Tellus (1987), *39B*, 72–79

Variations of atmospheric carbon dioxide concentration at Syowa Station (69°00′S, 39°35′E), Antarctica

By M. TANAKA, T. NAKAZAWA, M. SHIOBARA*, H. OHSHIMA**, S. AOKI***,
Upper Atmosphere Research Laboratory, Faculty of Science, Tohoku University, Sendai 980, Japan,
S. KAWAGUCHI and T. YAMANOUCHI, *National Institute of Polar Research, Kaga 1-9-10, Itabashi, Tokyo 173, Japan,* Y. MAKINO, *Meteorological Research Institute, Nagamine 1-1, Yatabe, Ibaraki 305, Japan,* and H. MURAYAMA, *Department of Chemistry, Faculty of Education, Yokohama National University, Yokohama 240, Japan*

(Manuscript received November 4, 1985; in final form June 24, 1986)

ABSTRACT

Precise measurements of the atmospheric CO_2 concentration were initiated at Syowa Station, Antarctica in 1983. Preliminary inspection of the data obtained up to the present showed that: (1) a regular diurnal variation is not observable; (2) irregular variations are sometimes observed with extremely small amplitudes of 0.2 ppmv at most; (3) a seasonal variation with the minimum concentration in mid-April and the maximum concentration in mid-October; and peak-to-peak amplitudes of about 1.2 ppmv are detected; (4) annual mean values of the CO_2 concentration are 341.2 and 342.6 ppmv for 1983 and 1984, respectively.

1. Introduction

Systematic measurements of the atmospheric CO_2 concentration are currently made at several places in the Antarctic region, either by continuous sampling with an in situ analyzer or by discrete flask sampling with subsequent laboratory analysis (Keeling et al., 1976; Beardsmore et al., 1984; Komhyr et al., 1985). We initiated CO_2 measurements at Syowa Station (69°00′S, 39°35′E) using a flask sampling technique in January 1983 and by operating a continuous measurement system since February 1984. Since the station is isolated from vegetated lands and industrial regions, it is expected that not only the mean rate of annual increase of the CO_2 concentration but also its small year-to-year fluctuations can be detected precisely, both quantities being very important for the accurate interpretation of the global carbon cycle. In this paper, we report a general description and preliminary results of our new measurements.

2. Sampling site and experimental procedures

2.1. Sampling site

Syowa Station is located on Ongul Island about 4 km off the coast of the Lützow-Holm Bay (Fig. 1). The Ongul Island is about 11 km^2 in area and 29 m above sea level. The surface of the island is composed of naked rocks with some lichen growth and is covered with snow except in summer. The Ongul Strait is usually frozen throughout the year, but since 1980, open water has been observed on occasion in summer to autumn.

Syowa Station has been established in 1957 for the Japanese Antarctic Research Expedition and at present, semi-permanently accommodates about 35 staff. All facilities of the station are

* Present affiliation: Meteorological Research Institute.

** Present affiliation: International Meteorological and Oceanographic Consultant, Shintomi 2-14-7, Chuo, Tokyo 104, Japan.

*** Present affiliation: National Institute of Polar Research.

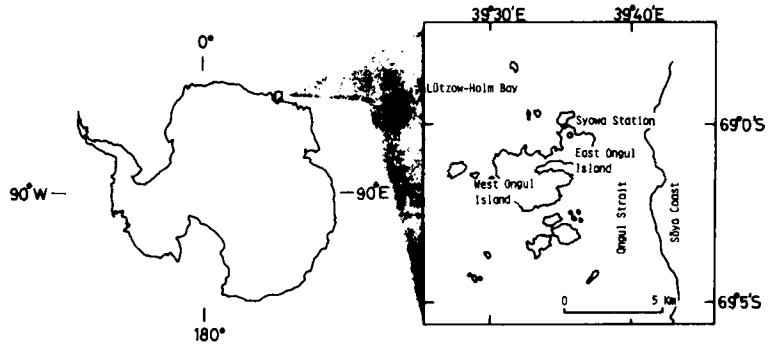

Fig. 1. Location of Syowa Station and its surrounding area.

powered by an electric dynamo with diesel engines.

