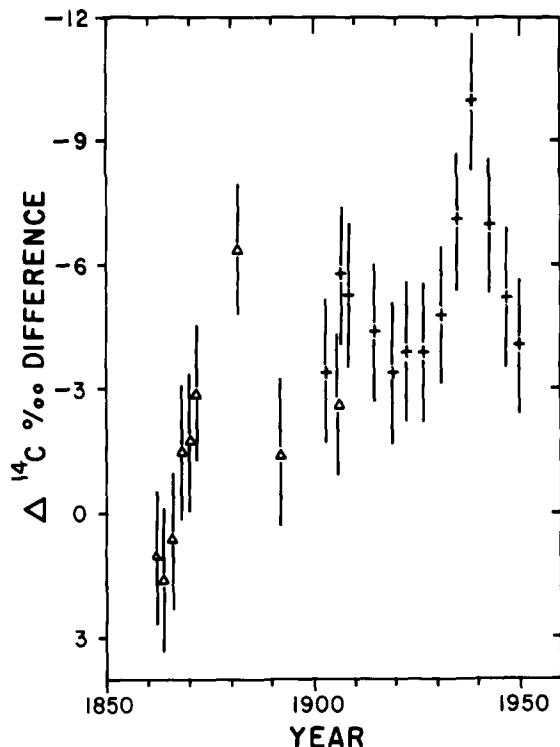


Fig. 3. The difference in $\Delta^{14}\text{C}$ levels of wood from trees of the Netherlands and the state of Washington. The graph indicates by how much the $\Delta^{14}\text{C}$ values of two Dutch trees (triangles and pluses) are below the three-year moving average $\Delta^{14}\text{C}$ values of the Washington tree.

4. Natural atmospheric ^{14}C variability

Our measurements of the atmospheric ^{14}C levels during the last 1000 years indicate that the carbon reservoirs are not in steady state equilibrium with respect to atmospheric ^{14}C levels. The response of such a dynamic system to a fossil fuel CO_2 pulse depends on the point in time when such a perturbation is imposed. The 19th and 20th century atmospheric ^{14}C dilution is therefore uniquely tied to the natural ^{14}C levels of these centuries. Furthermore, the calculated ^{14}C dilution in a dynamic model would not be identical in size to the dilution calculated from models where the fossil fuel CO_2 pulse is superimposed on steady state conditions.

The ^{14}C record of the current millennium clearly shows that the $\Delta^{14}\text{C}$ values observed in the mid-20th century are not exceptionally low (lower curve

in Fig. 4) when compared to the ^{14}C activities encountered in the 12th and 13th centuries. This similarity in $\Delta^{14}\text{C}$ levels is most likely the result of a long-term increase in ^{14}C production rates that relates to the decrease in the earth's geomagnetic field intensity [12].

If we approximate the long-term $\Delta^{14}\text{C}$ trend (attributed to geomagnetic field intensity changes over the past several thousand years) by a sinusoidal curve [13], and remove this trend from the observed record, the 20th century "geomagnetically" corrected $\Delta^{14}\text{C}$ levels now fall below the pre-1900 natural levels (upper curve in Fig. 4). This at least agrees with the concept of an anthropogenic dilution of the atmospheric ^{14}C reservoir.

On a shorter time scale the fine structure in the annual ^{14}C levels may be related to 11- and 22-year solar cycle modulation of the cosmic ray flux. However, our annual record (Fig. 2) indicates a magnitude of such ^{14}C variability not much beyond the uncertainty of the measurements (circa 1.5‰). This contrasts with the earlier work by Baxter and Farmer [14] on English oak, who suggested large year to year changes. As shown in Fig. 5, our high-precision ^{14}C determinations of three wood samples (each containing three rings) from an oak tree of the same English forest do not indicate a large annual ^{14}C variability in England. A further discussion of these short time scale ^{14}C variations is given in section 7.

Regional differences in natural ^{14}C levels should be considered also. We have not been able to detect any differences beyond our measuring precision of 1.5‰ in natural ^{14}C levels of contemporaneous wood of northern hemispheric origin between 32°N and 52°N latitude. $\Delta^{14}\text{C}$ levels also appear independent of altitude because high-altitude Bristlecone pine has the same ^{14}C levels as low altitude Douglas fir of the Pacific Northwest. The ^{14}C levels of contemporaneously grown wood pairs are given in Table 2. The work of Lerman et al. [4] suggests a $\Delta^{14}\text{C}$ level about 4‰ lower for part of the southern hemisphere. However, our preliminary work on cellulose samples from the southern hemisphere yields $\Delta^{14}\text{C}$ levels comparable to the Washington state $\Delta^{14}\text{C}$ record. Three samples (1920–1922, 1922–1925 and 1932–1934) of a *Nothofagus* tree (51°6'S, 72°54'W) averaged only

