THE EFFECT OF ANTHROPOGENIC CO_2 AND ^{14}C SOURCES ON THE DISTRIBUTION OF ^{14}C IN THE ATMOSPHERE

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ABSTRACT. ^{14}C measurements on continuous weekly samples of atmospheric CO_2 and hydrocarbons, collected in a rather densely populated area are presented. The deviation of the measured ^{14}C data from the clean air level is primarily due to CO_2 from the combustion of fossil fuels. This is confirmed by fossil fuel admixture estimates individually calculated with an atmospheric dispersion model. Up to 10 percent admixture is predicted by this model and observed from the ^{14}C shift for weekly averages, particularly during the winter season. Natural CO_2 admixture due to soil respiration, however, even in winter, is of the same order of magnitude, but much larger in the warm season: the considerable variations in CO_2 concentration in summer are almost exclusively controlled by natural sources. Using tree leaf samples, we have been able to identify boiling water reactors (BWR) as weak sources of $^{14}CO_2$. Atmospheric samples taken in the environment of the pressurized water reactors (PWR) Biblis show that the ^{14}C release of these reactors is primarily in the form of hydrocarbon ^{14}C. The source strength of the various power plants, calculated on the basis of our observations in their environment, ranges from 0.5 to 7Ci per year.

INTRODUCTION

The clean air ^{14}C level is modified in densely populated areas by anthropogenic sources: 1) fossil fuel CO_2 (^{14}C free) causes a depletion of the regional ^{14}C level in industrialized areas (Vogel and Uhlitzsch, 1975). 2) The emission of ^{14}C from nuclear power plants ($^{14}CO_2$ mainly from boiling water reactors, radioactive hydrocarbons from pressurized water reactors [Kunz, Mahoney, and Miller, 1974; 1975]) leads to an increase of the local ^{14}C concentrations.

A study has been made in the Rhine Neckar area (Mannheim/Ludwigshafen/Heidelberg) to distinguish between the influence of fossil fuel combustion CO_2 from the industrialized area around Mannheim and the ^{14}C emission from the Biblis nuclear power plants.

In addition to this study, based on direct atmospheric CO_2 and hydrocarbon measurements, we collected tree-leaf and tree-ring samples in the vicinity of a number of German power plants to monitor any $^{14}CO_2$ releases from the nuclear reactors.

Clean air ^{14}C background

The identification of the different anthropogenic CO_2 sources by isotopic analysis requires knowledge of the clean air isotopic composition. From 1959 (beginning of nuclear weapon testing) to the present, we have made atmospheric CO_2 measurements at several clean air stations in Western Europe and South Africa (Berdau and Münnich, 1972; Vogel and Marais, 1971) and since 1972, primarily at the stations, Vermunt, Vorarlberg, Austria, 1800m, and Schauinsland, near Freiburg, West Germany, 1284m. The time variation is shown in figure 1. An exponential regression, due to exchange between atmosphere and ocean (Münnich, 1963), of the data points gives a clean air ^{14}C concentration in January 1979 of $\Delta^{14}C = 323 \pm 1‰$. The fitted curve was used as clean air back-
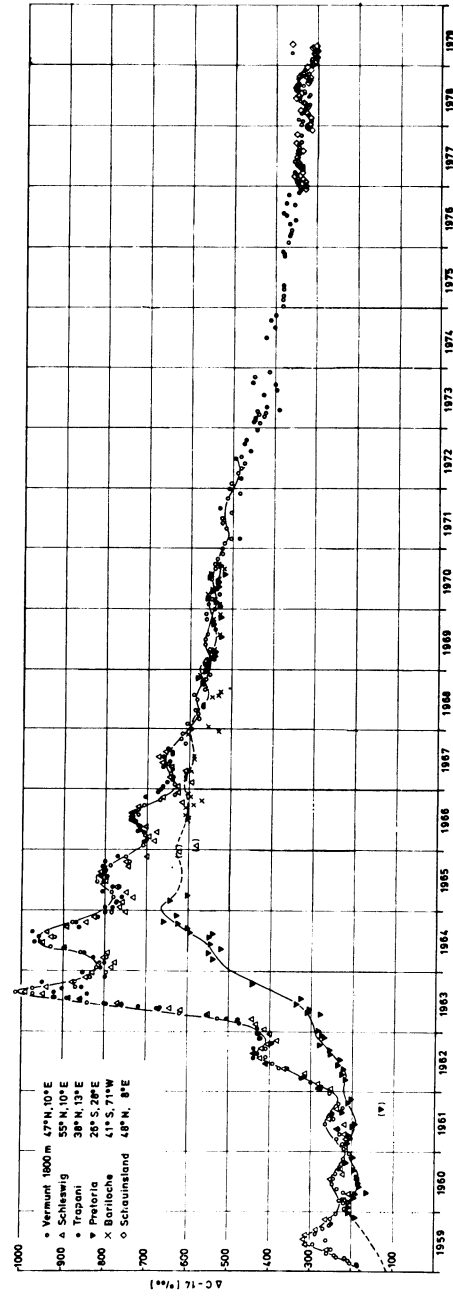
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Fig 1. ¹⁴C concentration of tropospheric CO_2 since 1959: the lower curve represents the ¹⁴C concentration in the southern hemisphere (Pretoria and Bariloche, South Africa) and the upper one shows the time variation in the northern hemisphere (Trapani, Schleswig, Vermunt and Schauinsland, Western Europe) (Münnich and others, ms in preparation).

