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Time and space variations of the carbon isotopic ratio of tropospheric carbon dioxide over Japan

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ABSTRACT

CO_2 samples collected in the troposphere over Japan during the period from April 1984 to November 1990 were analyzed for $\delta^{13}C$ with a precision of better than $0.03\,‰$. The amplitudes of the seasonal cycles of $\delta^{13}C$ and CO_2 concentration decreased with increasing height, with a phase delay of about 1 month between the lower and upper troposphere. From a comparison of the observed seasonal variation of the CO_2 with that of $\delta^{13}C$, it was found that the rate of change in $\delta^{13}C$ with respect to the CO_2 concentration is about $-0.05\,‰$/ppmv. This suggests that the seasonal CO_2 cycle over Japan is mainly produced by seasonally-dependent biospheric activities. However, air transport from different latitudes is also important for the seasonal CO_2 cycle, particularly in the upper troposphere. $\delta^{13}C$ decreased secularly at an average rate of about $-0.04\,‰$/year, due mainly to combustion of fossil fuel with isotopically light CO_2. Interannual variations of $\delta^{13}C$, superimposed on the long-term trend, were also observed, which were approximately opposite in phase with those of the CO_2 concentration. The comparison of both interannual variations suggested that the cause could be primarily attributed to an imbalance in the CO_2 exchange between the atmosphere and the biosphere rather than between the atmosphere and the oceans.

1. Introduction

Systematic measurements of the background concentration of atmospheric CO_2 are currently being performed at many sites around the world (Pearman and Hyson, 1986; Keeling et al., 1989a; Ferguson, 1991; Enting and Pearman, 1992). The data from this station network provide us with valuable information about exchange of carbon between the atmosphere and the earth's surface, which is indispensable for predicting future levels of atmospheric CO_2 concentration and for evaluating strategies for limiting or reducing future emissions of CO_2 into the atmosphere. However, the role of the biosphere in the carbon cycle is not yet well understood. To solve this difficulty, measurements are required for the carbon isotopic ratio, $\delta^{13}C$, of atmospheric CO_2 as well as for its concentration (Gillette and Box, 1986; Pearman and Hyson, 1986; Tans et al., 1989; Keeling et al., 1989a). It is expected that the CO_2 exchange between the atmosphere and the biosphere can be quantitatively separated from that between the atmosphere and the oceans, by using the different isotopic fractionations of CO_2 in these exchange processes; the former yields a change in the atmospheric $\delta^{13}C$ at a rate of approximately $-0.05\,‰$/ppmv and the latter at a rate of approximately $-0.005\,‰$/ppmv, at present levels of the CO_2 concentration and $\delta^{13}C$ in the atmosphere (Siegenthaler and Münnich, 1981; Pearman and Hyson, 1986; Keeling et al., 1989a).

$\delta^{13}C$ values of atmospheric CO_2 have been

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measured for air samples taken from fixed stations on land, ships, aircraft and balloons, but they are still sparse (Keeling, 1958; Mook et al., 1983; Keeling et al., 1984; Francey, 1985; Francey and Goodman, 1985; Gamo et al., 1989; Keeling et al., 1989a; Francey et al., 1990). Measurements with aircraft are one of the most promising methods for detecting temporal and spatial variations of the atmospheric $\delta^{13}C$, because air samples collected on board aircraft are fairly free from the influence of regional CO_2 sources and sinks (Bischof, 1962; Tanaka et al., 1983a, 1987a; Pearman and Beardsmore, 1984; Nakazawa et al., 1991a). Therefore, the data from aircraft measurements are especially useful for constraining the carbon cycle models which are in use for elucidating causes of the CO_2 increase in the atmosphere. However, only two aircraft programs have been reported so far for measurements of atmospheric $\delta^{13}C$ (Friedli et al., 1987; Francey et al., 1990).

We have collected air samples for measurements of the tropospheric CO_2 concentration over Japan since 1979, using commercial jet airliners and chartered aircraft (Tanaka et al., 1983a, 1987a). The samples obtained after 1984 have also been analyzed for $\delta^{13}C$. In this paper, we report the results for the air samples collected during the period from April 1984 to November 1990, and discuss variations of $\delta^{13}C$ of tropospheric CO_2 over Japan, supplemented by the CO_2 concentration data.

2. Experimental procedures

The air samples analyzed in this study were collected in the troposphere over Japan once per month during the period from April 1984 to November 1990. The collection of the air samples was made using a Piper PA-28 (Japan Flying Service) below 4 km over the Pacific Ocean about 50 km off the coast of Sendai (38°N) and a McDonnell Douglas DC-9 (Japan Air System) at heights of 4–11 km between Sendai and Fukuoka (34°N). Each air sample was collected into a 550 ml Pyrex glass flask or a 350 ml stainless-steel flask by pressurizing up to 3.0×10^5 Pa with an electric diaphragm pump or a manual stainless-steel-plunger pump. Air samples were taken from the intake mounted on the nose of the PA-28 and from the so-called "fresh air" nozzle in the cockpit of the DC-9. Before air sampling, all flasks were evacuated to lower than 0.13 Pa with heating at 100°C for at least 3 h. Air samples collected in the flasks were returned to our laboratory and their CO_2 concentrations were determined using a non-dispersive infrared analyzer with a precision of 0.01 ppmv against our CO_2-in-air standard gases. Then, gas chromatographic analyses were made to determine the concentrations of CH_4, CO and N_2O. These analyses were done within 1 or 2 days after collection. More details of our sampling and analysis procedures have been described elsewhere (Tanaka et al., 1983a, b, 1987a, Nakazawa et al., 1992).

Within a few days after the gas chromatographic analyses, CO_2 was extracted cryogenically from the remaining air in the 550 ml flasks. The procedures were as follows. Each air sample was evacuated from the flask with a rotary pump first and then a diffusion pump through H_2O and CO_2 traps which were held at −100 and −197°C, respectively, maintaining the pressure in the traps to lower than 133 Pa. The temperature of the CO_2 trap was then increased to −100°C and sublimated CO_2 was collected into a sample vial cooled to −197°C. After the collection of CO_2, the vial was flamed off. Typical amounts of CO_2, thus extracted, were about 200 μl STP. Traps for both H_2O and CO_2 are made of quartz glass and contain many thin glass tubes to increase the trapping efficiency of the gases. The sample vial is a Pyrex glass tube with an outer diameter of 6 mm. The vial was dried by evacuating to 1.33×10^{-4} Pa and heating with a gas burner prior to use. Our extraction procedures are similar to those of Keeling (1958), Francey and Goodman (1985) and Friedli et al. (1987).

The mass spectrometer used in this study was a Finnigan MAT-δE installed at the National Institute of Polar Research in Tokyo. Since the amount of CO_2 available for the mass spectrometer analysis was rather limited, we used a cold finger inlet to introduce CO_2 samples into the mass spectrometer. Internal and external reproducibilities of our mass spectrometer analysis for carbon isotope were estimated to be within 0.02 and 0.03 ‰ (one standard deviation), respectively, by measuring 52 CO_2 samples extracted from a CO_2-in-air standard gas.

