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On the ^{13}C record in tree rings. Part II. Registration of microenvironmental CO_2 and anomalous pollution effect

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ABSTRACT

^{13}C data on two sets of Eifel (Germany) trees are presented, which demonstrate severe non-temperature environmental influences disturbing the normal trend of data in this century. For five isolated trees exposed during the last 25 years to higher than normal CO_2 content and other pollution gases, an unexpected increase in ^{13}C values has been found, which is explained as pollution effect altering the photosynthetic CO_2 fixation. For five other formerly forest trees of the same location, increasing ^{13}C values during the youth stage have been observed, which later became adapted to the normal trend with clearing of their habitat. The ^{13}C record for both sets of trees is similar at time periods of similar atmospheric environment. Ring width data of the trees and pollution experiments on barley confirm the observed effects.

1. Introduction

In preceding papers (Freyer, 1978, 1979), ^{13}C measurements in rings of northern hemispheric trees covering the period of the last 150 years have been reported. An overall ^{13}C decrease during the last 100 years has been found, which was discussed as due to variations in the isotopic content of atmospheric CO_2 that resulted from the increasing production of fossil and biospheric CO_2. It has been pointed out, however, that the ^{13}C curves in their actual shape, though decreasing, are superimposed by other effects, possibly by environmental and climatic influences. Neglecting these influences, Stuiver (1978) and Freyer (1978) have used the trend of the measurements for estimations of the past biospheric CO_2 source. Pearman et al. (1976), on the other hand, have interpreted their ^{13}C curves on southern hemispheric trees only as a consequence of climatic implications, Libby and Pandolfi (1974) likewise.

In this paper additional ^{13}C measurements on trees are presented, which have been used partly for calculations of the overall ^{13}C trend (Freyer, 1978, 1979). The trees analysed in this series have been selected primarily for more heavier confirmation of the ^{13}C record for increasing CO_2 levels. However, effects have been observed which demonstrate severe environmental influences disturbing the normal trend. Measurements of the climatic response on the ^{13}C record in trees will be reported in a succeeding paper.

2. Location and habitat of analysed trees

Five isolated trees were selected, which grow in the main exhaust direction at a distance of about 50–100 m from a hard coal-fired foundry, located in a small valley in Mechernich, Eifel, Germany (50°40N, 6°40E). This foundry has been in operation since 1890 and closed down from 1929 to 1949. It had been renewed and restarted in 1950. As a result, the trees had been exposed to a higher than normal CO_2 content from 1950 up to now; they had also been exposed to other pollution gases, such as SO_2, and dust particles. For comparison, five additional similar trees were selected growing in pasture land in a neighbouring valley at a distance of about 2–3 km from the foundry. The older trees in this habitat had been surrounded in their youth stage by a small forest,

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Table 1. *Atmospheric CO_2 and SO_2 concentrations and $\delta^{13}C$ values in CO_2 for the polluted and control habitat of trees*

Date	Polluted	Control habitat
	a. CO_2 [p.p.m.]*	
	b. $\delta^{13}C$ [‰ (PDB)]†	
1974-8-28	a. 331 ± 7 (3)	318 ± 3 (3)
	b. −7.6 (1)	−7.2 (1)
1974-9-3	a. 346 ± 13 (5)	316 ± 2 (5)
	b. −8.6 ± 0.2 (3)	−6.9 ± 0.1 (3)
1977-4-29	b. −8.4 ± 0.2 (3)	−7.6 ± 0.1 (3)
1977-6-14	a. 339 ± 3 (3)	327 ± 2 (3)
	b. −8.1 (1)	−7.4 (1)
	SO_2 [p.p.b.]‡	
1976-4-21	54 ± 10 (3)	—
1976-4-28	63 ± 8 (4)	7 ± 2 (4)
1976-5-5	28 ± 9 (4)	≤2 (4)

The number of measurements is given in parentheses. The values are expressed as mean ± S.D.