ground for the atmospheric samples from 1976 to 1977. The strong variation, $\Delta^{14}C$ maximum in early summer, observed in clean air in 1978, possibly resulting from later atmospheric nuclear weapon tests (Chinese) and induced by the exchange between troposphere and stratosphere (Münnich, 1963), were taken into account by a separate fit of the clean air values for 1978.

Sampling methods

Since August 1976, continuously collected weekly samples of atmospheric CO_2 and total carbon (CO_2 plus oxidized hydrocarbons) were taken about 4km east of the nuclear power plants in Biblis (Levin, 1978). The sampling system is shown schematically in figure 2. About 15m³ of air are sampled by a small aquarium pump. The exact volume of air is measured by a gas meter. The air then passes through a glass column filled with 4n sodium hydroxide solution. To strip the air quantitatively from CO_2, the glass column contains a packing of small Raschigrings (hardglass) to enlarge the absorption surface. The column rotates around its axis causing permanent renewal of the NaOH film on the column packing. Parallel to this, in a second path, the atmospheric hydrocarbons are oxidized catalytically at 600°C to CO_2 and are then absorbed together with the atmospheric CO_2 in an absorption system identical to the one described before.

The glass columns are changed once a week. The absorbed CO_2 sample is extracted directly in the sampling device in a laboratory vacuum system (fig 3) by addition of half-concentrated H_2SO_4 (40 percent) to the sodium carbonate solution. The CO_2 samples are cleaned in a charcoal column and measured in a CO_2 proportional counter (*cf* Schoch and others, 1980).

The tree-leaf samples, mainly from old fruit trees, standing rather isolated, were collected in 1976, 1977 and 1978 at the German reactors Biblis (PWR, 2500 MWe), Brunsbüttel (BWR, 806 MWe), Gundremmingen (BWR, 252 MWe), Karlsruhe (PWR, 57 MWe), Lingen (BWR,
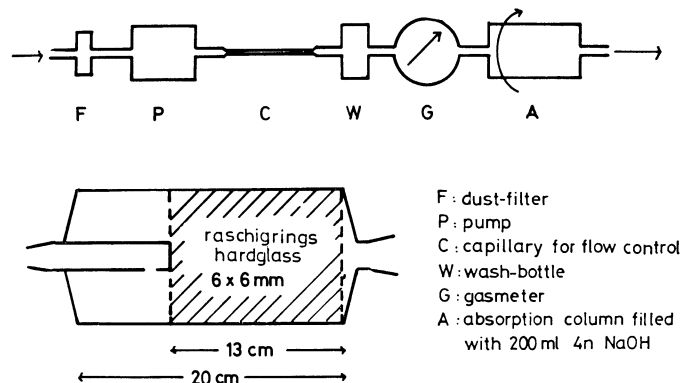

F   P   C   W   G   A

raschigrings
hardglass
6 x 6 mm

← 13 cm →
← 20 cm →

F : dust-filter
P : pump
C : capillary for flow control
W : wash-bottle
G : gasmeter
A : absorption column filled
    with 200 ml 4n NaOH

Fig 2. Absorption system for atmospheric CO_2 samples with a rotating NaOH absorption column.

