Tellus (1987), *39B*, 21–28

Atmospheric CO_2 in continental Europe—an alternative approach to clean air CO_2 data

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(Manuscript received November 28, 1985; in final form April 30, 1986)

ABSTRACT

A 5-year record of continuous atmospheric CO_2 concentration data from the Schauinsland mountain top station (48°N, 8°E, 1205 m a.s.l.) is analysed for contributions from different continental sources, e.g., fossil fuels and by the natural biosphere. The fossil fuel contribution is determined from monthly averages of parallel carbon isotope data (^{14}C, (^{13}C)) collected from 1977 to 1984. The observed short-term fluctuations are identified as "local contamination" with help of continuous atmospheric ^{222}Radon data from the same location. The combination of all tracer data, carbon isotopes and ^{222}Radon activity, in addition to CO_2 concentration makes it possible to evaluate a CO_2 concentration record representative for "*continental clean air*" not influenced locally by natural and anthropogenic sources. Comparison of the processed record with CO_2 data from a marine station (Ocean Weather Station P, 50°N, 145°W) (Wong et al., 1984) shows a significant phase shift at the continental compared to the marine site. This is attributed to the continental biosphere acting as a *net sink* in early summer (April to June) and as a *net source* in autumn and winter (October to January).

1. Introduction

In view of its climatic implications, the study of global atmospheric CO_2 concentrates on background observations at remote sites, delivering the presumably most representative input data for global carbon cycle models. Equally important information, however, can be drawn from continuous CO_2 observations at "contaminated" sites if parallel data records of certain "tracers" are available which allow identification of the different CO_2 sources and parameterization of atmospheric transport.

Measurements of the $^{13}C/^{12}C$ isotopic ratio in atmospheric CO_2 give the possibility to distinguish between atmosphere-biosphere and atmosphere-ocean CO_2 exchange: due to *strong* isotopic fractionation during CO_2 *uptake* by living plants ($\delta^{13}C \approx -18‰$), and *no* fractionation during CO_2 *release* from the biosphere, CO_2 concentration variations caused by biogenic activity are coupled with considerable ^{13}C variation. This is not the case for concentration variations caused by atmosphere-ocean exchange showing only very little kinetic fractionation (Siegenthaler and Münnich, 1981).

^{14}C analysis is used to quantitatively determine the contribution of fossil fuel CO_2 at the sampling site: any contamination by anthropogenically produced ^{14}C free CO_2 will cause a ^{14}C depletion in the sample CO_2.

Continuous atmospheric ^{222}Radon measurements are used to determine the coupling between atmospheric concentration and ground level sources. The radioactive noble gas ^{222}Rn ($t_{1/2} = 3.8$ days) is produced only on the continent (source strength ≈ 0 over the ocean) by radioactive decay of ^{226}Radium and is released nearly homogeneously by all soils. Thus atmospheric ^{222}Rn activity is a good parameter for the "contact time" of air with ground-level sources.

The purpose of this paper is to illustrate the power of accompanying tracer data in atmospheric CO_2 studies. Applying these tracers, the CO_2 concentration data observed at the BAPMon station Schauinsland, are used to

evaluate a CO_2 record representative for "continental air" over Central Europe, i.e., continental air not *directly* (locally in space and time) influenced by the continental biosphere or by fossil fuel pollution.

2. Sampling site

The Schauinsland station is located in southern Germany in the Black Forest on the mountain top Schauinsland (48°N, 8°E) at 1205 m a.s.l. With an elevation about 1000 m above the regional level (e.g., the broad Rhine valley), it is usually above the ground level inversion layer during night, but within the ground level boundary layer during day-time. The station is an isolated house with electric heating only. Only occasional contamination from local traffic (station personnel) occurs. The sample air is collected from a heated stack with its air inlet ~ 5 m above the ground. The station is surrounded by meadows and woods; during winter the ground is largely snow covered.