* CO_2 measurements under field conditions with an UNOR2 infrared gas analyser against flowing CO_2/N_2 calibration gas.

† Isotopic measurements after collection and processing of air samples (Craig, 1953) with a Micromass 602C mass spectrometer. The data have not been corrected for N_2O contamination (Craig and Keeling, 1963).

‡ SO_2 measurements after West and Gaeke (1956).

which had been cleared between 1920 and 1930. The measurements of atmospheric CO_2 and SO_2 and $\delta^{13}C$ in CO_2 given in Table 1 illustrate the present local environment of both sets of trees when the foundry had been working during the day.

Table 2. *Tree species and recorded periods*

Polluted species (Recorded periods)	
	Qu 14 (1890–1973)
	Qu 15 (1908–1973)
	Ae 1 (1854–1973)
	Fr 2 (1888–1973)
	Pi 6 (1924–1973)
Control species	
	Qu 10 (1890–1975)
	Qu 11 (1896–1975)
	Qu 12 (1914–1975)
	Fr 1 (1920–1975)
	Qu 13 (1932–1975)

The trees specified earlier (Freyer, 1979) and classified as polluted and control species according to the different habitats are given in Table 2.

3. Experimental procedure

Wood samples of the trees were taken with a drilling corer used in tree-ring analysis. Two-year blocks of wood were prepared, converted to cellulose, burned and analysed for their $^{13}C/^{12}C$ ratios as described earlier.

4. Results and discussion

4.1. ^{13}C *and ring width curves of polluted and control Eifel tree species*

The ^{13}C variations over the time record of the tree have been calculated in the same manner described earlier as deviations from the tree specific isotopic value within the years A.D. 1930–1950. This time interval has been chosen because of the history of the trees. Polluted and control species had been exposed to normal atmospheric CO_2 between 1930 and 1950, while the environment of both tree habitats had been different at other time periods.

The mean deviations from the average 1930–1950 values of the individual trees are given in Fig. 1. The bars represent the mean reproducibility of deviations (t-distribution); the lower reproducibility for the beginning (measurements of 2 and

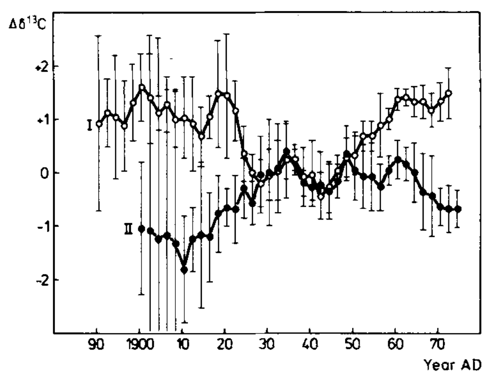

Fig. 1. $\Delta\delta^{13}C$ variations in polluted (I, open circles) and control Eifel tree species (II, full circles) based on the average 1930–1950 individual tree specific values. The bars represent the deviations (t-distribution), assuming an error probability of 90%.

3 trees, respectively) and the higher one for the end of the record (measurements of 5 control and polluted trees each) result mainly from the different numbers of trees analysed. It is obvious that the environment of the habitat influences the ^{13}C record severely. Only during the 1930–1950 time interval is the ^{13}C record for both sets of trees similar. After 1950, the control species show the normal ^{13}C decrease as observed in other trees from different locations (Freyer, 1978, 1979). For the polluted species an even sharper decrease was expected during this time interval, because these trees had been exposed to a higher CO_2 content with lower $\delta^{13}C$ values (cf. Table 1) than the control species. However, an unexpected ^{13}C increase is observed which will be discussed in the following as a pollution effect. Before 1930, the control species show lower ^{13}C values than in the years after. This effect has been explained as youth trend in forest trees due to the uptake of the environmental CO_2 in a forest stand which is mixed with ^{13}C-depleted respiration CO_2 (Freyer, 1979). After forest clearing in the 1920s the ^{13}C values of these trees become adapted to the values of the polluted ones. The polluted species, isolated over the whole period of record, exhibit higher ^{13}C values before 1930 than during the 1930–1950 time interval. This effect may be the normal trend, as observed in the other trees (Freyer, 1978, 1979). However, especially for the peak ^{13}C values between 1915 and 1925, a pollution influence cannot be excluded, because the foundry had been in operation during that period.

