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Effects of Long-Range Transport on Atmospheric Trace Constituents at the Baseline Station Tenerife (Canary Islands)

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Abstract. First results of baseline observations from the new BAPMoN station Tenerife give information about the atmospheric background in this latitude of about 25° N in the North Atlantic. The influence of the meridional exchange with the northern part of the hemisphere as well as transport from the African continent is evident. Changes of air mass are strongly reflected in the concentration records of carbon dioxide, methane, and ozone depending on the seasonal and meridional distribution of these components. Transport of Sahara dust results in an increase of optical thickness and an ozone depletion. According to the seasonal frequency of characteristic transport conditions, these influences are reflected in the annual cycle of the records.

Key words. Atmospheric background concentrations, ozone, carbondioxide, carbon isotopes, methane, optical thickness, North Atlantic, long-range transport.

1. Introduction

In June 1984, the new WMO background air pollution monitoring station (BAPMoN) Izaña (Tenerife) commenced operation. This high-altitude observatory is the first continuously operating station in the southern part of the North Atlantic monitoring atmospheric trace gases in air which most of the time is representative for the free mid-troposphere at this latitude.

With these characteristics, the remote site of Izaña already has been used in previous investigations studying the atmospheric background level of trace constituents (see, e.g., Abel *et al.*, 1969).

The purpose of this paper is

(a) to give a brief overview of the observation program at Izaña,
(b) to present the data of a 15 months operation period for carbon dioxide and carbon isotopes, methane, and ozone, and
(c) to illustrate the influence of long-range transport of these trace gases from their anthropogenic and non-anthropogenic source regions on the variabilities observed.

2. Characteristics of the Sampling Site

The baseline station Tenerife is located at 28° 18′ N and 16° 29′ W on a mountain plateau at 2376 m above sea level. The location is representative for the unpolluted troposphere over the middle and southern parts of the North Atlantic, being influenced on a large scale by three main types of air masses:

- trade winds (45% of the time),
- air which passed the Saharan desert (30%),
- air from the northern part of the North Atlantic (low pressure systems) (25%).

During the summer months, May to October, the observation site most of the time (*ca.* 90 %) is separated from the lower atmosphere due to a strong inversion layer below 2000 m. The same is true in the winter period for 70% of the time. During stable atmospheric conditions, the local orography leads to a local wind system which affects the area of the station site: at daytime upslope winds transport air from the surrounding lowland areas to the elevated sampling site. As a result, the air analyzed is often influenced by local biogenic activity during daytime. During night, however, there are no local wind systems because the station is on top of a large plateau, and the samples represent the free atmosphere. Particularly, the diurnal variation of ozone, carbon dioxide, water vapor, and condensation nuclei (absolute concentrations and standard deviations of the half hour mean values) strongly show this influence. In order to get representative concentrations, a careful data selection procedure had to be applied to the data set.

3. Monitoring Program

The baseline station equipment is housed in a newly built tower at the building of the meteorological observatory Izaña. The instrumentation for the meteorological parameters, the sun photometer, and two dust samplers are installed at a platform on top of the tower above the roof of the main building. The main air inlet (stainless steel and glass) is at a height of 13 m above the ground, which is 2.5 m above the observation platform.

The signals of the continuously working instruments are automatically recorded every 10 sec by a data acquisition unit and processed to half-hour mean values and their standard deviations (for methane one single half-hour value, for turbidity the half-hour minimum is stored).

Table I gives a summary of the parameters measured and of the corresponding instrumentation.

To achieve international compatibility, special emphasis has been put on the technical equipment for the CO_2 and CH_4 analyses and on the related calibration procedures:

Table I. Trace constituents and meteorological parameters observed at baseline station Tenerife

Parameter	Instrumentation/method	Sampling frequency
Ozone (surface)	Dasibi 1003 AH/UV Absorption	continuous
Condensationnuclei	General Electric CNC2/ Cloud chamber	continuous
	Scholz-counter, manually	discontinuous
Carbon Dioxide	Ultramat 3, Siemens/NDIR	continuous
Methane	Dani-MPI Mainz/GC FID	1 value per 30 min.
Carbon Isotopes of CO_2 (^{13}C, ^{14}C)	chemical absorption; radioactive counting, MS	3 days resp. 2 weeks integrating
Optical thickness 336, 500, 778 nm	WRC 2-Davos/3-channel sun photometer	continuous
Precipitation	Erni/automatic rain gauge	on event
Meteorology dd, ff, TT, Td	Thiess	continuous
Rawinsonds	Väisälä operated by the Spanish Met. Service Sta. Cruz de Tenerife	twice per day

The CO_2 system has been described in detail by Schmitt and Levin (1985). CO_2-in-air calibration gases (working gases) are used. The CO_2 concentrations are given relative to an internal scale (based on three 'primary' CO_2-in-nitrogen tanks and eight 'secondary' CO_2-in-air tanks which have been checked twice a year since 1982). This scale will be compared with international WMO CO_2 calibration standards in the near future. The reproducibility of the CO_2 analysis including all calibration and data processing procedures, is better than ± 0.1 ppmv.