3. Experimental and calibrations

3.1. CO_2 concentration

Continuous atmospheric CO_2 concentration measurements, being part of the BAPMon network (Background Air Pollution Monitoring network) (Manning, 1982), were started in 1967. The station is now operated by the German Federal Environment Agency. During the period 1974 till September 1982, an NDIR URAS 2 (Hartmann & Braun, Frankfurt, FRG), and from October 1982 till the present time, an Ultramat 3 (Siemens, Karlsruhe, FRG) was used. During the whole period of observation, CO_2 in N_2 reference gases calibrated by the Scripps Institution of Oceanography (1959 Adj. Index Scale) have been used. The data reported here are corrected for carrier gas effect and converted to the WMO-1974 scale. The carrier gas correction is based on a preliminary experimental comparison carried out for the two analysers as described by Levin (1984). The accuracy of the CO_2 concentration data (analysis and conversion to the WMO-1974 CO_2/air scale) is $\approx \pm 2$ ppm.

3.2. Carbon isotopes

^{14}C and ^{13}C analysis has been performed on about two-weekly integrated CO_2 samples continuously collected by quantitative absorption in sodium hydroxide solution. After transfer to the Heidelberg laboratory, CO_2 has been extracted from the solution in a vacuum system by adding hydrochloric or sulfuric acid. For the ^{14}C analysis, CO_2 gas is purified over charcoal and counted in a high precision proportional counter system. From small aliquots of the NaOH solution, CO_2 is extracted quantitatively and the $^{13}C/^{12}C$ ratio is measured by mass spectrometry. All sampling and laboratory procedures are described in greater detail by Levin et al. (1980), Schoch et al. (1980), and Dörr and Münnich (1980).

All ^{14}C activities are expressed as the permill deviation ($\Delta^{14}C$ (‰)) from the NBS oxalic acid activity corrected for decay (Stuiver and Polach, 1977). As all sampling as well as laboratory procedures have been made quantitatively, the Δ-values presented here are not corrected for fractionation using individual $\delta^{13}C$-values. To allow a direct comparison with plant material ($\delta^{13}C \approx -25‰$), they have been corrected to a $\delta^{13}C = -25‰$ assuming all samples having a $\delta^{13}C = -8.08‰$ (mean value of all samples in the period from 1977 to 1985). The precision (1σ) of a single ^{14}C analysis is typically $\Delta^{14}C = \pm 4‰$.

All $^{13}C/^{12}C$ isotopic ratio values are expressed as the permill deviation from the international PDB standard: $\delta_{PDB}{}^{13}C$ (‰) (Craig, 1957). For scale comparison with $\delta^{13}C$ data by other laboratories (compare Gonfiatini, 1984) we quote the $\delta^{13}C$ results obtained by the Heidelberg laboratory on various isotope standards: NBS-16: $-41.57‰$; NBS-17: $-4.51‰$; NBS-18: $-5.07‰$; NBS-19: $+1.83‰$. As the CO_2 sampling technique by chemical absorption in sodium hydroxide solution is specific for CO_2, in contrast to a cryogenic extraction, the $\delta^{13}C$ values presented here need not be corrected for N_2O contributions; they rather represent the real $^{13}C/^{12}C$ ratio of atmospheric CO_2. The precision (1σ) of a ^{13}C analysis is typically $\delta^{13}C = \pm 0.05‰$.

4. Results and discussion

Monthly mean CO_2 concentrations at the Schauinsland station observed from 1974 to 1984

are shown in Fig. 1 (Grosch et al., 1981; Grosch, pers. comm.).

As will be shown later (compare Figs. 5 and 6), the seasonal variation seen in this record is basically the one generally observed in the zonal band of this latitude (Conway, 1985, pers. comm.). Due to the comparatively small net flux into or out of the sea, the CO_2 concentration observed over the ocean (Wong et al., 1984) even at ship's level is not much modulated by air-sea exchange. This is different over the continent where the CO_2 flux to and from the plant cover is larger by about an order of magnitude. Therefore, here we have to be careful not to be mislead by only local effects of the biosphere or even by pollution.

The CO_2 variation observed at the Schauinsland station can conveniently be sorted into three scale classes:

(1) the whole latitude belt;
(2) the European continent;
(3) the immediate neighbourhood.