N_2O contained in the air samples cannot be removed from CO_2 by the above procedures. Since

the mass numbers of N_2O are the same as those of CO_2, the contribution of N_2O has to be corrected for in order to determine precise values of $\delta^{13}C$ and $\delta^{18}O$ of CO_2. Respective isotopic components are defined as

$$\delta^{13}C = \left\{ \frac{(^{13}C/^{12}C)_{sa}}{(^{13}C/^{12}C)_{st}} - 1 \right\} \times 1000, \quad (1)$$

$$\delta^{18}O = \left\{ \frac{(^{18}O/^{16}O)_{sa}}{(^{18}O/^{16}O)_{st}} - 1 \right\} \times 1000, \quad (2)$$

where subscripts $_{sa}$ and $_{st}$ denote the sample and the standard, respectively. In this study, the correction factors for measured values of δ^{45} and δ^{46} of CO_2 samples were estimated by analyzing pure CO_2, pure N_2O and CO_2-N_2O mixtures, according to Mook and Van der Hoek (1983) and Friedli and Siegenthaler (1988). Here, δ^{45} and δ^{46} represent current intensity ratios of the mass spectrometer for masses of 45 and 46, respectively. The correction factors, $\Delta\delta^{45}$ and $\Delta\delta^{46}$, are approximated by

$$\Delta\delta^{45} = \rho E(\delta_c^{45} - \delta_n^{45}), \quad (3a)$$

$$\Delta\delta^{46} = \rho E(\delta_c^{46} - \delta_n^{46}), \quad (3b)$$

where δ_c and δ_n are measured δ-values of pure CO_2 and pure N_2O relative to some CO_2 standard gas, respectively, ρ the concentration ratio of N_2O to CO_2, and E the relative ionization efficiency of N_2O against CO_2 for the MAT-δE, which was determined to be 0.75 ± 0.02. By substituting measured values of E, δ_c and δ_n into eqs. (3a) and (3b), $\Delta\delta^{45}$ and $\Delta\delta^{46}$ were found to be $(256 \pm 8)\rho$ and $(358 \pm 11)\rho$, respectively. Eqs. (3a) and (3b) can also be expressed by

$$\Delta\delta^{45} = C^{45}\rho, \quad (4a)$$

$$\Delta\delta^{46} = C^{46}\rho, \quad (4b)$$

where C's are constant values to be determined. We measured CO_2-N_2O mixtures with concentration ratios of 0 to 26×10^{-3}, and found respective factors to be $(234 \pm 3)\rho$ and $(334 \pm 8)\rho$ by applying a least squares fitting technique to the measurements. Since there were only slight differences between the results of the two methods, we simply averaged them. After eliminating the contribution of ^{17}O on the basis of the correction method by Mook and Grootes (1973), we obtained

$$\Delta\delta^{13}C = 250\rho \ (‰), \quad (5)$$

$$\Delta\delta^{18}O = 347\rho \ (‰). \quad (6)$$

Since ρ of the air samples collected for the period covered by this study can be regarded to be nearly constant, i.e., $\rho = 0.88 \times 10^{-3}$ (Elkins et al., 1988; our unpublished data), a correction of $+0.22‰$ was applied to all measured values of $\delta^{13}C$. In this analysis, the values of $\delta^{18}O$ were also determined. The results obtained will be described elsewhere.

Standards for our isotope measurements included 3 types; primary, secondary and working. The primary standard was CO_2 gas produced by reacting NBS-18 ($\delta^{13}C = -5‰$ and $\delta^{18}O = -23‰$ with respect to PDB) with 100% phosphoric acid at 25°C (Coplen et al., 1983). The secondary standards were obtained by purifying CO_2 gas prepared industrially and by extracting CO_2 from the atmosphere. The working standard gas, which was used in analyses of the CO_2 samples, was made by extracting CO_2 from the atmosphere, and its $\delta^{13}C$ value was determined by using secondary standard gases calibrated against the primary standard. The calibration of the secondary and working standards was repeated 6 times during 2 years of this analysis, and it was confirmed that both standards were stable within our measurement precision. By comparing the primary standard with a new primary prepared in the same way at the end of this study, we found differences of $\delta^{13}C$ and $\delta^{18}O$ between the gases of 0.02 and 0.1‰, respectively. Each standard CO_2 gas was stored in a Pyrex glass container with a metal-seal stop valve at one end. The volume of the containers for the primary, secondary and working standard gases are 20, 200 and 2300 ml, respectively.

Tanaka et al. (1983b, 1987b) found that a deterioration of the air samples occurred for the CO_2 concentration during storage in the flasks. To examine this problem, 16 flasks were filled with CO_2-in-air standard gas and their $\delta^{13}C$ values were measured after storing them for different periods from 0 to 80 days. The results showed a gradual, slightly positive shift in $\delta^{13}C$ with storage time; the shift amounted to $+0.05‰$ at 80 days after the flasks were filled with gas. In this study,

CO_2 extraction was usually performed within 1 week after sample collection. Therefore, the deterioration of air samples during their storage was negligible, the shift in $\delta^{13}C$ being within our measurement precision.

Francey and Goodman (1985) showed that CO_2 samples extracted and stored in glass flasks for longer than 80 days are affected by their storage. In the present study, the time between CO_2 extraction and mass spectrometer analysis was as long as 6 years. However, air samples collected at the same height interval and date showed almost identical values of $\delta^{13}C$, and deviations of measured $\delta^{13}C$ from a fitted curve for a particular height interval were independent of their storage time. Therefore, the deterioration of the extracted CO_2 samples stored in the flamed-off glass tubes appears to be very small.

3. Data analysis

Approximately 3200 air samples were collected over Japan from April 1984 to November 1990. Since the CO_2 extraction procedure is time consuming, 729 samples, which were thought to be representative of the CO_2 concentration in respective height intervals on the basis of the vertical CO_2 profiles measured in individual flights, were selected and analyzed for $\delta^{13}C$.

To examine height-dependent variations of $\delta^{13}C$, the data were first grouped into 5 intervals of 0–2, 2–4, 4–6, 6–8 and 8 km-tropopause, and then 2 or 3 data in the same month and height interval were simply averaged to calculate monthly mean values of $\delta^{13}C$. At this stage, 9 data were excluded from the data set. These data showed exceptionally high or low values, probably due to the influence of stratospheric air intruding into the troposphere or a failure in CO_2 extraction. Measurements of $\delta^{13}C$, thus obtained, showed clear evidence of a seasonal cycle and a long-term trend. To separate respective contributions, we applied a digital-filtering technique including Fourier harmonics, linear interpolation and a Butterworth filter (Hamming, 1977) to the time series of measurements. The technique has been described by Nakazawa et al. (1991a, 1992). Therefore, only a brief description and supplemental explanation are given here. In this study, the average seasonal cycle was first approximated by an annual cycle consisting of the fundamental and first and second harmonics, and then was smoothed by a 16th-order Butterworth filter with a cutoff period of 4 months for which a signal is attenuated by 50%. The residuals obtained by subtracting the average seasonal cycle from the data were interpolated linearly to calculate daily values of $\delta^{13}C$. Daily $\delta^{13}C$ values were smoothed by the 26th-order Butterworth filter with a cutoff period of 21 months to derive the long-term trend. The long-term trend thus obtained was subtracted from the data and the average seasonal cycle was determined again from the residuals. These steps were repeated 2 or 3 times to obtain an unchangeable long-term trend. Once the long-term trend and the average seasonal cycle were determined, these components were removed from the data. Then, daily $\delta^{13}C$ values were calculated from a linear interpolation of the residuals and were smoothed by the above-mentioned 16th-order Butterworth filter to derive irregular parts of the seasonal cycle. In this data process, we found that the long-term trends of $\delta^{13}C$ are different for different cutoff periods of the filter, as shown in Fig. 1. This phenomenon is seen especially in the results for the 4–6 km height interval. However, we assumed that the long-term trends in different height intervals of the troposphere are similar with each other and we employed 21 months as the cutoff period of the filter. The approximate average seasonal cycle, which was necessary in the first step of the iterative procedure, was obtained by fitting the observed data to the above Fourier harmonics and Reinsch-

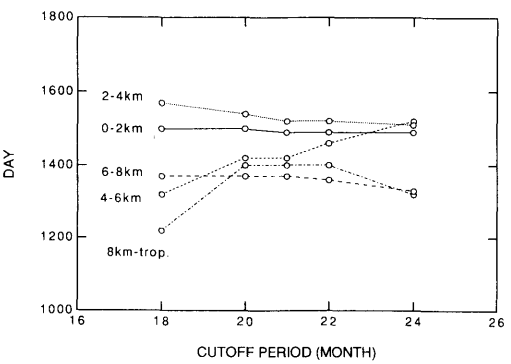

Fig. 1. Days on which the annual increase rates of $\delta^{13}C$ of atmospheric CO_2 at selected height intervals over Japan reach a minimum around late 1987, obtained by changing the cutoff period of the Butterworth filter. The days are the elapsed time relative to 1 January 1984.

type spline with a cutoff period of 5 years (Cox, 1983; Enting, 1987).