Half-hourly methane data are obtained by an automatically working FID gas chromatographic system, alternating calibration gas and ambient air every 15 min. The station standards have been calibrated twice, at the Max Planck Institut für Chemie (Mainz, F.R.G.) and the Fraunhofer Institut für Atmosphärische Umweltforschung (Garmisch, F.R.G.). A calibration against NBS standard reference material will be performed in the near future. Including all calibration and data processing procedures, the standard deviation of a single analysis is $\pm 0.4\%$.

Carbon dioxide samples for carbon isotope analysis are collected continuously integrating over periods of 3 or 14 days for ^{13}C and ^{14}C, respectively. The sampling and analysis techniques are described in 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 NBS oxalic acid standard activity corrected for decay (Stuiver and Polach, 1977). The precision (1σ) is

typically ±4‰. The $^{13}C/^{12}C$ isotopic ratio values are expressed as the permill deviation from the PDB standard $^{13}C/^{12}C$ ratio: $\partial^{13}C$ [‰] (Craig, 1957). The total precision (1σ) of a ^{13}C analysis is typically ±0.05‰.

4. Data

Continuous records of atmospheric carbon dioxide, methane and ozone over a period of 15 month (May 1984 through September 1985) are now available in preliminary form. As has been mentioned above, to achieve data from the free atmosphere, values influenced by local sources and sinks had to be removed from the continuous records. Tests applied have demonstrated that the standard deviation of the half-hour mean vlaues can be used to discriminate between locally influenced and undisturbed situations, respectively. The large-scale homogeneous CO_2 distribution causes standard deviations of less than 0.1 ppmv within half an hour. With an instrument noise of less than 0.03 ppmv, the upper limit standard deviation for CO_2 at baseline conditions was set to 0.075 ppmv for half-hourly means. Corresponding to the frequency distribution of CO_2 standard deviations, this baseline criterion is satisfied for 50% of all nighttime and 20% of all daytime observations.

This strong selection criterion originally deduced from the variability of the CO_2 signal was also used to remove data not representative of large scales from the records of other trace gases (e.g. CH_4 and O_3). As a consequence of this selection method, the data records discussed below (except the records for carbon isotopes) are representative of the identical time periods and air masses, respectively.

4.1. *Carbon Dioxide*

The CO_2 record (selected daily mean values) is presented in Figure 1. The total range of 9 ppmv between the minimum concentration in September and maximum values in April/May corresponds to the expected seasonal amplitude in this latitude and altitude (Conway *et al.*, 1988). Short-term fluctuations caused by long-range transport from different latitudes, are small in the period from May to October due to the persistent Saharan and trade-wind influence. In winter, however, meridional exchange by Atlantic low pressure systems becomes more frequent, and the day-to-day fluctuations of the CO_2 concentration increase significantly.

4.2. *$^{13}C/^{12}C$*

The $\partial^{13}C$ record obtained during the period from August 1984 to April 1985 is shown in Figure 2. A decrease of the $^{13}C/^{12}C$ isotopic ratio is observed from October to December according to the concentration increase of CO_2 during this

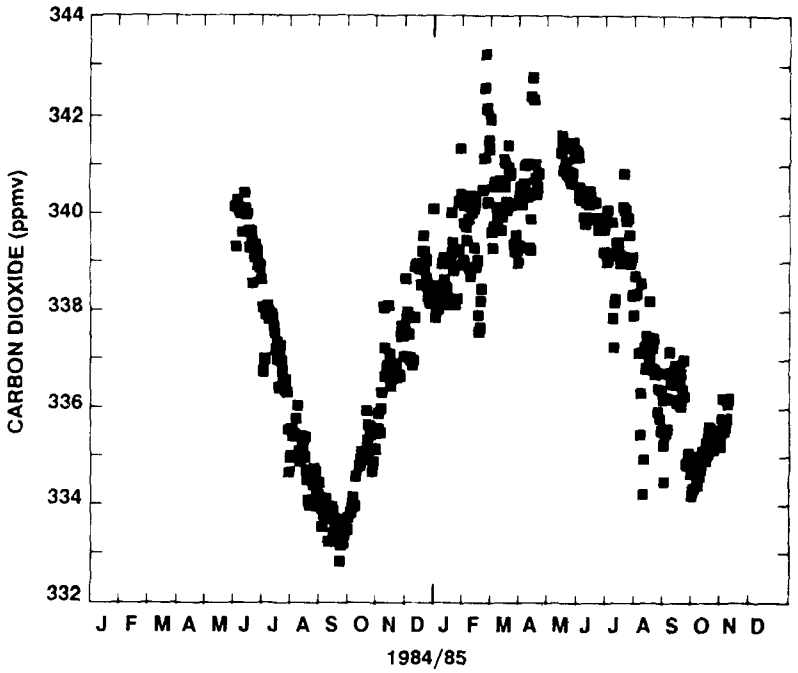

Fig. 1. Selected daily mean CO_2 concentration values at Baseline Tenerife (the concentrations are given relative to an internal standard, see text).

