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Temporal variations of the CO_2 concentration and its carbon and oxygen isotopic ratios in a temperate forest in the central part of the main island of Japan

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ABSTRACT

Using discrete air sampling, values of $\delta^{13}C$ and $\delta^{18}O$ in atmospheric CO_2, as well as its concentration, were measured in a forest in the central part of the main island of Japan during the period from June 1994 to June 1996 to examine the biospheric contribution to their temporal variations. $\delta^{13}C$ shows a prominent diurnal variation with high values in the daytime and low values in the nighttime, especially during the warm season. $\delta^{13}C$ also vary seasonally, showing a maximum in summer and a minimum in spring. The diurnal and seasonal variations of $\delta^{13}C$ are opposite in phase with those of the CO_2 concentration. The rate of change in $\delta^{13}C$ with respect to the CO_2 concentration is found to be approximately -0.05‰/ppmv. This suggests that the diurnal and seasonal variations of the CO_2 concentration are produced primarily by diurnally- and seasonally-dependent photosynthetic-respiratory processes of the biosphere near the observation site, respectively. In the warm season, $\delta^{18}O$ also increases in the daytime and decreased in the nighttime, which is similar to the diurnal variation of $\delta^{13}C$, but opposite to that of the CO_2 concentration. The diurnal $\delta^{18}O$ variation is thought to be caused by the release of isotopically heavy CO_2 during photosynthesis, and light CO_2 during respiration. However, an interpretation of the seasonal $\delta^{18}O$ variation is found to be much more difficult than those of $\delta^{13}C$ and the CO_2 concentration. This is likely due to complicated combinations of different seasonally varying fluxes of biospheric CO_2 into the atmosphere, as well as to various weather-dependent factors governing the $\delta^{18}O$ composition in CO_2.

1. Introduction

In connection with possible climate change due to human activities, substantial efforts have been devoted to monitoring background levels of the atmospheric CO_2 concentration over a long time period (Pearman and Beardsmore, 1984; Beardsmore and Pearman, 1987; Keeling et al., 1989a, 1995; Trivett et al., 1989; Conway et al., 1994; Nakazawa et al., 1991, 1993, 1997a). The data from such systematic measurements have established a steady secular increase of the CO_2 concentration, and they have also contributed to developing and validating global carbon cycle models for use in quantitative evaluation of the CO_2 exchange among the main carbon reservoirs (atmosphere, terrestrial biosphere and ocean). However, the role of the terrestrial biosphere is not yet well understood quantitatively (Schimel et al., 1995).

For a better understanding of the global carbon

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cycle, measurements of carbon isotopic ratio, $\delta^{13}C$, of atmospheric CO_2 would be very useful. It is expected to quantitatively distinguish the CO_2 exchange between the atmosphere and the terrestrial biosphere from that between the atmosphere and the oceans, on the basis of 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, based on the present levels of the atmospheric CO_2 concentration and $\delta^{13}C$ values in the atmosphere, the surface oceans and the terrestrial biosphere (Siegenthaler and Münnich, 1981; Pearman and Hyson, 1986; Keeling et al., 1989a; Nakazawa et al., 1993, 1997a). Indeed, several comprehensive measurements of the atmospheric $\delta^{13}C$, as well as of the CO_2 concentration have been made, and their results have been applied to elucidate the global carbon cycle (Keeling et al., 1989a, b, 1995; Nakazawa et al., 1993, 1997a; Ciais et al., 1995a, b; Francey et al., 1995).

A molecule of CO_2 also contains oxygen atoms with different masses. Systematic measurements of oxygen isotopic ratio, $\delta^{18}O$, of atmospheric CO_2 were first made by Mook et al. (1983) and Keeling et al. (1984), and then by Francey and Tans (1987), Francey et al. (1990), Murayama et al. (1996) and Trolier et al. (1996) to examine its seasonal variation and latitudinal distribution. However, the atmospheric $\delta^{18}O$ has not been investigated extensively as much as the CO_2 concentration and $\delta^{13}C$. One of the reasons for this is related to the technical difficulty of removing water vapor from air in flask samples to prevent oxygen exchange between CO_2 and H_2O during their storage. In addition, fundamental mechanisms of the processes governing temporal and spatial variations in the atmospheric $\delta^{18}O$ are very complicated and difficult to understand.

