

Long-term observations of atmospheric CO₂ and carbon isotopes at continental sites in Germany

By INGBORG LEVIN*, ROLF GRAUL¹ and NEIL B. A. TRIVETT², *Institut für Umweltphysik, University of Heidelberg, Germany*; ¹*Umweltbundesamt, Meßstelle Schauinsland, Germany*; ²*Atmospheric Environment Service, Toronto, Canada*

(Manuscript received 20 December 1993; in final form 1 August 1994)

ABSTRACT

A network for regional atmospheric CO₂ observations had already been established in Germany by 1972, consisting of 5 stations with basically different characteristics: Westerland, a coastal station at the North Sea, 2 regional stations, Waldhof and Deuselbach, as well as 2 mountain stations, Brotjacklriegel at the eastern boarder of Germany and Schauinsland in the Black Forest. In addition to CO₂ concentration observations, from 1977 onwards quasi-continuous ¹³CO₂ and ¹⁴CO₂ measurements were performed on samples from the Schauinsland site, and for the short period 1985–1988, ¹⁴CO₂ measurements were also made on Westerland samples. CO₂ data selection based on wind velocity allows for an estimate of the representative continental CO₂ level over Europe. The peak-to-peak amplitude of the seasonal cycles is between 12.1 ppmv (Schauinsland) and 17.6 ppmv (Waldhof). The phase of the seasonal cycles at the German sites is shifted if compared to maritime background sites with the concentration maxima occurring already between beginning of February and beginning of April, the minima in August. The long-term mean CO₂ increase rate in the last 20 years at Westerland and Schauinsland is 1.49 and 1.48 ppmv yr⁻¹, respectively. The mean $\delta^{13}\text{C}$ of the seasonal source CO₂ at Schauinsland is calculated from unselected $\delta^{13}\text{C}$ and CO₂ data to be -25.1‰ . From the ¹⁴C observations in unselected CO₂, we derive yearly mean fossil fuel contributions at Westerland of 4 ppmv, and at Schauinsland of only 2.5 ppmv. Based on the seasonality of the fossil fuel CO₂ component at Schauinsland and on concurrently observed atmospheric ²²²Radon activities, we derive a seasonal amplitude of the fossil fuel CO₂ source which is higher by a factor of 3 compared to emission estimates for Europe.

1. Introduction

Since the pioneering measurements of atmospheric CO₂ started by Keeling in 1957/58 at Mauna Loa, Hawaii, and at the South Pole (Keeling et al., 1989), numerous sites for CO₂ monitoring have been established all over the world (Tans, 1990). The principal aim of this global network is to document the abundance of CO₂ in the remote atmosphere, and to gain a better insight into the sources and sinks of this important atmospheric greenhouse gas, by using

the spatial and temporal variations of CO₂ in combination with atmospheric transport models. One shortcoming of the present global CO₂ network is, however, the lack of representative observations over the continents. The CO₂ climatology in the remote maritime atmosphere seems to be well documented today, which allows for budgeting the large-scale CO₂ fluxes between atmosphere and the surface reservoirs (oceans and terrestrial biosphere) to within $\pm 20\%$. A better quantification of the uptake of anthropogenic CO₂ by different reservoirs, however, needs an improved knowledge of the sources and sinks on smaller scales, and particularly of the diverse terrestrial biosphere. One approach to gain this

* Corresponding author.

information uses observations over continents describing the CO₂ climatology on the continental or even the regional scale.

A German network of regional atmospheric CO₂ observations has been established since 1972 (see Fig. 1). This network consists of five stations with basically different characteristics: The northernmost station Westerland (55°N, 8°E, 8 m a.s.l.) is situated on the island Sylt in the North Sea. Particularly during northwesterly winds, the air collected here most directly represents maritime conditions in this latitudinal belt. The stations Waldhof (53°N, 11°E, 73 m a.s.l.), in a flat agricultural area of northern Germany, and Deuselbach (50°N, 7°E, 480 m a.s.l.), in a hilly terrain at the western border of Germany are strongly influenced by regional biogenic and anthropogenic sources or sinks. Their diurnal CO₂ cycle is also strongly modulated by the changing stability of the atmospheric boundary layer. The mountain stations Brotjacklriegel (49°N, 13°E, 1016 m a.s.l.) at the eastern border of Germany, and Schauinsland (48°N, 8°E, 1205 m a.s.l.) in the Black Forest in south west Germany are less influenced by contamination through local sources. In particular the Schauinsland station, during moderate or strong winds is shown to be representative for mean atmospheric CO₂ conditions over Western Europe at this elevation of about 1000m above mean sea level.

In addition to continuous concentration observations, from 1977 onwards quasi-continuous

¹³CO₂ and ¹⁴CO₂ measurements were made at the Schauinsland site. For the period of about two years ¹⁴CO₂ measurements are also available for the station Westerland. These supplementary isotopic data provide insight into the nature of the dominant sources and sinks—biogenic or anthropogenic—influencing the station in question.

The complex problems and the challenges associated with the interpretation of highly variable continental CO₂ and isotope records are discussed in this paper. The aim is to develop a method of interpretation and selection of continental CO₂ data. Finally, representative continental data records for the Schauinsland and the Westerland station will be provided, and made available for validation of regional as well as global scale carbon cycle models.