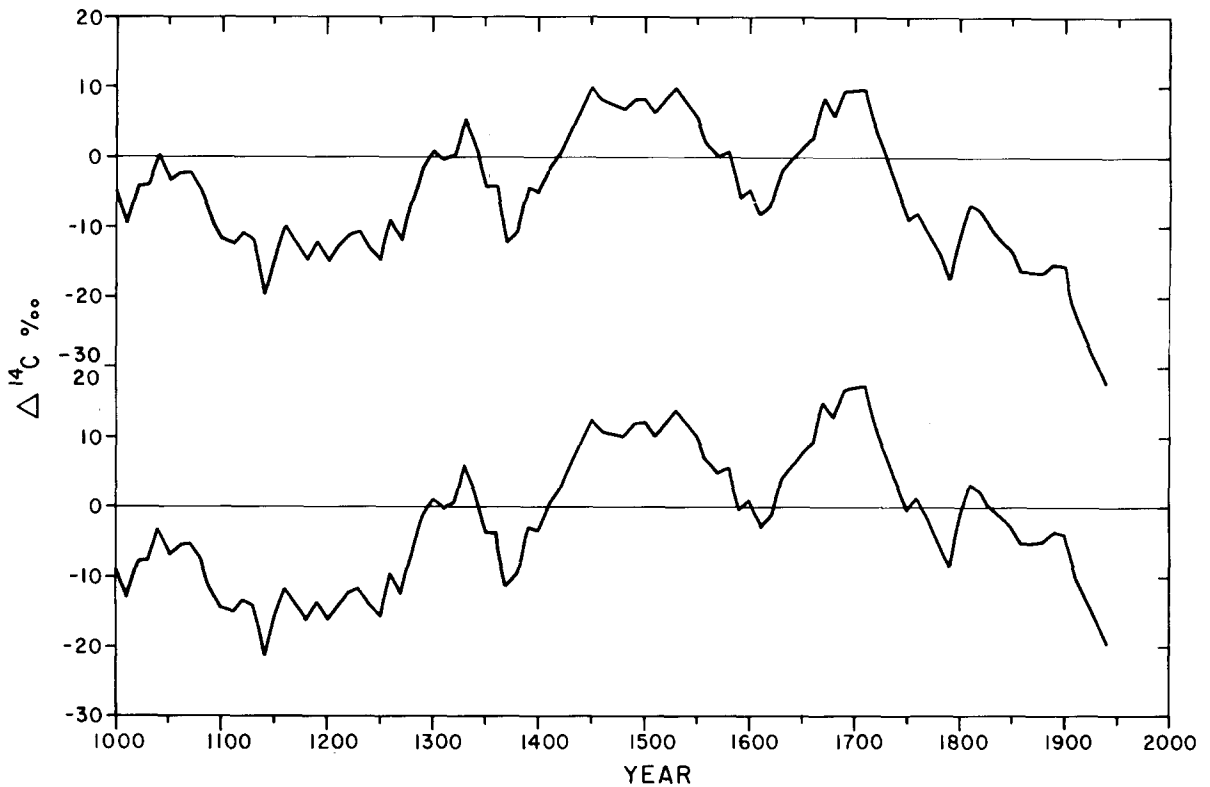


Fig. 4. Atmospheric $\Delta^{14}\text{C}$ levels of the current millennium, uncorrected (lower curve) and corrected for long-term geomagnetic induced changes (upper curve).

$0.6 \pm 1.3\%$ below the values reported for the C tree.

5. Model calculations

A box-diffusion model as described by Oeschger et al. [15] was constructed to parameterize global carbon exchange. Important exchange parameters in this model are the CO_2 gas transfer rate (F , in $\text{moles m}^{-2} \text{ yr}^{-1}$), the vertical diffusion rate in the ocean (K_z , $\text{cm}^2 \text{ s}^{-1}$) and the biospheric residence time (τ , years). Many uncertainties surround the biological growth factor. We therefore assumed a constant biomass for all the calculations discussed in this section.

The natural variability of the measured atmospheric ^{14}C levels during the current millennium (Fig. 4) indicate that the atmospheric ^{14}C content

would not have been constant after 1860 even if fossil fuel CO_2 had not been released. This natural variability is related by us to the solar modulation of the cosmic ray flux and associated ^{14}C production in the upper atmosphere [7]. To evaluate the solar modulation for our present investigation we first calculated, using a box-diffusion model, the ^{14}C production rate (Q_M , in $\text{atoms s}^{-1} \text{ cm}^{-2}$ earth surface) during the 1600-year interval prior to fossil fuel addition. Average Q_M values over the time interval of the recorded A.D. 1723–1855 sunspot cycles (each lasting on average of about 11 years) were calculated as were average sunspot numbers (\bar{S}) over these cycles [16]. A regression procedure was used to calculate the dependence of \bar{Q}_M and \bar{S} , as described previously [7]. With this information, we then used the sunspot record between 1855 and 1953 to estimate \bar{Q}_M over this time interval and calculate the atmospheric $\Delta^{14}\text{C}$

