In-situ measurement of the atmospheric CO concentration at Syowa Station, Antarctica

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Abstract: A high-precision measurement system for the atmospheric CO concentration was developed. With some modifications to a gas chromatograph CO analyzer, instrumental reproducibility of 0.5 ppbv was achieved. This could be sufficient for detection of short-term, seasonal and long-term variations of the atmospheric CO concentration in the Antarctic region. A standard gas system to maintain a consistent calibration scale for the CO measurements was also prepared. The measurement system was installed at Syowa Station in March 2000 and has been maintained up to the present. The first-year's observation showed a clear seasonal cycle of CO concentration.

1. Introduction

Carbon monoxide (CO) is one of the reactive gases in the atmosphere and plays an important role in atmospheric chemistry through its influence upon the concentrations of atmospheric oxidants, such as ozone (O_3), hydroxyl radical (OH) and hydroperoxy (HO_2). In particular, up to 75% of OH radical loss is induced by reaction with CO in remote marine regions (Thompson, 1992). Therefore, an increase of anthropogenic and natural CO emission leads to decrease of the atmospheric content of the OH radical, causing other reduced trace gases to accelerate their concentration increase (Khalil and Rasmussen, 1988). Since the most significant sink process for tropospheric methane (CH_4), one of the greenhouse gases, is reaction with the OH radical, it is expected that an increase of CO emission will influence radiative properties of the atmosphere through the CO-OH-CH_4 system (Daniel and Solomon, 1998)

To elucidate the temporal and spatial variations of the tropospheric CO concentration, many monitoring programs have been conducted around the world (Khalil and Rasmussen, 1988; Brunke *et al.*, 1990; Manning *et al.*, 1997; Novelli *et al.*, 1998; Langenfelds *et al.*, 2001) by using a discrete flask sampling method with subsequent laboratory analysis and an *in-situ* continuous measurement method. The flask sampling method has the advantage that spatially wide data can be acquired with less instrumentation; however, there is a problem of sample deterioration during storage in the flask (Novelli *et al.*, 1998) and it is difficult to obtain information on short-term

variations of the CO concentration.

Syowa Station is one of the most suitable sites to monitor background levels of atmospheric trace gases such as CO_2 (Nakazawa *et al*., 1991) and CH_4 (Aoki *et al*., 1992), since Antarctica is far from vegetated and industrial regions. Therefore, continuous CO concentration data at the station will provide useful information concerning seasonal and long-term variations and will help us to interpret the CO_2 and CH_4 variations. We have developed a high-precision measurement system for the atmospheric CO concentration to start *in-situ* CO observations at Syowa Station ($69.0°$S, $39.5°$E), Antarctica. The observation system was installed at the station in March 2000 by the 41st Japanese Antarctic Research Expedition (JARE-41).

In this paper, technical aspects of the in-situ observation system for the atmospheric CO concentration are reported in detail and an outline of the first-year's observation is presented.

2.   Measurement system

We have developed an *in-situ* measurement system for atmospheric CO concentration at Syowa Station. A schematic diagram of the system is shown in Fig. 1. The system consisted of a CO analyzer, a gas handling system, a data acquisition system and three kinds of standard gas, two working and one check. To maintain the in-situ measurements at the remote site for a long time, it is required for the system to be high-precision, stable for the long-term and of simple construction. In addition, it is preferable that the observed data can be monitored from Japan to reduce the burden on the person who operates the system at the station.

2.1.   CO analyzer

The gas chromatograph with a hot mercuric oxide reduction detector (RGA3; Trace Analytical Inc., U.S.A.) was adopted for the CO analyzer in the system. The configuration of the analyzer is listed in Table 1. An air sample introduced in a sampling volume (1 m*l*) of the analyzer was injected by carrier gas flow into column 1, where contaminants such as CO_2 and H_2O were separated from the sample, and only eluted components were forwarded to column 2. The stream selection valve was a Valco 10 port valve rotated by pressurized air. CO was separated from other components in column 2 and introduced into the detector, where mercuric oxide was reduced to mercury vapor by reacting CO gas and the amount of the mercury vapor was detected by absorption of ultraviolet radiation. Ultra-pure air manufactured by Nippon Sanso Co. was employed for the carrier gas. A combustion filter in the carrier gas flow path inside the RGA3 removes reactive impurities contained in the carrier gas. The flow rate of the carrier gas was controlled to be 15 m*l*/min by two stages of pressure control. The carrier gas was depressurized down to 0.2 MPa by a pressure regulator first, and then down to 0.1 MPa by a bellows pressure valve.