2. Techniques

2.1. CO₂ concentration measurements

Continuous atmospheric CO₂ measurements by NDIR were performed with URAS-2 (Hartmann & Braun) analysers at all five sites till 1982. From there on, Ultramat-3 (Siemens) analysers were used. CO₂-in-N₂ calibration gases provided by the Scripps Institution of Oceanography (SIO) were used (1959 Adj. Index Scale) until 1991. The standards in the concentration range of 290–355 ppmv were recalibrated with CO₂-in-N₂ calibration gases in the concentration range of 290–375 ppmv kindly provided by NOAA/CMDL. This allowed us to transfer all our concentration values into the WMO 1985 CO₂-in-N₂ scale. A linear transformation function was used:

$$c(\text{WMO 1985}) = c(\text{1959 adj. ind.}) \times 1.0404 \\ - 12.86 \text{ [ppmv]}. \quad (1)$$

From 1992 onwards, CO₂-in-synthetic-air mixtures, calibrated by SIO in 1990 (WMO 1987 mole fraction scale) have been used in the network. All data obtained by URAS-2 and Ultramat-3 instruments with CO₂-in-N₂ gases had to be corrected for carrier-gas-effect (Griffith et al., 1982). The carrier-gas-effect of one URAS-2 instrument which was still available in the network has been determined experimentally using CO₂-in-N₂ (WMO

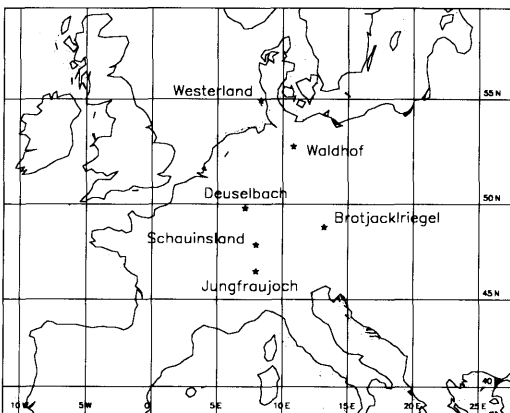


Fig. 1. Map of Central Europe with CO₂ and carbon isotope measurement sites.

1985 scale) and CO₂-in-air (WMO 1987 mole fraction scale) gases:

$$c_{\text{URAS}}(\text{WMO 1987}) = c_{\text{URAS}}(\text{WMO 1985}) + 4.39 \text{ [ppmv]}. \quad (2)$$

The correction function (2) has then been applied to all records derived with URAS-2 instruments (the same correction was used at all 5 stations).

For the Ultramat-3 instruments individual carrier gas corrections have been applied on the basis of experimental determinations. The five analysers and one additional instrument of the Institut für Umweltp Physik fell into two groups showing carrier gas effects differing by 0.5 ppmv over the concentration range of 320–360 ppmv. For the stations Schauinsland, Westerland, and Brotjacklriegel the correction function

$$c_{\text{Ultramat}}(\text{WMO 1987}) = c_{\text{Ultramat}}(\text{WMO 1985}) \times 1.0044 + 1.882 \text{ [ppmv]} \quad (3)$$

was used. For Deuselbach and Waldhof the correction function

$$c_{\text{Ultramat}}(\text{WMO 1987}) = c_{\text{Ultramat}}(\text{WMO 1985}) \times 0.999 + 4.47 \text{ [ppmv]} \quad (4)$$

has been applied to all measurements performed with this instrument from 1982–1991. The errors associated with the scale and carrier gas corrections are estimated to be less than ± 0.5 ppmv. The overall precision of daily mean concentration values is estimated to be ± 1 ppmv.

2.2. Isotope measurements

Carbon isotope measurements have been performed on large volume CO₂ samples continuously collected by dynamic quantitative absorption of atmospheric CO₂ in carbonate free sodium hydroxide solution. ¹³C analyses of the CO₂ are by mass spectrometry, ¹⁴C analyses by high precision proportional counting of the purified CO₂ sample. All sampling and analysis procedures are described by Levin et al. (1980) and Schoch et al. (1980). $\delta^{13}\text{C}$ values are given relative to the V-PDB standard (Hut, 1987), the overall precision of a single analysis is typically $\pm 0.1\text{‰}$. $\Delta^{14}\text{C}$ data

are given relative to NBS oxalic acid activity corrected for decay (Stuiver & Polach, 1977), the precision of a single $\Delta^{14}\text{C}$ measurement is typically $\pm 5\text{‰}$.

3. Results and discussion

3.1. Diurnal concentration variations

The CO₂ climatology of the 5 stations can be derived from their short term (diurnal) CO₂ concentration variability, and from their absolute concentration level compared to background conditions. Fig. 2 shows the typical mean diurnal cycles at all 5 stations for January, April, July, and September, calculated from *unselected* hourly mean values during the period of 1973–1980. The straight solid lines represent the monthly mean values calculated for the same period from the *selected* Schauinsland data, assumed to represent the respective background concentration level over Western Europe. During the winter months (c.f., Fig. 2a), we observe almost no diurnal cycle at any of the stations. The two mountain sites show a mean concentration level which is only several ppmv higher than the respective background level. The mean concentration increases towards low elevation sites, and is highest at Waldhof, probably due to frequent strong ground level inversions at that site.

During spring, and more pronounced during the summer months, the stations Waldhof and Deuselbach experience large diurnal cycles with mean night time concentrations rising up to 50 ppmv above the assumed background level. The daytime values at these sites are only slightly lower than the background concentration. This behaviour is a consequence of the large diurnal variation of vertical mixing in the continental boundary layer, particularly during summer, in combination with maximum CO₂ fluxes from soil and plant *respiration*. Obviously, the signal of the ground level plant *assimilation* sink during daytime is strongly weakened by enhanced vertical mixing. At the mountain sites Schauinsland and Brotjacklriegel the behaviour is just opposite: night time concentrations are close to the background level whereas the daytime concentration values, due to the influence of local vegetation on the upslope winds, are depleted in their CO₂ concentration. This behaviour of the diurnal

CO₂ cycle is a common phenomenon generally observed at mountain sites (Schmitt et al., 1988).

The diurnal CO₂ cycles at the coastal station Westerland show amplitudes which are between those observed at the regional sites Waldhof and Deuselbach and those at the two mountain sites. Here we have basically two meteorological regimes, maritime or continental. The maritime air masses show background concentration levels whereas the continental air masses typically show similar diurnal amplitudes as observed at the two regional sites.

From this CO₂ climatology it seems obvious that only the two mountain sites Schauinsland and Brojtackriegel are potential candidates for selecting CO₂ concentration data representative for the large scale continental CO₂ level over Western Europe. Westerland also experiences background concentrations when the wind is off the North Sea, which are comparable to observations over the North Atlantic.