Further data selection was made statistically on the basis of the assumption that time-to-time changes in the background $\delta^{13}C$ value are small; data lying more than 3 standard deviations from the fitted curve were regarded as outliers and were rejected from the data set. This procedure was repeated 1 or 2 times for each data set until no further outliers were identified. Sixteen data were rejected by this procedure.

The procedures described above were also applied to the CO_2 concentration data obtained from the same air samples.

4. Results and discussion

Monthly mean values of $\delta^{13}C$ at the selected height intervals are shown in Fig. 2, together with the best fit curves and the long-term trends. The standard deviations of the data from the curves are

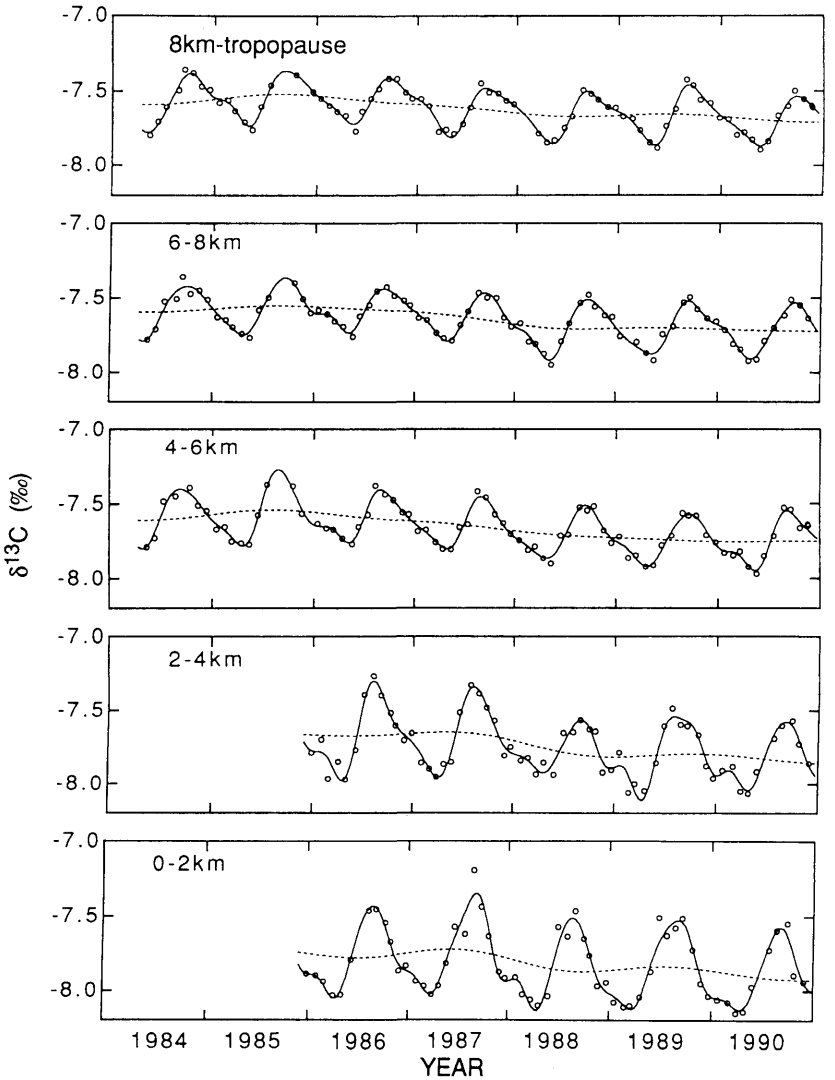

Fig. 2. $\delta^{13}C$ of atmospheric CO_2 at selected height intervals of the troposphere over Japan. Open circles represent monthly mean values of observed $\delta^{13}C$, thin lines the best fit curves of the data and broken lines the long-term trends.

0.069, 0.059, 0.038, 0.035 and 0.031 °/₀₀ for 0–2, 2–4, 4–6, 6–8 and 8 km-tropopause, respectively. The results of the CO_2 concentration are given in Fig. 3; these are consistent with those reported previously (Tanaka et al., 1983a, 1987a). The standard deviations at the respective intervals are 1.31, 1.00, 0.66, 0.50 and 0.62 ppmv.

The average seasonal cycles of $\delta^{13}C$ are shown in Fig. 4. As seen in this figure, the amplitude of the seasonal cycle decreases and its phase delays with increasing height. The peak-to-peak amplitude of the seasonal cycle is about 0.62 °/₀₀ in the lower troposphere and about 0.36 °/₀₀ in the upper troposphere. The minimum value of the cycle appears in early April and in early May, and the maximum value in mid- or late August and in mid-September in the lower and upper troposphere, respectively. These seasonal cycles are quite similar to those of the CO_2 concentration shown in Fig. 5, but the signs of the cycles are opposite to each