To achieve better reproducibility for the CO analysis, it was necessary to reduce the noise level in the detector output signal. The intensity of the ultraviolet radiation was sensed by photo diodes and then amplified by a series of operational amplifiers. We added $0.1\,\mu$F ceramic condensers to the electric detector circuit to bypass noise from the
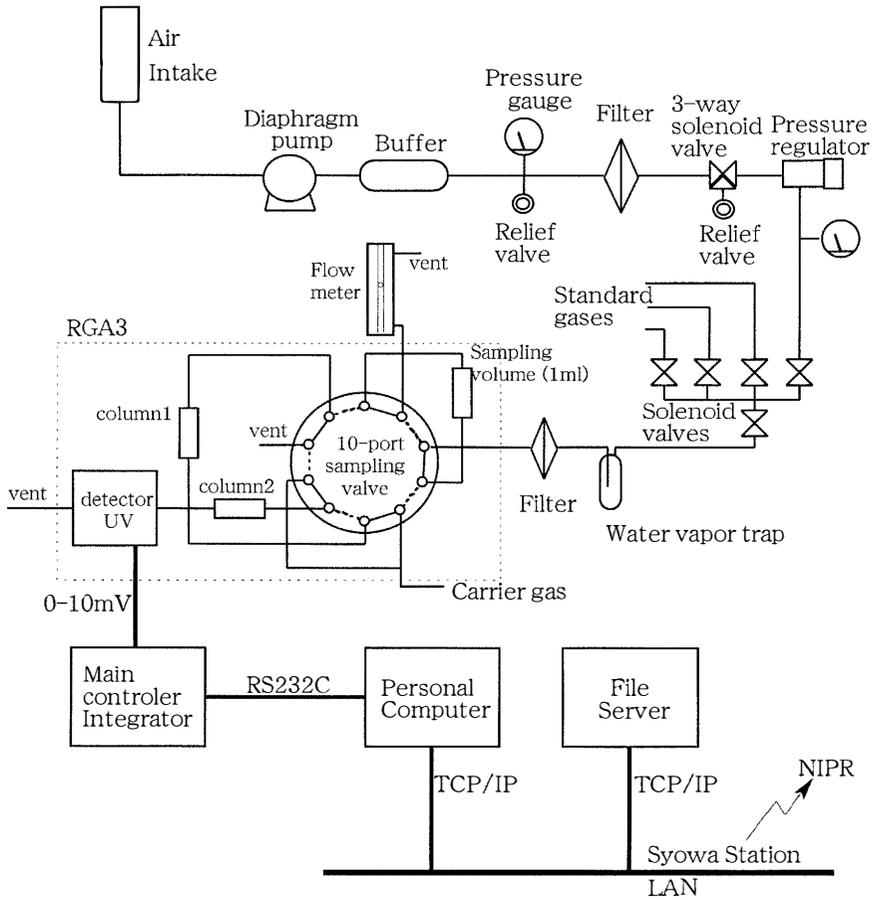
Fig. 1. Schematic diagram of the in-situ measurement system for the atmospheric CO concentration.

Table 1. Configurations of the CO analyzer, RGA3.

Column 1	Unibeads 1S (60–80 mesh) $1/8'' \times 30\ 1/4''$ temperature: 110℃
Column 2	Molecular Sieve 5A (60–80 mesh) $1/8'' \times 30\ 1/4''$ temperature: 110℃
Carrier gas	Ultra-pure air (Nippon Sanso Co.) Impurities' concentrations are certified below: 0.1 ppmv for CO, CO_2 and CH_4 and below 0.01 ppmv for NO_x and SO_2
Detector	HgO/UV temperature: 265℃
Sample	volume: 1 ml

power source lines.   In addition, the cutoff frequency of the low pass filter at the final stage of the circuit was changed from 10 Hz to 2.3 Hz to suppress short period noise. Variations of frequency and voltage of the power source could be another noise source. Therefore, a frequency converter, EP-400A (NF electric instruments, Japan), was inserted between RGA3 and the station power supply to regulate the frequency and voltage to be 50.00 Hz and 100.0 V AC.   By the modifications described above, the noise level in the output of the RGA3 detector was reduced to about 2μVp-p, about half of that before the modifications.   Furthermore, standard deviations of the CO peak height were improved from 0.7% to 0.3% of the average value, when CO-in-air standard gas was analyzed repeatedly.