The annual mean value of air temperature at the station is $-11\,^{\circ}C$, and its monthly mean value decreases down to $-20\,^{\circ}C$ in August and increases up to $-1\,^{\circ}C$ in January. The annual mean value of wind velocity is about 6 m s^{-1}. Prevailing winds are north-northeasterly, northeasterly or easterly for more than 70% of the windy condition. The occurrence of calm condition is about 14% of the year.

2.2. *Continuous measurements*

Our continuous measurement system consists of a nondispersive infrared analyzer, gas handling system and data acquisition system (Tanaka et al., 1984), and it was installed in an air-conditioned laboratory. The analyzer of the type VIA was manufactured by Horiba, Japan and improved by ourselves as described by Tanaka et al. (1983a) to attain an imprecision of ± 0.01 ppmv in an arbitrary concentration range of 50 ppmv span. In this measurement, a reference gas with a CO_2 concentration of about 333 ppmv was always flowed through the reference cell at a uniform rate of 15 ml min^{-1}.

The inlet of the analyzer was separated into 3 channels by solenoid valves; 2 channels were allotted to standard gases and the remainder to air samples. Solenoid valves were activated by an electromechanical controller with 6 channel circuits, the 1st and 2nd channels of which were connected to valves for the standard gases and remaining 4 channels to that for the air sample. The circuits of the controller were switched successively every 5 min. Thus each standard gas and the air sample were introduced into the analyzer once and 4 times every 30 min, respectively. The instrumental drift of the analyzer was normally of the order of ± 0.2 ppmv/day and was corrected by a linear interporation of successive calibrations. Each solenoid valve was opened only for 3 min, allowing a flow of air sample or standard gas of 350 ml min^{-1} through the analyzer and then closed for 2 min to record the response of the analyzer. This operation of the valve was used not only to economize the consumption of standard gases but also to avoid the uncertainties of the analyzer response caused by the slight difference between flow rates of air sample and standard gas. The number of air samples analyzed by this measurement system amounts to about 70,000 for each year.

The intake of air samples was mounted atop a 8 m-high mast (19 m above sea level) at the coast line of the island, being away from the laboratory by about 30 m and facing to the sea for a sector between northwest and south-southwest measured clockwisely. Air samples were introduced into the analyzer by pumping through an annealed copper tube from the intake. Water vapor was removed from air samples by a glass trap cooled at $-60\,^{\circ}C$ by an electric refrigerator, and dust particles by glass and membrane filters. The tubing of our measurement system, except for the intake tube of air sample and the water vapor trap, was made of stainless steel, and the respective parts were connected to each other by using a metal-to-metal seal.

The output signals of the analyzer were recorded digitally on printing paper with uncertainties corresponding to 0.005 ppmv, as well as on a stripchart serving as a back-up with a scale factor of 0.25 ppmv div^{-1}. A digital cassette

recorder was also added to this data acquisition system in January 1986 to simplify the data analysis.

The concentration of each air sample was first derived from analyzer responses for the air sample and standard gases, assuming a linear relationship between the CO_2 concentration and the analyzer response, and then corrected for the deviation from a non-linear relationship, which amounted to 0.08 ppmv at most. A non-linear relationship was confirmed once every 10 days by using a standard gas with CO_2 concentration nearly equal to the air sample to be measured, and the values interpolated from respective results were used for the above correction.

2.3. Standard gases

To maintain the consistency of measurements for a long time, our standard gases were classified into 3 categories, primary, secondary and working. All standard gases were CO_2-in-air mixtures prepared by Nippon Sanso, Japan. The purity of CO_2 was higher than 99.995% and the CO_2 concentration in the air with which it was mixed was lower than 0.05 ppmv, as determined by a gas chromatographic analysis before mixing the gases together. The dew-point temperature of respective gases were also confirmed by a conductivity hygrometer to be below $-70°C$. The working and secondary standard gases were stored in 47 l manganese-steel cylinders, the primary standard gases in 10 l aluminum cylinders.

New steel cylinders selected as storage containers for our standard gases were washed by an acid solution and steamy water, dried out with pure N_2 gas, and evacuated to a pressure of $\sim 10^{-3}$ mm Hg for 5 or 6 h at a temperature of 150°C. Whenever the cylinders were filled with standard gases, the above evacuation procedure was first carried out and a CO_2-in-air mixture with CO_2 concentration of about ten times that of the standards was then put in the cylinder to a pressure of about 0.5 atm for three days. Then known amounts of CO_2 and air were introduced in order using two precise pressure gauges with different ranges after evacuating the cylinders to a pressure of $\sim 10^{-3}$ mm Hg for about 1 h. The total pressures of the standard gases thus prepared were about 100 kg cm^{-2}.