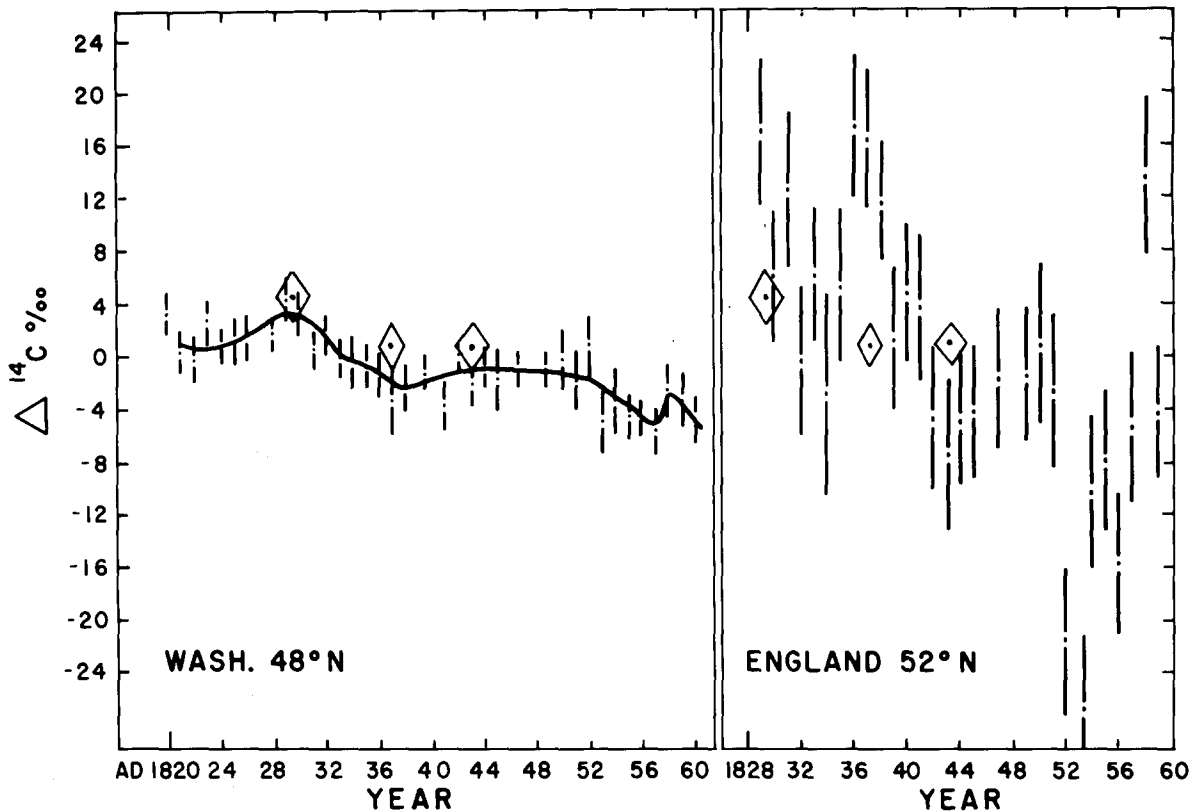


Fig. 5. A comparison of annual $\Delta^{14}\text{C}$ variability of wood from the state of Washington and England. The measurements of English wood in our laboratory (diamonds) do not confirm the large variability reported previously [14].

level that would occur with and without the fossil fuel perturbations.

Three versions of the box diffusion models were used to calculate atmospheric ^{14}C levels and to examine the sensitivity of our analysis to the magnitude of the exchange parameters. The description of the three model versions is found in Table 3. Model A is the version described by Siegenthaler and Oeschger [17], model B differs from A by having a $K_z = 3 \text{ cm}^2 \text{ s}^{-1}$ and $F = 21 \text{ moles m}^{-2} \text{ yr}^{-1}$ whereas model C is the same as B with $\tau = 30$ years [18,19].

The higher F and K_z values in models B and C are derived from the oceanic distribution of bomb-produced ^{14}C [20–22]. However, this higher value of K_z implies a steady state ^{14}C activity in the deep ocean ($> 2000 \text{ m}$) that is significantly higher (-100%) than that measured between 50°N and

50°S during GEOSECS (-190%) [21]. We chose to use a K_z value reflecting ocean transport processes that apply over a time scale closer to that of the fossil fuel addition, even though it violates steady state equilibrium.

For each model version Q_M values were calculated, and the dependence of \bar{Q}_M and \bar{S} were determined (Table 3). The next step is to use the sunspot record and an appropriate relationship between Q_M and S to calculate the ^{14}C production rates and atmospheric ^{14}C levels during the time interval of fossil fuel addition. The uncertainty of these model calculations depends in part on the uncertainty of the \bar{Q}_M and \bar{S} relationship. As mentioned previously [7], variations in the atmospheric ^{14}C levels may be caused by variables other than production rate changes (i.e. climate, biospheric reservoir size, ocean mixing and chem-

TABLE 2

A comparison of $\Delta^{14}\text{C}$ levels of pairs of contemporaneous wood grown in different regions (the alphabetical listing of the trees follows our laboratory code)