The raw detector signal in volts was measured by an integrator unit (Shimadzu C-R5A, Japan), where numeric parameters of the CO peak, such as peak area, peak height and retention time, were determined.   These parameters were transferred to a PC through a serial data connection.   The CO analysis for a sample requires 3.5 min after the sample injection is completed.   The C-R5A and optional interfaces of the parallel I/O and relay unit (Shimadzu PC-17N and PRG-102A, Japan) controlled valves inside the RGA3 and in the gas-handling unit described below.   Data receiving software on the PC was designed to store the data into a floppy disk and hard disk and display the time series of received data.   Observed date and time were inserted into the data record using a PC clock that was adjusted using a network timeserver once a day.   Observed data could also be stored on a file server connected to a local area network (LAN) by a data copy program working on the PC.

2.2.   Gas handling system and measurement sequence

The gas handling system is also shown in Fig. 1.   Sample air and standard gases were selected at solenoid valves and introduced into the sample volume inside the CO analyzer through a water trap cooled at $-60°$C and a 2 μm inline filter.   In the system, we used two CO-in-air standard gases, of which CO concentrations were about 100 and 50 ppbv (hereafter denoted as High and Low gases, respectively) to calibrate the response of the CO analyzer and one standard gas (around 30 ppbv) to check the analyzer linearity (also denoted as Check gas).   The sample air was pumped from an air intake by a diaphragm pump (GAST type MOA, U.S.A.) into the solenoid valve unit.   A buffering volume and a three-port solenoid valve were placed in the sample-air line so as to absorb the pressure pulsations due to vibration of the pump and to prevent overload of the pump when the sample line was not selected, respectively.   Tubing was primarily made of stainless steel.   Teflon tubes were employed for the parts between standard gas cylinders and the gas handling system for easy handling while the cylinders were being exchanged.   Vacuum-tight fittings were adopted as connectors in the system and special attention was paid to confirm that there was no leakage in the tubing or connection.

It was verified that the complete exchange of the gas within the CO analyzer could be attained at a flow rate of 300 ml/min for 2 min.   Thus, an interval of 5.5 min was necessary for the sequential CO analysis, when 3.5 min for the GC analysis were considered.   Since time-to-time variations of the CO concentration had been expected to be small at Syowa Station, we had programmed the *in-situ* observation sequence as the

series analyses of High and Low gases and two times of the sample air at an interval of 10 min.   Therefore, the atmospheric CO concentration could be determined twice every 40 min.   In addition to the normal sequence as above, an analysis for the Check gas was inserted once every 12 hours to monitor the linearity of the analyzer's response.

2.3. Performance of the system

Instrumental reproducibility of the system was examined by analyzing a CO-in-air standard gas as the sample with two kinds of CO standard gases to calibrate the CO analyzer, repeatedly.   The CO concentrations of the standards were chosen to be 215 and 78 ppbv, respectively.   The CO concentration of the sample was calculated using the peak height of CO which appeared in the chromatogram and by linear interpolation of the CO analyzer responses against the two standard gases of which CO concentration were assigned.   The distribution of deviation for each measured value from the average is given in Fig. 2.   The total number of sample measurements and the average CO concentration of the sample were 58 and 120.2 ppbv, respectively.   As seen in the figure, the standard deviation of the analyses was within 0.5 ppbv.   When the peak area was adopted for the calculations, the deviation increased to ± 1.5 ppbv.   Considering the fact that peak height measurements showed less scatter around the average CO concentration, we chose the peak height as the measure of CO amount.

