Scientific paper

Temporal variations of atmospheric CO_2 concentration and carbon isotope ratio in Ny-Ålesund, Svalbard

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Abstract: Ground based observation of the atmospheric CO_2 concentration and its carbon isotope, $\delta^{13}C$, have been performed in Ny-Ålesund, Svalbard since 1991. The CO_2 concentration and $\delta^{13}C$ observed in 1991–1999 showed clear seasonal cycles with peak-to-peak amplitudes of 16.5‰ ppmv and 0.8, respectively. From comparison of the seasonal cycles, it was found that the seasonal CO_2 cycle in Ny-Ålesund is mainly caused by seasonal change of biospheric activities. Interannual variations of the CO_2 concentration and $\delta^{13}C$ superimposed on their secular trends were also observed. Comparing both of the interannual variations revealed that the cause was primarily ascribed to the imbalance of the CO_2 exchange between the atmosphere and the terrestrial biosphere.

1. Introduction

For better understanding of the global carbon cycle on the earth's surface, it is necessary to obtain a precise and long-term data set of the background CO_2 concentration in the atmosphere over geographically wide areas. For this purpose, many monitoring programs have been initiated around the world and the data obtained by these measurements provide us with global pictures of the distribution of the atmospheric CO_2 concentration (*e.g.* Conway *et al.*, 1994). Based on the present understanding, about half of the industrially released CO_2 remains in the atmosphere and the rest is absorbed by the surface ocean and the terrestrial biosphere (Keeling *et al.*, 1989b). However, individual roles of the surface ocean and the terrestrial biosphere in the global carbon cycle are not well understood (Francey *et al.*, 1995; Keeling *et al.*, 1995; Morimoto *et al.*, 2000).

Carbon isotopic ratio, $\delta^{13}C$, of atmospheric CO_2, defined as:

$$\delta^{13}C = \left(\frac{(^{13}CO_2/^{12}CO_2)_{sample}}{(^{13}CO_2/^{12}CO_2)_{standard}} - 1 \right) 10^3, \tag{1}$$

has been used as an effective tool for separating the net air-sea fluxes of CO_2 from those between the atmosphere and the terrestrial biosphere, since the degree of isotopic fractionation effect is different between these exchange processes. When a net CO_2 exchange occurs between the atmosphere and the terrestrial biosphere, $\delta^{13}C$ of the atmospheric CO_2 varies at a rate of -0.05‰/ppmv (Keeling *et al.*, 1989b). On the other hand, the net CO_2 exchange

between the atmosphere and the ocean causes only about $-0.005‰/ppmv$ change in $\delta^{13}C$ (Siegenthaler and Münnich, 1981).

We have maintained a systematic air sampling program at ground level in Ny-Ålesund, Svalbard (78°55′N, 11°56′E) since 1991 for measuring the atmospheric CO_2 concentration and carbon isotope ratio, $\delta^{13}C$, of CO_2 (Yamanouchi et al., 1996). In this paper, we will present temporal variations of the atmospheric CO_2 concentration and $\delta^{13}C$ for 1991–1999 and 1996–1999, respectively. The $\delta^{13}C$ data before 1995 were removed from the analyses since there were some experimental and sample quality problems. Using the available data, seasonal and secular variations of the atmospheric CO_2 concentration and their causes will be discussed.