| Years A.D. | $\Delta^{14}\text{C}$ (‰) | Tree | Location | Species |
|------------|---------------------------|------|-------------------|------------------|
| 1846–1855 | -1.8 ± 0.6 | A | 47°46'N, 124°06'W | Douglas fir |
| 1846–1855 | -2.7 ± 1.7 | AR | 32°23'N, 110°41'W | Douglas fir |
| 1842–1844 | 0.7 ± 1.7 | FD | 51°48'N, 2°37'W | Oak |
| 1842–1844 | -1.6 ± 0.7 | A | 47°46'N, 124°06'W | Douglas fir |
| 1836–1838 | 0.7 ± 1.8 | FD | | |
| 1836–1838 | -1.6 ± 0.7 | A | | |
| 1829–1831 | 3.9 ± 1.8 | FD | | |
| 1829–1831 | 2.6 ± 1.0 | A | | |
| 1810–1819 | 2.3 ± 1.7 | F | 43°7'N, 123°40'W | Douglas fir |
| 1810–1819 | 3.0 ± 0.6 | B | 46°45'W, 121°45'W | Douglas fir |
| 1790–1799 | -9.1 ± 1.7 | F | | |
| 1790–1799 | -6.2 ± 0.6 | B | | |
| 1480–1489 | 9.7 ± 1.6 | R | ~47°N, ~122°W | Douglas fir |
| 1480–1490 | 8.6 ± 1.8 | BP | ~36°N, ~118°N | Bristlecone pine |
| 1080–1089 | -8.5 ± 1.1 | S | 48°40'N, 123°40'W | Douglas fir |
| 1080–1090 | -7.2 ± 2.7 | BP | ~36°W, ~118°N | Bristlecone pine |
| 1310–1319 | -3.5 ± 1.8 | S | 48°40'N, 123°40'W | Douglas fir |
| 1310–1319 | -0.7 ± 1.6 | R | ~47°N, ~122°W | Douglas fir |
| 1300–1309 | 2.3 ± 1.2 | S | | |
| 1300–1309 | -1.8 ± 1.8 | R | | |
| 880–899 | -15.1 ± 1.8 | S | 48°40'N, 123°40'W | Douglas fir |
| 880–899 | -14.5 ± 1.4 | RC | ~36.5°N, 118.5°W | Sequoia |
| 240–249 | -12.7 ± 1.4 | RC | ~36.5°N, 118.5°W | Sequoia |
| 240–249 | -15.4 ± 1.5 | SR | ~36.5°N, 118.5°W | Sequoia |

TABLE 3

Model versions and parameters used for the calculations

| | Model A | Model B | Model C |
|--|-------------------------------|-------------------------------|-------------------------------|
| K_z ($\text{cm}^2 \text{s}^{-1}$) | 1.25 | 3 | 3 |
| F ($\text{moles m}^{-2} \text{yr}^{-1}$) | 19 | 21 | 21 |
| τ (yr) | 60 | 60 | 30 |
| N_B/N_A | 2.4 | 2.5 | 2.5 |
| Q_∞ at $\text{sec}^{-1} \text{cm}^{-2}$ | 1.57 | 1.71 | 1.71 |
| CO_2^* (ppm) | 292 | 297 | 297 |
| A.D. 1723–1855 | | | |
| $d\bar{Q}_M/d\bar{S}$ | $-(60 \pm 26) \times 10^{-4}$ | $-(62 \pm 29) \times 10^{-4}$ | $-(78 \pm 31) \times 10^{-4}$ |
| Q_0 | 1.61 ± 0.13 | 1.73 ± 0.15 | 1.80 ± 0.16 |
| A.D. 1798–1855 | | | |
| $d\bar{Q}_M/d\bar{S}$ | $-(29 \pm 10) \times 10^{-4}$ | $-(29 \pm 12) \times 10^{-4}$ | $-(65 \pm 30) \times 10^{-4}$ |
| Q_0 | 1.58 ± 0.04 | 1.69 ± 0.06 | 1.86 ± 0.13 |

K_z is the vertical diffusion coefficient, F the ocean-atmosphere gas exchange rate, τ the biosphere residence time, N_B/N_A the ratio of the biospheric and atmospheric carbon reservoirs, and Q_∞ the steady state ^{14}C production rate of the model. The model calculated ^{14}C production rates (in atoms $\text{s}^{-1} \text{cm}^{-2}$ of earth surface), and average sunspot number \bar{S} per 11-year solar cycle, yield the listed $d\bar{Q}_M/d\bar{S}$ values and the production rate Q_0 for $\bar{S}=0$. The geomagnetically corrected ^{14}C record was used for these calculations. The initial assumed CO_2 level, prior to anthropogenic releases, is labelled CO_2^* .

istry, etc.). However, the strong correlation between calculated changes in \bar{Q}_M and solar activity [7,23–25] suggest this is a first-order effect, and only this effect has been incorporated into the calculations.

By extrapolating the \bar{Q}_M - \bar{S} relationship calculated from the ^{14}C record prior to 1855 to the following 100 years, we assume that whatever processes cause the \bar{Q}_M changes continue to do so in a similar manner. The uncertainty in this assumption is debatable, but using a \bar{Q}_M - \bar{S} relationship is preferable to assuming the anthropogenically unperturbed atmospheric $\Delta^{14}\text{C}$ levels would have remained constant up to 1955. Another complication in the modeling procedure is less obvious and involves the choice of the time at which to start the model calculations. At this starting time, the model's reservoirs are assumed to be in chemical and isotopic equilibrium, and then are perturbed from this condition. However, as seen in Fig. 4, the long-term atmospheric ^{14}C record indicates that the atmospheric carbon reservoir oscillates about an equilibrium condition. Thus, the imposition of an equilibrium state at a particular time is arbitrary. Generally, the further back in time the models' initial conditions are set, the less sensitive the model calculations at a succeeding time are to these conditions. Thus, starting the model calculations in 1855 was not considered to be the best approach. Instead we imposed steady state initial conditions in either 1735 or 1815, for which \bar{Q}_M - \bar{S} relationships determined over the 1723–1855 and 1798–1855 time intervals were used, respectively, to calculate atmospheric ^{14}C levels. This procedure allows the model to feed back into the post-1860 atmospheric ^{14}C calculations, ^{14}C changes that are close to observed atmospheric values.