3.2. Long-term CO₂ records: data selection

As could already be inferred from the mean diurnal cycles, due to the influence from continental sources and sinks the unselected monthly mean CO₂ concentrations at all 5 stations deviate considerably from background conditions. During high wind speeds, and thus strong atmospheric mixing conditions, the observations even at regional sites become more representative of a larger area. As a first step towards more representative data records, the raw hourly values have been selected for high wind speeds. The typical wind velocity distribution differs very much from station to station; individual criteria have thus been used at the 5 sites (see Table 1). Hourly CO₂ values were assumed as representative for a site when the wind velocity was higher than the long term mean seasonal value at the station in the summer or in the winter half-year, respectively. Daily mean values and standard deviations (1σ) have then been calculated from the selected hourly

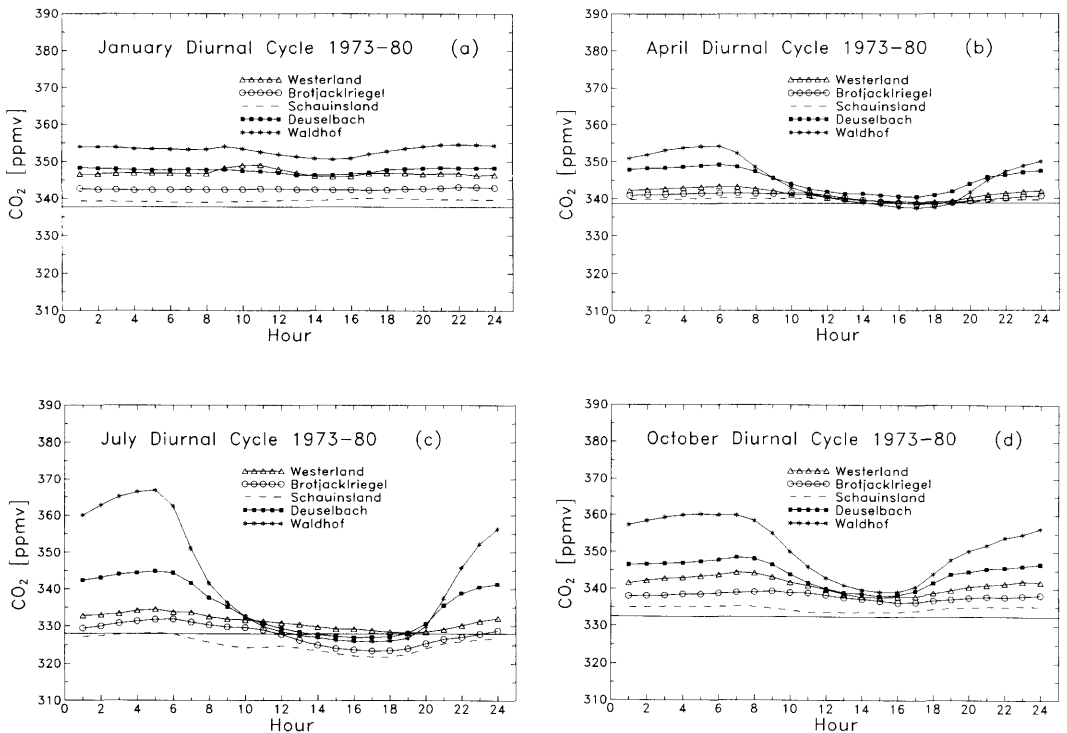


Fig. 2. Mean diurnal cycle of unselected atmospheric CO₂ at the 5 German sites calculated for the period of 1973–1980 for January (a), April (b), July (c), and October (d). The straight solid lines represent the respective background level over Europe determined from the selected Schauinsland data (compare Fig. 4a).

Table 1. Selection criteria for "background data" and parameters of the selected CO₂ records from the German stations

Station	Minimum velocity [m s ⁻¹]		% of "background" observations	Peak to peak amplitude [ppmv]	Seasonal Cycle	
	summer	winter			max. [day No.]	min. [day No.]
Waldhof	2.0	2.5	11.1	17.6	31	217
Deuselbach	4.0	5.0	13.1	15.7	46	229
Brotjacklriegel	2.5	3.0	16.2	12.5	71	229
Schauinsland	2.5	3.5	17.1	12.1	90	239
Westerland	7.5	7.5	17.6	16.5	57	239

means if more than six hourly values were selected for a day. The calculated daily mean value was finally accepted as representative when the standard deviation (1σ) of the selected hourly values of the day was less than ± 1.5 ppmv.

Harmonic curves have then been fitted through the selected daily mean values (Trivett, 1989). The mean seasonal cycles show significant differences in amplitude and phase at the individual sites (Fig. 3): the seasonal amplitude is largest (15.7 to 17.6 ppmv, Table 1) at the low elevation sites Waldhof, Westerland, and Deuselbach. Smallest

yearly amplitudes are observed at the mountain stations Schauinsland and Brotjacklriegel which is in accordance to the generally observed decrease of the seasonal CO₂ amplitude in the troposphere with height in the northern hemisphere (Bolin & Bischof, 1970; Nakazawa et al., 1993). The concentration decrease at Waldhof and Deuselbach occurs already in February, at the northernmost station Westerland only at the beginning of April. The dates of maximum and minimum concentrations are listed in Table 1. Also the absolute concentration levels at the five stations differ