2. Experimental procedures

Air samples analyzed in this study were collected at the Japanese Observatory, called "Rabben", in Ny-Ålesund, Svalbard (78°55′N, 11°56′E) during the period from August 1991 to October 1999. Figure 1 shows the location of Ny-Ålesund. An air sample was pumped from an air intake mounted on the roof of Rabben and pressurized up to 9.9×10^5 Pa into an 0.800×10^{-3} m³ stainless-steel flask with stop-valves at both ends. The air sampling was performed once a week by the staff of the Norwegian Polar Institute without any sampling criterion, e.g., wind direction or wind speed. The flasks filled with air samples were returned to the National Institute of Polar Research (NIPR) once per two months and
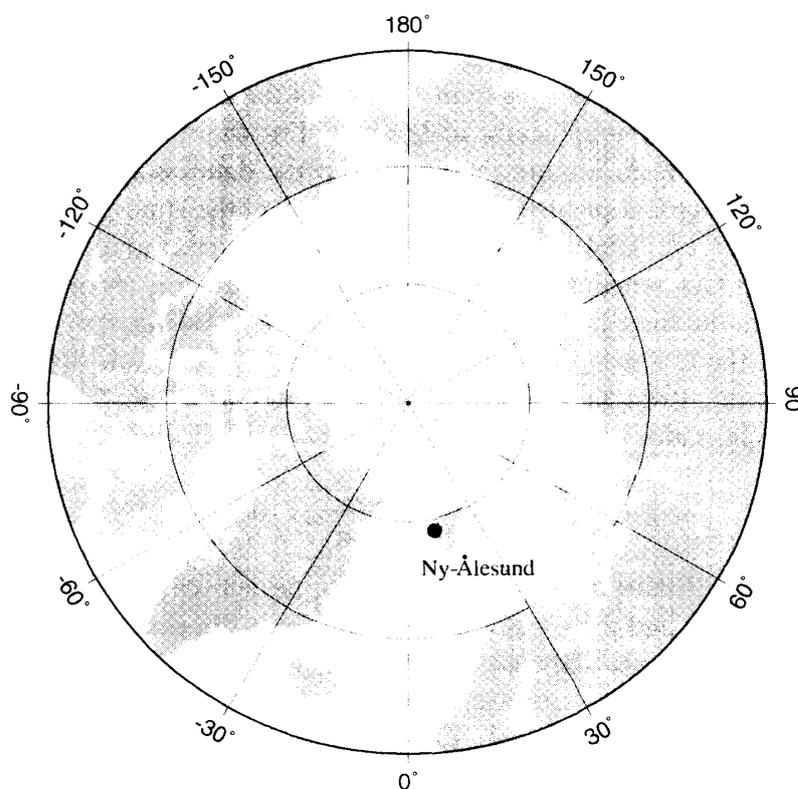

Fig. 1.   Location of Ny-Ålesund, Svalbard.

subsequent analyses were performed. The time between air sampling and concentration analysis is ordinarily about 2.5–3 months.

The CO_2 concentrations of the air samples were determined against our CO_2-in-air standard gases using a non-dispersive infrared (NDIR) analyzer (Tanaka *et al.*, 1983) with a precision of 0.1 and 0.02 ppmv before and after August 1996, respectively, when our NDIR analyzer was exchanged. After the CO_2 concentration analysis, part of the air sample was used for determining CH_4 concentration by a gas chromatograph with a flame ionization detector (GC/FID) (Aoki *et al.*, 1992). The CO_2 sample used for $\delta^{13}C$ measurement was cryogenically extracted from the remaining air sample in the flask using an automatic extraction system at NIPR.

The automatic CO_2 extraction system consists of a mass flow controller, pneumatic valves, H_2O trap, temperature controlled CO_2 trap, turbo molecular pump and oil rotary pump. A computer automates the CO_2 extraction procedure, described below. After the system was sufficiently evacuated to lower than 1.3×10^{-4} Pa, H_2O and CO_2 traps were cooled at about -80 and $-197°C$, respectively. The air sample was pumped through the traps at a constant flow rate of 50×10^{-6} m³/min (50 cc/min). The extracted CO_2 was sublimed by increasing the temperature of the CO_2 trap and transferred into a sample tube cooled at $-197°C$. When the transfer of CO_2 was finished, the tube was flamed off by a gas burner. The reliability of the NIPR extraction system was confirmed by comparing $\delta^{13}C$ values of the extracted CO_2 samples with those extracted at Tohoku University (Nakazawa *et al.*, 1993, 1997a). A typical amount of a CO_2 sample was about 0.280×10^{-6} m³$_{STP}$ (280 μl_{STP}). The $\delta^{13}C$ values of the CO_2 samples were analyzed by a mass spectrometer, Finnigan MAT-δS at Tohoku University. The instrumental reproducibility for the $\delta^{13}C$ analysis was within 0.02‰ (Nakazawa *et al.*, 1997a).