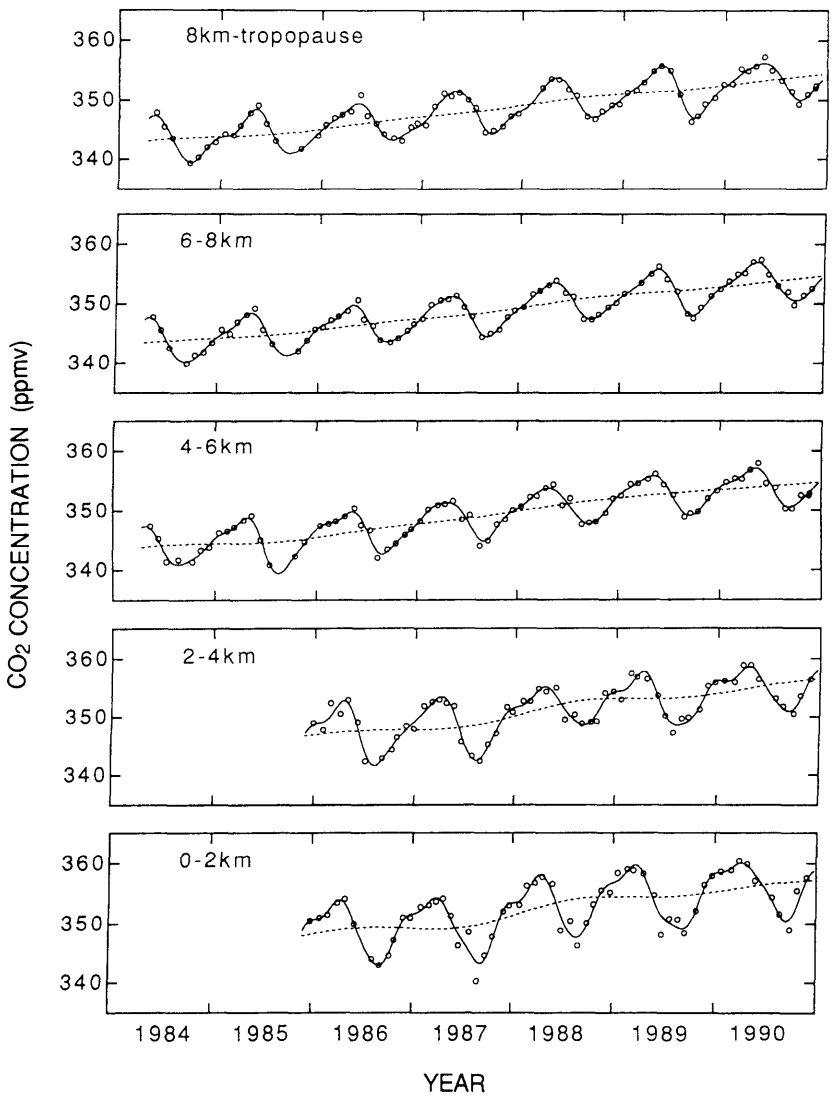

Fig. 3. The same as in Fig. 2, but for the CO_2 concentration.

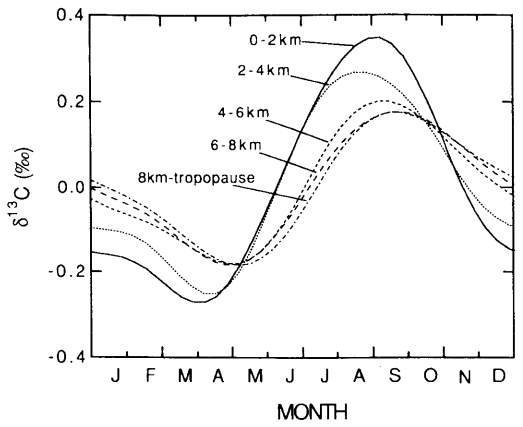

Fig. 4. Average seasonal cycles of $\delta^{13}C$ of atmospheric CO_2 at selected height intervals over Japan.

other. A similar relationship between the phase of the seasonal cycles of CO_2 concentration and $\delta^{13}C$ has been observed before at other locations in the northern hemisphere (Mook et al., 1983; Keeling et al., 1984; Friedli et al., 1987). It is also found from Figs. 4 and 5 that the seasonal cycle of the CO_2 concentration reaches a minimum and that of $\delta^{13}C$ a maximum later at 0–2 km than at 2–4 km. Such a behavior of the CO_2 concentration is inconsistent with the results obtained when all of the measured CO_2 data are used. This is probably an artifact related to the scatter of the data in the lower troposphere.

When CO_2 is added to the atmosphere from a

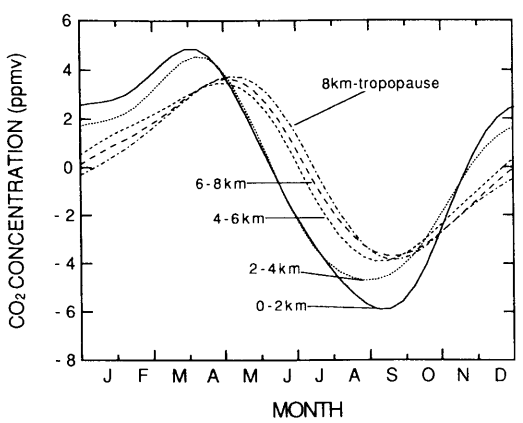

Fig. 5. The same as in Fig. 4, but for the CO_2 concentration.

single carbon reservoir, the balance equation for $^{13}CO_2$ in the atmosphere is given by

$$C\,\delta^{13} = C_0\,\delta_0^{13} + \delta_I^{13}(C - C_0), \tag{7}$$

where C_0 and C denote the CO_2 concentrations (in ppmv) before and after adding CO_2, respectively, δ_0^{13} and δ^{13} are the corresponding values of $\delta^{13}C$ ($^\circ/_{oo}$) and $\delta_I^{13}\,\delta^{13}C$ ($^\circ/_{oo}$) of CO_2 added to the atmosphere. Differentiating eq. (7) with respect to C, we obtain

$$d\,\delta^{13}/dC = (\delta^{13} - \delta_0^{13})/C. \tag{8}$$

Here, we assumed that the present levels of the concentration and $\delta^{13}C$ of atmospheric CO_2 and $\delta^{13}C$ in the biosphere (in the context of this paper, this means the terrestrial biosphere) are 350 ppmv, -7.8 and $-25\,^\circ/_{oo}$, respectively. From these values, eq. (8) and the fractionation factors given by Keeling et al. (1989a, p. 189), the rate of change in $\delta^{13}C$ with respect the CO_2 concentration is calculated to be $-0.05\,^\circ/_{oo}$/ppmv for the CO_2 exchange between the atmosphere and the biosphere (i.e., addition of CO_2 by ± 1 ppmv). While, the respective change rates of -0.002 and $-0.005\,^\circ/_{oo}$/ppmv are obtained for the CO_2 release from and uptake to the ocean using the kinetic fractionation factors given by Siegenthaler and Münnich (1988), $\delta^{13}C$ of about $1.6\,^\circ/_{oo}$ in the surface oceans and eq. (8). Therefore, the CO_2 exchange between the atmosphere and the ocean could affect the atmospheric $\delta^{13}C$ at rates of less than $-0.005\,^\circ/_{oo}$/ppmv.

To examine causes of the observed seasonal CO_2 cycles, the CO_2 and $\delta^{13}C$ data were compared with each other, after subtracting their long-term trends. The results are shown in Fig. 6. The relationship between the CO_2 concentration and $\delta^{13}C$ is almost linear for all height intervals. Slopes obtained by applying a least squares fitting technique are about $-0.05\,^\circ/_{oo}$/ppmv and correlation coefficients are better than 0.98, as shown in Table 1. These results suggest that the seasonal cycle of the tropospheric CO_2 over Japan is produced mainly by CO_2 exchange between the atmosphere and the biosphere. It is also seen in Table 1 that the rate of change in $\delta^{13}C$ with respect to the CO_2 concentration decreases with increasing height. This phenomenon may be attributed to the fact that tropospheric air over Japan is transported from different areas in different seasons,