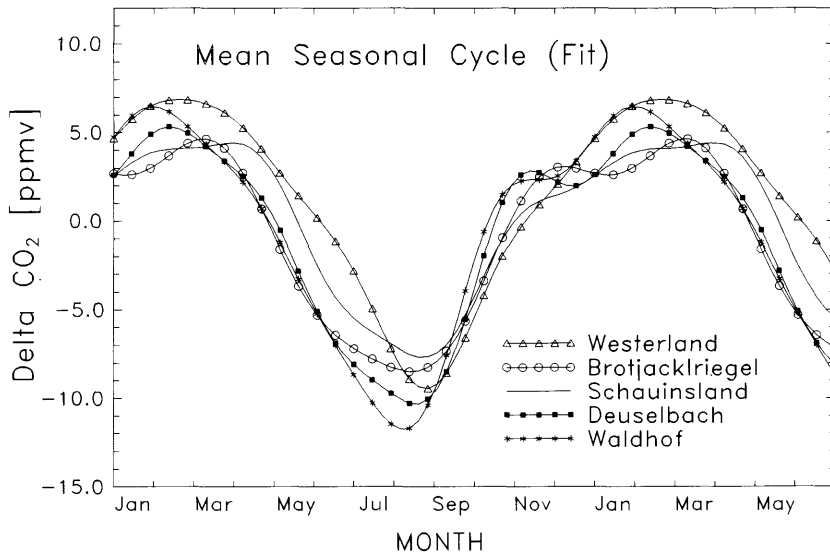


Fig. 3. Mean seasonal cycles determined from selected daily values of atmospheric CO₂ over the period of 1972–1990 at the 5 German sites. Peak-to-peak amplitudes are largest at the regional stations Waldhof and Deuselbach and decrease towards high elevation sites (e.g., Schauinsland). Whereas the CO₂ minimum is generally observed in August, the maximum concentration at the regional sites occurs already in February/March, at the mountain station Schauinsland only in April (compare Table 1).

considerably: the yearly mean concentrations at Brotjackriegel, Deuselbach and Waldhof are higher by approximately 3 ppmv, 4 ppmv, and 4.5 ppmv respectively when compared to Schauinsland and Westerland. The mean yearly increase rates are similar at all sites and lie between $1.38 \text{ ppmv yr}^{-1}$ and $1.49 \text{ ppmv yr}^{-1}$ for the 20 years period of 1972 to 1992.

No complete record of clean air CO_2 data in comparable latitudes (about 45°N to 55°N) is available for the measurement period; between about 50°N and 75°N , however, the yearly mean meridional concentration gradient is usually less than 1 ppmv (e.g., Tans et al., 1989). For the last 10 years, the individual yearly mean concentrations observed at the coastal site Westerland and at the Schauinsland station (Figs. 4a, b) have

therefore been compared with data from (clean air) sites in higher latitudes of the northern hemisphere, namely Barrow (76°N , 119°W) and Mould Bay (71°N , 157°W) (see Table 2). The agreement of yearly mean concentrations at these four stations is usually better than 1 ppmv. This is partly due to the fact that the data selection for high wind speeds results in an implicit selection of predominately westerly winds (maritime air masses). Nevertheless, at Schauinsland, and even at Westerland there still remains a significant percentage (about 10 and 20%, respectively) of "continental data" in the record.

3.3. $^{13}\text{CO}_2$ at the Schauinsland

As a by-product from the $^{14}\text{CO}_2$ analyses of large volume CO_2 samples, the stable isotope ratio

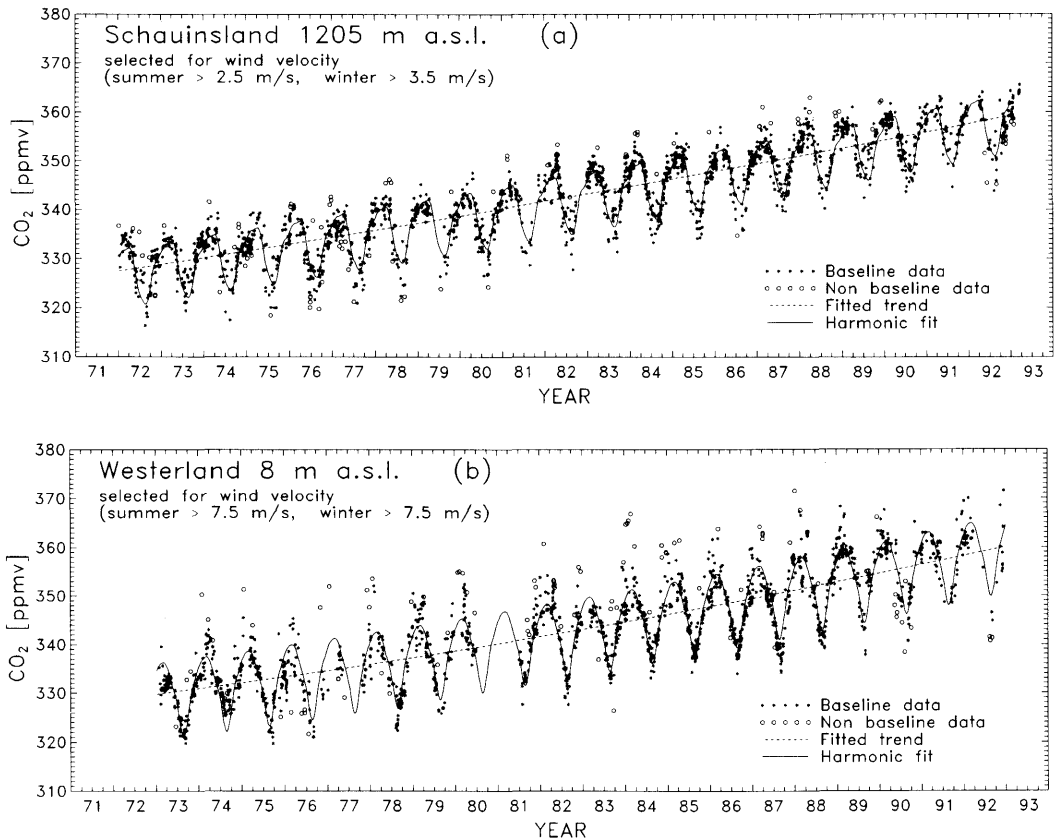


Fig. 4. Long-term records of selected daily mean values for Schauinsland (a) and Westerland (b). The solid lines are harmonic fit curves through the selected values (Trivett, 1989). Data are considered as *baseline data* if they fall into the 1σ range of all deviations from the curve, *non-baseline data* fall into the respective 2σ range. The mean increase rates (dashed lines) have been calculated to 1.48 and $1.49 \text{ ppmv yr}^{-1}$ for Schauinsland and Westerland, respectively.