3. Results and discussions

From August 1991 to October 1999, about 370 air samples were collected at Ny-Ålesund and analyzed in Japan. Figures 2a and b show the observed CO_2 concentrations and $\delta^{13}C$ values, respectively, together with their best fit curves to the data, long-term trends and annual increase rates. These fitted curves were calculated by a digital filtering technique including Fourier harmonics, linear interpolations, Reinsch-type splines and a Butterworth filter. Details of the curve fitting procedures were presented in Nakazawa *et al.* (1997b). In the curve fitting procedures, data lying more than 3 standard deviations from the best fit curve were regarded as 'non-baseline data', mainly due to local human activities, and were eliminated from the data set. The $\delta^{13}C$ data obtained before 1996 had problems in their quality, since some of the air samples were stored in the flasks for more than one year, and/ or there might have been problems in the mass spectrometer analyses. Therefore, we did not include the $\delta^{13}C$ data obtained before 1995 in the present study.

As seen in Fig. 2, the CO_2 concentration and $\delta^{13}C$ show secular increase and decrease, respectively, due mainly to fossil fuel combustion, as well as seasonal cycles and interannual variation. The seasonal cycles of $\delta^{13}C$ are quite similar to those of CO_2 concentration, but they are 180° out of phase. The average seasonal amplitudes of CO_2 concentration and $\delta^{13}C$ are about 16.5 ppmv and 0.8‰ peak-to-peak, respectively. These values are almost the same as those obtained for 40°–55°N in the western Pacific during 1984–1991 (Nakazawa *et al.*,
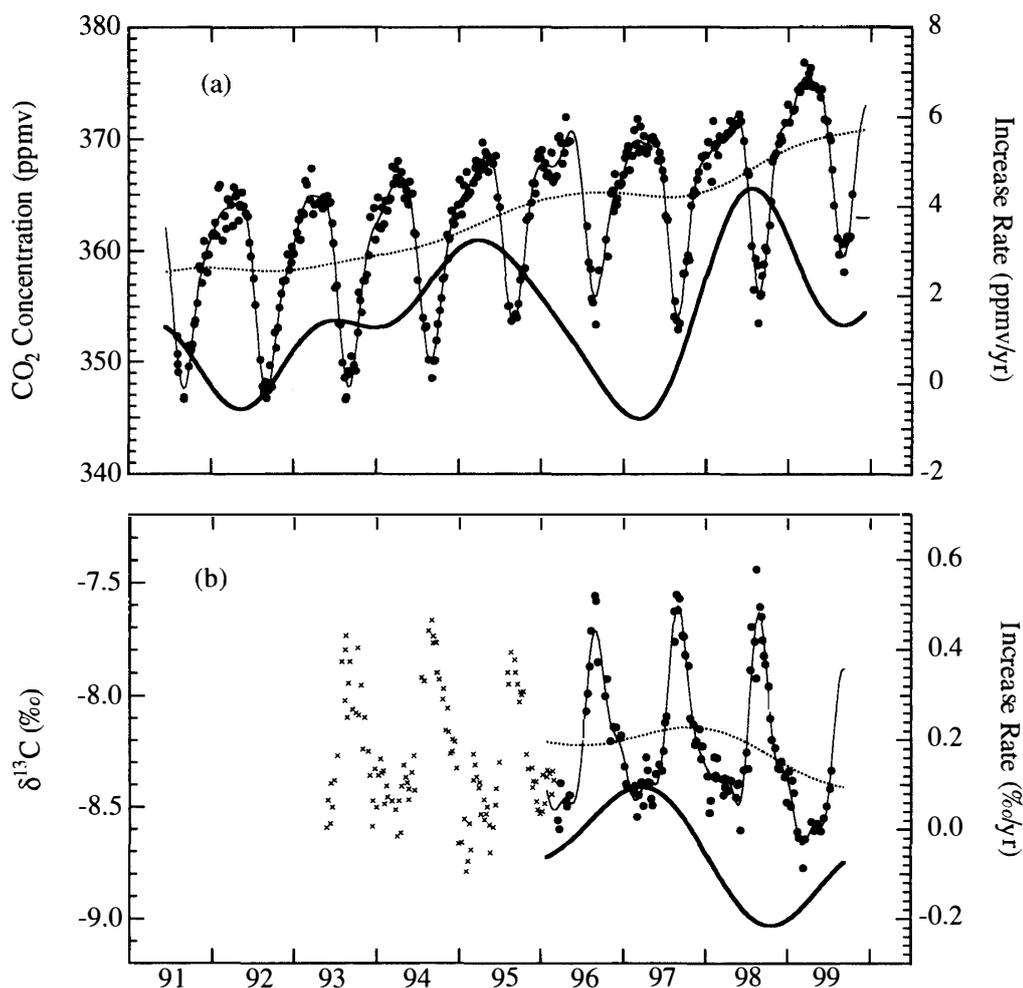
Fig. 2a. The CO_2 concentration observed at Ny-Ålesund from 1991 to 1999. Closed circles, thin and broken lines represent observed data, best fit curve to the data and long-term trend, respectively (left axis). Thick line shows the increase rate of the CO_2 concentration (right axis).