The incisions in the history of the trees, which are well marked by the ^{13}C record, seem to be observable to a lesser extent even by the ring-width data. These ring-width data have not been processed with the commonly used ring indices (e.g. Fritts, 1976), but by the same calculation applied to the ^{13}C values. The relative deviations in ring width from the mean tree specific ring width within the years A.D. 1930–1950 are given in Fig. 2 for both sets of trees. It is shown that broad ring width in the polluted trees during the first two decades of the record is followed by narrow ring width at about 1920, which, however, cannot be attributed to a pollution effect because the control species follow the same pattern. From 1920, the control species exhibit a sudden increase in ring width, which is common for forest trees becoming isolated due to the higher nutrient and light supply. The pattern for both sets of trees during the 1930–1950 time interval looks similar only for one decade. For the last two decades of the record, the ring width of the polluted trees decreases faster than those of the control species, which may possibly be due to the pollution influence. The statistical significance of all observations in the ring-width pattern, however, is not as established as the significance of the ^{13}C record.

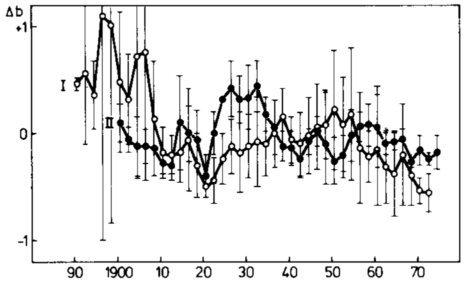

Fig. 2. Relative ring width data $\Delta b = (b - \bar{b})/\bar{b}$ of polluted (I, open circles) and control Eifel tree species (II, full circles) based on the average ring width $\bar{b}$ in the 1930–1950 time period. The bars represent the deviations (t-distribution), assuming an error-probability of 90%.

The measurements on both sets of trees have been considered for calculation of the overall ^{13}C trend (Freyer, 1978, 1979) at time intervals, at which the trees had been exposed to normal free atmospheric CO_2, i.e. control species from 1930 to 1975 and polluted ones from 1926 to 1949.

4.2. *Explanation of the pollution effect on ^{13}C values*

The polluted trees had been exposed during the pollution period to higher CO_2 content and lower $\delta^{13}C$ values than the control species. Nevertheless, the ^{13}C record of the polluted trees shows an opposite trend to the expected. Preliminary experiments on barley (*Hordeum distichum*) confirm the SO_2 pollution effect on $\delta^{13}C$ values. Barley seedlings were hydroponically cultured in two identical glass chambers at room temperature and flushed with air at the same rate. One chamber was supplied with SO_2 from a permeation tube. The plants were harvested at different times after germination, the shoots were freeze-dried and subjected to the same experimental procedure as cellulose from the wood samples. Table 3 shows the $\delta^{13}C$ values for the shoots. It is observed that the

Table 3. *Effects of SO_2 pollution on $\delta^{13}C$ values of barley after different times of germination (SO_2 concentration 4.1 ± 0.4 p.p.m.)*

	$\delta^{13}C$ (‰ PDB)	
	Polluted	Control plants
5 days*	−25.6 ± 0.2 (5)	−25.7 ± 0.1 (5)
11 days	−26.4 ± 0.1 (5)	−26.8 ± 0.3 (5)
18 days	−25.7 ± 0.4 (8)	−26.9 ± 0.4 (8)

The number of measurements of individual plants is given in parentheses. The values are expressed as mean ± S.D.