A CO_2 source contribution to each of these scale classes can further be classified as being due to (a) the biosphere, and (b) to fossil fuel combustion. Each direct source/sink contribution evidently decreases with the (vertical as well as horizontal) distance from the source or sink.

We first show by the correlation in Fig. 2 that all concentration variations observed at the Schauinsland are basically of "biogenic" nature. A linear regression of $\delta^{13}C$ and the reciprocal CO_2 concentration leads to a $\delta^{13}C_s$ of the source CO_2 of -25.7 ± 1.4‰. Similar source values have been observed by Friedli et al. (1987) over Switzerland. The calculated $\delta^{13}C$ value is very close to the isotopic ratio of the living biosphere (Vogel, 1980), but also not far from fossil fuel CO_2: $\delta^{13}C = -27$ to -28‰ (Tans, 1981).

Having thus shown the non-ocean origin of the CO_2 variations, we do not use ^{13}C any further.

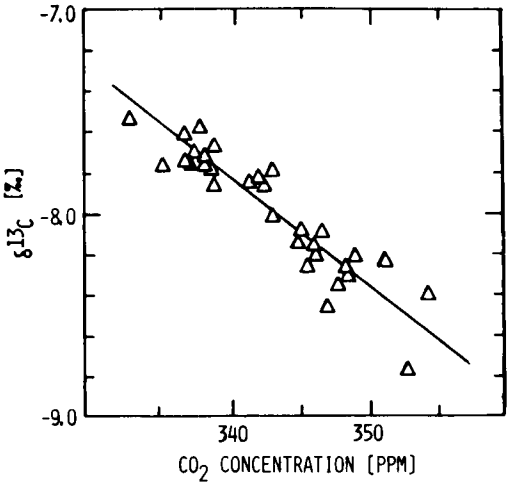

Fig. 2. Relation between $\delta^{13}C$ and CO_2 concentration: the straight line is a calculated least squares fit through the data points: $\delta^{13}C = 6083/c_{CO_2} - 25.7$ (‰).

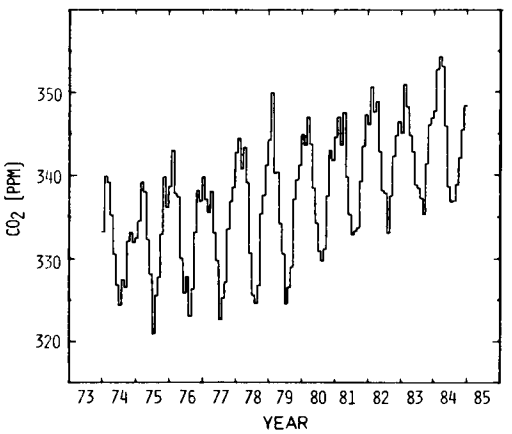

Fig. 1. Atmospheric CO_2 concentration observed at the BAPMon station Schauinsland (48°N, 8°E) (Grosch et al., 1981; Grosch, pers. comm.).

4.1. Contributions from fossil fuel sources

The CO_2 "contamination" by fossil fuel combustion is sensitively determined by ^{14}C analysis of the atmospheric CO_2. Continuous measurements have been made since 1977. The result is shown in Fig. 3. The tropospheric ^{14}C level is still generally decreasing due to atmosphere-surface ocean equilibration of the pre-1962 nuclear weapon ^{14}C spike in the atmosphere (Levin et al., 1985). Significant summer/winter variations with a peak to valley distance of up to $\Delta^{14}C = 20$‰ (spline curve in Fig. 3; Reinsch, 1967) are superimposed on this decrease, with presently about 15‰ per year. The pre-1980 data—particularly those from 1978—may still be influenced by artificial ^{14}C originat-