6. The relationship between ^{14}C production rates and solar activity

The calculated production rate changes $\Delta\bar{Q}_M$ (the percent difference from A.D. 300–1860 average production rate) have been attributed to changes in solar modulation of the cosmic ray flux [7,23–25]. The model calculated relationship between \bar{Q}_M and \bar{S} (Table 3) can be compared with

the relationship derived from observed post-1937 atmospheric neutron fluxes, which yield a $d\bar{Q}/d\bar{S}$ value of -0.0041 ± 0.0010 [7,23]. Previously we calculated a $d\bar{Q}_M/d\bar{S} = -0.0048$ for the 1800–1860 interval from atmospheric ^{14}C variations, using reservoir model A [7,23]. The data base for our present calculations is more extensive, and we now obtain a $d\bar{Q}_M/d\bar{S}$ value of -0.0029 ± 0.0010 for the 1798–1855 interval (Table 3). Between 1723 and 1855, $d\bar{Q}_M/d\bar{S}$ is -0.0060 ± 0.0026 , which suggests an increase in solar modulation when approaching the Maunder minimum in the late 17th century. For model version C the calculated $d\bar{Q}_M/d\bar{S}$ values for these time intervals are the same, within the error of the calculations (Table 3). Thus the model with the shorter biosphere residence time indicates a similar degree of cosmic ray flux modulation when approaching the Maunder minimum.

All calculations suggest, for the 1723–1855 interval, a ^{14}C production rate–sunspot dependency slightly stronger than indicated by the $d\bar{Q}/d\bar{S} = -0.0051$ upper limit obtained from post-1937 neutron flux observations [7]. However, within the error of the $d\bar{Q}_M/d\bar{S}$ calculations (Table 3) the values agree with the independently determined \bar{Q} - \bar{S} relationship derived from 20th century neutron flux measurements.

The model calculated values of $d\bar{Q}_M/d\bar{S}$ are derived from a geomagnetically corrected ^{14}C record. It should be noted that differences between $d\bar{Q}_M/d\bar{S}$ values derived from the observed atmospheric $\Delta^{14}\text{C}$ record, and the geomagnetically corrected record, are very small. For example, using model B and the geomagnetically corrected ^{14}C record results in $d\bar{Q}_M/d\bar{S} = -0.00617$ whereas $d\bar{Q}_M/d\bar{S} = -0.00622$ using the uncorrected record. Although the differences are small, we removed the geomagnetic long-term trend because otherwise the derived \bar{Q}_M - \bar{S} relationship is influenced by geomagnetically induced change in atmospheric $\Delta^{14}\text{C}$ level.

7. Results of model calculations

Atmospheric ^{14}C levels were calculated from models A, B, and C for both the anthropogenically

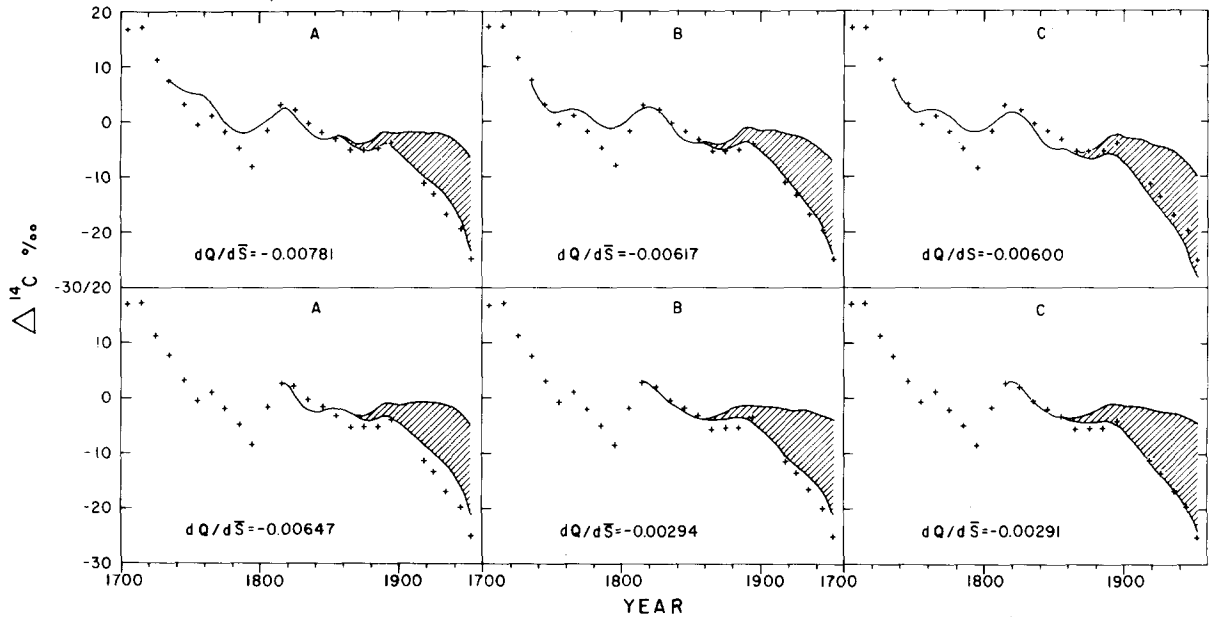


Fig. 6. Carbon reservoir model calculated $\Delta^{14}\text{C}$ levels of the 19th and 20th century. In each section the upper curve represents the calculated natural atmospheric $\Delta^{14}\text{C}$ level, whereas the lower curve gives the calculated level when the release of fossil fuel CO_2 is taken into account. Plus points are the decade averaged measured $\Delta^{14}\text{C}$ levels, except for the 1952 endpoint. Calculations start either in 1735 (top) or 1815 (bottom). Model A, B, and C parameters are given in Table 3. The shaded area represents the influence of fossil CO_2 release.

perturbed and unperturbed conditions. For each model, two solar modulation (1723–1855 and 1798–1855) dependencies between \bar{Q}_M and \bar{S} were used. A comparison between the measured atmospheric ^{14}C levels and model calculated ^{14}C time change is presented in Fig. 6. The shaded area represents the ^{14}C depletion due to fossil fuel CO_2 addition. Annual CO_2 production rates were taken from Keeling [26]. The atmospheric CO_2 concentrations calculated by each of the three models agreed to within 1 ppm with the observed CO_2 increase between 1960 and 1974 [8].