Previous studies have revealed that the variations of $\delta^{18}O$ in atmospheric CO_2 depend on factors such as isotopic equilibrium of oxygen with sea water, different diffusive processes of isotopically different CO_2 through stomata during photosynthesis, isotopic exchange of oxygen with chloroplast water in leaves during photosynthesis and with soil water during respiration of living plants and decomposition of organic matter, and equilibrium of oxygen with isotopically heavy O_3 in the stratosphere (Bottinga and Craig, 1969; Mook et al., 1983; Friedli et al., 1987; Francey and Tans, 1987; Yung et al., 1991; Gamo et al., 1989, 1995; Farquhar et al., 1993). Recently, it has been suggested that the exchange of oxygen between atmospheric CO_2 and terrestrial biospheric water plays an important role in the $\delta^{18}O$ variations of tropospheric CO_2 (Friedli et al., 1987; Francey and Tans, 1987; Hesterberg and Siegenthaler, 1991; Farquhar et al., 1993; Yakir and Wang, 1996). It is therefore expected that measurements of the atmospheric $\delta^{18}O$ provide some useful and valuable information about the role of the terrestrial biosphere in the global carbon cycle.

In order to understand the mechanisms and factors controlling the CO_2 exchange between the atmosphere and the terrestrial biosphere, it is important to measure the CO_2 concentration and its $\delta^{13}C$ and $\delta^{18}O$ simultaneously near or in a forest region where their biospheric signals are especially enhanced. We therefore collected air samples in a temperate forest land in the central part of Japan, and then analyzed them for those components for the period June 1994 to June 1996. In this paper, the results of the measurements are reported and discussed, especially in terms of the diurnal and seasonal variations of the CO_2 concentration and its $\delta^{13}C$ and $\delta^{18}O$ composition.

2. Observation site and experimental procedures

The location of our air sampling site (36°N, 137°E; 1420 m a.s.l.) and its surrounding are shown in Fig. 1. The site was situated about 15 km east of Takayama City. The vegetation around the site consisted mainly of deciduous broadleaf trees such as birch and oak and partly of conifers. The ground surface was also covered by short bamboo grass. The prevailing wind was southwesterly or northeasterly throughout the year, reflecting mainly the topographical features around the site. Annual mean air temperature was about 7.3°C, and monthly averaged temperature reached 20.0°C in August and -4.8°C in January. The ground surface was usually covered with snow in the cold months from December to April.

The collection of air samples was carried out about once per month for the period from June 1994 to June 1996. In each month, air samples

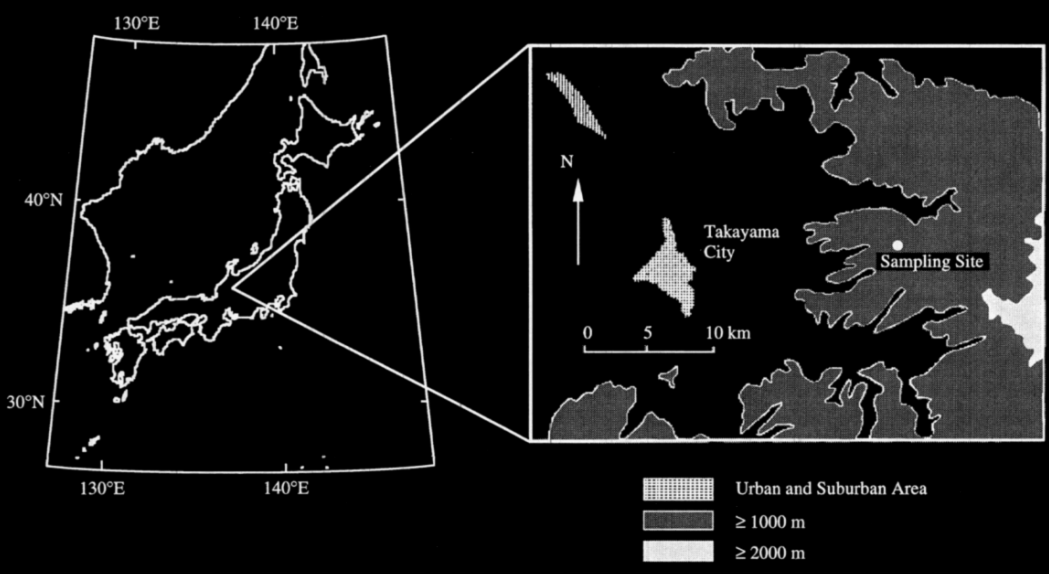

Fig. 1. Location of Takayama observation site where air samples were collected for this study and its surrounding area.