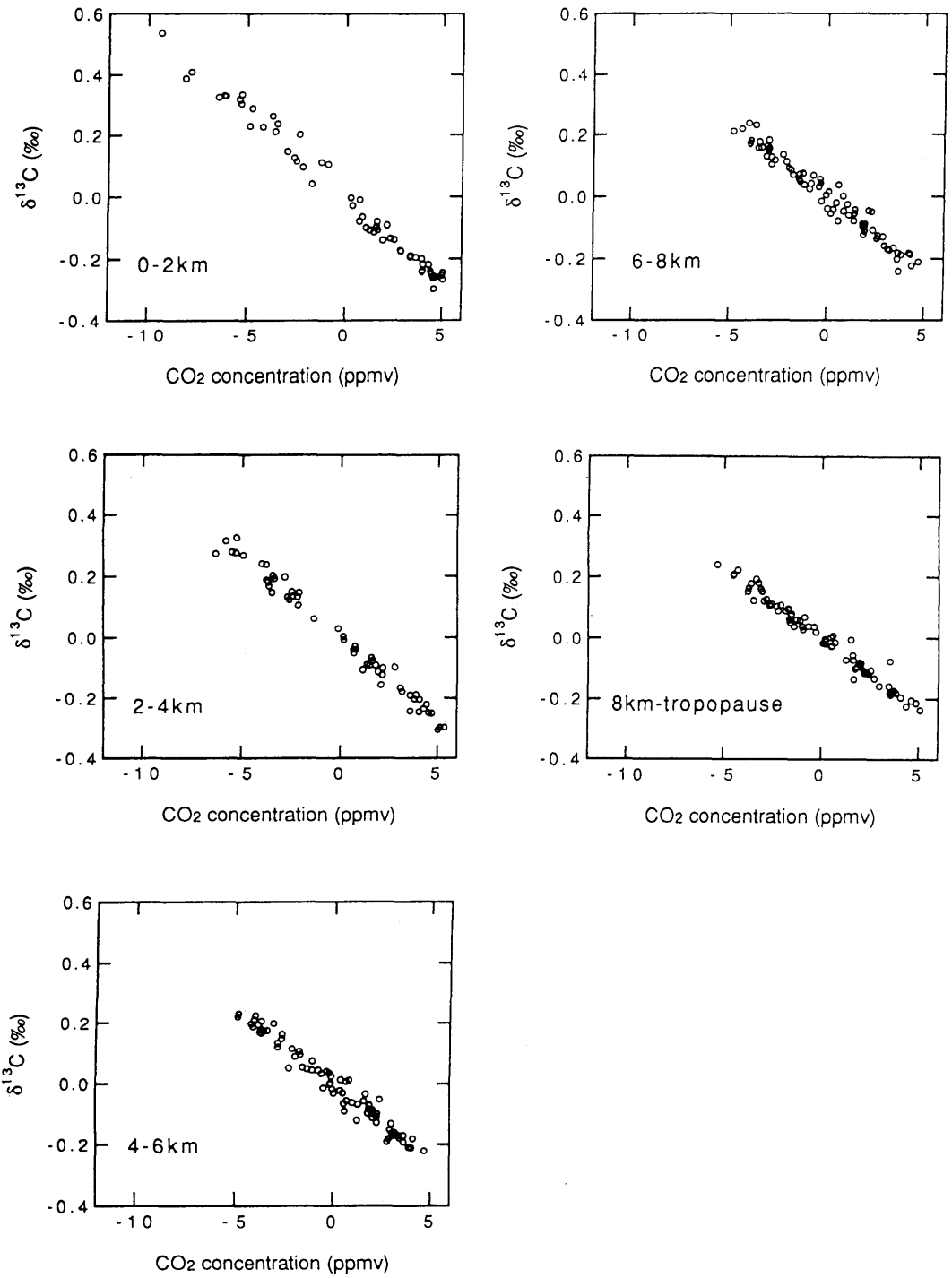

Fig. 6. Relationships between the seasonal cycles of CO_2 and its $\delta^{13}C$ at selected height intervals over Japan.

Table 1. *Rates of change in $\delta^{13}C$ with respect to the CO_2 concentration and regression coefficients obtained by approximating the relationship between the seasonal cycles of CO_2 and its $\delta^{13}C$ at selected height intervals over Japan as a straight line*

Altitude (km)	d δ^{13}C/dC (°/oo/ppmv)	Regression coefficient
0–2	−0.055	−0.992
2–4	−0.054	−0.992
4–6	−0.050	−0.982
6–8	−0.049	−0.980
8-tropopause	−0.047	−0.986

especially in the upper troposphere. In comparison, from measurements at stations remote from land, Francey (1985) and Keeling et al. (1989a) found more complicated relationships than found in this study. Their results suggested exchange of atmospheric CO_2 with both the biosphere and the oceans as well as seasonally varying air transport from different areas.

As seen in Figs. 2 and 3, the CO_2 concentration increases and $\delta^{13}C$ decreases with time at all height intervals, presumably as a result of fossil fuel combustion and deforestation. Average rates of the long-term $\delta^{13}C$ decrease are −0.039, −0.045, −0.035, −0.029 and −0.027 °/oo/year for 0–2, 2–4, 4–6, 6–8 and 8 km-tropopause, respectively. The absolute value for the lowest level is slightly larger than those obtained by Mook et al. (1983) from measurements at La Jolla (−0.041 °/oo/year), Cape Kumukahi (−0.013 °/oo/year), Fanning Island (−0.031 °/oo/year) and the South Pole (−0.021 °/oo/year) around 1980, as a whole, possibly reflecting different periods of both measurements. The rates of change in $\delta^{13}C$ relative to the CO_2 concentration at respective height intervals are −0.021, −0.023, −0.020, −0.017 and −0.016 °/oo/ppmv. The rates in the lower troposphere agree well with those observed at Fanning Island (−0.021 °/oo/ppmv) and La Jolla (−0.024 °/oo/ppmv) for the period from 1978 to 1981 (Mook et al., 1983, Table 7) and with the calculated global average (−0.021 °/oo/ppmv) using a 2-dimensional transport model (Pearman and Hyson, 1986). The change rates of approximately −0.02 °/oo/ppmv are however smaller than the rate −0.05 °/oo/ppmv expected for fossil fuel combustion or biospheric CO_2 sources and larger than −0.005 °/oo/ppmv expected for oceanic CO_2 sources. This implies that CO_2 released into the atmosphere by fossil fuel combustion and deforestation is exchanged between the atmosphere and the oceans and between the atmosphere and the biosphere for a long time, by which the isotopic signal is diluted faster than that of the CO_2 in the atmosphere (Siegenthaler and Oeschger, 1987). The fact that the rate of the $\delta^{13}C$ decrease with respect to both CO_2 concentration and time depends on height is probably caused by the horizontal advection of CO_2 from other latitudes, especially in the upper troposphere. Irregular variations of the long-term CO_2 and $\delta^{13}C$ trends were slightly different at different height intervals, as discussed later.

It is well-known that the long-term CO_2 trend shows interannual variations with periods from a few to several years (Bacastow, 1976; Bacastow et al., 1980; Bacastow and Keeling, 1981; Thompson et al., 1986; Tanaka et al., 1987a; Conway et al., 1988; Keeling et al., 1989a; Nakazawa et al., 1991b). Seasonally adjusted CO_2 concentrations at selected height intervals of the troposphere over Japan are given in Fig. 7, together with the annual CO_2 increase rates. These results show that a quasi-biennial oscillation is superimposed on the persistent increase of the CO_2 concentration; the CO_2 concentration increased rapidly at all height intervals early in 1986, 1988 and 1990. Such an oscillation was also found in our continuous measurements at Syowa Station, Antarctica (Nakazawa et al., 1991b). The interannual CO_2 variations are largest in the lower troposphere and decrease with increasing height. The rapid increase of the CO_2 concentration early in 1988 could be related to the 1987 ENSO event, but the increase in 1986 and 1990 occurred in the absence of ENSO events. It is therefore thought that the interannual CO_2 variations are associated not only with ENSO events but also with other factors. Similar variations are also seen in the results of $\delta^{13}C$ shown in Fig. 8, but the sign of the variations is almost opposite to that of the CO_2 concentration. Interannual variations of $\delta^{13}C$ have also been observed by Francey et al. (1990) at the South Pole, Cape Grim, Mauna Loa and Pt. Barrow and by Keeling et al. (1989a, p. 181) at the South Pole and Mauna Loa. Their results also showed a rapid decrease of $\delta^{13}C$ from 1987 to 1988, but amplitudes of the interannual $\delta^{13}C$