The primary standard gases were prepared gravimetrically using aluminum cylinders and an extremely precise balance with a standard deviation of 1.5 mg in a wide range of 1 mg to 100 kg. The cylinders used were treated by almost the same procedure as above, but without washing with the acid solution. Details of our gravimetric method have been described elsewhere (Tanaka et al., 1983a). The concentration scale of the standard gases employed for this measurement was based on the primary standard gases prepared by a 3-stage dilution in 1983; original gas of about 5% concentration was first prepared by mixing the CO_2 and air, the second stage gas of about 3700 ppmv by diluting it with dry air and then the 6 standard gases ranging from 320 to 370 ppmv were obtained by further dilution. Total pressure of the primary standard gases was about 120 kg cm^{-2}. The imprecision (one standard deviation) in the concentrations was estimated to be 0.13 ppmv, on the basis of the estimated uncertainty of ± 25 mg in weighing each component gas on the balance due mainly to adhesion of dust particles and adsorption of water vapor on the outer wall of the cylinder. To minimize the uncertainties in calibrated values, CO_2 concentrations of the primary standard gases were corrected by a least-square-fit technique assuming a quadratic relation between the response of our analyzer and the CO_2 concentration. In Table 1 are shown the original calibration values and those corrected by the above-mentioned procedure. The amount of correction hardly exceeded the range of ± 0.04 ppmv. To confirm the stability of this primary standard gas system, a new primary standard gas system was prepared again in 1985 by the same procedure. The differences in the CO_2 concentration between both systems were within the estimated uncertainties as shown in Table 1.

The CO_2 concentrations of the working standard gases used in this measurement were determined before and after their use with an imprecision of ± 0.01 ppmv by comparing with our secondary standard gas system. A typical example of the results is shown in Table 2, together with the analyzer responses for the respective standards. The concentration of each working standard gas was derived by a quadratic interpolation from analyzer responses for the secondary standard gases, which were obtained by averaging 2 values before and after the

Table 1. *CO_2 concentrations of the primary standard gases prepared gravimetrically in 1983 and 1985; values in parentheses were obtained by a least-square-fit technique assuming a quadratic relation between the analyzer response and the CO_2 concentration*

1983		1985		
Cylinder	CO_2(ppmv)	Cylinder	CO_2(ppmv)	Calibration by the 1983 standards
DC4753	320.76±0.12 (320.77)	DC7338	320.02±0.12 (320.04)	320.04
DC4754	329.81±0.12 (329.81)	DC7339	328.92±0.12 (328.89)	328.87
DC4755	339.74±0.13 (339.73)	DC7340	341.00±0.13 (340.97)	340.91
DC4756	350.12±0.13 (350.11)	DC7341	350.45±0.13 (350.49)	350.39
DC4757	359.49±0.13 (359.53)	DC7342	360.95±0.13 (360.97)	360.82
DC4758	368.26±0.13 (368.24)	DC7343	369.64±0.13 (369.62)	369.41

Table 2. *Example of the calibration of working standard gases against the secondary standard gas system*

	Secondary standard gas				Working standard gas			
Measurements	NSN75-19 (331.59ppmv)	NSR06-72 (338.49ppmv)	NSL 3-25 (352.19ppmv)	PLB70388 (364.07ppmv)	PLB36417		NSK10-19	
	(mv)	(mv)	(mv)	(mv)	(mv)	(ppmv)	(mv)	(ppmv)
1	48.2	204.7	512.4	775.7	156.0	336.34	165.1	336.74
2	48.8	205.5	512.9	776.2	157.0	336.35	166.2	336.76
3	49.3	205.6	513.5	776.9	156.8	336.33	166.0	336.73
4	49.7	206.0	514.0	777.7	157.6	336.35	166.6	336.74
5	49.6	205.1	514.1	777.8	157.3	336.33	166.5	336.74
Mean (ppmv)						336.34		336.74
St. dev. (ppmv)						±0.010		±0.011

working standards were analyzed. The concentrations of all working standard gases used are given in Table 3. The drift in concentration was almost within ±0.1 ppmv. Therefore, the results of both calibrations were simply averaged to calculate the CO_2 concentration in air samples.