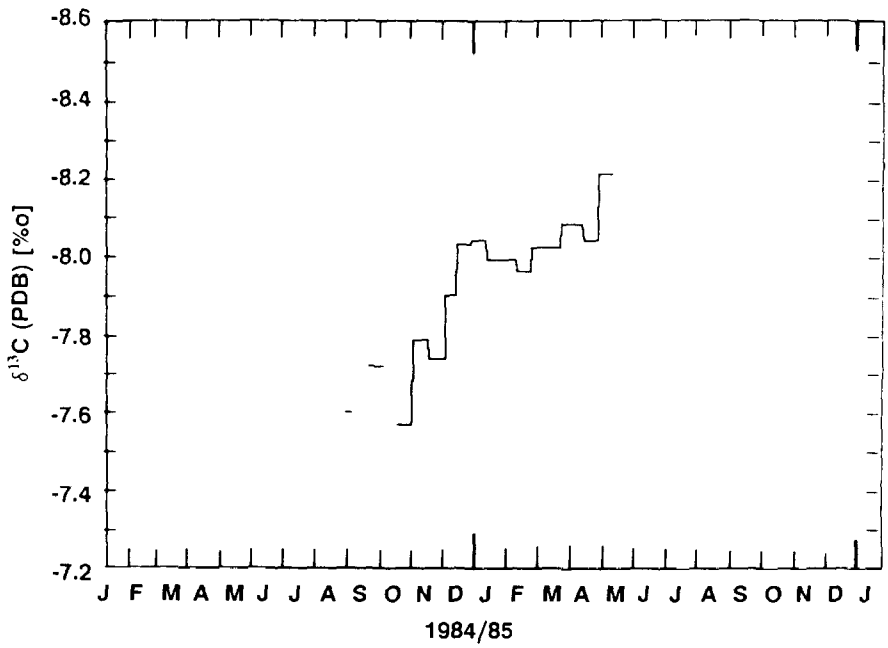

Fig. 2. $^{13}C/^{12}C$ isotopic ratio in atmospheric CO_2 at Baseline Tenerife.

time of the year: Assuming a two-component-mixing of constant background concentration and CO_2 from a variable source/sink the $\delta^{13}C$ of this source CO_2 can be determined from the linear correlation of $\delta^{13}C$ and the reciprocal of the CO_2 concentration. The intercept of the regression line is for the Izaña data $\delta^{13}C = -28.1 \pm 2.1‰$. This value is slightly lower than the mean ^{13}C value for biogenic CO_2 ($\delta^{13}C = -25‰$) and slightly, but not yet significantly lower than observed at Continental stations in the Northern Hemisphere, e.g. Schauinsland ($\delta^{13}C = -25.7 \pm 1.4‰$; Levin, 1987). For this short observation period, we can, however, only conclude that the parallel changes of the CO_2 concentration and $\delta^{13}C$ demonstrate the origin of these variations mainly being biogenic, whereas the contribution from a proposed seasonal cycle of the ocean-atmosphere CO_2 gas exchange is of minor importance at the Tenerife site.

4.3. $^{14}C/^{12}C$

The variability of the ^{14}C activity in atmospheric CO_2 observed at baseline station Izaña (Figure 3) is rather small and does not show a significant seasonal cycle, as being observed, e.g., at Continental European sites (Levin *et al.*, 1985; Levin, 1987). Evidently there is little direct influence from a seasonally varying (^{14}C-free) anthropogenic fossil fuel CO_2 source at this clean air station. (Note that the ^{14}C data are not selected.) A one ppmv contribution from this source to the seasonal cycle of atmospheric CO_2 concentration would, however, only

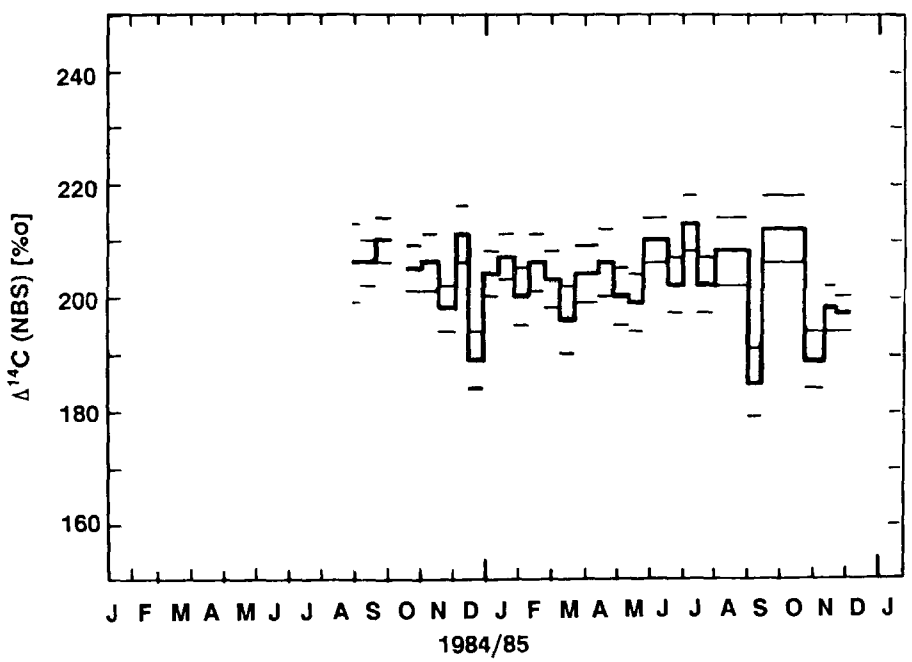

Fig. 3. $^{14}C/^{12}C$ isotopic ratio in atmospheric CO_2 at Baseline Tenerife.

lead to a seasonality of 3‰ in $\Delta^{14}C$ and could be significantly detected only in a longer-term record of $\Delta^{14}C$.