were taken over a few days, and their sampling interval was set to 1–2 h in the warm season and 2–2.5 h in the cold season, to detect the diurnal variations of the CO_2 concentration, $\delta^{13}C$ and $\delta^{18}O$. An air intake was mounted at 18 m on a 27 m-height tower, which was 2–3 m above the crown of the trees (the canopy height). Each air sample was collected into a Pyrex glass flask with a volume of about 550 ml by pressurizing up to 2×10^5 Pa with an electric diaphragm pump. Prior to use, the sample flasks were evacuated to 1.3×10^{-1} Pa at 100°C for 6 h. Water vapor contained in the air sample was removed by passing it through a stainless steel tube (50 cm in length and 1 cm in inner diameter) filled with anhydrous magnesium perchlorate, to minimize the oxygen exchange between H_2O and CO_2 in sampled air during its storage in the flask. To reduce possible selective adsorption of CO_2 on anhydrous magnesium perchlorate, air was passed sufficiently through the tube and then each air sample was collected into the flask. By this procedure, the decrease of the CO_2 concentration was reduced to be less than about 0.3 ppmv. The measured values of the CO_2 concentration were shifted up by this amount. We also confirmed that the values of $\delta^{13}C$ and $\delta^{18}O$ were not affected by anhydrous magnesium perchlorate, at least not exceeding our analytical precision, and the dew point of the air after passing through the tube was lower than −60°C.

The tower was also used by the National Institute for Resources and Environment (NIRE) for continuous measurements of the CO_2 concentration at 4 heights of 5.8, 8.8, 18, and 27 m, as well as for those of meteorological factors such as temperature, humidity, wind speed, wind direction and solar radiation at 2 heights of 9 and 26 m.

The flasks filled with air samples were returned to our laboratory for analysis. The CO_2 concentrations of the air samples were determined against our air-based standard gases by using a non-dispersive infrared analyzer with a precision of 0.01 ppmv (Tanaka et al., 1983a, 1987a; Nakazawa et al., 1992). Our standard gases were classified into three categories of primary, secondary and working. The working standard gases were used for usual concentration analyses of the flask samples, and their CO_2 concentrations were determined against the secondary standard gas system. The CO_2 concentrations of the secondary standard gases were calibrated by using the primary standards prepared gravimetrically within uncertainties of 0.13 ppmv.

After gas chromatographic analyses for the CH_4, N_2O and CO concentrations, pure CO_2 was

extracted cryogenically from the remaining air in the flask sample. Each air sample was evacuated from the flask through H_2O and CO_2 traps which were held at $-100°$ and $-197°C$, respectively. The temperature of the CO_2 trap was then increased to $-100°C$ and sublimated CO_2 was collected into a Pyrex glass tube cooled to $-197°C$. After the collection of CO_2, the tube was flamed off. This was done within 3–5 days after sampling, to reduce the oxygen exchange of CO_2 with slightly residual H_2O in the flasks during storage as much as possible. The details of the extraction procedures have been described elsewhere (Nakazawa et al., 1993, 1997a). Typical amounts of CO_2, thus obtained, were about 200 μL_{STP}.

Respective isotopic components of $\delta^{13}C$ and $\delta^{18}O$ of CO_2 are defined as