Our secondary standard gas system currently used consisted of 5 cylinders with different CO_2 concentrations ranging from 317 to 364 ppmv and were calibrated against the primary standard gas system twice or three times per annum. The relative drifts in the concentration of the secondary standards did not exceed the range of ±0.1 ppmv for the last 3 years, as shown in Fig. 2. The uncertainty in the concentration of the NSK 63-29 standard may be somewhat larger than others, since its value was determined by extrapolating the analyzer responses for the primary standard gases. However, this gas was used only for calibrating the approximate concentration of the reference gases. The lifetimes of our secondary standards ranged between 4 and 6 years.

The secondary and working standard gases were calibrated after being aged one month or two before their use, to minimize a possible initial drift of the CO_2 concentration. The usage of all gases was terminated at a pressure of about 30 kg cm^{-2} because a drift in concentration is likely to occur with further decrease of the pressure in the cylinders.

Table 3. *CO_2 concentrations of the working standard gases used at Syowa Station for the period February 1984–January 1985*

Cylinder	Before use (ppmv)	After use (ppmv)	Difference (ppmv)
PLD33420	353.47	353.56	+0.09
NSE35-83	353.33	353.22	-0.11
NSC89-46	353.13	353.23	+0.10
NSN39-35	353.50	353.59	+0.09
MLC15489	352.92	353.05	+0.13
NSL10-50	352.76	352.76	0.00
MLE17015	352.75	352.79	+0.04
CLB70047	352.99	353.06	+0.07
NSK26-49	336.89	337.00	+0.11
NSN 6-24	335.09	335.10	+0.01
NSL32-42	337.06	337.07	+0.01
PLB36417	336.30	336.34	+0.04
NSK75-17	335.23	335.27	+0.04
NSL31-80	337.01	337.08	+0.07
NSK10-19	336.66	336.74	+0.08
NSJ78-46	335.15	335.23	+0.08
NSK34-87	342.09	342.11	+0.02

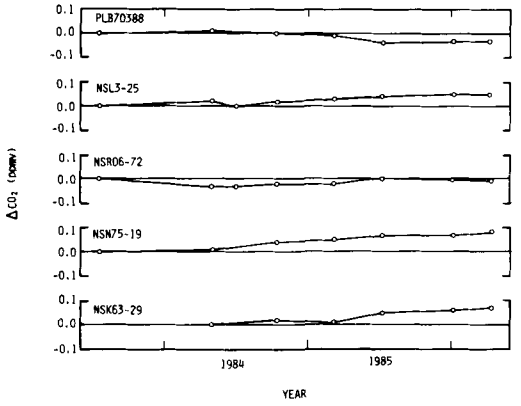

Fig. 2. Relative drifts in CO_2 concentration of the secondary standard gases over the last 3 years.

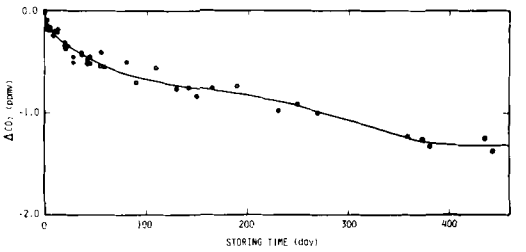

Fig. 3. Deterioration of standard gas samples filled in the sample flasks for a long time. The sample pressures were about 3 atm. The CO_2 concentrations are shown as a deviation from the concentration of the standard gases used. The solid curve represents a 4th-order polynomial fitting to the data.

2.4. Measurement by flask sampling

Air-sample containers were cylindrical Pyrex glass flasks of 550 ml capacity with greaseless stopcocks fitted at both ends as used by Tanaka et al. (1983a, b). The flasks were cleaned by washing in an aqueous detergent solution activated by ultrasonic waves, and then evacuated to a pressure below 1×10^{-3} mm Hg at approximately 100°C for more than 5 h.

Air samples were collected under strong wind conditions by pressurizing up to about 3 atm with an electric rubber-diaphragm pump. The intake of the air sample was mounted atop the mast for the continuous measurement or a 4 m-high mast in its vicinity. The flasks filled with air sample were protected from breakage by a shock absorbing material and stored in the dark inside of a thick paper box which prevents extreme change of temperature.