All the model calculations of ^{14}C activity in the post-1860 interval agree within a few permil with the measured values. As mentioned above, the date for the start of the model calculations (i.e. either 1735 or 1815) was chosen to obtain a good fit to the observed ^{14}C record between 1815 and 1855. Interestingly, with the \bar{Q}_M - \bar{S} dependencies presently used, none of the models can completely account for the dip in ^{14}C activity measured between 1780 and 1800. However, under-reporting of sunspot numbers is possible for the record prior to

1800 (J.A. Eddy, personal communication).

The pattern of atmospheric ^{14}C change from 1860 to 1955 is presented in closer detail in Fig. 7, where the permil differences from the 1860 ^{14}C activity level is examined. The similarity of the model calculations suggests that the ^{14}C record alone cannot be used to choose one model over another, especially when one considers the uncertainty of the \bar{Q}_M - \bar{S} relationship and the error in the cumulative CO_2 release (ca. 10% [26]), and to a lesser degree the error in the ^{14}C measurements ($\pm 0.6\%$) for the decade averages. We prefer to examine further the results for model B because this version uses F and K_z values which are more representative of the oceanic bomb ^{14}C distributions, as discussed above. We also prefer to use the \bar{Q}_M - \bar{S} relationship that represents the 1723–1855 interval (i.e. $d\bar{Q}_M/d\bar{S} = -0.00617$) as this longer time interval provides a better representation of solar modulation and sets the initial steady state conditions in the model further back in time, as discussed above.

The results of calculations using model B indi-

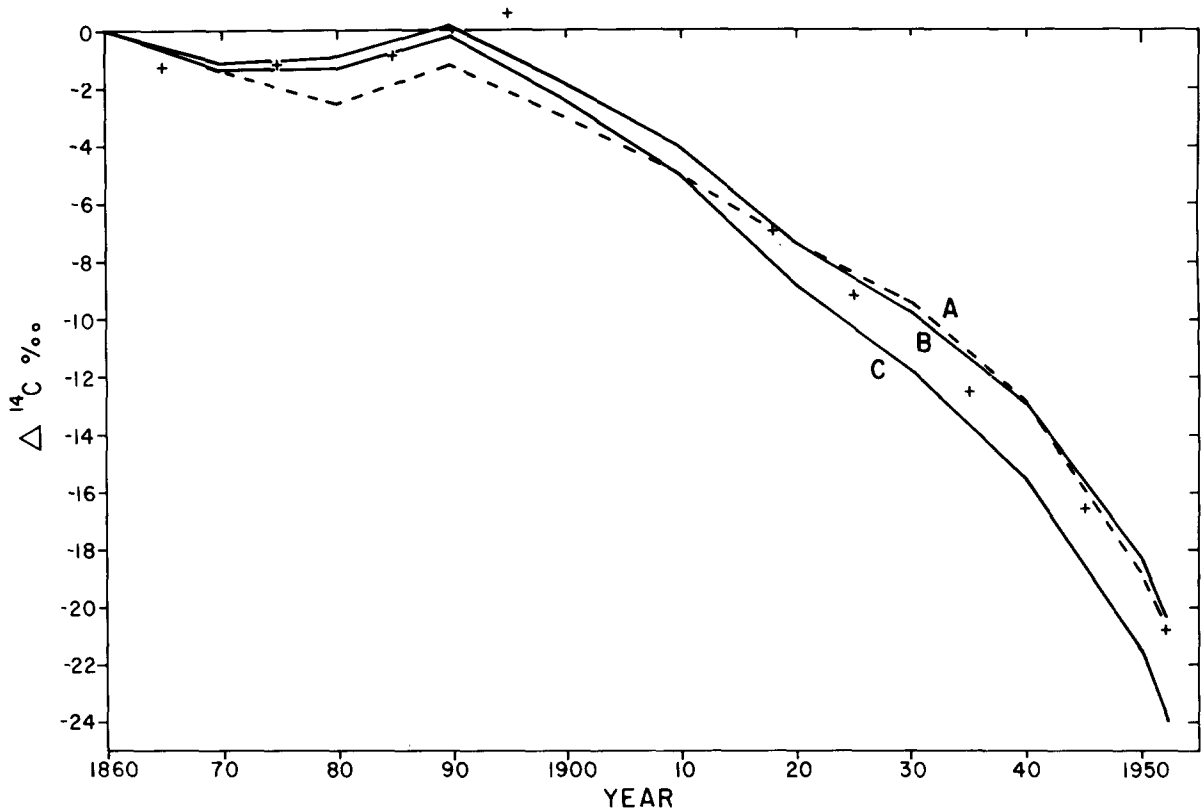


Fig. 7. A comparison of measured decade averaged $\Delta^{14}\text{C}$ values (squares), and model calculated $\Delta^{14}\text{C}$ levels, all relative to the year 1860 (see text).

cate a change in $\Delta^{14}\text{C}$ between 1860 and 1950 of -18.4% when both the predicted natural variability and the fossil fuel CO_2 release are included. The measured ^{14}C change between the 1855–1864 decade and the years 1949–1951 is $-20.0 \pm 1.2\%$ (Table 1).