b. Same as (a), but for $\delta^{13}C$ data from 1996 to 1999. Crosses are data that were not included in this study.

Table 1. Annual mean values of the CO_2 concentration and $\delta^{13}C$ observed in Ny-Ålesund, Svalbard.

	1991	1992	1993	1994	1995	1996	1997	1998	1999
CO_2 (ppmv)	358.15	358.34	358.95	360.45	363.16	365.04	364.95	367.13	370.18
$\delta^{13}C$ (‰)	–	–	–	–	–	−8.216	−8.162	−8.217	−8.386

1997a). Annual mean values of the CO_2 concentration and $\delta^{13}C$ observed in Ny-Ålesund are listed in Table 1.

To investigate causes of the seasonal CO_2 cycles, the observed CO_2 concentration and

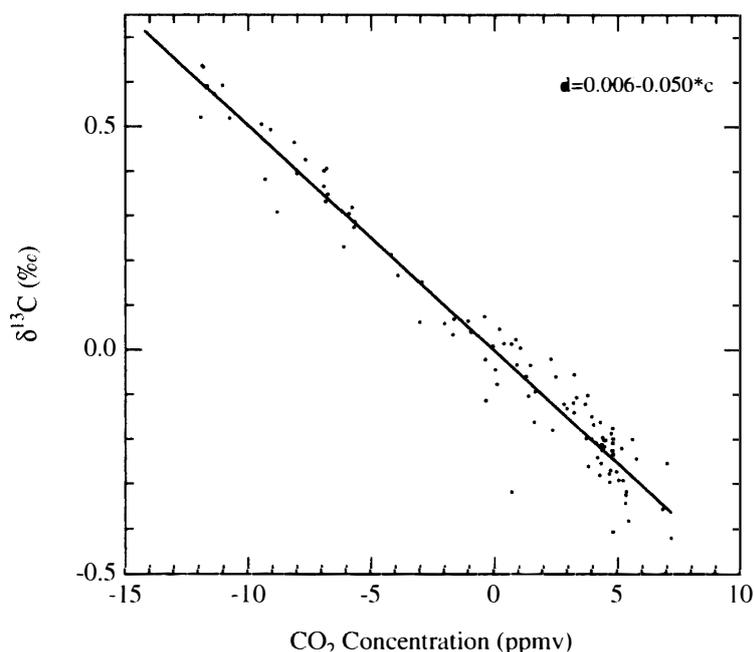*Fig. 3. Relationship between the seasonal cycles of the CO_2 concentration and $\delta^{13}C$ observed at Ny-Ålesund during the period from 1996 to 1999. Closed circles represent the observed data and the thin line is the fitted line.*