Air samples (usually single flasks) were collected at irregular intervals 2 to 4 times per month. They were returned to the Tohoku University and analyzed by the nondispersive infrared analyzer (Tanaka et al., 1983a) and our air-based standard gases mentioned before. Water vapor was removed from air samples by 2 glass traps cooled at −78°C. In this measurement, the lapse in time between air sampling and subsequent laboratory analysis reached 440 days at maximum. The possible deterioration of air samples stored in the flasks, which is probably due to a selective adsorption of CO_2 on the inner wall of the flask, was corrected in the light of laboratory experiments with dry standard gases as shown in Fig. 3 (Tanaka et al., 1983a). The maximum correction amounted to 1.3 ppmv. The standard deviation of a single measurement from this line is approximately 0.1 ppmv.

3. Results and discussion

To examine whether or not a systematic diurnal variation of the CO_2 concentration due to natural and anthropogenic activities exists at Syowa Station, monthly means of hourly mean CO_2 concentrations were derived from the continuous record for each month between February 1984 and January 1985. The results of December and July 1984 are shown in Fig. 4 as examples for the summer and winter seasons. The concentration of atmospheric CO_2 is stable, and no regular diurnal CO_2 variation is observable. This is a great advantage for a station which is monitoring the background concentration of atmospheric CO_2.

Fig. 4 also shows irregular variations of the CO_2 concentration with amplitudes of about 0.5 ppmv. As seen in Fig. 5, considerably high CO_2 concentrations were sometimes observed when the wind dropped and vehicles passed near the intake of air sample. Such locally contaminated data are responsible for the above variations and have to be deleted to obtain a data set representative of an area larger than the regional scale. As mentioned before, the present continuous measurement provides a large amount of the CO_2 concentration data. Therefore, an objective statistical selection scheme was tentatively used in this study, assuming that a homogeneous

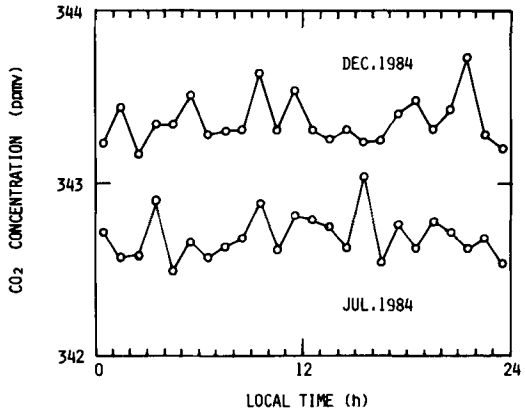

Fig. 4. Monthly means of hourly mean CO_2 concentrations obtained from all available data for July and December 1984 at Syowa Station.

airmass free from local contamination has small within-hour and hour-to-hour CO_2 concentration changes. We first calculated hourly mean values of the eight individual concentration readings and classified them into 5 groups such that the standard deviation of an individual reading during one hour is less than 0.5, 0.4, 0.3, 0.2 or 0.1 ppmv. Hourly means with standard deviation greater than 0.5 ppmv were rejected. The same procedure was also applied to mean values of 2, 3 and 4 h. Then, we calculated daily mean values from these 20 sets of data and fitted respective values to Fourier harmonics:

$$S(t) = C_1 \sin 2\pi t + C_2 \cos 2\pi t + C_3 \sin 4\pi t + C_4 \cos 4\pi t, \quad (1)$$

and a cubic spline with knots at both ends of the record (i.e. a single cubic function), to separate respective contributions of the seasonal variation and the secular increase of the CO_2 concentration. Here, t is the elapsed time (in year) relative to January 1, 1984 and C_i's are parameters determined by the fitting. Table 4 shows the mean values of the CO_2 concentration for the period February 1984–January 1985, together with %s of the selected data and standard deviations from the above function. Corresponding values of the CO_2 concentration and standard deviation for all available data are 342.73 and 0.26 ppmv, respectively. The results for the selected data are in excellent agreement with each other, except for %s of selected data, and are improved considerably as compared with those for all available data.