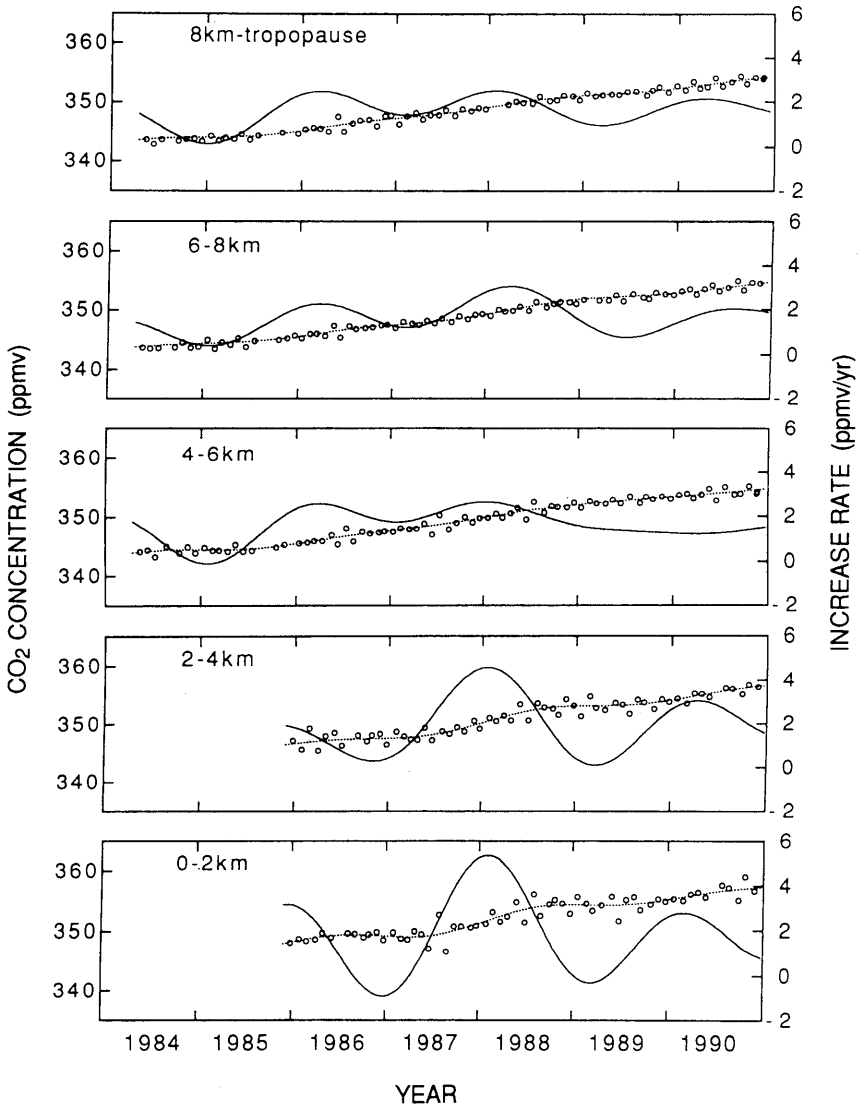

Fig. 7. Seasonally adjusted CO_2 concentrations (open circles) at selected height intervals over Japan. The long-term trends (dotted lines) and the annual increase rates (solid lines) of the atmospheric CO_2 concentration are also shown.

variations observed in the troposphere over Japan, which ranged between 0.04 and 0.10‰, are obviously larger than those of Francey et al. (~0.015‰) and somewhat smaller than those of Keeling et al. (~0.12‰), as a whole. These different amplitudes may be partly attributed to the different smoothing approaches of the observed data.

To examine causes of the interannual CO_2 variations observed over Japan, we first subtracted the contribution of fossil fuel combustion from the long-term trends of the CO_2 concentration and $\delta^{13}C$ by the following procedures. Taking account of the fact that our data records are rather short and that fossil fuel combustion increased almost linearly with time during the period from 1983 to

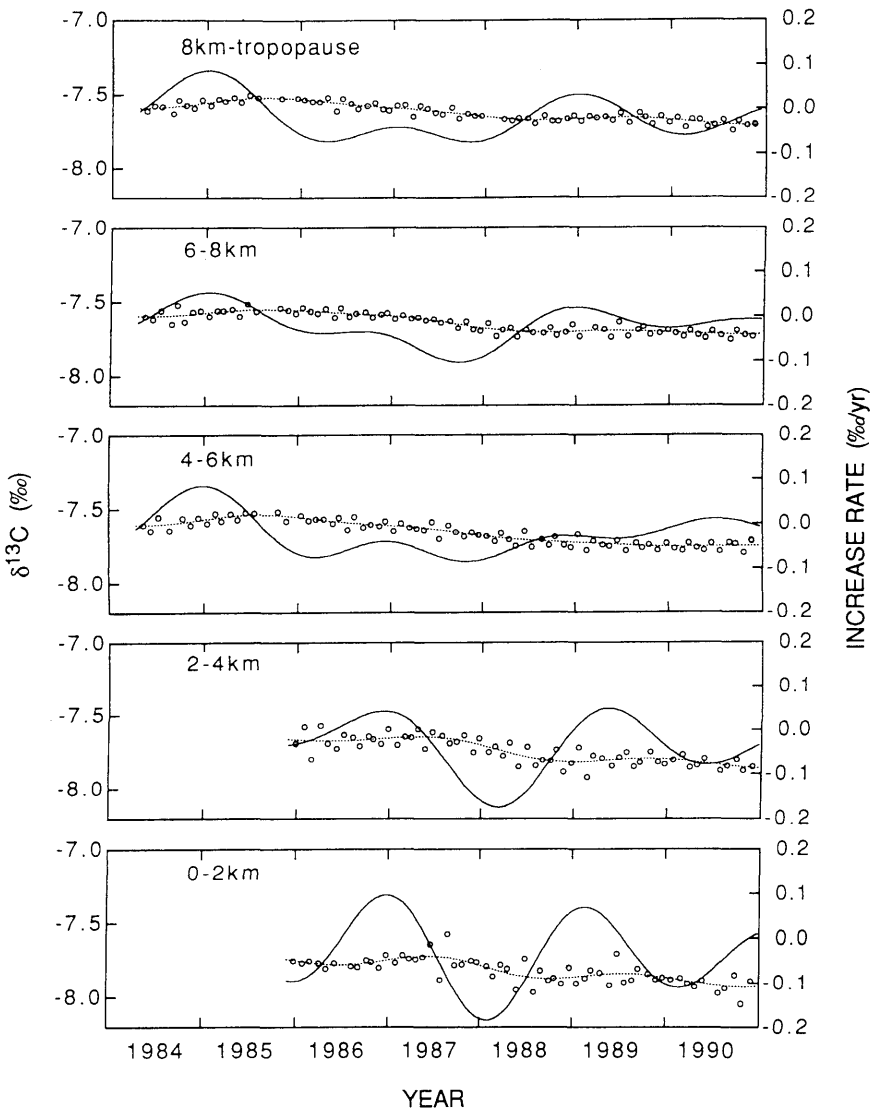

Fig. 8. The same as in Fig. 7, but for $\delta^{13}C$ of atmospheric CO_2.