Linearity of the analyzer response was examined by analyzing several air samples of which CO concentration was determined to be from 20 to 200 ppbv.   The air samples were prepared by the dynamic dilution method with a CO-in-air standard gas (200.7 ppmv) and purified air, and the CO concentration of the sample was calculated using their flow rates measured by mass flow controllers.   These mass flow controllers were calibrated against a film flow meter and the precision of the CO concentration, thus
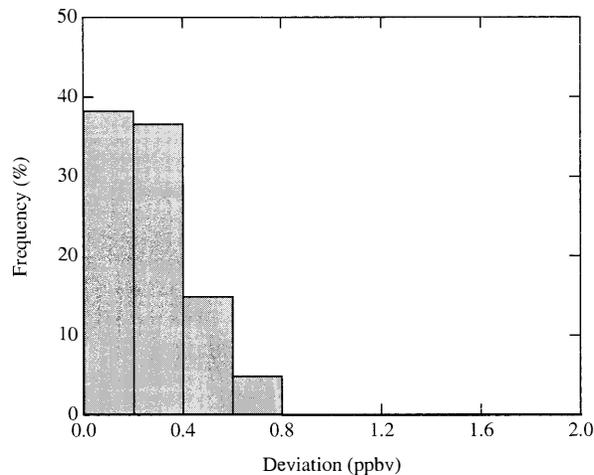

Fig. 2.   *Frequency distribution of the absolute difference of each measured value for a CO-in-air standard gas from the average.   The total number of the analyses was 58.*
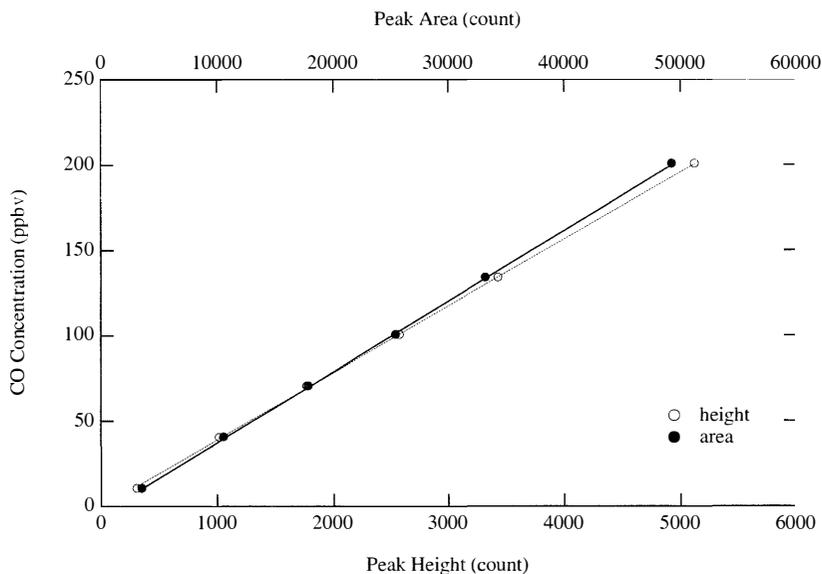
Peak Area (count)

Fig. 3. *Relationships between the CO concentration of the sample gas and the peak area (top axis) and peak height (bottom axis), respectively, determined by the CO analyzer, RGA3. The sample gas was prepared by the dynamic dilution method and its CO concentration was assigned independently (see text).*
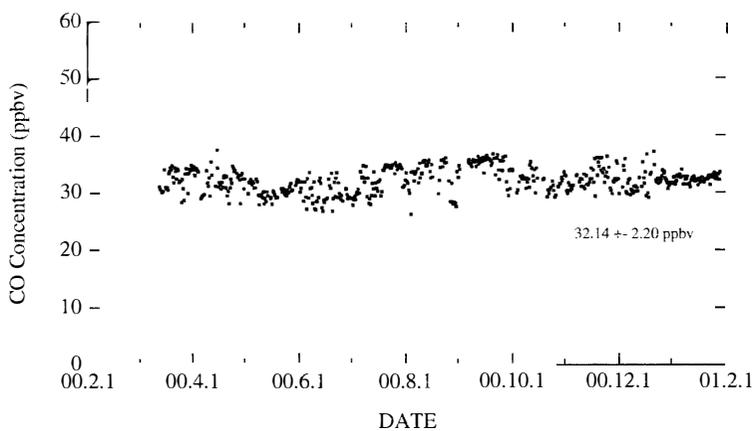

Fig. 4. *Time variations of the Check gas concentration determined at Syowa Station during the period of JARE-41.*

obtained, was estimated to be within 0.8% (1σ). The relationship between the CO concentration and peak area and height of CO, thus obtained, is shown in Fig. 3. It is clearly seen in this figure that both peak area and height correlate linearly with the assigned CO concentration in the range of 20–200 ppbv. The two experiments, the reproducibility and linearity tests described above, were conducted at the National Institute of Polar Research, Tokyo.