268 MWe), Neckarwestheim (PWR, 855 MWe), Stade (BWR, 662 MWe), and Würgassen (BWR, 670 MWe). The leaves were cleaned in distilled water, dried and combusted to CO_2. The ^{14}C activity was measured in a CO_2 proportional counter.

We also measured the ^{14}C concentration in tree rings from 1968 to 1978 from two trees near the Obrigheim reactor. Individual rings were identified by Bernd Becker, Universität Hohenheim. The samples were treated and measured in the same way as tree-leaf samples.

Interpretation of the atmospheric sample data from Biblis reactor environment

The time variation of ^{14}C in atmospheric CO_2 and CO_2 + hydrocarbon samples is shown in figure 4. The major results are:

1) Nearly all $\Delta^{14}C$ values of the CO_2 samples are below the clean air ^{14}C level.

2) The samples of total carbon (CO_2 and hydrocarbons) show little, but significantly higher $\Delta^{14}C$ values.

The interpretation of these results is as follows:

1) A $^{14}C/^{12}C$ ratio lower than the clean air level indicates the influence of fossil fuel combustion CO_2 sources in the environment of the sampling site, which, in most cases, exceed the influence of the reactor-produced ^{14}C. The sampling location is in the middle of the Rhine valley, a region rather densely and homogeneously populated. The highly industrialized area of Mannheim/Ludwigshafen is no more than about 25km south of
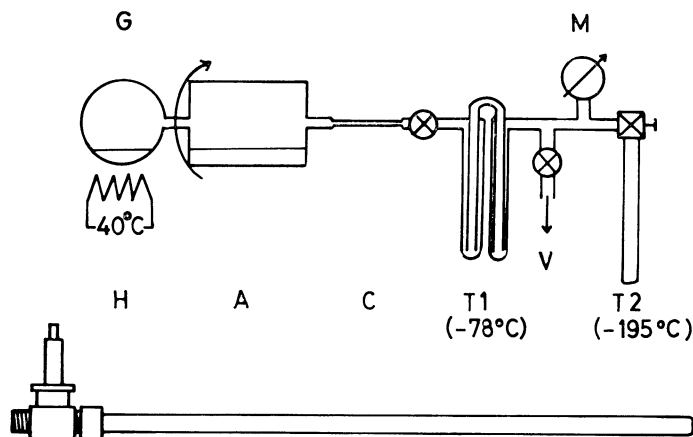
T2: CO2 cold trap (stainless steel pressure container, Swagelokfitting all metal, pressure valve: Nupro SS-(12MM)BW)

G : 1000 glass bulb with 100 ml 40 % H2SO4
H : heater
A : absorption column with 200ml 4n NaOH + carbonate (rotating)

C : capillary for H2O – vapor flow control
T1 : H2O cold trap
V : vacuum pump
M : manometer

Fig 3. Extraction system for atmospheric CO_2 samples.

the sampling station. Two other large sources in the vicinity of the sampling site are Darmstadt and Mainz.