The calculated $\Delta^{14}\text{C}$ values include estimated geomagnetic induced changes of the atmospheric $\Delta^{14}\text{C}$ levels, as described above. This correction amounts to a $+2.1\%$ increase in ^{14}C level between 1860 and 1950. The change in atmospheric ^{14}C levels that would have resulted from the solar-induced variability in ^{14}C production rates during the 1860 and 1950 interval was calculated to be -4.8% . When fossil fuel is added in the model calculations, the ^{14}C level in 1950 changes an additional -15.7% . Our estimated natural depletion in atmospheric ^{14}C levels is greater in the more recent part of the 1860–1950 interval, as

seen in Fig. 6. Before 1930 almost all (i.e. $> 95\%$) of the model calculated ^{14}C depletion is due to fossil fuel addition. In 1950, natural variability accounted for 15% of the measured Suess effect.

The previous discussion of model calculations of atmospheric ^{14}C levels uses ^{14}C production rates and sunspot numbers averaged over approximately 11-year cycles. So far we have not taken into account annual variations in production rate within a single solar cycle. Whereas the long-term trend in 20th century neutron flux observations gives a $d\bar{Q}/d\bar{S}$ of -0.0041 , the modulation within a solar cycle yields $dQ/dS = -0.00242$ [7,27]. To determine the effect of yearly variations in ^{14}C production rates, we incorporated the following solar modulation relationship in model B to calculate annual changes in atmospheric $\Delta^{14}\text{C}$ level:

$$Q_M = 1.735 - 0.00617 \bar{S} - 0.00242(S - \bar{S}).$$

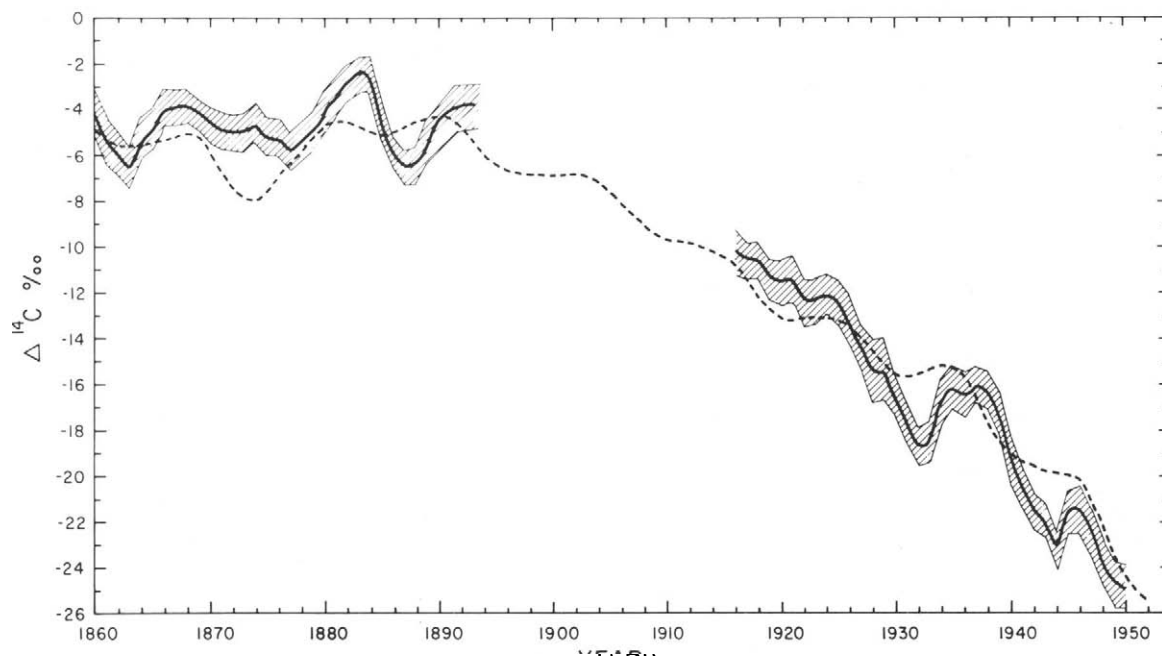


Fig. 8. Model calculated $\Delta^{14}\text{C}$ levels (dashed line) that take into account the year to year solar modulation. The calculated amplitude of the 11-year cycle is about 1‰. The heavy solid line is the three-year moving average of single-year tree-ring measurements, with standard deviation (shaded area). Suitable single-year measurements are not yet available for the 1895–1915 interval (see text).

A comparison between the calculated atmospheric $\Delta^{14}\text{C}$ curve and the measured tree-ring $\Delta^{14}\text{C}$ levels is made in Fig. 8. To facilitate such a comparison, we matched the calculated and measured decade (1855–1864) averaged $\Delta^{14}\text{C}$ values, and as a result lowered all calculated $\Delta^{14}\text{C}$ values by 1.4‰.