Novelli *et al.* (1998) pointed out that the linearity of the RGA3 CO analyzer could change over time, depending on the age of the HgO reaction bed in the detector. As mentioned in Section 2.2, we inserted Check gas analyses into the normal observation sequence to monitor long-term variations of the linearity. Figure 4 shows temporal variations of the CO concentration for the Check gas determined at Syowa Station from March 2000 to January 2001. From this figure, no clear trend can be found in the concentration variation for a whole year. Therefore, it can be concluded that the CO analyzer used at Syowa Station for JARE-41 had shown good linearity at least for the year. As can be seen from the figure, the standard deviation of the Check gas analyses was four times larger than the system's reproducibility (0.5 ppbv). It could be possible that the Check gas that stayed at the pressure regulator and Teflon tube for long time had deteriorated before being introduced into the analyzer, since the interval between Check gas analyses was set to be 12 hours.

2.4. Standard gas

To maintain high precision observation of the CO concentration for a long time, we categorized our standard gases into primary, secondary and working gases. The primary gas was produced by the gravimetric method using a precise balance with a
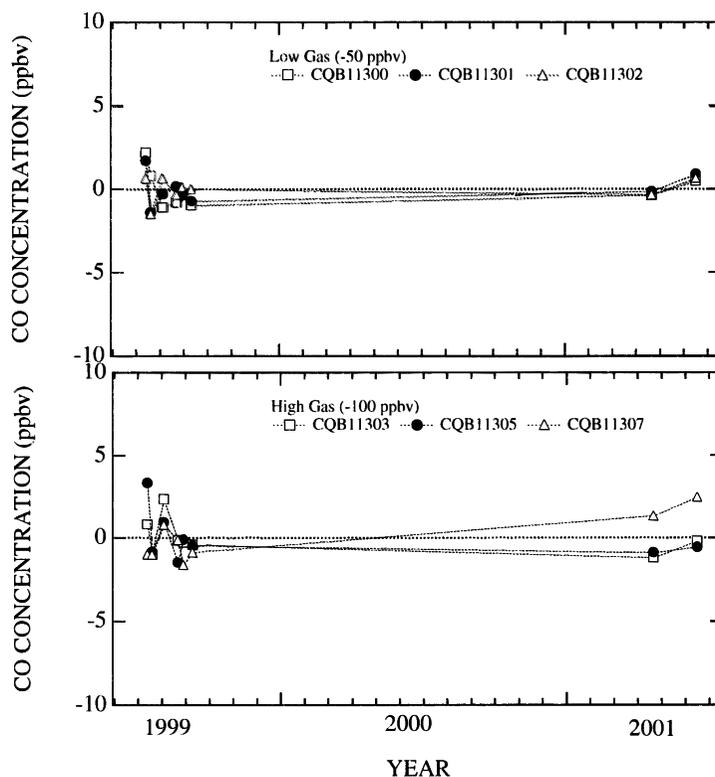

Fig. 5. *Stability of the CO working standard gases used by JARE-41. Each point denotes a deviation from the average value.*

precision better than $3\sigma=4.6$ mg for the range from 1 mg to 100 kg. Since detailed descriptions of the method have already been reported by Tanaka *et al.* (1983) and Aoki and Kawaguchi (1990), only a brief explanation will be given here.   The original gas of 1.508% concentration was first prepared by mixing pure nitrogen, oxygen and CO. Then, intermediate gases of 200.7 ppmv and 2.501 ppmv were produced by dilution of the 1.508% gas with the Ultra-pure air in which the amount of CO had been determined to be 1.6 ppbv.   Finally, four primary gases ranging from 50 to 300 ppbv were obtained by dilution of the 2.501 ppmv gas with the purified air.   The absolute accuracy of the primary standards was estimated to be on the order of 0.3%.   The secondary standard gases were air-CO mixtures of which CO concentration ranged from 50 to 200 ppbv determined by the primary gases and stored in 47 liter aluminum high-pressure cylinders.