In order to distinguish between the influence of the reactor and of the combustion sources which compensate each other to a certain extent, we first estimated the fossil fuel admixture at the sampling point with an atmospheric dispersion model. The model is based on a circular area source for fossil CO_2 (fig 5) around the sampling point with a radius of 40km. All sources outside this area are assumed not to contribute to the depression at the sampling point. The circular area is cut off in the east and west due to the specific topography of the Rhine valley. Sources on the hills, about 300m above the valley, presumably do not contribute due to a larger vertical dispersion. The source strength has been assumed to be proportional to the population density. This assumption has been checked with the sales statistics of fossil fuel for individual areas: average consumption is presumably 3t of carbon per person per year (Statistisches Landesamt Baden-Württemberg, 1976). This leads to a mean area source strength in the model area (500 inhabitants per km²) of 1500t carbon per km² per year; assumed seasonal variation: summer, 75 percent, winter, 125 percent. Big cities such as Mannheim/Ludwigshafen, Darmstadt, and Mainz are considered as additional sources (see fig 5). Together with three-hour synoptical data, wind direction and velocity, cloudiness, solar radiation (Deutscher Wetterdienst, 1976-1979), we calculated the theoret-
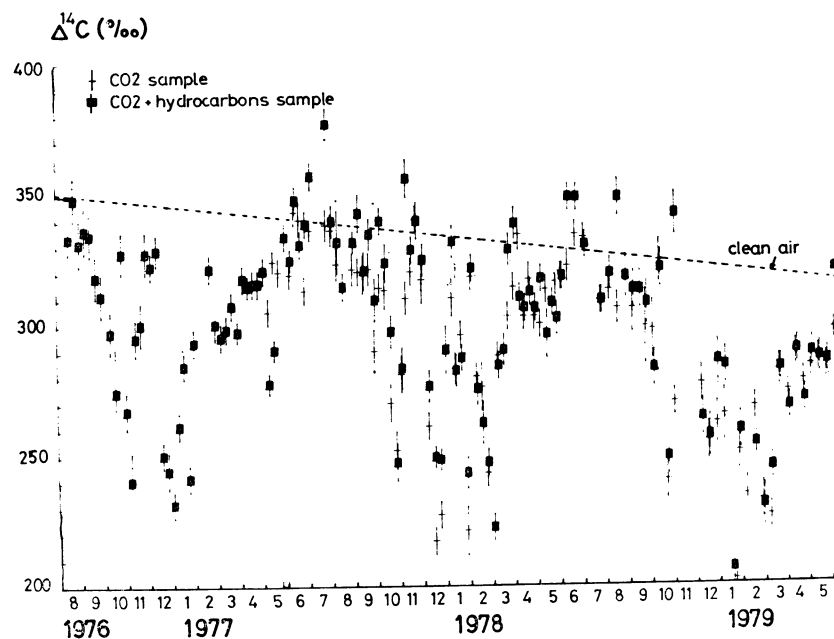

Fig 4. Time variation of ^{14}C in atmospheric CO_2 (+) and CO_2 + hydrocarbons (■) samples, collected near the nuclear plants in Biblis (FRG). The dotted line indicates the interpolated clean air ^{14}C level.

ical fossil fuel admixture at the sampling location for each weekly sample. Depending on individual wind direction and speed, air has varying durations over the source area and carries varying concentrations of fossil CO_2 on arriving at the sampling site. The fossil fuel concentration observed at the sampling point further depends on actual atmospheric mixing conditions (stability) controlling vertical dilution of the source CO_2 (Klug, 1964; 1969).

The results of the model calculation are shown in figure 6. The correlation between the estimated CO_2 admixture and the one observed is quite good ($\chi^2 = 0.68$, [Bevington, 1969]). Assuming that the sample contains only two components, clean air CO_2 and fossil fuel CO_2, neglecting, for the time being, any reactor influence (the Biblis reactors are of pressurized water type and emit ^{14}C primarily in reduced form) and assuming (cf Dörr and Münnich, 1980) that, at present, ^{14}C in soil-born CO_2 is not significantly different from the atmosphere, the fossil fuel mixing ratio can be calculated from the $\Delta^{14}C$ value observed, compared to the clean air concentration from the following equation:

$$\frac{C_{\text{fossil fuel}}}{C_{\text{clean air}}} = \frac{\Delta^{14}C_{\text{clean air}} - \Delta^{14}C_{\text{sample}}}{\Delta^{14}C_{\text{sample}} + 1000} \; (\%) \qquad (1)$$

The linear regression in figure 6 does not show a significant reactor influence that would cause a decrease of the measured ^{14}C depression