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

and

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

where subscripts sa and st denote the sample and the standard, respectively. In this study, a Finnigan MAT-δS was used for the mass spectrometer (Nakazawa et al., 1997a). External reproducibilities of our mass spectrometer analysis were estimated to be within 0.02 and 0.05‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively. N_2O contained in the air samples could not be removed from CO_2 by the above extraction procedures. Since the mass numbers of N_2O are the same as those of CO_2, N_2O must be taken account of in order to determine precise values of $\delta^{13}C$ and $\delta^{18}O$ of CO_2. The contribution of N_2O to measured values of $\delta^{13}C$ and $\delta^{18}O$ was corrected by using formulae determined experimentally for our mass spectrometer and the concentration values of atmospheric CO_2 and N_2O measured in this study. The corrections for $\delta^{13}C$ and $\delta^{18}O$ amounted to 0.21–0.24 and 0.29–0.34‰, respectively. Standards for our isotope measurements consisted of the primary, secondary and working gases (Nakazawa et al., 1993, 1997a). The working standard, which was used in the analyses of the CO_2 samples, was made by extracting CO_2 from the atmosphere, and its $\delta^{13}C$ and $\delta^{18}O$ values were determined against the primary standard through the secondary standard. The primary standard was CO_2 gas produced by reacting NBS–18 with 100% phosphoric acid at 25°C. Its recommended values of $\delta^{13}C$ and $\delta^{18}O$ with respect to PDB are -5.029 and -23.035‰, respectively (IAEA, 1995).

3. Results and discussion

During the period from June 1994 to June 1996, air sampling was conducted 25 times and the total number of collected air samples amounted to 381. However, 13 samples were excluded from the present data analysis, due to failure in their collection or analysis. The information related to each air sampling, such as date, weather, temperature, humidity, wind speed and the number of collected samples, is summarized in Table 1. As seen from this table, the air samples were taken mostly on sunny days in 1994, on rainy days in 1995 and on sunny days in 1996.

3.1. *Diurnal variation*

To see the characteristic features of the seasonal difference in the diurnal variations of the CO_2 concentration, $\delta^{13}C$ and $\delta^{18}O$, their measured values on 29, 30 July 1994 and 27 and 28 February, 1995 are plotted in Fig. 2 as representative of warm and cold seasons, respectively. As seen in this figure, the diurnal variation is clearly observable for all components in the warm season from May to September, and is almost non-existent in the cold season from October to April. In the warm season, the diurnal variation of the CO_2 concentration reaches a minimum in the afternoon and a maximum early in the morning. On the other hand, the $\delta^{13}C$ and $\delta^{18}O$ values show a diurnal variation that is almost opposite to that of the CO_2 concentration. The maximum peak-to-peak amplitudes of the diurnal variations of the CO_2 concentration, $\delta^{13}C$ and $\delta^{18}O$ amounted to approximately 35 ppmv, 2.0 and 1.5‰, respectively.

It is thought that the atmospheric CO_2 concentration is affected largely by biospheric activities near the site, i.e., CO_2 uptake by photosynthesis and CO_2 release by plant respiration and soil respiration (decomposition). To confirm this, we have used measured values of the CO_2 concentration and $\delta^{13}C$. It is well known that when CO_2 is

Table 1. *Summary of measurements at Takayama Site in the central part of the main island of Japan*

Date	Weather	Temperature (°C) (humidity %)	No. flasks
1994/06/23–06/24	cloudy	13.9 (98.6)	11
07/28–07/30	sunny	21.2 (95.2)	30
08/24–08/25	sunny	19.9 (87.5)	25
09/27–09/28	rainy	14.3 (100.0)	20
11/01–11/02	sunny	7.4 (78.6)	16
11/30–12/01	sunny	4.4 (77.1)	13
12/26–12/27	cloudy/rainy	2.7 (99.6)	12
1995/01/26–01/27	rainy/cloudy	−7.5 (94.1)	8
02/27–02/28	snow/sunny	−6.8 (93.2)	12
03/24–03/25	rainy	2.2 (98.7)	12
04/12–04/13	snow/rainy	−2.5 (94.6)	14
05/11–05/12	rainy	8.2 (96.6)	14
06/13–06/14	rainy	10.7 (100.0)	13
07/03–07/04	rainy	15.5 (98.2)	13
07/26–07/28	sunny	21.8 (82.1)	30
08/21–08/22	cloudy	19.4 (87.0)	13
09/21–09/22	sunny	12.1 (86.6)	13
10/24–10/25	rainy	6.8 (99.0)	13
11/20–11/21	rainy	−1.6 (100.0)	13
12/25–12/26	snow	−13.3 (94.4)	12
1996/01/23–01/24	snow	−8.5 (96.3)	13
02/20–02/21	snow	−10.2 (81.9)	9
03/18–03/19	sunny	−7.4 (76.1)	13
04/22–04/23	sunny	3.6 (52.9)	13
05/23–05/24	sunny	9.1 (57.6)	13
06/20–06/21	sunny/rainy	15.9 (92.1)	13