4.4. *Methane*

As has also been reported from other sites in the Northern Hemisphere (Steele *et al.*, 1987), an annual cycle is indicated in the CH_4 concentration record at the Tenerife station (Figure 4), with a minimum in summer. (With respect to the absolute CH_4 concentration values, they are in good agreement with values of the free troposphere in this latitude reported by Scheel (1987).) A 15 month period is, however, not sufficient to evaluate amplitudes or trends. Similar to the carbon dioxide (and ozone records, Figure 5), short-term fluctuations with a period of days are superimposed on the long-term variation. Due to the intensity of the meridional transport processes, these variations are again stronger in winter than in summer.

4.5. *Ozone*

Again, the one year record of surface ozone (Figure 5) is not sufficient to establish a seasonal cycle or trend. Obviously there is no minimum in summer, as has been observed at the comparable site of Mauna Loa. In contrast, very

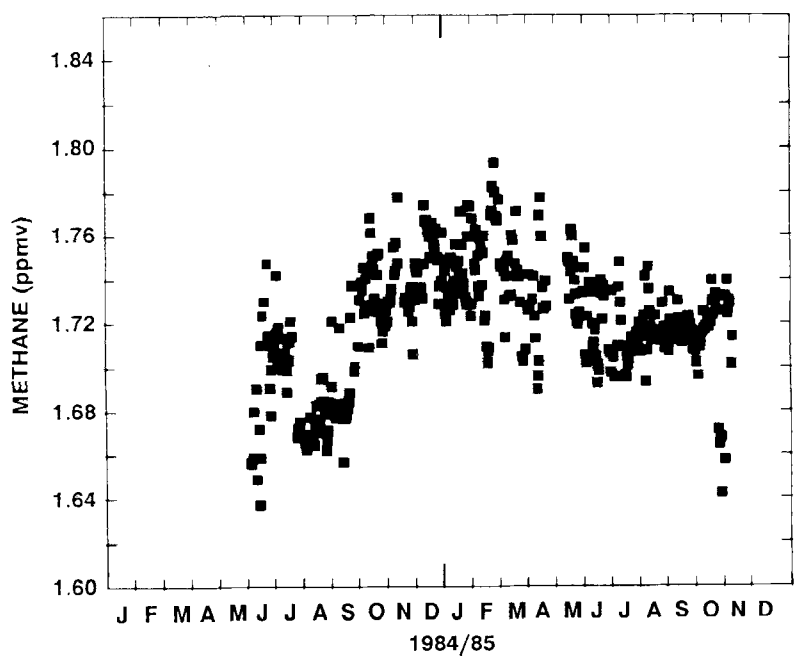

Fig. 4. Daily mean selected methane concentrations at Baseline Tenerife.

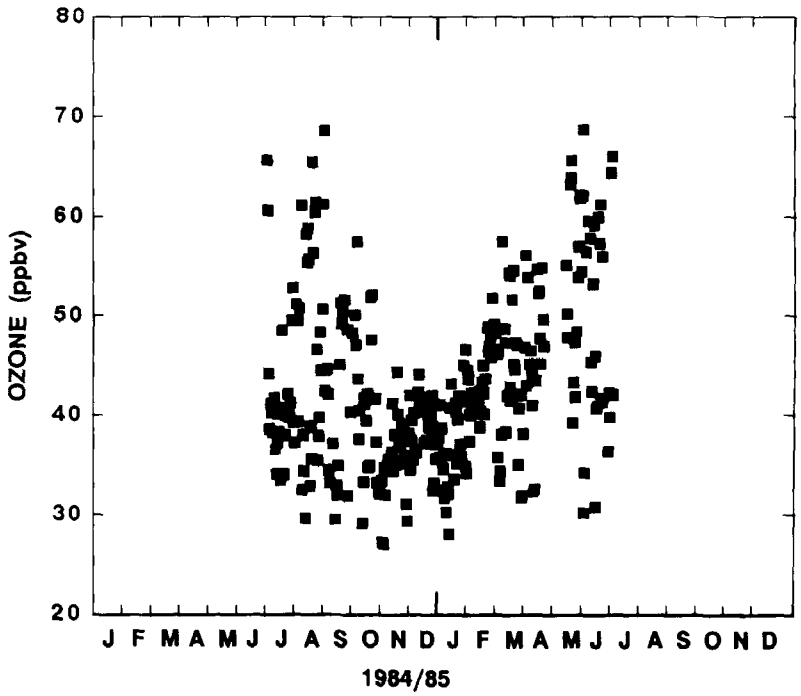

Fig. 5. Daily mean selected ozone concentrations at Baseline Tenerife.

high concentrations (daily means up to 70 ppbv) are observed in summer at Tenerife. Contrary to CO_2 and CH_4, the day-to-day and the intensive short-term variations are more frequent in summer than in winter. The average concentration for the period considered is 40 ppbv compared to, e.g., 25 ppbv at Mauna Loa (Oltmans and Komhyr, 1986).