We also prepared CO-in-air working standard gases of around 100 and 50 ppbv, which were also stored in aluminum cylinders and calibrated against the secondary gases, for usual calibrations of the CO analyzer at Syowa Station.   The working standard gases were calibrated 6 times before being shipped to Syowa in 1999 and 2 times after return to Japan in 2001.   The calibration results for the 6 working gases used in JARE-41 are shown in Fig. 5 as deviations from their averaged values.   As shown in these figures, all working standard gases except for that in cylinder no. CQB 11307 were stable within a range around 1.5 ppbv (1σ) for the two years.   The CO concentration of CQB11307 increased by 3.5 ppbv during its usage, which could be caused by oxidation of organic substances which remained and adhered to the inner wall of the cylinder.

3.   Preliminary results for the JARE-41 period

The *in-situ* measurement system for the CO concentration was installed at Syowa Station in March 2000 by JARE-41.   The air intake was mounted at the top of an 8 m-high mast, 30 m from the laboratory building, facing prevailing winds.   The air sample was introduced through Teflon tubing of 1/2-inch o.d. and about 40 m long from the intake into the gas handling system.   The in-situ measurement was started on March 12, 2000 and has continued up to the present without serious problems.   The CO analyzer and working standard gases used in the JARE-41 period were replaced by new ones at the end of January 2001 and were shipped to Japan for maintenance and re-calibrations.   In this section, we will present preliminary results for the CO concentration at Syowa Station measured by JARE-41.

A total of 20877 data were obtained at Syowa Station from March 2000 to January 2001.   All available data are plotted in Fig. 6a.   It can be seen that some of the data are scattered toward higher values, probably due to local station activities such as exhaust gas from the power plant and vehicles.   To eliminate the contaminated data, a simple selection scheme was applied to the data set, assuming that CO concentration variation over time was small in an air mass free from local contamination and the contaminated air showed higher CO concentration than background values.   We first calculated apparent daily mean concentrations and daily standard deviations using all available data.   Then, data showing higher values more than 2 standard deviations
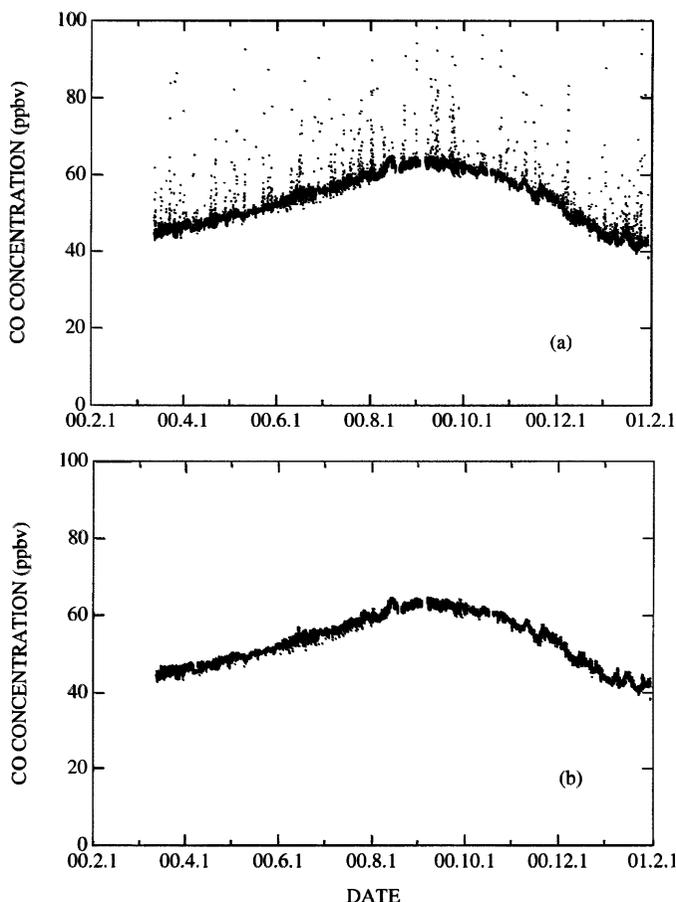
Fig. 6. (a) All available CO concentration data measured at Syowa Station.
(b) Same as (a), but for selected data.

from the daily mean were removed from the data set as outliers and the daily means were calculated again. These procedures were repeated until no outliers were identified, with the result that 1978 data corresponding to 9.5% of all available data were rejected. The selected data are shown in Fig. 6b.