added to the atmosphere from a single carbon reservoir, the balance equation for $^{13}CO_2$ in the atmosphere is given by:

$$C\delta^{13} = C_0\delta_0^{13} + \delta_I^{13}\,(C - C_0), \tag{3}$$

where C_0 and C denote the CO_2 concentrations (ppmv) before and after adding CO_2, respectively, δ_0^{13} and δ^{13} are the corresponding values of $\delta^{13}C$ (‰) and δ_I^{13} is $\delta^{13}C$ (‰) of CO_2 added to the atmosphere. Differentiating eq. (3) with respect to C, we obtain

$$\frac{d\delta^{13}}{dC} = \frac{\delta_I^{13} - \delta^{13}}{C}. \tag{4}$$

By assuming the respective values of 360.0 ppmv, −8.0 and −25.0‰ for the present levels of the CO_2 concentration, $\delta^{13}C$ in atmospheric CO_2 and $\delta^{13}C$ in the biosphere, it is obtained from eq. (4) that the rate of change in $\delta^{13}C$ with respect to the CO_2 concentration is −0.047‰/ppmv for the CO_2 exchange between the atmosphere and the biosphere.

The CO_2 concentrations measured on 24–25 August and 30 November–1 December, 1994 are plotted in Fig. 3 against their corresponding $\delta^{13}C$ values, as examples of the relationship between these components. As seen from this figure, the CO_2 concentration and $\delta^{13}C$ are linearly related with each other; the rates of change in $\delta^{13}C$ relative to the CO_2 concentration, calculated by applying a least squares fitting technique, are −0.048 and −0.050‰/ppmv for the respective cases. The change rates and the regression coefficients for all measurements, obtained by the same procedure as above, are summarized in Table 2. Average values of the change rates and the regression coefficients are −0.048‰/ppmv and 0.938, respectively. The observed values of the change rate are therefore in excellent agreement with that calculated by assuming the CO_2 exchange between the atmosphere and the biosphere. This agreement is consistent with the idea that the diurnal CO_2 variation observed at Takayama is locally induced by the diurnal photosynthetic-respiration plant cycle.