5. Characteristic Types of Air Masses and their Influence on the Trace Gas Concentrations

As has already been mentioned above, strong short-term fluctuations are superimposed on the long-term seasonality of the trace gas records. These fluctuations may be attributed (a) to the influence of different air masses, resp. long-range transport to the area of the observation site, or (b) to chemical reactions within the air mass.

As a first approach to classify long-range transport phenomena, three basic types of weather situation and different air masses, respectively, can be distinguished in the region of the Canary Islands by analyzing the synoptic situation of the surface, the 850 hPa, and the 500 hPa levels:

(1) During trade wind situations, the air has aged within the subtropical high pressure system. Due to weak pressure gradients, and thus a long resi-

dence in the area, it normally cannot be assigned to a specific geographic origin or to a transport path.

(2) Associated with Atlantic low pressure systems, the present air mass has its origin most frequently in the northern part of the North Atlantic or in the adjacent continents.

(3) Under high pressure situations, the air may also be transported via North Africa (Sahara) to the Canary Islands in connection with easterly waves (Prospero and Carlson, 1980).

A change of air mass is almost always reflected in a distinct change of the atmospheric trace compounds corresponding to their characteristic distribution in space and time. As trade winds are the most frequent situation, and the corresponding air mass may be regarded as aged or local, the other types can be described in terms of deviations from these trade wind situations.

To illustrate this behavior, typical examples for both the summer and winter seasons – supported by backward trajectories – are given below.

During summer, with a carbon dioxide concentration minimum in high northern latitudes and a relative maximum in the latitude of the Canary Islands (Schmitt, 1976; Conway *et al.*, 1988), the observed CO_2 concentration is several ppmv lower under the influence of northern air than under trade winds or Sahara conditions. As an example, see Figure 6(A)–(C) (3 through 8 August, 1984): a carbon dioxide concentration draw down of 4 ppmv has been observed on 4 August; at the same time, concentrations of ozone and methane increase by 30 and 70 ppbv, respectively, due to the generally higher levels of these gases in the northern part of the hemisphere (Blake and Rowland, 1986; Steele *et al.*, 1987). The backward trajectory analysis shows a change of air mass origin from the trade wind situation on 3 August to a northern origin on 4 and 5 August back to the trade winds on 6 August.

The ozone increase (from about 35 ppbv to up to 60–70 ppbv) exceeds the expected surface background level. This may be explained by photochemical reactions during the long-range transport of a polluted air mass. Another possibility for increasing ozone could be stratospheric intrusion in connection with meridional transport. But in the case of stratospheric intrusion, the concentration of carbon dioxide should have increased because of the higher stratospheric values in August if compared to the troposphere (Schmitt, 1976; Bischof *et al.*, 1985), methane readings should have decreased due to the significant lower stratospheric level (Fabian *et al.*, 1981).

Similar conditions in winter, i.e. transport from the north (period of 4 through 9 December, Figure 7(A)–(C)), also result in an increase of ozone, but the peak values are lower (55 ppbv) according to the overall lower concentrations in the northern troposphere and the lesser importance of photochemical reactions at this time of the year. The simultaneous increase of methane by 50