Table 2. Yearly mean CO₂ concentrations at the German stations Schauinsland and Westerland (selected) in comparison with sites from the NOAA/CMDL network^{a)} (Conway et al., 1990; WMO, 1992)

Year	Mould Bay ^{a)} (76°N, 119°W)	Barrow ^{a)} (71°N, 157°W)	Schauinsland (48°N, 8°E)	Westerland (55°N, 8°E)
1982	342.4	342.7	343.4	343.3
1983	343.6	343.7	345.0	342.1
1984	345.6	345.3	345.1	345.8
1985	346.7	346.4	346.9	346.3
1986	348.6	348.6	348.1	346.8
1987	349.8	349.7	350.4	348.7
1988	353.5	353.4	353.2	352.1
1989	355.5	355.0	354.3	356.2
1990	356.0	356.0	354.9	354.6
1991	357.6	357.5	357.7	357.5

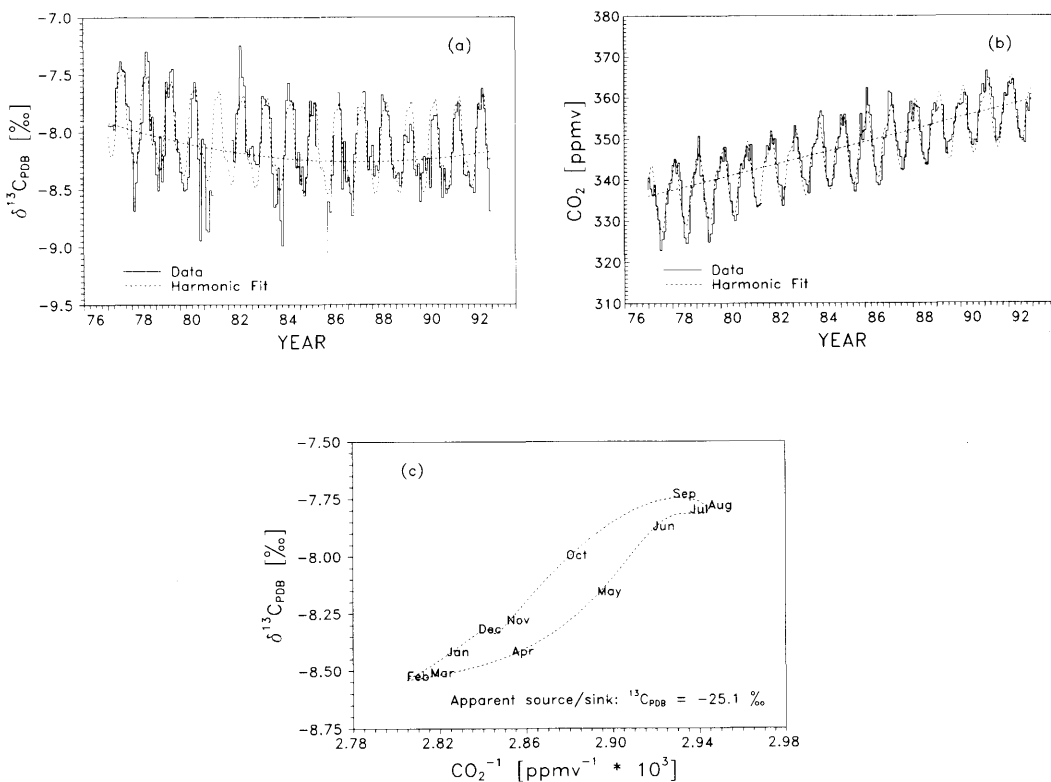


Fig. 5. Monthly mean values of $\delta^{13}C$ (a) in atmospheric CO₂ (b) at the Schauinsland site (unselected data), the dashed curves represent harmonic fits calculated through the data sets; the correlation of $\delta^{13}C$ and invers CO₂ concentration (c) (calculated from the detrended fit curves) leads to an isotopic signature of the mean source responsible for the observed $\delta^{13}C$ seasonality at Schauinsland of $\delta^{13}C = -25.1$ ‰.

$^{13}\text{C}/^{12}\text{C}$ in CO_2 has been measured at Schauinsland during the period of 1977–1992 (Fig. 5a). A large seasonal cycle with a mean peak to peak amplitude of $\delta^{13}\text{C} = 0.8\text{‰}$ is observed which is strongly anti-correlated with the unselected CO_2 concentrations (Fig. 5b). The mean $\delta^{13}\text{C}$ is decreasing from 1977 to 1992 by about 0.02‰ yr^{-1} , with a larger decrease in the first part of the record, and nearly no trend in the second part. Harmonic fits have been obtained for both unselected CO_2 and $\delta^{13}\text{C}$ monthly means. With the assumption that only one source or sink is responsible for the observed CO_2 seasonality, the isotopic composition of CO_2 from this apparent source (resp. the fractionation of the sink) can be calculated from the correlation of the $\delta^{13}\text{C}$ values and the inverse concentrations (Levin, 1987). From the detrended data a mean $\delta^{13}\text{C} = -25.1\text{‰}$ of the source is derived (Fig. 5c). This value represents the mean isotopic composition of all sources, biogenic and anthropogenic, contributing to the CO_2 variations at Schauinsland on the regional as well as on the continental and hemispheric scale. It is characteristic for exchange with terrestrial biota, and somewhat greater than the $\delta^{13}\text{C}$ of fossil fuels (-27‰ to

-28‰). It compares very well with values observed at background sites (Keeling et al., 1989), and the source $\delta^{13}\text{C}$ derived from recent observations of the concentration and stable isotopes on flask samples collected at the Schauinsland during supposedly good mixing conditions (Neubert, unpublished data).

3.4. $^{14}\text{CO}_2$ at the Schauinsland

The $^{14}\text{C}/^{12}\text{C}$ ratio, expressed as $\Delta^{14}\text{C}$, in unselected atmospheric CO_2 at the Schauinsland station shows a steady and approximately exponential decrease from 1977 until today with a time constant of about $T = 16$ years (Fig. 6, histogram). Overlying this trend is a seasonality with minimum values occurring during the winter half year. The decline is the consequence of bomb ^{14}C still equilibrating with the world oceans and the biosphere, as well as an ongoing input of ^{14}C -free fossil fuel CO_2 into the atmosphere. The seasonality is mainly attributed to a seasonally varying contribution of fossil fuel CO_2 at the measurement site being largest in the winter half year (Levin et al., 1989).