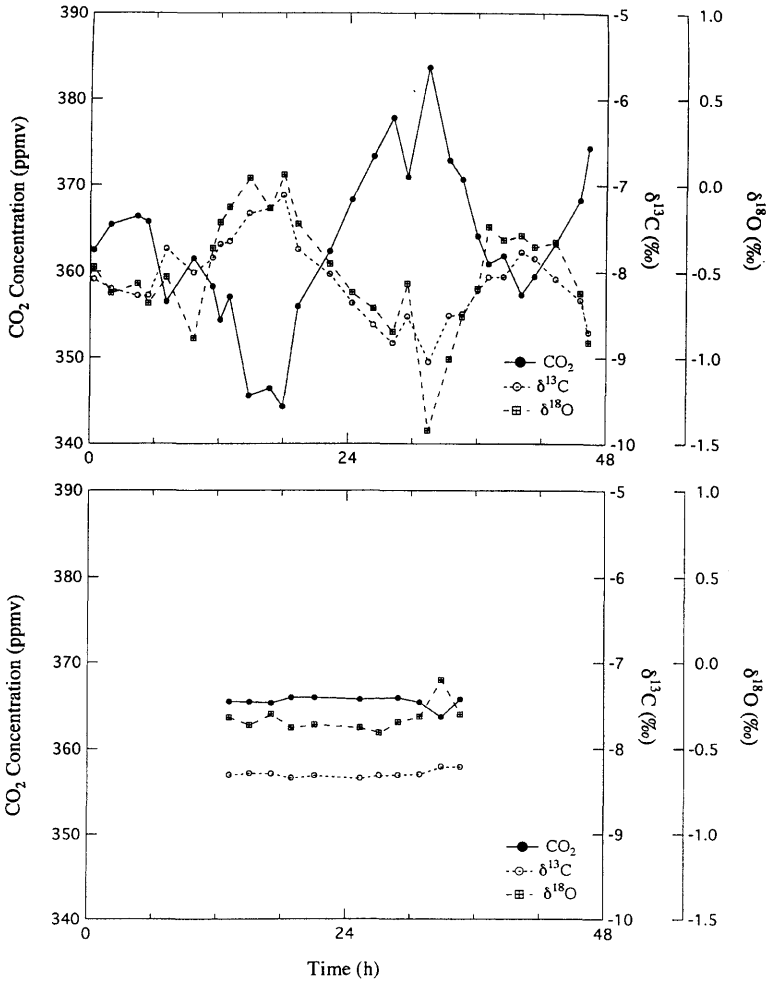

Fig. 2. Measured values of the CO_2 concentration and its $\delta^{13}C$ and $\delta^{18}O$ at Takayama air sampling site on 29–30 July, 1994 (upper panel) and 27–28 February, 1995 (lower panel).

As seen in Fig. 2, the diurnal variation of $\delta^{18}O$ in atmospheric CO_2 in the warm season show a maximum in the afternoon and a minimum early in the morning, which is in phase with that of $\delta^{13}C$ but opposite to that of the CO_2 concentration. This is suggestive of a diurnal $\delta^{18}O$ variation produced mainly by the CO_2 exchange between the atmosphere and the biosphere. In order to understand these changes of $\delta^{18}O$ in atmospheric CO_2, it is necessary to consider oxygen isotope exchange between CO_2 and waters in leaf, plant body and soil (Friedli et al., 1987; Francey and Tans, 1987; Farquhar et al., 1993; Yakir and Wang, 1996).

Oxygen isotopes of CO_2 released into the atmosphere through plant respiration and soil respiration are thought to be in equilibrium with oxygen isotopes of waters in plant body and soil, respectively, because CO_2 is in contact with these waters long enough to exchange oxygen isotopes. In general, no isotopic fractionation occurs when plants absorb water in soil through roots (Zundel et al., 1978; Förstel, 1982; Flanagan and Ehleringer, 1991). Therefore, CO_2 molecules ori-

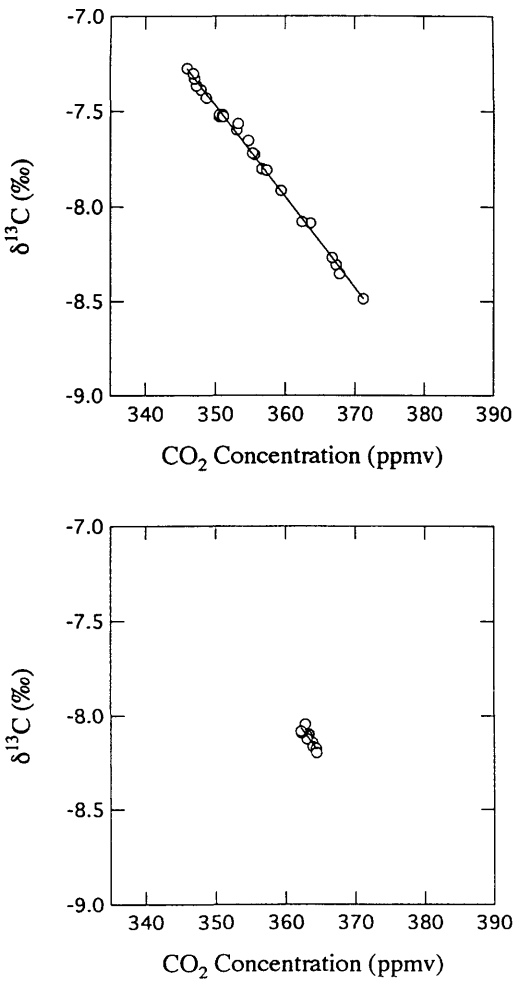

Fig. 3. Relationships between measured values of the CO_2 concentration and $\delta^{13}C$ at Takayama air sampling site on 24–25 August, 1994 (upper panel) and 30 November–1 December 1994 (lower panel).

ginating in biospheric respiration (soil, root and aboveground plant) all have similar $\delta^{18}O$ values, which are lower than those in the atmosphere (Hesterberg and Siegenthaler, 1991; Farquhar et al., 1993).