1989 (Boden et al., 1991), the contribution of fossil fuel combustion was approximated by fitting a Reinsch-type cubic spline with a cutoff period of 7 years to the long-term CO_2 and $\delta^{13}C$ trends. The fitted curves, being nearly straight lines, were subtracted from the long-term trends. The residuals, thus obtained, were regarded as the interannual CO_2 and $\delta^{13}C$ variations. The cutoff frequency of the splines was chosen arbitrarily in this study, but we confirmed that its choice has little effect on the results to be discussed later. As stated before, the rates of change in the atmospheric $\delta^{13}C$ with respect to the CO_2 concentration are -0.05 and $-0.005\,‰$/ppmv for biospheric and oceanic CO_2, respectively, at present levels of the CO_2 concentration and $\delta^{13}C$ in the atmosphere. We also confirmed that the change rate of $-0.05\,‰$/ppmv for biospheric CO_2 is applicable to the CO_2 and $\delta^{13}C$ variations with periods less than a few years, by calculating

the CO_2 concentration and $\delta^{13}C$ in the atmosphere, using a box-diffusion model (Oeschger et al., 1975; Seigenthaler and Oeschger, 1987). In this calculation, the time-dependent CO_2 source was first deduced by analyzing the CO_2 and $\delta^{13}C$ records from ice core analyses and systematic measurements at Mauna Loa (Friedli et al., 1986; Keeling et al., 1989a), and then the CO_2 with $\delta^{13}C$ of $-25‰$ was released periodically from the biosphere into the atmosphere, in addition to a continuous CO_2 release due to fossil fuel combustion at a rate of about 6 Gt/year. Therefore, we calculated variations of $\delta^{13}C$ by multiplying the residuals of the CO_2 concentration obtained above by the respective change rates. The results are shown in Fig. 9, together with the observed variations of $\delta^{13}C$. It can be seen from this figure that the observed variations are in close agreement

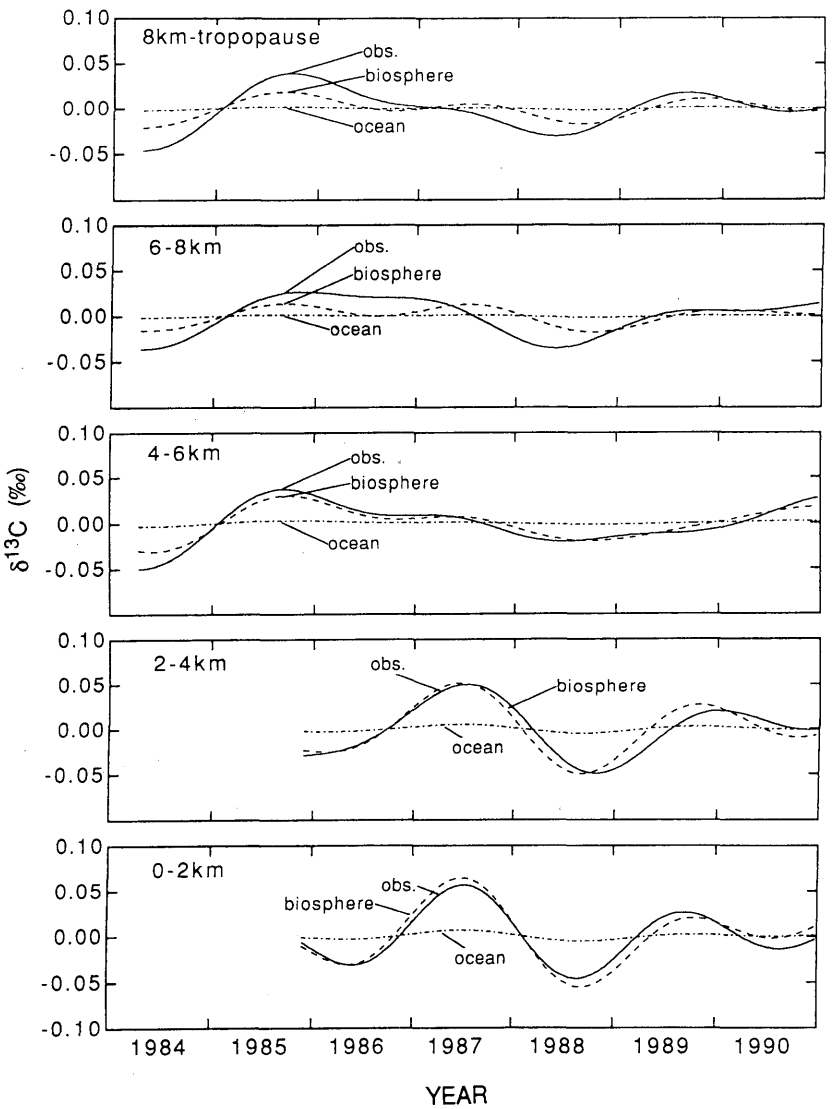

Fig. 9. Comparison of observed interannual variations of $\delta^{13}C$ of atmospheric CO_2 (obs.) with those calculated on the basis of oceanic (ocean) and biospheric (biosphere) CO_2 at selected height intervals over Japan.

with those calculated on the basis of biospheric CO_2 especially below 6 km. This fact suggests that the interannual CO_2 variations over Japan are primarily attributable to net CO_2 exchanges between the atmosphere and the biosphere rather than between the atmosphere and the oceans. Such an imbalance may occur in association with global climate change due to the ENSO event and other factors.

It is also seen in Fig. 9 that the agreement of the observed variations of $\delta^{13}C$ with those calculated for biospheric CO_2 is better in the lower and middle troposphere than in the upper troposphere. Taking account of the fact that the amplitude of the interannual variations is enhanced in the lower troposphere, biospheric activities in Japan and the Asian Continent could be substantially responsible for the variations of the CO_2 concentration and $\delta^{13}C$ below the middle troposphere over Japan. On the other hand, seasonally dependent horizontal transport of air from other areas with different values of CO_2 concentration and $\delta^{13}C$ may be important in the upper troposphere, in addition to a gradual upward transport of CO_2 from the lower troposphere around Japan. In this regard, it is noted that latitudinal distributions of $\delta^{13}C$ are different from those of the CO_2 concentration at least in the lower troposphere, and that interannual variations of the CO_2 concentration and $\delta^{13}C$ are different in magnitude and phase in different areas, due to a complicated distribution of CO_2 sources and sinks on the earth's surface (Tanaka et al., 1987c; Keeling et al., 1989a, b; Francey et al., 1990; Ferguson, 1991; Nakazawa et al., 1991a, 1992).

From a combined Mauna Loa-South Pole isotopic record, Keeling et al. (1989a, p. 182) found anomalous peaks of negative $\delta^{13}C$ late in 1980, 1983 and 1988, which were nearly coincident with anomalous increases of the CO_2 concentration, and attributed this to a substantial release of biospheric CO_2 in association with the ENSO event. They also found that in 1983, the CO_2 concentration did not increase as much as expected from the observed fluctuation of $\delta^{13}C$, and suggested that this discrepancy resulted from a simultaneous ocean uptake of CO_2. However, such a discrepancy cannot be seen in our results obtained over Japan at least during the period covered by this study. As stated above, our results suggest that not only the seasonal CO_2 cycle

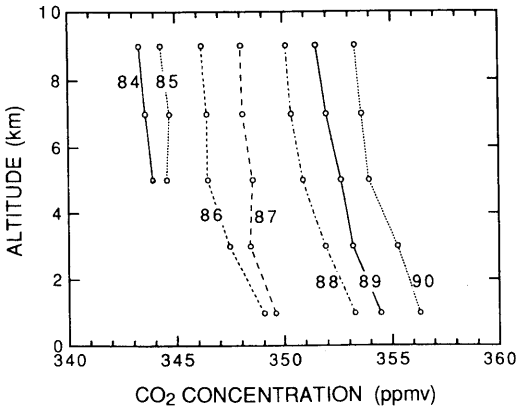

Fig. 10. Vertical profiles of annual mean CO_2 concentration in the troposphere over Japan.

but also the interannual CO_2 variations can be attributed to CO_2 exchange between the atmosphere and the biosphere, on the basis of the change rate of $-0.05\,‰$/ppmv. This may imply that the oceans do not respond quickly to variations of the atmospheric CO_2 concentration with periods shorter than a few years.