The ^{14}C background level in mid latitudes of the northern hemisphere can be derived from observa-

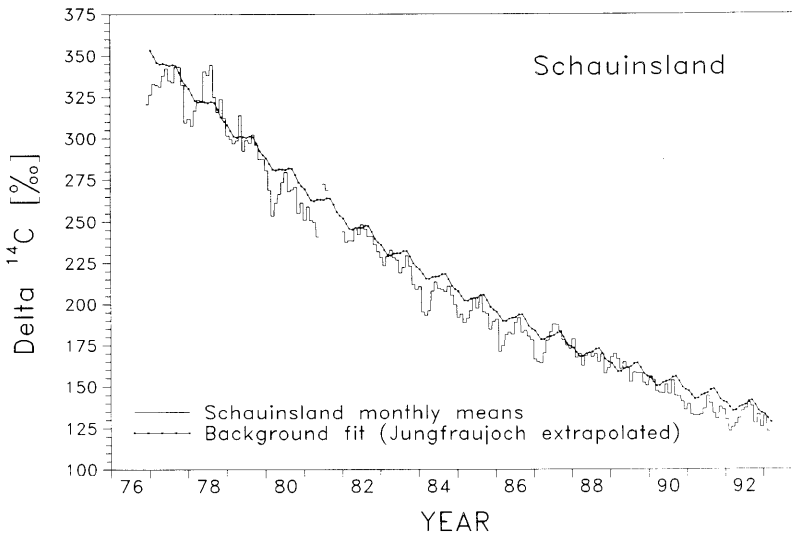


Fig. 6. Monthly mean $\Delta^{14}\text{C}$ in atmospheric CO_2 at Schauinsland (histogram) compared to values in background air over Europe (fitted curve). The seasonal cycle of the background fit has been derived from continuous $^{14}\text{CO}_2$ observations at Jungfraujoch (1986–1991). The long-term trend of the background fit curve is the same as observed at the Schauinsland, but we added a constant value of $\Delta^{14}\text{C} = +6\text{‰}$ (mean $\Delta^{14}\text{C}$ difference between Schauinsland and Jungfraujoch in 1986–1991).

tions at the High Alpine Research Station Jungfraujoch in the Swiss Alps (47°N, 8°E, 3450 m a.s.l.; see Fig. 1). At this site quasi-continuous ¹⁴CO₂ samples have been measured from 1986 onwards (Fig. 6, smooth curve). A harmonic fit curve and the mean trend have been calculated from the Jungfraujoch data. In the period of 1986 to 1991 the mean Schauinsland ¹⁴CO₂ level was constantly lower by about $\Delta^{14}\text{C} = 6\text{‰}$ if compared to Jungfraujoch. This offset is attributed to a general pile up of fossil fuel CO₂ over central Europe. To derive the ¹⁴CO₂ background level in mid latitudes of the northern hemisphere for the time period of 1977 to 1986 we used the trend curve calculated for the Schauinsland data and added the mean difference between Jungfraujoch and Schauinsland to this curve. The seasonal variation of the ¹⁴CO₂ background was derived from the mean seasonality at Jungfraujoch from 1986 to 1991 (Levin et al., 1992).

From the ¹⁴C depletion at Schauinsland relative to the background curve derived from the Jungfraujoch data we calculated monthly mean ¹⁴C-free fossil fuel contributions at the Schauinsland site according to Levin et al. (1989). A mean seasonal cycle for 1977–1992 was derived from these monthly data (Fig. 7). During winter the

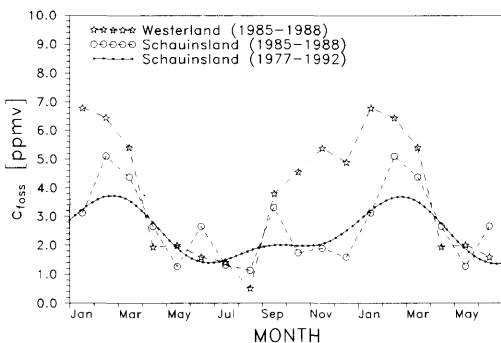


Fig. 7. Mean fossil fuel CO₂ contribution derived from the respective negative $\Delta^{14}\text{C}$ deviations from the background fit (c.f., Figs. 6 and 8) at Schauinsland for the period of 1977–1992 (smooth curve) and the period of 1985–1988 (cycles) in comparison with Westerland data for the same time span (stars). The fossil fuel CO₂ contribution during the summer months is similar at both sites. During the winter months, probably due to suppressed vertical mixing over the continent, the Schauinsland mountain station experiences much lower fossil fuel contributions than the coastal station Westerland.

fossil fuel component is about a factor of two higher than during summer. Part of this seasonality at the Schauinsland is due to a seasonality of the fossil fuel source (see Fig. 9), but also the atmospheric mixing height is considerably larger during the summer than during the winter season. The ¹⁴C draw down during winters of 1987/88, 1988/89 and 1989/90 is much smaller than in the earlier and later years. This can be explained by the extraordinary warm European winters coupled with a high frequency of maritime (unpolluted) air masses reaching the Schauinsland station. This special situation in the late 1980s is also manifested in low ²²²Rn concentrations observed at this site during these winter half years (Sartorius, IAR-Freiburg; see also Subsection 3.6).