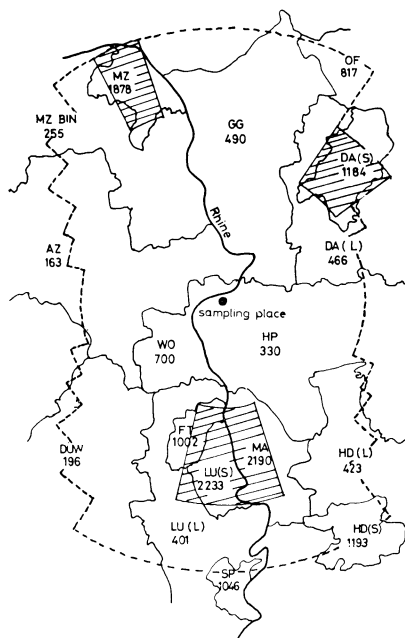

Fig 5. Map of the area source of fossil fuel combustion CO_2 in the Rhine valley around the sampling site near the Biblis reactor. The map shows the mean population density (number of inhabitants per km²) of the various districts.

(the regression line passes, in fact, through the origin). This finding agrees well with results of spot measurements made directly in the reactor stacks (Riedel and Gesewsky, 1977). The points in brackets seem to indicate short-term ^{14}C releases from the reactor. They were sampled between 16.5. and 21.5.78, and between 29.5. and 8.6.78. Indeed, there has been a maintenance period of the Biblis reactor B during June 1978, so that a ^{14}C release from the reactor might be possible. In these two specific cases the appropriateness of the depression estimated by the model is also supported by the observed ^{13}C values. A fossil fuel, but likewise a soil CO_2 admixture changes the δ^{13}C due to the different $(^{13}C)/(^{12}C)$ ratios of fossil fuel and plant material in general ($\delta^{13}C = -25\%_0$) and of global atmospheric CO_2 ($\delta^{13}C = -8\%_0$). Thus, observed δ^{13}C values of one week's integrated samples from low altitude locations vary in the range of -8 to $-11\%_0$ in good correlation with individual CO_2 concentration (Esser, 1975). Note that the slope of the regression line in figure 6 is not exactly equal to 1. This might be due to a source strength assumed too high in our calculation.

2) The higher Δ^{14}C values observed for oxidized samples in Biblis can only result from reactor-released ^{14}C in reduced form. The observed effect could not result from natural methane because mean Δ^{14}C methane values much greater (about $1000\%_0$) than ever observed were necessary for
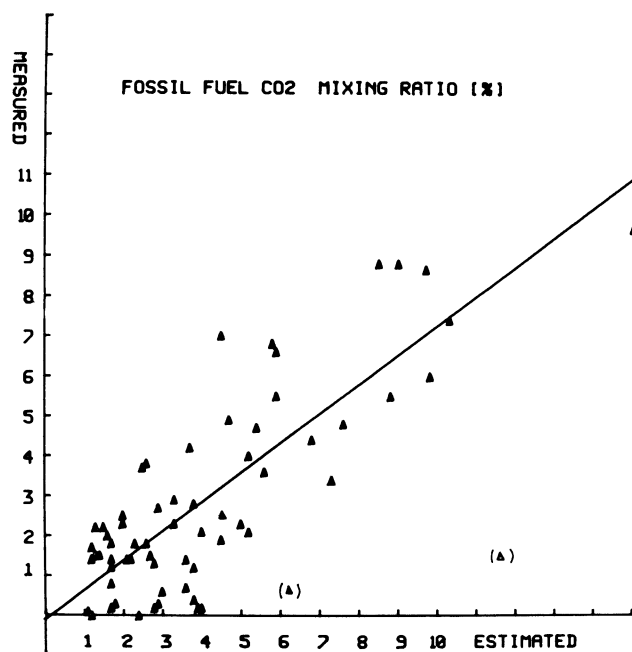

Fig 6. Correlation between the measured fossil fuel CO_2 admixture (calculated from the observed ^{14}C depression in the samples) and the CO_2 admixture estimated by the dispersion model.

the increase in the composite sample. Atmospheric methane indeed shows $\Delta^{14}C$ values of about 0‰ (Levin, 1978). ^{14}C excess of the hydrocarbons was calculated by subtraction from the $\Delta^{14}C$ values of the CO_2 samples simultaneously collected. Estimated excess of the oxidized samples is shown in figure 7. The mean value over the whole period is $\Delta^{14}C = + (8.3 \pm 1.4)$‰ corresponding to an excess of 6‰ relative to the clean air $^{14}CO_2$ concentration. With a long-term dispersion factor of $f = 8.2 \cdot 10^{-8}$ s/m³ for the sampling point, with respect to a point source represented by the Biblis reactors, this increase leads to a source strength of 3.5Ci per year.