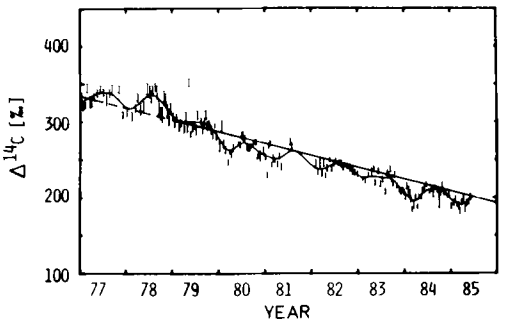

Fig. 3. ^{14}C activity in atmospheric CO_2 at the Schauinsland site. The seasonal variations (spline curve) are mainly due to a seasonally varying European "Suess effect". The straight line is the proposed northern hemisphere ^{14}C clean air level (Levin et al., 1985).

ing from the most recent Chinese bomb tests. The ^{14}C modulation from 1980 onwards is, however, mainly due to seasonal variation of fossil fuel CO_2 over the European continent. We propose to use the straight line "upper envelope" of the observed data to represent the ^{14}C level of this latitude (e.g., to be measured over the ocean) for the period from 1980 onwards. Any negative deviation from this line (straight line in Fig. 3) is interpreted as an admixture of ^{14}C free fossil fuel CO_2. The position of this line, i.e., the undisturbed ^{14}C level has been checked by comparing continuous SO_2 concentration data from the Schauinsland site (data by courtesy of the Federal Environment Agency, Grosch, pers. comm.): a linear correlation of anthropogenic SO_2 and CO_2 simultaneously produced by burning of fossil fuels yields an approximately zero intercept of the regression line if the "undisturbed" ^{14}C level has been determined correctly. Further justification of the level chosen here comes from a comparison with recent ^{14}C data at the maritime baseline station Tenerife (Schmitt and Levin, 1985).

The mean monthly fossil fuel contribution to the Schauinsland station CO_2 record (Fig. 1) identified by the depression of the ^{14}C level is shown in Fig. 5B. The mean "contamination" amounts to about 1–2 ppm in summer and about 3–4 ppm in winter months. These values turn out surprisingly low in view of the fact that Central Europe is one of the strongest fossil CO_2 source regions!

4.2. Contribution from local biogenic sources

As indicated already, the CO_2 concentration measured at the mountain top Schauinsland is influenced by local sources from the immediate neighbourhood as well as by larger scale sources from the European continent. Direct source influence *on the average* decreases regularly with increasing distance from the ground and its plant cover. This can be formulated mathematically by introducing a *time independent* diffusion constant increasing with the distance from the ground. If we use an average vertical diffusion constant of $5 \cdot 10^4$ cm^2/s (Machta, 1974), we get an exponential decrease of ground influence with altitude at a scale height of about 1 km *on the average*. However, the daily variation of vertical mixing is very pronounced, and, due to strong mixing in the middle of a clear day in summer, we may find nearly "continental clean air" even at ground level, whereas here at night the ground source influence is very extreme. At about 1 km above ground in the *free atmosphere* on the other hand, the concentration observed during night practically represents the soil and plant contribution of a more extended area of the continent only. This is also true for an exposed site on a mountain top of about this altitude: during night, efficient radiative cooling of the ground produces cool air which flows down the mountain slopes and sucks fresh air from aloft.

For the Schauinsland site, this typical behavior is illustrated by the atmospheric radon record (Civil Defense Agency, Institute of Atmospheric Radioactivity, W. Weiss, pers. comm.). A strong concentration peak before sunrise is observed in the Rhine valley (Fig. 4C), in contrast with nearly constant, slightly decreasing Rn activity on the mountain top (Fig. 4B). This record further shows a pronounced peak around noon which is explained as the passage of radon accumulated in the valley during the preceding night, now being lifted by radiative heating and dispersed. The corresponding behaviour is seen in the CO_2 concentration record (Fig. 4A): we observe nearly constant concentration during night and a "noon peak" of soil and plant respiration CO_2 also stored in the Rhine valley during the preceding night (compare Dörr et al., 1983) and now lifted to the mountain level and dispersed. Contrary to radon, the CO_2 concentration is also influenced by very local plant