$\delta^{13}C$ from 1996 to 1999 were compared after their long-term trends had been subtracted. The relationship of the seasonal component between the CO_2 concentration and $\delta^{13}C$ is plotted in Fig. 3. It is clearly seen in this figure that the relationship is almost linear. The change rate of $\delta^{13}C$ with respect to the CO_2 concentration was calculated by a least square method to be around $-0.05‰$/ppmv. This result suggests that the seasonal variation of the CO_2 exchange between the atmosphere and the terrestrial biosphere is responsible for the observed CO_2 seasonal cycles in Ny-Ålesund. Aoki *et al.* (1996) observed extremely low partial pressure of CO_2 (pCO_2) in Greenland Sea surface water in summer and speculated that the Greenland Sea acted as a strong sink for atmospheric CO_2 in summer. However, the relationship between CO_2 concentration and $\delta^{13}C$ shown in Fig. 3 demonstrates that the seasonal change of the terrestrial biospheric activity caused the observed variations of the CO_2 concentration in Ny-Ålesund on the seasonal time scale.

Engardt *et al.* (1996) analyzed their CO_2 concentration and $\delta^{13}C$ data observed in Ny-Ålesund and concluded that, on time scales of a few days in spring and early summer when phytoplankton blooms occurred in Greenland Sea, an oceanic air mass depleted in CO_2 by oceanic uptake produced dips of 2–4 ppmv in the CO_2 concentration in Ny-Ålesund.

As shown in Fig. 2, short-term variations of CO_2 concentration and $\delta^{13}C$ are more prominent in winter than in other seasons. Similar phenomena have also been reported by Engardt and Holmén (1999) in Ny-Ålesund and at other Arctic stations such as Alert (Trivett *et al.*, 1996; Yuen *et al.*, 1996) and Point Barrow (Conway *et al.*, 1994). To obtain information on the source of the short-term variations observed in Ny-Ålesund, we

compared deviations of the CO_2 concentration and $\delta^{13}C$ data from their best-fit curves. The relationship between the deviations of the CO_2 concentration and $\delta^{13}C$ showed a negative correlation, of which the slope was $-0.047\pm0.008‰/ppmv$. As stated above, when a net CO_2 exchange occurs between the atmosphere and the terrestrial biosphere, the change rate of $\delta^{13}C$ with respect to the CO_2 concentration is about $-0.05‰/ppmv$. Taking into account that the $\delta^{13}C$ signature of the fossil fuel CO_2 is close to that of the terrestrial biosphere (Andres *et al.*, 1999), the source of the short-term variations observed in Ny-Ålesund was ascribed to the biospheric and/or fossil fuel CO_2 in origin. This result is in agreement with the 3-dimensional model analysis by Brandefelt and Holmén (2001). They showed that the cause of sporadic high CO_2 concentrations observed in Ny-Ålesund is ascribed to advection of an air mass from Europe, where both biospheric and fossil fuel CO_2 are released in winter.

It has been pointed out that the increase rate of the CO_2 concentration fluctuates in association with El Niño and Southern Oscillation (ENSO) events (Bacastow, 1976; Keeling *et al.*, 1989a). As shown in Fig. 2a, such interannual variations of the CO_2 increase rate have been observed in Ny-Ålesund; rapid increase of the CO_2 concentration in relation to the occurrence of ENSO events was found in 1995 and 1998. It is also noticeable that the CO_2 increase almost stopped in 1997. The long-term trend of $\delta^{13}C$ data in Fig. 2b shows rapid increase and decrease in the beginning of 1997 and 1998, respectively, which correspond well to variations of CO_2 concentration but for the opposite sign.