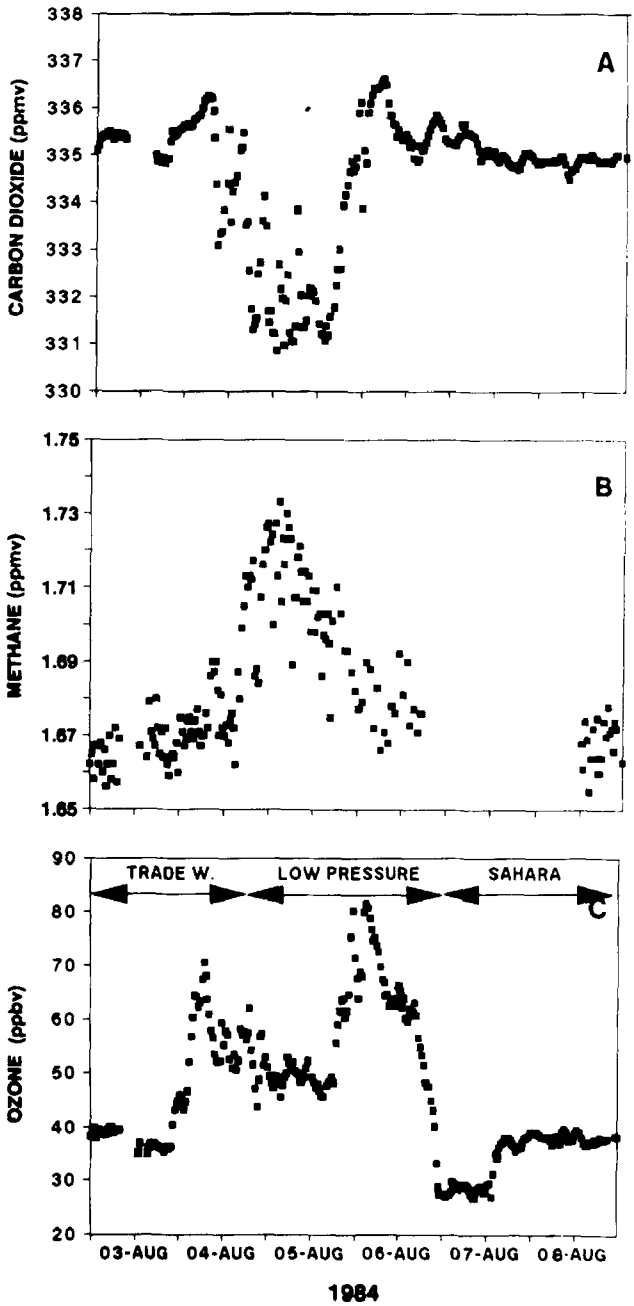

Fig. 6. Unselected half-hour mean concentration values at Baseline Tenerife for the period 3 to 8 August 1984. (A) carbon dioxide, (B) methane, (C) ozone. During Atlantic low pressure system events in summer, a steep decrease in CO_2 concentration is connected with a steep increase of methane and ozone.

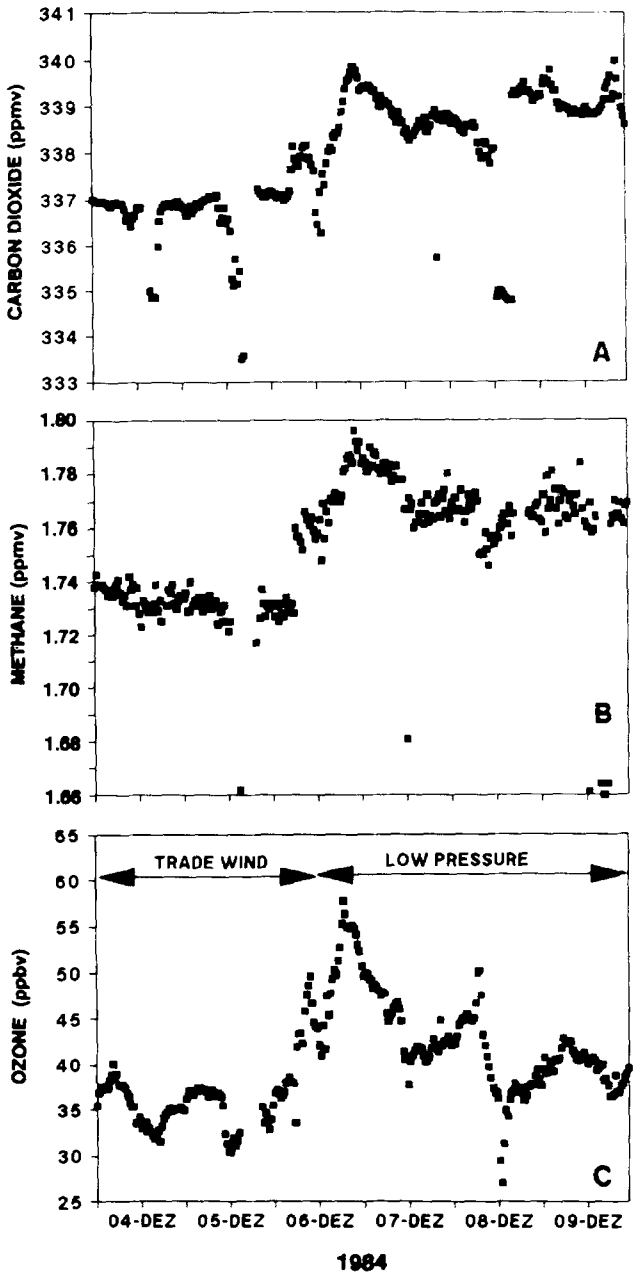

Fig. 7. Unselected half-hour mean concentration values at Baseline Tenerife for the period 4 to 9 December 1984. (A) carbon dioxide, (B) methane, (C) ozone. A low pressure system transports highly polluted air from the north to the sampling site.