Annual mean values of the CO_2 concentration and $\delta^{13}C$ are shown in Figs. 10, 11 and Table 2. The annual mean CO_2 concentrations decrease and $\delta^{13}C$ increase gradually with increasing height. These profiles suggest that a large amount of isotopically light CO_2 is released into the atmosphere from the ground surface, due possibly to fossil fuel combustion at northern high and middle

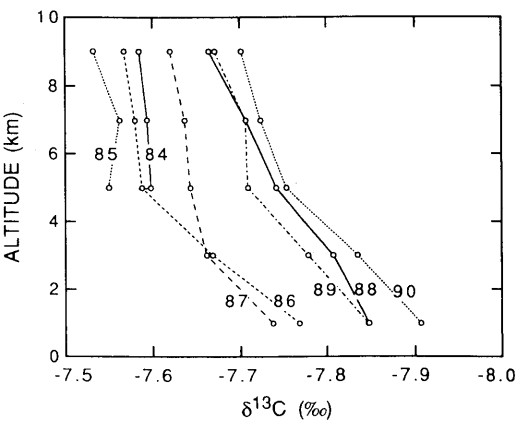

Fig. 11. The same as in Fig. 10, but for $\delta^{13}C$ of atmospheric CO_2.

latitudes. In contrast, the results of aircraft measurements over Australia show that the annual mean values of the CO_2 concentration and $\delta^{13}C$ increase with increasing height (Pearman and Beardsmore, 1984; Francey et al., 1990). Such a vertical CO_2 profile can probably be ascribed to the southward transport of air from the northern hemisphere and low latitudes through the upper troposphere and to ocean uptake of CO_2 in the southern hemisphere (Pearman and Beardsmore, 1984; Tans et al., 1989; Nakazawa et al., 1991a). The effect that $\delta^{13}C$ of lower tropospheric CO_2 is decreased especially in high latitudes of the southern hemisphere, due to the temperature dependence of the air-sea isotopic fractionation factor and the greater extent of sea area than in the northern hemisphere, may be much more important for the observed vertical $\delta^{13}C$ profile, taking precedence over the above two processes (Kroopnick, 1974; Keeling et al., 1989b, p. 323).

The annual mean CO_2 concentration increased steadily throughout the troposphere, showing almost the same vertical profile from year to year. The annual mean $\delta^{13}C$ showed more complicated variations than the CO_2 concentration did. In general, the annual mean value of $\delta^{13}C$ decreased gradually with time. However, a temporary but rapid decrease of $\delta^{13}C$ occurred conspicuously in the upper and middle troposphere in 1984 when the annual mean CO_2 concentration was lower than those of 1985 and 1986, as seen in Figs. 10, 11. Similar behavior was also seen in latitudinal distributions of the annual mean $\delta^{13}C$ observed in the lower troposphere (Keeling et al., 1989a, p. 177). A substantial release of biospheric CO_2 associated with the 1983 ENSO event may be responsible for this reversal. From 1986 to 1987, the annual mean value of $\delta^{13}C$ increased slightly in the lower troposphere and decreased rapidly in the middle and upper troposphere, while the annual mean CO_2 concentrations increased throughout the troposphere. This fact suggests that a large amount of biospheric CO_2 was released into the atmosphere from the ground surface around Japan in 1985 or 1986, and/or that in 1987, air with isotopically light CO_2 and high CO_2 concentrations was transported anomalously from other latitudes to the middle and upper troposphere over Japan or vertical mixing of the air was enhanced in the middle and upper troposphere over Japan. In this connection, the results of our aircraft measurements over Japan show that a rapid increase of the CO_2 concentration occurred from 1985 to 1986, especially in the lower troposphere, and that the annual mean CO_2 concentrations in respective layers of the free atmosphere over Japan became almost constant independent of height whenever the ENSO event occurred (Tanaka et al., 1987a; our unpublished data). It is also seen in Fig. 11 that the annual mean value of $\delta^{13}C$ decreased rapidly from 1987 to 1988 throughout the troposphere, consistent with the enhanced increase in the CO_2 concentration. This phenomenon is thought to be related to the 1987 ENSO event.

Table 2. *Annual mean values of the CO_2 concentration (upper row, ppmv) and $\delta^{13}C$ (lower row, $^o/_{oo}$) at the selected height intervals over Japan*

Altitude (km)	1984	1985	1986	1987	1988	1989	1990
0–2	—	—	349.03	349.58	353.26	354.48	356.33
	—	—	−7.769	−7.738	−7.847	−7.848	−7.907
2–4	—	—	347.49	348.43	351.93	353.17	355.28
	—	—	−7.669	−7.662	−7.779	−7.807	−7.835
4–6	343.93	344.59	346.49	348.55	350.92	352.64	353.95
	−7.598	−7.550	−7.588	−7.643	−7.709	−7.742	−7.754
6–8	343.60	344.71	346.47	348.12	350.38	352.01	353.62
	−7.594	−7.562	−7.580	−7.637	−7.707	−7.707	−7.724
8-tropopause	343.31	344.32	346.24	348.04	350.15	351.56	353.33
	−7.585	−7.533	−7.567	−7.621	−7.672	−7.665	−7.702

5. Conclusions

To contribute to a better understanding of the global carbon cycle, temporal and spatial variations of $\delta^{13}C$ of tropospheric CO_2 over Japan were examined by analyzing the CO_2 samples collected by aircraft during the period from April 1984 to November 1990. Conclusions obtained in this study are as follows:

The amplitude of the seasonal cycle of $\delta^{13}C$ decreased with increasing height and the phase delay between the lower and upper troposphere was about 1 month. Such a seasonal cycle was very similar to that of the CO_2 concentration. The relationship between the seasonal cycles of the CO_2 concentration and $\delta^{13}C$ was found to be approximately a straight line with a gradient of around $-0.05\,‰$/ppmv, suggesting that the cause of the seasonal CO_2 cycle is primarily attributable to seasonally dependent biospheric activities. It was found however that air transport from other latitudes is also important for the cycle, especially in the upper troposphere.

$\delta^{13}C$ decreased secularly at an average rate of about $-0.04\,‰$/year throughout the troposphere due to fossil fuel combustion and deforestation. The rate of change in $\delta^{13}C$ with respect to the CO_2 concentration was approximately $-0.02\,‰$/ppmv, which lies between that expected from fossil fuel combustion or biospheric CO_2 sources and that from oceanic CO_2 sources. This fact implies that CO_2 from fossil fuel combustion and deforestation is exchanged between the atmosphere and the oceans and between the atmosphere and the biosphere for a long time after its release into the atmosphere.

Interannual variations with a period of about 2 years were found in $\delta^{13}C$ as well as in the CO_2 concentration. From the comparison of both variations, it was suggested that such interannual variations are primarily induced by an imbalance in the CO_2 exchange between the atmosphere and the biosphere, which may occur in association with climate change, rather than between the atmosphere and the oceans at least over Japan.

The results obtained in this study provide useful information for elucidating the carbon cycle on the earth's surface. However, the data sets of $\delta^{13}C$ are still sparse. Further measurements, especially with aircraft and ships, over a geographically wide area are required for depicting a global picture.

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