* Time after germination.

values for polluted and control plants harvested after 5 days are identical, which reflect mainly those of the barley kernel ($\delta^{13}C = -25.3 \pm 0.3\%$). During the course of the experiment, however, the isotopic values of polluted and control plants became different. The polluted plants exhibit higher $\delta^{13}C$ values than the control plants by about one per mill over the entire duration of the experiment (18 days), which could not be continued further because of later necrosis of the polluted plants. Experiments on barley cultivated on soil showed similar $\delta^{13}C$ differences for polluted and control plants.

The biochemical mechanism of SO_2 damage in plants is not understood in detail. As net effects, an inhibition of photosynthesis and an increase in respiration intensity are observed, which have been investigated in many studies (cf. summary given by Ziegler, 1973). Both effects should alter the carbon isotope composition of the plant material, as ascertained by the experiments. An inhibition of photosynthesis possibly lowers the fractionation factor of carbon isotopes between atmospheric CO_2 and plant material, which should be similar, as has been observed by Park and Epstein (1960) on plants grown under different CO_2 concentrations. An increase in respiration intensity could have the same effect, i.e. a ^{13}C enrichment in the polluted plants (relative to the control plants), possibly because of a lower rate of reassimilation of the respired carbon dioxide.

5. Conclusions

The normal trend of ^{13}C values in tree rings recording increasing atmospheric CO_2 levels can be severely disturbed by other environmental influences. By measurements on selected trees for which the history is known, two non-temperature effects have been demonstrated which reverse the normal trend. The pollution effect which seems to diminish the carbon isotope fractionation factor between atmospheric CO_2 and vegetation has to be pointed out. The decrease in ^{13}C data during the late nineteenth and the early twentieth centuries in different analysed trees has been shown to be nearly the same, while the ^{13}C record among individual twentieth-century trees exhibits larger variations (Freyer, 1979). This may reflect at least partly increasing ambient pollution levels and more acid rain, during this century, even when the trees had not been exposed to local pollution sources. For wet and dry deposition of sulphur compounds on continents, e.g. a present increase of more than three times the pre-industrial value as a result of anthropogenic emissions has been estimated; the deposition on the oceans is much less anthropogenically influenced (Granat et al., 1976). Therefore it has to be concluded that only measurements on a large number of carefully selected trees, especially in maritime areas, can prove ^{13}C variations of past atmospheric CO_2 levels. As yet, the SO_2 pollution effect or effects of other pollution sources (other than increasing CO_2 levels) cannot be quantified. These effects, however, have to be considered in the interpretation of ^{13}C tree-ring data in the future.

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О СОДЕРЖАНИИ ^{13}C В КОЛЬЦАХ ДЕРЕВЬЕВ. II.РЕГИСТРАЦИЯ CO_2 В БЛИЖАЙШЕЙ ОКРЕСТНОСТИ И АНОМАЛЬНЫЙ ЭФФЕКТ ЗАГРЯЗНЕНИЯ

Представлены данные по содержанию изотопа ^{13}C в двух выборках деревьев из Эйфеля (ФРГ), которые указывают на серьезные нетемпературные влияния окружающей среды, нарушающие нормальный тренд данных в этом столетии. В пяти изолированных деревьях, росших в последние 25 лет в условиях повышенного содержания CO_2 и других загрязняющих газов, найдено неожиданное повышение содержания ^{13}C, что объясняется влиянием загрязнений, изменяющих фотосинтетическую фиксацию CO_2. Для пяти других деревьев, выросших в лесу в том же районе, наблюдалось повышенное содержание ^{13}C на ранней стадии, которое потом адаптировалось к нормальному тренду при очищении места их роста. Данные по ^{13}C для обеих выборок деревьев подобны для периодов времени, когда атмосферное окружение было подобным. Данные по толщине древесных колец и эксперименты по загрязнению на ячмене подтверждают наблюдаемые эффекты.