The daily mean values of the CO concentration and their standard deviations calculated from the selected data are shown in Fig. 7. The standard deviations of daily concentration variation ranged from 0.1 to 1.2 ppbv, an average value being 0.5 ppbv that was comparable to the instrumental reproducibility of the measurement system. This fact indicates that there had been no diurnal cycle in the CO concentration above our detection limit throughout the year. It is clearly seen in Fig. 7 that the CO concentration shows a seasonal cycle with peak-to-peak amplitude of around 20 ppbv. Maximum and minimum concentrations appeared at the beginning of September and in late austral summer, respectively. These characteristics of the CO seasonal cycle were also observed in southern middle and high latitudes by the NOAA/CMDL flask
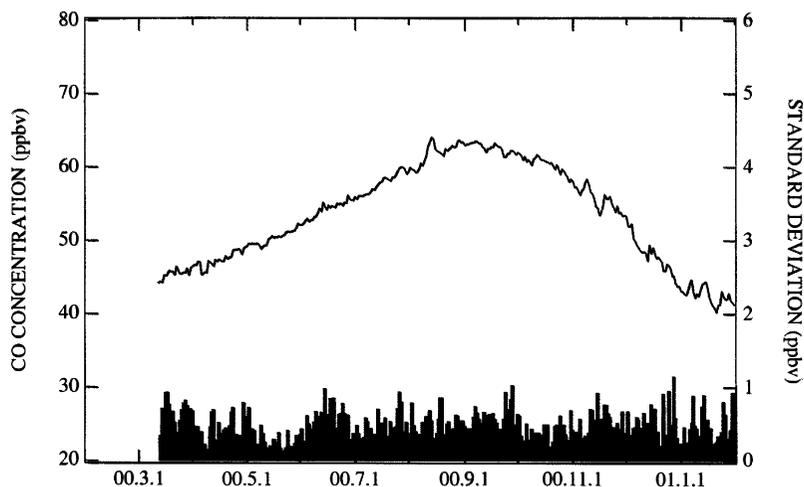
Fig. 7. *Daily mean CO concentrations (solid line; left axis) and daily standard deviations (bars; right axis) at Syowa Station.*

sampling network (Novelli *et al.*, 1998). It is also noticeable from the figure that short-term variations of the CO concentration, of periods from several days to 10 days, are superimposed on the seasonal variation. Such a short-term variation could not be detected by discrete flask sampling of sampling interval longer than a week. Nakazawa *et al.* (1991) reported that a similar short-term variation was found in our continuous CO_2 concentration record observed at Syowa Station. These phenomena could be induced by air mass exchange in association with synoptic scale disturbances.

4. Concluding remarks

We have developed a high precision, *in-situ* measurement system for the atmospheric CO concentration. A standard gas system for the CO measurements to maintain a consistent calibration scale for a long time was also prepared. The measurement system was installed at Syowa Station in March 2000 and has been maintained up to the present without serious problems. The first-year's results showed a clear seasonal cycle and short-term irregular variations in the CO concentration. Since our primary standard scale was established independently, it will be necessary to compare our calibration scale with other measurement programs in the future.

By continuing the *in-situ* observation of the CO concentration at Syowa Station, it will become possible to obtain knowledge of seasonal and secular variations of the CO concentration. As stated above, we have maintained an in-situ measurement system for CO_2 and CH_4 concentrations at Syowa Station. Since sources and sinks for the species, CO_2, CH_4 and CO, are partly different from each other, comparisons between the temporally dense data records will provide us useful information about the origin of concentration variations and about gas and aerosol transports to the Antarctic region.

Acknowledgments

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