Measurements of plant material near several German power plants

Interpretation of tree-leaf and tree-ring samples requires knowledge of the exact growth (CO_2 collection) period of the plant material to enable us to account for the proper clean air ^{14}C level. For this purpose, we defined general "sample periods" for tree leaves — beginning of April to end of May — and for wood — beginning of April to end of October — (Becker, 1978, pers commun). For these periods, we calculated the clean air reference value as a mean of the observed clean air ^{14}C concentrations:

$$1976 : \Delta^{14}C = 368 \pm 3‰$$

$$1977 : \Delta^{14}C = 347 \pm 1‰$$

$$1978 : \Delta^{14}C = 336 \pm 1‰$$
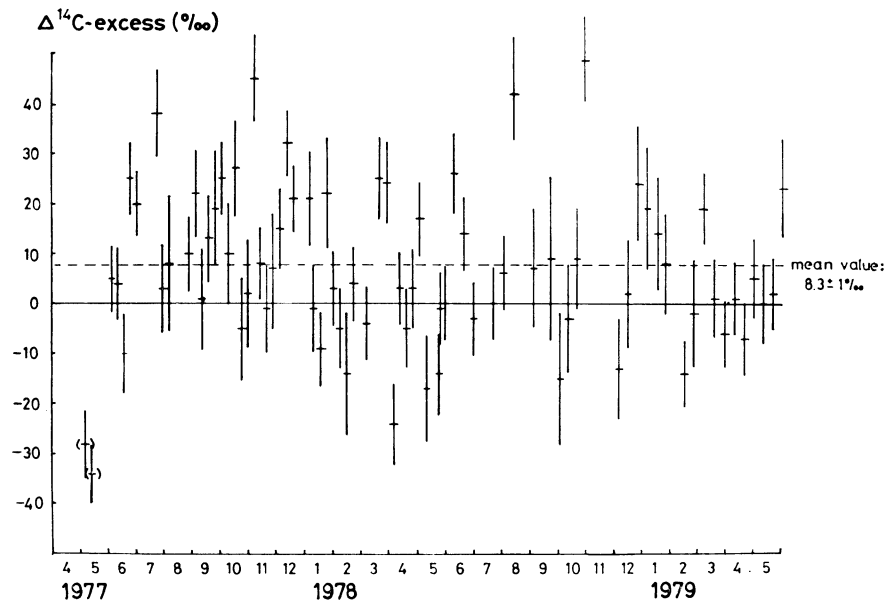
Significant increases above these levels were only found in leaf samples

Fig 7. $\Delta^{14}C$ excess of the combined CO_2 + hydrocarbons samples compared to CO_2 samples collected near Biblis reactors. The mean excess is $\Delta^{14}C = + (8.3 \pm 1.4‰.)$

collected near the Würgassen and Obrigheim reactors in 1976 and near the Brunsbüttel reactor in 1977:

$$\text{mean } \Delta^{14}C_{\text{increase}} \text{ (Obrigheim 1976)} = 19 \pm 2\text{‰}$$

$$\text{mean } \Delta^{14}C_{\text{increase}} \text{ (Würgassen 1976)} = 17 \pm 2\text{‰}$$

$$\text{mean } \Delta^{14}C_{\text{increase}} \text{ (Brunsbüttel 1977)} = 19 \pm 2\text{‰}$$

These values correspond to a ¹⁴C excess of about 2 percent of the natural ¹⁴C concentration.

The results of the Obrigheim tree-ring measurements are plotted in figure 8. In accordance with the tree-leaf data, we found an average excess in the concentration of wood of $\Delta^{14}C = 27 \pm 3\text{‰}$ over the whole period, 1968 to 1978. Particularly in the years 1970, 1974, 1975, and 1978, we observed a significant excess of $\Delta^{14}C = 35 \pm 9\text{‰}$ to $49 \pm 9\text{‰}$.