3.5. ¹⁴CO₂ at Westerland

Quasi-continuous observations of ¹⁴CO₂ at the coastal site Westerland in the period of 1985–1988 show a much larger seasonality and also bigger deviations from the Jungfraujoch ¹⁴C background level than the Schauinsland data (Fig. 8). During winter, the fossil fuel component at Westerland is, thus, a factor of two higher than at the mountain site Schauinsland whereas during the summer half year the fossil fuel contributions at both sites are comparable (Fig. 7). Although the Schauinsland station is situated further inside the continental source area, its elevation above ground level leads to generally smaller contamination by ground level sources, particularly during winter. This behaviour is also confirmed by the significantly smaller seasonal amplitude of the selected CO₂

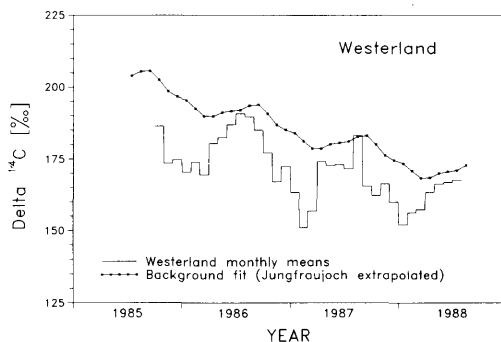


Fig. 8. Monthly mean values of $\Delta^{14}\text{C}$ in atmospheric CO₂ at Westerland (histogram). The smooth curve represents background air over Europe, as in Fig. 6.

concentrations at Schauinsland if compared to Westerland (compare Fig. 3).

3.6. Determination of the fossil fuel source strength

A tracer to estimate the residence time of an air mass over the continent as well as the atmospheric mixing conditions is the trace gas ^{222}Rn (Dörr et al., 1983; Levin, 1987). The radioactive noble gas ^{222}Rn emanates from all continental surfaces rather homogeneously and constantly with time. We used continuous atmospheric ^{222}Rn observations (kindly provided by H. Sartorius, Institut für Atmosphärische Radioaktivität, Freiburg) and the fossil fuel CO_2 component derived from ^{14}C data at the Schauinsland station to estimate the source strength of fossil fuel CO_2 in the catchment area of the Schauinsland site (e.g., Germany and South-West Europe). We made the simple assumption that the ^{222}Rn flux from continental surfaces is homogeneous and constant with time, and that the flux from ocean surfaces is negligible (Dörr & Münnich, 1990). The observed atmospheric ^{222}Rn activity (c_{Rn}) then mainly reflects the residence time of the respective air mass over the continent divided by the vertical mixing height. With the further assumption that the fossil fuel sources are similarly homogeneously distributed at ground level on the continents, from the known ^{222}Rn flux density of $j_{\text{Rn}} = (53 \pm 20) \text{ mBq m}^{-2} \text{ h}^{-1}$ (Dörr & Münnich, 1990), and the fossil fuel component c_{foss} , the fossil fuel flux density j_{foss} is estimated according to:

$$j_{\text{foss}} = j_{\text{Rn}} \times c_{\text{foss}} / c_{\text{Rn}} \quad (5)$$

For the catchment area of the Schauinsland site (i.e., Germany and South Western Europe) a mean flux density of $2 \text{ mMole m}^{-2} \text{ h}^{-1}$ is calculated with a sinusoidal seasonal amplitude of $\pm 30\%$ (Fig. 9). The mean flux density is considerably smaller than the $3\text{--}4 \text{ mMole CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ expected from statistically derived emission data of the relevant European countries (Marland, 1990). Possibly, the Jungfraujoch station is still partly influenced by the fossil fuel sources on the European continent, and the $^{14}\text{CO}_2$ background level was estimated too low. However, the mean $^{14}\text{CO}_2$ level at the maritime background station Izaña, Tenerife, is only higher by about 2‰ , suggesting an underestimation of the fossil fuel contamination at Schauinsland by 30% at most.

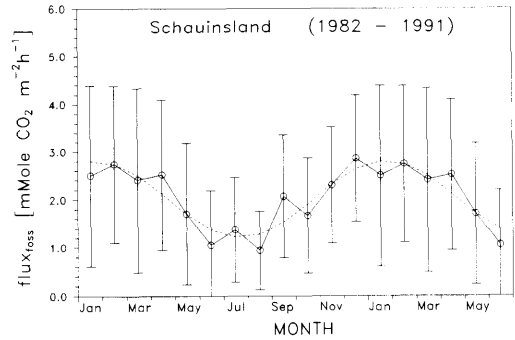


Fig. 9. Monthly mean fossil fuel CO_2 flux densities (calculated from parallel ^{222}Rn observations) in the catchment area of the Schauinsland station. The error bars show the variability of flux densities calculated in individual years.

Also the mean ^{222}Rn flux density has large error margins of $\pm 30\text{--}50\%$. Within these uncertainties the estimated mean fossil fuel flux density is in reasonable agreement with direct emission statistics.

An important finding is, however, that the seasonality of the fossil fuel flux density from Europe is about three times higher than the seasonality estimated from emission statistics (Rotty, 1987). Rotty's estimate had been derived from sales statistics which may be considerably different to the seasonality of the actual fossil fuel emission. A large seasonality of the fossil fuel emissions is also needed to explain the seasonal cycle of $^{14}\text{CO}_2$ observed at northern hemispheric background sites like Izaña, Tenerife or Alert, Canada (Levin et al., 1992). If we attribute the $^{14}\text{CO}_2$ seasonality at these sites mainly to fossil fuel contributions, a significant part (at least 10%) of the seasonal cycle in CO_2 concentration in mid to high latitudes of the northern hemisphere has to be attributed to this source and not to atmosphere-biosphere exchange, as has generally been assumed.

4. Summary and conclusions

The long-term records of atmospheric CO_2 carefully conducted at continental sites in Germany provide an important contribution to establishing the global atmospheric CO_2 budget:

- there is clear observational evidence for differences in seasonal cycles driven by the continental sources and sinks;

- accompanying isotopic observations (¹³C and ¹⁴C) at sites subject to largely different pollution levels are shown to provide a quantitative identification of sources;
- the relative anthropogenic CO₂ contribution can be furthermore related to respective fluxes by the ²²²Radon approach.

Data selection based on meteorological parameters have been shown to provide representative continental records which now can be used to validate regional, continental, and also global scale CO₂ models.

All data presented in this paper will be made available to other investigators through the Carbon Dioxide Information Analysis Center, P.O. Box 2008, Oak Ridge, TN 37831-6335, USA.