In order to compare more quantitatively the magnitude of the interannual variations in the CO_2 concentration and $\delta^{13}C$, we first extracted the interannual components from the long-term trends by the following procedures. It should be noted that the following analyses were performed during the period from 1996 to 1999, during which our $\delta^{13}C$ data were available. (1) Assuming that the year-to-year change of the fossil fuel combustion rate is small, the contribution of the fossil fuel CO_2 was approximated by a linear fit to the long-term CO_2 trend. (2) The fitted line, thus obtained, was subtracted from the observed long-term trend of the CO_2 concentration and the residual was regarded as the interannual component of the CO_2 concentration. (3) Similarly, the contribution of the fossil fuel combustion and isotopic disequilibrium flux (Tans *et al.*, 1993) to the $\delta^{13}C$ trend was approximated by a linear fit to the long-term $\delta^{13}C$ trend and was subtracted from it. (4) The residual, thus obtained, was regarded as the interannual component of $\delta^{13}C$. Figure 4a shows the interannual component of the CO_2 concentration in Ny-Ålesund from 1996 to 1999. We then calculated the $\delta^{13}C$ variations expected when only the oceanic CO_2 produced the interannual CO_2 variation and when only the terrestrial biospheric CO_2 did, respectively, by multiplying the respective values of $-0.005‰/ppmv$ and $-0.05‰/ppmv$ by the interannual variation of the CO_2 concentration shown in Fig. 4a. The rate of change of $\delta^{13}C$ with respect to the CO_2 concentration is calculated to be from -0.054 to $-0.050‰/ppmv$ for the terrestrial biospheric CO_2 when using the annual average values of the CO_2 concentration and $\delta^{13}C$ from 1996 to 1999, and -27 and $-28‰$ as the $\delta^{13}C$ value of the biospheric CO_2, respectively. Similarly, the change rates of $\delta^{13}C$ range from -0.0048 to $-0.0079‰/ppmv$ for the oceanic CO_2. In this case, we assume sea surface temperature and $\delta^{13}C$ values of the dissolved inorganic carbon in the Greenland Sea to be $2.4°C$ and $1.2–1.36‰$, respectively (our unpublished data, 2000). These calculations show that the respective change rate in $\delta^{13}C$ is not so sensitive to the long-term change in the atmospheric CO_2 concentration and
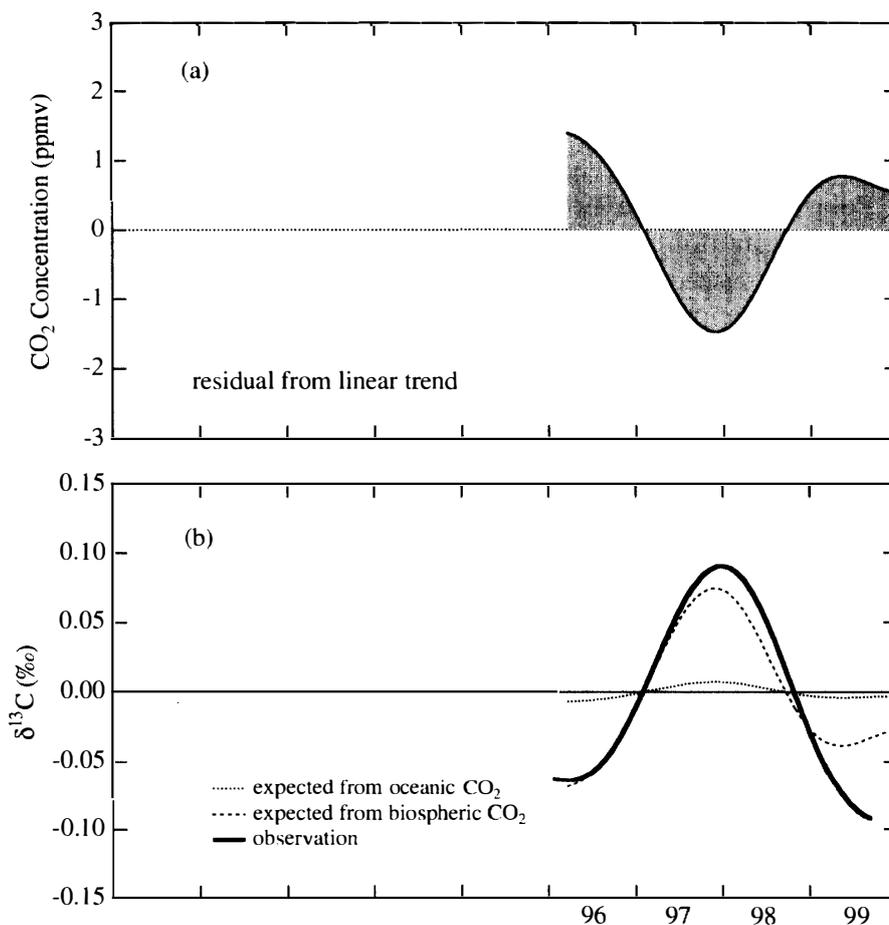
Fig. 4a. Interannual variation of the CO_2 concentration at Ny-Ålesund from 1996 to 1999.
   b. Comparison of observed interannual variation of $\delta^{13}C$ (thick line) with those calculated on the basis of biospheric CO_2 (broken line) and oceanic CO_2 (dotted line) at Ny-Ålesund.