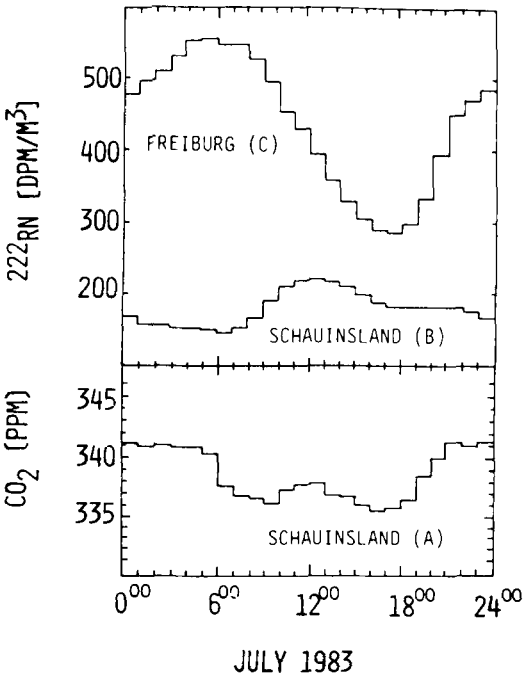

Fig. 4. (A) Mean diurnal cycle of atmospheric CO_2 observed at the Schauinsland mountain top in July 1983. (B) Mean diurnal ^{222}Rn activity observed during the same period at the same site as (A) (Weiss, pers. comm.). (C) Mean diurnal ^{222}Rn activity observed during the same period as (A) and (B) in Freiburg in the Rhine valley about 1000 m below the mountain station (Weiss, pers. comm.). Soil born tracers (e.g. CO_2 and ^{222}Rn) are accumulated in the Rhine valley inversion layer during night, and are transported to higher altitude and diluted in the morning. They lead to a concentration peak at the Schauinsland site around noon.

assimilation (steep concentration decrease after sunrise). This is due to the fact that the air intake at the Schauinsland station is only about 5 m over ground and not high enough to reach above the neighbouring wood.

This general behaviour of the daily variation of atmospheric CO_2 at the mountain station Schauinsland is in agreement with experience obtained elsewhere (e.g., on Hawaii; Mendonca (1969) and on Tenerife; Schmitt and Levin (1985)).

4.3. Central Europe clean air CO_2

The monthly mean CO_2 concentrations as observed at the Schauinsland sampling site (Fig. 1) can now, with the information basically drawn from the parallely observed radon data, be adjusted for the two contamination components, namely fossil fuel and local biogenic contributions, evaluated above.

Correction for the local plant assimilation, which actually means restricting the data-to-night values only, needs a positive adjustment of the observed mean data during the vegetation period (Fig. 5C). Of course, we still have to correct for the fossil fuel component: from the (daily integrated) ^{14}C data we can only determine the (daily) mean fossil fuel contamination. In this correction, we strictly should adjust the nighttime CO_2 concentration data for their fossil fuel contribution at night time only. However, correcting instead for the *daily mean* fossil fuel contribution makes a small error only: the maximum $\Delta^{14}C$ difference between the Rhine valley source region and the Schauinsland (as observed during winter time only) is about

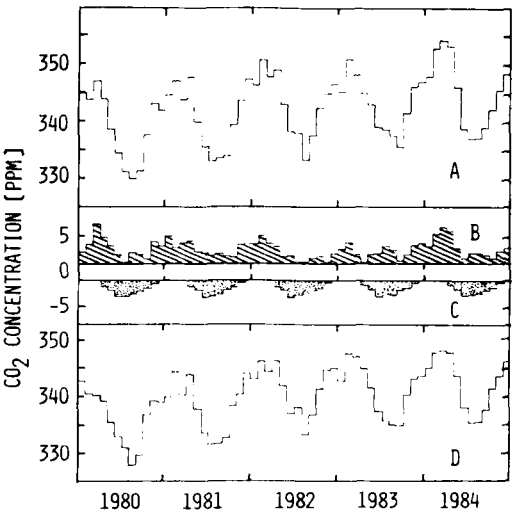

Fig. 5. (A) Monthly mean CO_2 concentration as observed at the Schauinsland station (same as Fig. 1). (B) CO_2 contribution from fossil fuel sources derived from the ^{14}C depletion form the proposed ^{14}C clean air level. (C) CO_2 depletion caused by local plant assimilation. (D) CO_2 record (A) corrected for contributions from fossil fuel sources (B), and assimilation sink (C) proposed to be representative for "clean air" CO_2 concentration over Central Europe.