Daily mean values of the CO_2 concentration obtained from hourly means of the data with a standard deviation of less than 0.5 ppmv are shown in Fig. 6. The results of February to June 1985 are also plotted in this figure, but these values should be regarded as a reference, because they were obtained by averaging only two CO_2 concentrations taken at 0000 and 1200 LT and the re-calibration of the standard gases is not yet made. Fig. 6 shows that the day-to-day variations of the atmospheric CO_2 concentration are surprisingly small, except that irregular variations with amplitudes of 0.2 ppmv at most and periods of 1–2 weeks are observed repeatedly. Such irregular CO_2 variations are not ascribed to the instrumental drift of the analyzer, and are probably attributed to the transport of different airmasses from other latitudes in association with synoptic scale weather disturbances.

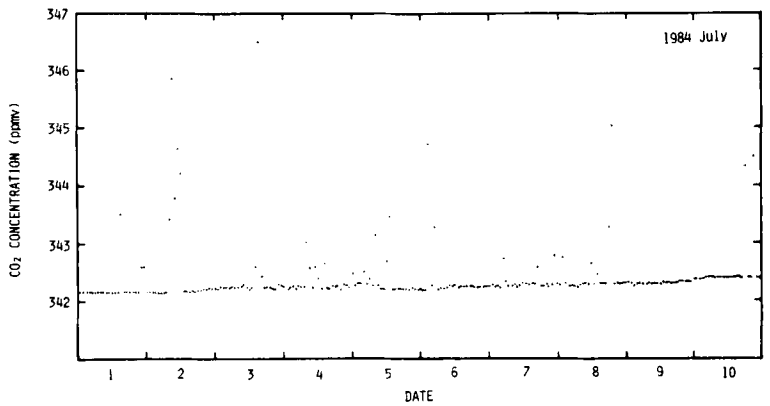

Fig. 5. Hourly mean CO_2 concentrations for the period 1–10 July, 1984 at Syowa Station.

Table 4. *CO_2 concentration (ppmv) at Syowa Station averaged over the period February 1984–January 1985, inclusive, obtained from respective data selection criteria; middle and bottom numbers show standard deviation and %, respectively, of selected data from the best fit function (ppmv)*

Time span for averaging (hr)	Standard deviation (ppmv) 0.5	0.4	0.3	0.2	0.1
	342.59	342.58	342.58	342.58	342.57
1	0.07	0.07	0.07	0.06	0.06
	89.3	88.1	86.9	85.0	82.1
	342.59	342.58	342.58	342.57	342.57
2	0.07	0.07	0.07	0.06	0.06
	84.7	83.5	81.4	78.9	75.0
	342.59	342.58	342.58	342.57	342.57
3	0.07	0.07	0.07	0.06	0.06
	81.1	79.7	77.5	74.6	69.9
	342.59	342.58	342.58	342.57	342.57
4	0.07	0.07	0.07	0.07	0.07
	79.7	76.9	75.1	71.6	66.0

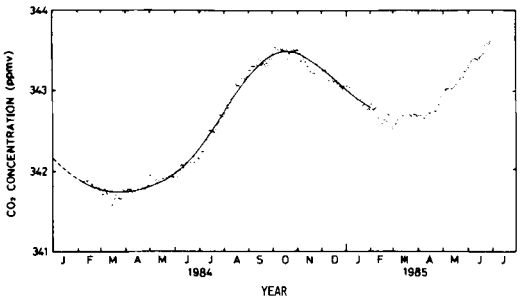

Fig. 6. Daily mean CO_2 concentrations at Syowa Station, obtained from hourly means with standard deviations of less than 0.5 ppmv. The solid curve shows the best fit of a time-dependent function (*cf.* text) to the data. Values for the period February–June 1985 are plotted for reference.

The values of seasonally adjusted CO_2 concentration obtained by applying the same procedure as before to these daily means were 342.13 and 343.05 ppmv for February 1, 1984 and January 31, 1985, respectively, and indicated a nearly linear increase during this period. The concentration difference of about 0.9 ppmv is a bit small as compared with an average rate of secular increase in recent several years, but a similar phenomenon was also found in the results obtained by our aircraft measurements over Japan (Tanaka et al., 1987). Such a temporal reduction of the rate of secular increase may be related to the El Niño event occurred in 1982 to 1983. Annual mean CO_2 concentration of 1984 was estimated to be 342.5 ppmv by supplementing the CO_2 concentration of January 1984 by an extrapolation.