$\delta^{13}C$ and uncertainties in the estimated $\delta^{13}C$ values of the biospheric and oceanic CO_2.

The results are shown in Fig. 4b. It is obvious from this figure that the observed $\delta^{13}C$ variations are well reproduced by those calculated based on the terrestrial biospheric CO_2. From this examination, it is suggested that the cause of the interannual variations of the CO_2 concentration observed in Ny-Ålesund from 1996 to 1999 were produced by an imbalance of the net CO_2 exchange between the atmosphere and the terrestrial biosphere. This finding will be further studied with the aid of global data sets of CO_2 concentration and $\delta^{13}C$. A recent phenomenological model study (Ito and Oikawa, 2000) showed that the terrestrial biosphere released excess CO_2 of 2.7 PgC/year (GtC/yr), which is equivalent to 1.26 ppmv CO_2 in the atmosphere, in 1998. Ito and Oikawa (2000) used a climate data set and their biosphere model, and concluded that higher temperatures and excess precipitation during the 1998 ENSO event accelerated plant respiration and soil decomposition. Their results are consistent with our findings obtained by atmospheric CO_2 concentration and $\delta^{13}C$ observations.

4. Conclusions

In order to clarify temporal variations of the atmospheric CO_2 concentration and $\delta^{13}C$, we have continued a systematic air sampling in Ny-Ålesund with cooperation of the Norwegian Polar Institute since 1991.

The CO_2 concentration and $\delta^{13}C$ observed in Ny-Ålesund during the periods 1991–1999 and 1996–1999, respectively, showed clear seasonal cycles with peak-to-peak amplitudes of 16.5 ppmv and 0.8‰. The amplitudes were similar to those observed at latitudes $40°–55°N$ in our previous study. It was also found that the CO_2 concentration and $\delta^{13}C$ data showed interannual variations in association with an ENSO event. From detailed comparisons of the CO_2 concentration and $\delta^{13}C$ data, it was found that the variations in the CO_2 exchange between the atmosphere and the terrestrial biosphere were responsible for the CO_2 variations on both seasonal and interannual time scales.

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