Because the use of \bar{S} over the 11-year cycle creates discontinuities in the production rates at the end of each solar cycle, we calculated five-year moving averages of \bar{Q}_M to which we added the calculated yearly change in Q (i.e., $-0.00242(S - \bar{S})$), so that a continuous production curve could be obtained. The 11-year ^{14}C production cycle causes rather small perturbations in the calculated atmospheric ^{14}C levels. The model calculated amplitude of the “cycle” is about 1‰, and cannot be observed in the actual record because the measuring precision of each point is only about 1.5‰. The comparison of a three-year moving average of the yearly data in Fig. 1 (with the omission of the 1895–1915 interval because the ^{14}C levels of these

samples are suspect, as discussed previously), indicates that the calculated long-term (1860–1950) change agrees with the measurements. However, the agreement between the fine structure of both curves is less good. To prove the existence of the 11-year $\Delta^{14}\text{C}$ oscillation one would need improved measuring precision to the 0.5‰ range. An independent confirmation of the measured $\Delta^{14}\text{C}$ perturbations of a few permil (such as the one near 1933) is also needed before such oscillations can be considered proven.

8. The global carbon cycle

The increase in atmospheric CO_2 level, calculated for model B, is from 297 ppm in 1860 to 311.8 ppm in 1950, or 5.0%. The corresponding 1.6% atmospheric $\Delta^{14}\text{C}$ change attributed to fossil fuel addition is smaller because part of the radiocarbon deficit is stored in the oceans and biosphere. By 1950 the atmospheric $^{14}\text{CO}_2/\text{CO}_2$ at-

tenuation factor is 0.32 for the industrial CO₂ release. In addition, the model calculations indicate a reduction in radiocarbon between 1860 and 1950 for the model biosphere from 97.8% to 96.5% and for the oceanic mixed layer from 94.5% ($\Delta^{14}\text{C} = -55\text{‰}$) to 93.7% ($\Delta^{14}\text{C} = -63\text{‰}$). The $\Delta^{14}\text{C}$ level measurements on annual coral rings provide a check on some of the calculated mixed layer $\Delta^{14}\text{C}$ values. Druffel and Linick [28] determined from a Florida Keys coral analogous mixed layer $\Delta^{14}\text{C}$ levels of $-51 \pm 2\text{‰}$ for the pre-industrial 19th century and of -61‰ for the year 1955. However, Nozaki et al. [29] measured between 1900 and 1950 a $\Delta^{14}\text{C}$ reduction of about 22‰ for a Bermuda coral. This large change, as discussed by Nozaki and co-workers, may be caused by a local exchange rate of ¹⁴C with the deep water that is smaller than the global world ocean average. The 10‰ change of the Florida coral agrees well with our model B calculated change of 8‰.

Recently, Druffel [30] has estimated a 6‰ decrease in mixed layer $\Delta^{14}\text{C}$ levels between 1930 and 1954 in the eastern Pacific using corals collected in the Galapagos. This compares to our model B calculated decrease of 4‰ over this same time interval. However, the inferred mixed layer $\Delta^{14}\text{C}$ record at this location is complicated by the variability of upwelling of deeper $\Delta^{14}\text{C}$ -depleted water, and thus may not reflect only atmospheric $\Delta^{14}\text{C}$ changes.

A recent point of debate has been the amount of carbon taken up, or released, by the biosphere during the current episode of anthropogenic disturbance. The biospheric reservoir size was kept constant for our calculations as discussed above. Thus, all industrial CO₂ not present in the atmosphere by 1950 is in the model ocean. We investigated the influence of biospheric CO₂ releases on atmospheric $\Delta^{14}\text{C}$ levels by reducing the biospheric reservoir size between 1860 and 1950 according to a biospheric pattern suggested previously [31,32] (i.e. Gaussian distribution centered at 1860 with a $\sigma = 20$ years, and CO₂ release totalling 120×10^9 tons). The differences with the model $\Delta^{14}\text{C}$ calculations made above are small because the released biological CO₂ has nearly the same ¹⁴C content as atmospheric CO₂. For this biospheric release pat-

tern the 1860–1950 change in model B calculated atmospheric $\Delta^{14}\text{C}$ level differs less than 0.5‰ from the -18.4‰ calculated earlier. However, to accommodate the large biospheric CO₂ flux the model calculations have to start with a lower atmospheric CO₂ content of 280 ppm.

9. Conclusions

Evidently, global carbon box-diffusion models can adequately account for the 1860–1950 change in atmospheric $\Delta^{14}\text{C}$ level when estimated fossil fuel CO₂ releases and predicted cosmic ray flux changes are incorporated in the model. For instance, model B, with a vertical eddy diffusion rate of $3.0 \text{ cm}^2 \text{ s}^{-1}$ in the oceans, correctly predicts the change in trend around 1937 when the gradient changes from -2.8‰ per decade to -6.8‰ per decade. Because the calculated results are not very sensitive to the choice of model parameters the Suess effect cannot be used for the fine tuning of models, especially since the fossil fuel CO₂ releases, cosmic ray flux modulation, and measured $\Delta^{14}\text{C}$ levels each have their inherent inaccuracies. The model calculations also show minimal changes in $\Delta^{14}\text{C}$ level when an anthropogenic reduction in biospheric reservoir size is simulated.

Model calculations indicate 11-year $\Delta^{14}\text{C}$ perturbations with an amplitude of about 1‰. The measured $\Delta^{14}\text{C}$ record is not yet sufficiently precise to confirm these oscillations.

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