The seasonal CO_2 variation reached at minimum in mid-April and at maximum in mid-October, and its peak-to-peak amplitude was about 1.3 ppmv. These results are in good agreement with measurements at the South Pole and Mawson Station (Keeling et al., 1976; Beardsmore et al., 1984; Komhyr et al., 1985).

The results of the flask sampling measurement in 1983 and 1984 are given in Fig. 7. Since no data selection was applied, the day-to-day variations are much larger than those of the continuous measurement, especially for 1984, but these data also show the seasonal CO_2 variation and secular CO_2 increase. We therefore separated the respective contributions by the same procedure as before, but added an internode to the cubic spline at the mid-point of the record. The results were very close to those of the continuous measurement for both seasonal and secular variations; (1) the seasonally adjusted CO_2 concentration increased rapidly in 1983 and more gradually through 1984; (2) annual mean values of the CO_2 concentration were 341.17 and 342.59 ppmv for 1983 and 1984, respectively; (3) the minimum of the seasonal CO_2 variation appeared in mid- or late April and the maximum in mid- or late October; and (4) its peak-to-peak amplitude was about 1.2 ppmv.

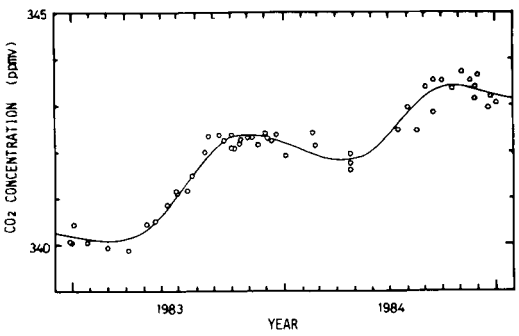

Fig. 7. Concentrations of atmospheric CO_2 obtained from single flask samples at Syowa Station. The solid curve represents the best fit function.

4. Conclusion

Measurements of the atmospheric CO_2 concentration were started at Syowa Station, Antarctica, using a discrete air sampling technique in January 1983, and an in situ continuous sampling technique in February 1984. Preliminary inspection of the data obtained up to the present showed that no regular diurnal CO_2 variation is observable, and that day-to-day CO_2 variations are also extremely small, except for outliers, due to station activities of appoximately 10–15% of all available data. We conclude from these facts that Syowa Station is a site suitable for background monitoring of the atmospheric CO_2 concentration.

5. Acknowledgements

We express our gratitude to the staffs of the 24, 25 and 26th Japanese Antarctic Research Expeditions for cooperating in this measurement. We also wish to thank the staff of the Nippon Sanso K.K. for their cooperative support in preparing our standard gases.

REFERENCES

Beardsmore, D. J., Pearman, G. I. and O'Brien, R. C. 1984. The CSIRO (Australia) atmospheric carbon dioxide monitoring program: surface data. *Division of Atmospheric Research Technical Paper No. 6*, 1–115.

Keeling, C. D., Adams, J. A. Jr, Ekdahl, C. A. Jr and Guenther, P. R. 1976. Atmospheric carbon dioxide variations at the South Pole. *Tellus 28*, 552–564.

Komhyr, W. D., Gammon, R. H., Harris, T. B., Waterman, L. S., Conway, T. J., Tayler, W. R. and Thoning, K. W. 1985. Global atmospheric CO_2 distribution and variations from 1968–1982 NOAA/GMCC CO_2 flask sample data. *J. Geophys. Res. 90*, 5567–5596.

Tanaka, M., Nakazawa, T. and Aoki, S. 1983a. High quality measurements of the concentration of atmospheric carbon dioxide. *J. Meteorol. Soc. Japan 61*, 678–685.

Tanaka, M., Nakazawa, T. and Aoki, S. 1983b. Concentration of atmospheric carbon dioxide over Japan. *J. Geophys. Res. 88*, 1339–1344.

Tanaka, M., Nakazawa, T., Shiobara, M., Ohshima, H., Kawaguchi, S. and Yamanouchi, T. 1984. A newly-developed system for continuous measurements of atmospheric CO_2 concentration at Syowa Station, Antarctica (in Japanese). *Antarct. rec. 82*, 1–11.

Tanaka, M., Nakazawa, T. and Aoki, S. 1987. Time and space variations of tropospheric carbon dioxide over Japan. *Tellus 39B*, 3–12.