To calculate ¹⁴C source strengths from the observed excess, a record of the actual atmospheric dispersion conditions during the growth period is needed. As such a record was not available to us, we tried to estimate the releases according to equation (2) using long-term dispersion factors, f, which describe the mean yearly dispersion conditions for the different sampling locations. Data was provided by H Riedel, Neuherberg, West Germany (1977, pers commun). The dispersion factors are calculated from long-term synoptical data records at the nuclear power plant sites.

$$Q = c_+/f \text{ [Ci/s]} \qquad \begin{array}{l} Q \ : \text{ source strength [Ci/sec]} \\ f \ \ : \text{ long-term dispersion factor [s/m}^3\text{]} \\ c_+ : \text{ additional } ^{14}C \text{ concentration [Ci/m}^3\text{]} \end{array} \qquad (2)$$

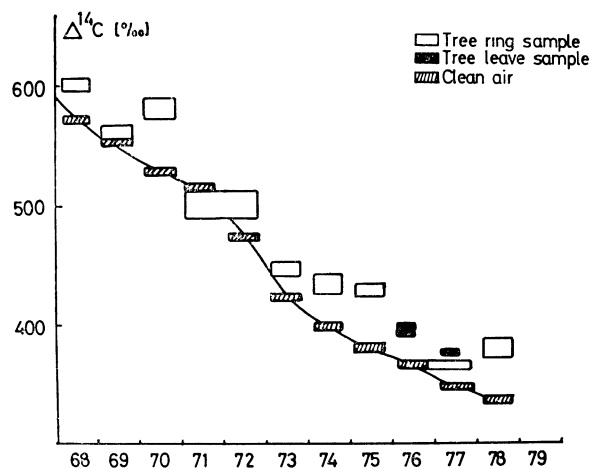Fig 8. Measured ¹⁴C concentrations of tree-ring samples collected near Obrigheim reactor (□) and tree leaf samples from Obrigheim, Würgassen, and Brunsbüttel reactor (■) compared with the mean clean air level (▨) during the growth period.

We estimated ^{14}C emissions of about 0.5 to 7Ci per year per nuclear power plant, which again agree well with direct emission measurements in the power plant stacks (Riedel and Gesewsky, 1977). Nevertheless, those estimates can only give the order of magnitude of the real ^{14}C emission because the long-term dispersion factors describe the mean dispersion condition during the whole year, which may differ considerably from the actual situation, especially if the ^{14}C release is not constant with time.

Tree leaves sampled around the Biblis reactors showed no ^{14}C increase above the clean-air level. They show a little but significant ^{14}C depression due to fossil fuel admixture. This behavior is similar to that found in CO_2 samples collected directly from the atmosphere, as discussed above. The ^{14}C depression in plant material is, however, much smaller, with an average reduction in $\Delta^{14}C$ of only $- (5 \pm 1)‰$, than it is in atmospheric CO_2 sampled during the same season, eg, spring. Reduction in $\Delta^{14}C$ in atmospheric CO_2 amounts to $- (24 \pm 1)‰$, on the average. This remarkable difference is due to the fact that CO_2 samples were collected all day, while plants, of course, only sample during the daytime when atmospheric stability is much lower and mixing is enhanced. In fact, our atmospheric mixing model correctly predicts varying fossil fuel contributions to plant material if it runs between sunrise and sunset only (Levin, 1978).

CONCLUSION

The data shows that reactor-produced radiocarbon is detectable in its environment, although the concentration is rather low in the cases
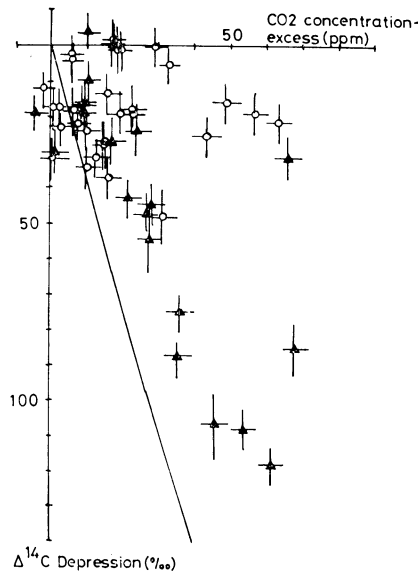