5. Acknowledgements

This work has been partly funded by the German Umweltbundesamt, Berlin, under contract

No. FE 104 02 627, and has been supported by the Bundesminister für Forschung und Technologie under contract No. 07KFT11, and via GKSS/IB in the framework of the Science and Technology Agreement between Germany and Canada, KAN ENV 25. We wish to thank the personnel at the Jungfraujoch, Schauinsland and Westerland stations for collecting the large volume CO₂ samples for isotope analysis, and K. Uhse (UBA-Pilotstation, Offenbach) for re-evaluation of the continuous CO₂ records from the German CO₂ network. H. Sartorius, Bundesamt für Strahlenschutz, Institut für Atmosphärische Radioaktivität, Freiburg, FRG, provided continuous ²²²Radon data from the Schauinsland site. The carbon cycle group at NOAA/CMDL, Boulder, USA, kindly provided CO₂-in-N₂ standards for re-calibration of our station standards. The staff of the Heidelberg Radiocarbon and Mass Spectrometer Laboratories are kindly acknowledged for their careful work doing the numerous isotopic analyses. We thank R. Francey for helpful suggestions concerning this manuscript.

REFERENCES

- Bolin, B. and Bischof, W. 1970. Variations of the carbon dioxide content of the atmosphere in the northern hemisphere. *Tellus* **12**, 431–442.
- Conway, T. J., Tans, P. and Waterman, L. S. 1990. Atmospheric CO₂ at Barrow and Mould Bay. In: *Trends '90, a Compendium of data on global change* (eds. T. A. Boden, P. Kanciruk and M. P. Farrell). ORNL/CDIAC-36, Oak Ridge, TE, USA, 54–55, 62–63.
- Dörr, H., Kromer, B., Levin, I., Münnich, K. O. and Volpp, H. J. 1983. CO₂ and Radon-222 as tracers for atmospheric transport. *J. Geophys. Res.* **88**, C2, 1309–1313.
- Dörr, H. and Münnich, K. O. 1990. ²²²Rn flux and soil air concentration profiles in West Germany. Soil ²²²Rn as tracer for gas transport in the unsaturated soil zone. *Tellus* **42B**, 20–28.
- Griffith, D. W. T., Keeling, C. D., Adams, J. A., Guenther, P. R. and Bacastow, R. P. 1982. Calculations of carrier gas effects in non-dispersive infrared analyzers. II. Comparisons with experiment. *Tellus* **34**, 385–397.
- Hut, G. 1987. Stable isotope reference samples for geochemical and hydrological investigations. In: *Report to the Director General, IAEA, Vienna*.
- Keeling, C. D., Bacastow, R. B., Carter, A. F., Piper, S. C., Whorf, T. P., Heimann, M., Mook, W. G. and Roeloffzen, H. 1989. A three-dimensional model of atmospheric CO₂ transport based on observed winds: 1. Analysis of observational data. *Geophysical Monograph* **55**, 165–236.
- Levin, I., Münnich, K. O. and Weiss, W. 1980. The effect of anthropogenic CO₂ and ¹⁴C sources on the distribution of ¹⁴C in the atmosphere. *Radiocarbon* **22**, 379–391.
- Levin, I. 1987. Atmospheric CO₂ in continental Europe, an alternative approach to clean air CO₂ data. *Tellus* **39B**, 21–28.
- Levin, I., Schuchard, J., Kromer, B. and Münnich, K. O. 1989. The continental European Suess-Effect. *Radiocarbon* **31**, 431–440.
- Levin, I., Bössinger, R., Bonani, G., Francey, R., Kromer, B., Münnich, K. O., Suter, M., Trivett, N. B. A. and Wölfli, W. 1992. Radiocarbon in atmospheric carbon dioxide and methane: global distribution and trends. In: *Radiocarbon after four decades: an interdisciplinary perspective* (Eds. R. E. Taylor, A. Long and R. Kra). Springer-Verlag, New York.
- Marland, G. 1990. CO₂ emissions. In: *Trends '90, a Compendium of data on global change* (eds. T. A. Boden, P. Kanciruk and M. P. Farrell). ORNL/CDIAC-36, Oak Ridge, TE, USA, 92–133.
- Nakazawa, T., Morimoto, S., Aoki, S. and Tanaka, M. 1993. Time and space variations of the carbon isotopic

- ratio of tropospheric carbon dioxide over Japan. *Tellus* **45B**, 258–274.
- Rotty, R. 1987. Estimates of seasonal variation of fossil fuel CO₂ emissions. *Tellus* **39B**, 184–202.
- Schmitt, R., Schreiber, B. and Levin, I. 1988. Effects of long-range transport on atmospheric trace constituents at the baseline station Tenerife (Canary Islands). *Atmos. Chem.* **7**, 335–351.
- Schoch, H., Bruns, M., Münnich, K. O. and Münnich, M. 1980. A multi-counter system for high precision carbon-14 measurements. *Radiocarbon* **22**, 442–447.
- Stuiver, M. and Polach, H. A. 1977. Discussion: Reporting of ¹⁴C data. *Radiocarbon* **19**, 355–363.
- Tans, P. P., Conway, T. J. and Nakazawa, T. 1989. Latitudinal distribution of the sources and sinks of atmospheric carbon dioxide derived from surface observations and an atmospheric transport model. *J. Geophys. Res.* **94**, D4, 5151–5172.
- Tans, P. P. 1990 (Ed.). Report of the WMO meeting of experts on carbon dioxide concentration and isotopic measurement techniques. *WMO Report No. 77*.
- Trivett, N. B. A. 1989. A comparison of seasonal cycles and trends in atmospheric CO₂ concentration as determined from robust and classical regression techniques. *Proceedings of the Third International Conference on Analysis and evaluation of atmospheric CO₂ data, present and past*. WMO Report No. 59.
- WMO 1992. Atmospheric CO₂ concentrations from Barrow and Mould Bay. *WMO WDCGG Data Report Part A (Carbon Dioxide)*, WDCGG No. 2, Published by Japan. Meteorol. Agency in Cooperation with WMO.