$\Delta^{14}C \approx 100‰$ (see Levin et al., 1980). A 1% (3 ppm) fossil fuel contamination *difference* between day and night would thus be accompanied by a $\Delta^{14}C$ difference between day and night of only 1‰, which is not detectable within our limits of accuracy. We therefore use the *daily integrated* ^{14}C data to correct for fossil fuel CO_2 (Fig. 5B).

The thus corrected CO_2 concentration is plotted in Fig. 5D: this CO_2 record is now supposed to be representative for "continental clean air" over Central Europe. Note that this record includes all meteorological conditions, continental and marine air masses; it represents the *mean* to be observed in the boundary layer between 1000 and 1500 m above ground at this specific geographic location at about 800 km distance from the coast. This record can now be used as *continental* background data for global carbon cycle models.

The typical error of the individual determinations of the monthly mean fossil fuel contamination is about ± 1–1.5 ppm. Correction for the local biogenic perturbations (restriction to night values) only causes a small additional error (± 0.5 ppm) in the determination of the continental clean air level defined above.

The corrected CO_2 concentration record in Fig. 5D still contains some large-scale influence of the biosphere over the European continent: Fig. 6 compares the adjusted Schauinsland concentration data derived before with a CO_2 record observed at a marine site, Ocean Weather Station P (50°N, 145°W) (Wong et al., 1984). (Unfortunately, during the period from 1980 to 1984 just discussed in detail above, there is only a 1½ years overlap of observations.) Although the yearly mean concentrations in 1980 turn out nearly equal at both stations lying in the same latitudinal band (Schauinsland: 337.3 ppm; Weathership P: 337.8 ppm), there is a significant "phase shift" between the two records. This can be interpreted as the influence of the biogenic source-sink seasonal pattern at the continental site.

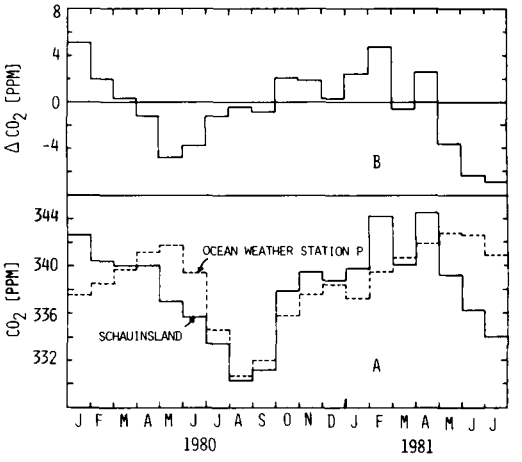

Fig. 6. (A) Monthly mean concentrations of atmospheric CO_2; solid line: at the Schauinsland station corrected according to FIg. 5; dashed line: observed at Ocean Weather Station P (Wong et al., 1984). (B) Monthly mean concentration difference between the two stations.

4.4. Estimate of the net biogenic CO_2 flux on the European continent

The monthly mean concentration difference between the two sampling sites plotted in Fig. 6B can be converted to monthly mean CO_2 flux values using additional information offered by the parallel monthly mean radon concentration observed at the Schauinsland by Weiss (pers. comm.). The radon activity of an airmass coming from the ocean and starting with zero activity increases with the time the air spends over the continent. Thus, the atmospheric radon activity links the soil-borne tracer sources to their concentration contribution observed in the atmosphere. Assuming the radon flux from the soil being homogeneous (and constant with time $j_{Rn} = 4000$ dpm m^{-2} h^{-1}; the observed variations fall into a range of a factor of two between the extremes—sandy or loamy soils; Dörr, 1984), we can calculate the net CO_2 flux (assumed to be homogeneous as well, but changing sign in the course of the year) based on the observed CO_2 concentration deviation (Fig. 6B) and the parallel observed radon activity from the following equation (we assume the CO_2 sources and sinks to be negligible over the ocean):