Fig 9. $\Delta^{14}C$ depression versus CO_2 concentration excess: the line represents the regression of CO_2 concentration excess and $\Delta^{14}C$ depression if caused by exclusive admixture of fossil fuel CO_2. The deviation from this line is due to admixture of soil respiration CO_2 (summer (—O—), winter (—▲—) samples.)

studied here. Air concentrations due to both reactor ^{14}C emissions as well as fossil fuel CO_2 emissions, strongly depend on the actual meteorological situation, primarily atmospheric stability. Even in a rather densely populated region, however, the source flux densities due to natural sources and sinks, soil respiration (see *cf* Dörr and Münnich, 1980) and plant assimilation during the daytime, are considerably greater than man-made ones, typically 25 to 50g CO_2/m^2 • day as compared with, for example, $15g/m^2$ • day due to fossil fuel in the Rhine-Neckar region study in this paper.

This becomes evident from figure 9 where the individual ^{14}C depression is plotted versus the observed excess in CO_2 concentration. Nearly all data points show a significantly larger CO_2 concentration excess than can be caused by the admixture of fossil fuel CO_2 (definitely known from the ^{14}C depression observed). This deviation from the fossil fuel regression line is due to admixture of plant and soil respiration CO_2. The interpretation is unambiguous since this CO_2 is not significantly different in ^{14}C from the normal atmospheric CO_2 (*cf* Dörr and Münnich, 1980). Thus, admixture of respiration CO_2 shifts the point into positive x direction only. One sees that this primarily occurs in summer when the admixture of natural CO_2 may be up to five times the fossil fuel one. The considerable variations in atmospheric CO_2 concentration observed (a range of about 30ppm, *ie,* 10 percent of the average atmospheric concentration, during the same day is often found in the summer even in a flat unforested area about 20m above ground) are primarily due to natural sources even in densely populated areas. Therefore, we now try to model these variations in a similar way to the one reported here. In this context, a simultaneous study of atmospheric CO_2 and atmospheric radon-222 seems to be very helpful.

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DISCUSSION

Loosli: You estimate admixtures of fossil fuel CO_2 to your weekly samples by using an atmospheric dispersion model. How precise are these estimated values and which sources are included in this error?

Levin: The coefficient of the calculated regression line from the correlation between model estimated and measured admixtures show an error of at least 30 percent. Due to the uncertainty in the synoptical data and the resulting diffusion parameters, an appreciably larger error (factor of 2) should be expected.

Haas: The soil gases reflect the type of vegetation growing in the area, *ie*, C-3 or C-4 type plants. In the USA, a range of $\delta^{13}C$ from $-17\%_0$ to $-26\%_0$ was observed according to plant types growing in Texas or North Dakota, respectively.

Levin: Our own measurements from this region show $\delta^{13}C$ values of soil respiration CO_2 of about $\delta^{13}C = -25\%_0$.

Siegenthaler: Through simultaneous ^{14}C *and* ^{13}C measurements the relative contributions of fossil and of respiration CO_2 could be estimated. How does this apply to your results on atmospheric CO_2?

Levin: We calculated the respiration CO_2 mixing ratio from a comparison of $\Delta^{14}C$ and measured CO_2 concentration (Levin, 1978). This led to admixtures about 3 times of the fossil fuel admixture in summer and

about the same as in winter time. Similar estimates could be made by simultaneous ^{13}C and ^{14}C measurements.

Fritz: Have you any information on ^{14}C variations with distance from a ^{14}C-emitting nuclear power station and have you compared ^{14}C with ^{3}H data?

Levin: 1) In tree-leaf samples from the environment of Würgassen and Obrigheim reactors we have measured ^{14}C increases only in the main wind direction and up to a distance of about 5km.

2) We have measured tritium in the washbottle water of the sampling system near the Biblis reactors and have not found unusual increases compared to the natural concentration.