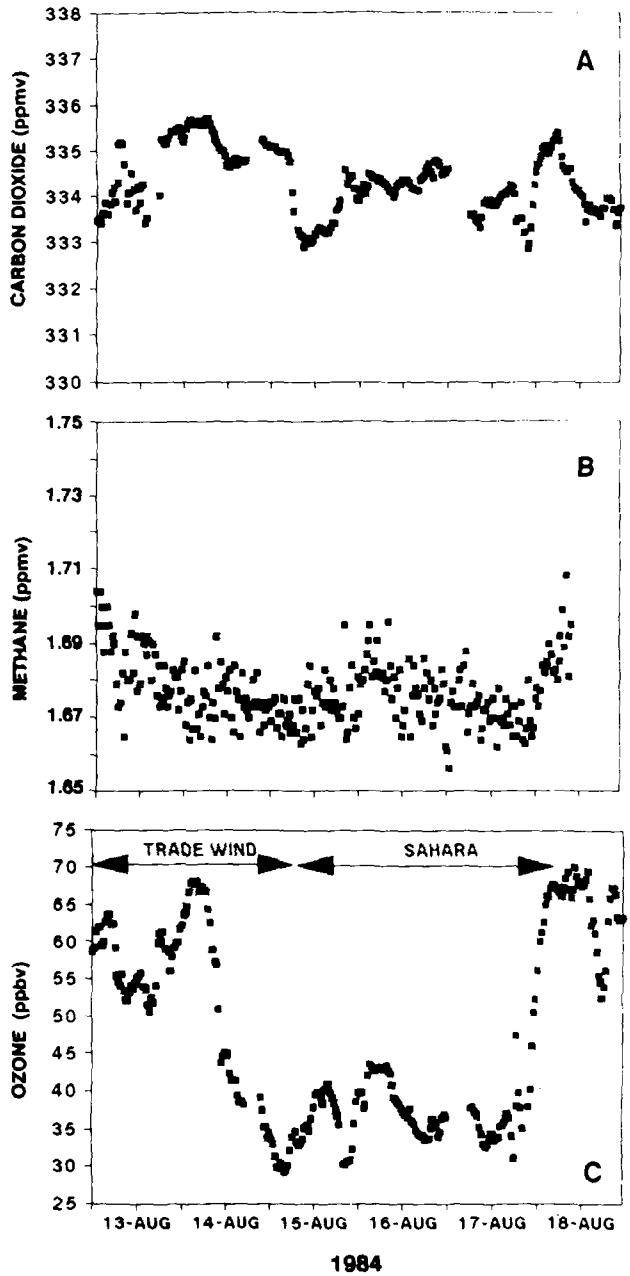

Fig. 8. Unselected half-hour mean concentration values at Baseline Tenerife for the period 13 to 18 August 1984. (A) carbon dioxide, (B) methane, (C) ozone. Air of Saharan origin is significantly depleted in ozone and methane.

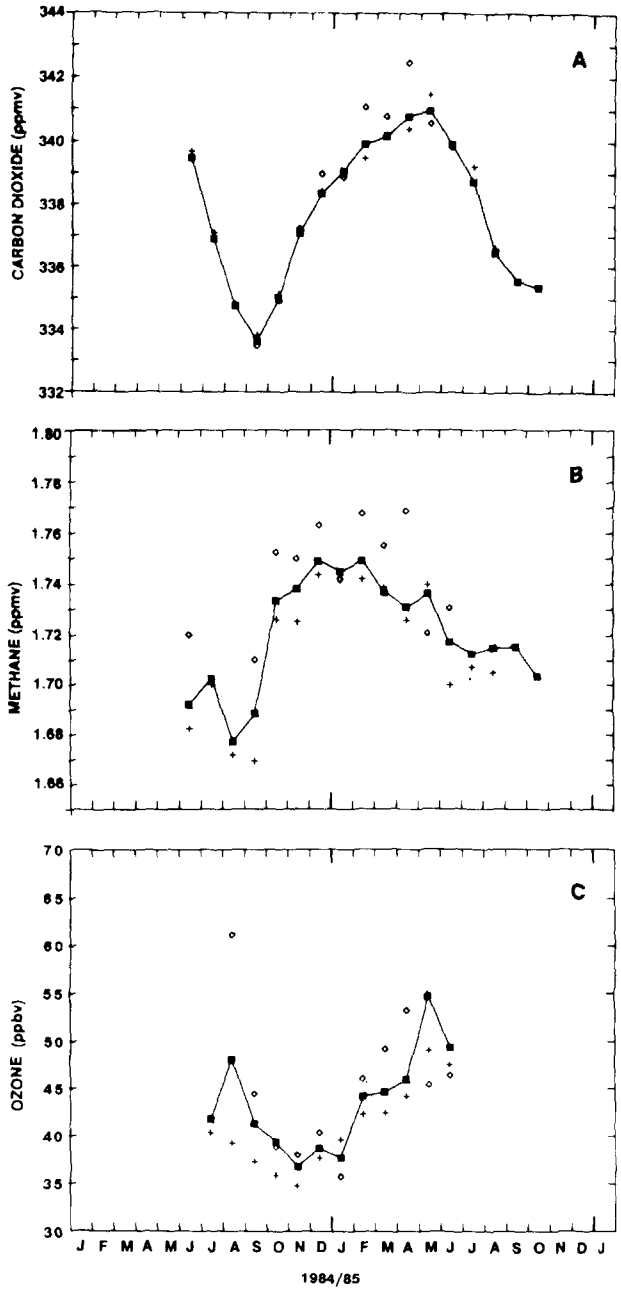

Fig. 9. Influence of different air masses (■: all values, +: Saharan air, ◇: low pressure) on the amplitudes of the seasonal cycles of the trace gases carbondioxide, methane, and ozone. (A) carbon dioxide, (B) methane, (C) ozone.

ppbv and of carbon dioxide by 3 ppmv suggests that the origin of the air mass is at a latitude between 40° and 60° N.

An example of the characteristic changes in trace-gas concentrations during Sahara dust events is given in Figure 8(A)–(C) (13 through 18 August, 1984). Whereas the carbon dioxide concentration does not change with the change of air mass, e.g. from the trade wind situation on 14 August to Saharan air on 15 to 18 August, the ozone concentration decreases steeply from about 70 to about 40 ppbv. A simultaneous depletion by about 20 ppbv is observed in methane concentration. The change of air mass origin on 15 August is also manifested by the five days backward trajectory analysis.