$$j_{CO_2} = c_{CO_2}/c_{Rn} \times j_{Rn} \qquad (1)$$

where $j_{CO_2} = CO_2$ flux; $j_{Rn} = {}^{222}Rn$ flux; $c_{CO_2} = CO_2$ concentration difference at Schauinsland-Station P; $c_{Rn} = {}^{222}Rn$ concentration.

The result of this simple estimate is shown in Fig. 7: during winter, the continent acts as a net

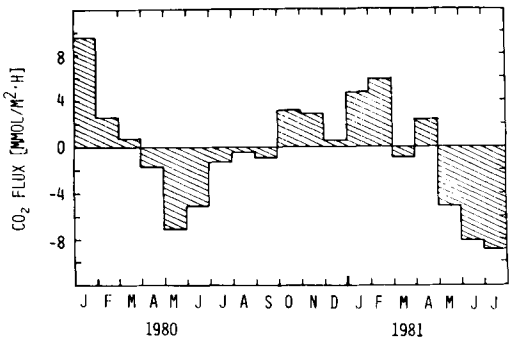

Fig. 7. Monthly mean biogenic CO_2 flux calculated according to (1) from the CO_2 concentration difference between the continental and the marine site (Fig. 6B), the mean ^{222}Rn concentration observed at the Schauinsland (Weiss, pers. comm.), and a homogeneous ^{222}Rn flux density of 4000 dpm m^{-2} h^{-1} (Dörr, 1984).

source for biogenic CO_2, during spring and late summer soil respiration and plant assimilation nearly cancel each other. A significant net sink is only observed in early summer during May to July. The absolute values of the winter time CO_2 flux estimated here (considering possible radon flux inhomogenities serious only within $\pm 50\%$) should be compared with direct soil respiration measurements performed by Dörr and Münnich (1987) in the southern part of Germany: fluxes between 2 and 4 mMol m^{-2} h^{-1} are rather commonly observed even in the cold period of the year in our temperate climate.

5. Conclusions

A supposedly uninterpretable record of continuous atmospheric CO_2 concentration data has been discussed. Local biogenic activity, leading to an additional amplitude of about 3 ppm in the yearly cycle, has been eliminated as well as the general European fossil fuel CO_2 level amounting to about 1–2 ppm in summer and 3–4 ppm in winter. The resulting supposedly representative concentration cycle to be observed in "clean air" over the continent in Central Europe shows special features, indicating the seasonal character of the continental biosphere activity, which has already been expected, considering the spatial distribution of continents and oceans in this latitudinal belt (40–50° N).

6. Acknowledgements

This study was partly funded by the Federal Minister of the Interior, Bonn, and the German Federal Environment Agency, Berlin. I am grateful to the staff of the BAPMon station Schauinsland for their help in obtaining the CO_2 samples for isotope analysis, and especially R. Graul for his cooperation in a preliminary intercalibration and determination of the carrier gas effect. I wish to thank W. Bischof for calibrating our CO_2/air standard gases; W. Grosch, Federal Environment Agency, Frankfurt, supplied the actual CO_2 concentration data. W. Weiss, Federal Civil Defense Agency, Institute of Atmospheric Radioactivity, Freiburg, supplied the $^{222}Radon$ concentration data of the Schauinsland site. I wish to thank all colleagues of the Heidelberg ^{14}C dating and the ^{13}C mass spectrometer laboratories for their careful work performing the numerous ^{14}C and ^{13}C analyses. W. G. Mook and I. Olsson are gratefully acknowledged for valuable discussions. I also wish to thank U. Siegenthaler and one anonymous reviewer for their helpful suggestions. Special thanks are to K. O. Münnich who was always available for extensive discussions.

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