The general influence of different air masses, e.g. Saharan air and low pressure systems, on the amplitudes of the seasonal cycles of the trace gases carbon dioxide, methane, and ozone is illustrated in Figures 9(A)–(C): Monthly means of CO_2 calculated for low pressure system situations are up to 2 ppmv higher than the total means during the winter months due to a strong biogenic and anthropogenic CO_2 source in northern latitudes. Saharan air does not induce significant changes on the monthly means of CO_2. During the summer months, the latitudinal CO_2 gradient is opposite in sign and smaller (Conway *et al.*, 1988), low pressure systems are rather sparse and, in addition, these situations in summer are very often connected to rather noisy half-hour means, and are rejected according to our strong clean air criterion. This seems to be the reason why the air mass influence in summer is not as pronounced as in winter.

For methane, with its major sources on the Northern Hemisphere continents, a steep latitudinal gradient is observed throughout the year (Blake and Rowland, 1986; Steele *et al.*, 1987). As a consequence, monthly mean values calculated for situations with an Atlantic low pressure system are higher by about 15 ppbv on the average if compared to the total mean (Figure 9(B)). For weather situations with a Saharan influence, we observe lower methane concentrations by about 10 ppbv if compared to the total monthly mean.

The deconvolution of the selected monthly means of ozone for air masses of different origin (Figure 9(C)) also shows higher values for northern low pressure systems if compared to the total mean which already has been explained by a possible influence of photochemistry in polluted air. An interesting feature is, however, a marked ozone depletion during Sahara dust events. From Figure 10 it seems as if ozone was generally depleted during the Sahara dust episodes. While methane and carbon dioxide do not show any significant correlation with optical thickness, ozone concentrations are confined to a lower range for increasing optical thickness. This means that a specific composition is not the reason for the observed ozone deficiency of Saharan air. It may rather be explained by decomposition of ozone on dust particles. (With respect to methane, this is not in contradiction to the positive correlation of the methane concentration with the occurrence of air from the Sahara, because only part of the Sahara air events is connected with high dust loads.)

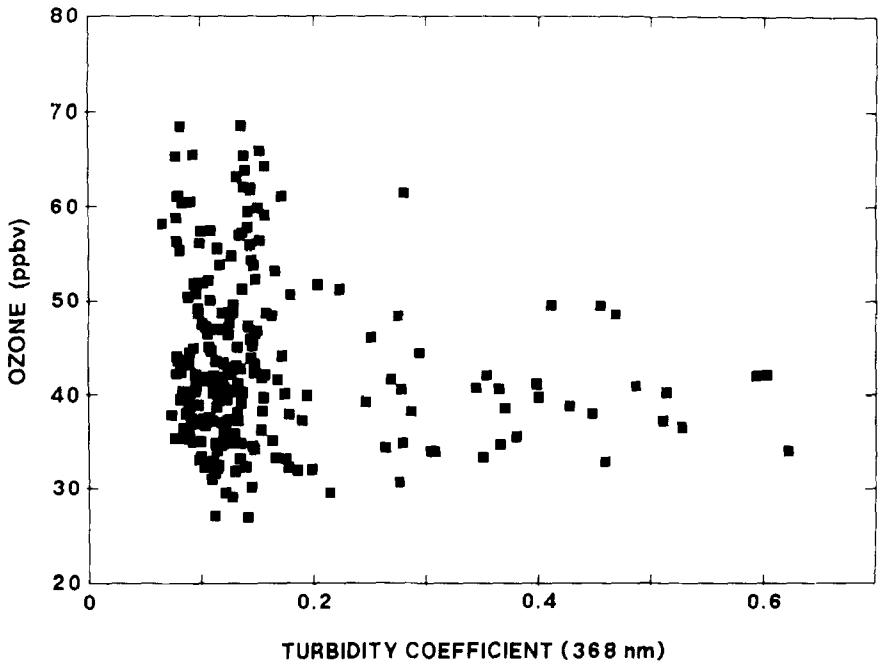

Fig. 10. Correlation of ozone and intensity of dust load of the air expressed as turbidity coefficient.

6. Summary and Outlook

This deconvolution of the seasonal cycles of carbon dioxide, methane, and ozone concentration clearly shows the problems that may arise with the interpretation of flask sample data: a selection of special weather situations for sample collection (e.g. determination of a 'clean air sector') will lead to an incomplete representation of the true mean concentration value at a particular site. Consequently, a three-dimensional atmospheric circulation model describing the trace gas concentration variations in space and time and including all weather situations, must fail in validating selected flask data records. This stresses the importance of continuous trace gas concentration records at newly established baseline stations.

The discussion of the carbon dioxide, methane, and ozone concentration records at the new baseline station Tenerife has shown that this site can be used for highly representative background concentration measurements of atmospheric trace constituents over the southern part of the North Atlantic. It may well be used as a background reference for the polluted continental European areas and can fill the gap in the global BAPMoN network in the Atlantic Ocean.

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