Plant respiration and soil respiration are activated with increasing air temperature and soil temperature, and surface air temperature can be used as a surrogate for soil temperature (Lloyd and Taylor, 1994; Fung et al., 1987). Therefore, the release of CO_2 by both respiration processes is more enhanced in the daytime than in the nighttime. As a result, $\delta^{18}O$ in atmospheric CO_2 is expected to be diluted in the daytime. However, the observational fact shows an opposite behavior, suggesting that a large fraction of CO_2 molecules that enter the leaves diffuses back to the atmosphere after exchanging oxygen atoms with isotopically heavy leaf water (Tans et al., 1985; Francey and Tans, 1987; Farquhar et al., 1993).

Water in leaves comes from water which is absorbed through roots from soil, and it is richer in ^{18}O compared with source (soil) water, due to evaporation processes at the air-water boundary in a leaf (Dongmann and Nürnberg, 1974; Zundel et al., 1978). Since most of the solar radiation is absorbed in chloroplasts in leaf cells, evapotranspiration occurs so that an increase in leaf temperature is suppressed. During this process, isotopically heavy $H_2{}^{18}O$ evaporates less readily than light $H_2{}^{16}O$. The $\delta^{18}O$ value of water at the evaporation site in leaves, δ_E, was formulated by Farquhar et al. (1993),

$$\delta_E = \delta_S + \varepsilon_k + \varepsilon^* + (\delta_V - \delta_S - \varepsilon_k)\frac{e_a}{e_i}, \quad (5)$$

where δ_S is the ^{18}O composition of soil water, δ_V is the ^{18}O value of water vapor in ambient (surrounding) air, e_a and e_i are the vapor pressures in the atmosphere and intercellular space, respectively, ε^* is the proportional depression of vapor pressure of $H_2^{18}O$ compared to $H_2^{16}O$, ε_k is the kinetic fractionation against $H_2^{18}O$ compared to $H_2^{16}O$ for diffusion in air. ε^* is slightly negatively dependent on temperature around ambient air temperatures, whose functional relationship was determined by Bottinga and Craig (1969). Soil water originates in precipitation water whose $\delta^{18}O$ varies as a function of temperature, the amount of precipitation, latitude and height (Dansgaard, 1964; Yursever and Gat, 1981). Therefore, the value of $\delta^{18}O$ in soil water is thought to be seasonally variable (Hesterberg and Siegenthaler, 1991), and will be discussed later. However, within the context of the discussion surrounding the diurnal variation, $\delta^{18}O$ in soil water can be assumed to be constant, as is with ε_k. Thus, δ_E in eq. (4) becomes influenced significantly by the terms which reflect weather conditions. Since it can be assumed that intercellular space in leaf is nearly saturated with water vapor, and that leaf temperature is almost the same as ambient temper-

Table 2. *Rates of change in $\delta^{13}C$ and $\delta^{18}O$ with respect to the CO_2 concentration and regression coefficients*

Date	$d\delta^{13}C/dC$ (‰/ppmv)	Regression coefficient	$d\delta^{18}O/dC$ (‰/ppmv)	Regression coefficient
1994/06/23–06/24	−0.041	0.983	−0.054	0.841
07/28–07/30	−0.049	0.994	−0.029	0.870
08/24–08/25	−0.048	0.998	−0.042	0.901
09/27–09/28	−0.044	0.995	−0.023	0.317
11/01–11/02	−0.054	0.984	−0.054	0.377
11/30–12/01	−0.050	0.885	−0.049	0.378
12/26–12/27	−0.024	0.939	0.030	0.598
1995/01/26–01/27	−0.050	0.962	−0.064	0.850
02/27–02/28	−0.044	0.658	−0.116	0.948
03/24–03/25	−0.052	0.993	−0.134	0.794
04/12–04/13	−0.037	0.860	−0.048	0.467
05/11–05/12	−0.037	0.869	−0.030	0.597
06/13–06/14	−0.082	0.854	−0.128	0.908
07/03–07/04	−0.053	0.997	−0.017	0.303
07/26–07/28	−0.050	0.987	−0.044	0.733
08/21–08/22	−0.052	0.974	−0.020	0.777
09/21–09/22	−0.050	0.998	−0.038	0.780
10/24–10/25	−0.064	0.961	−0.064	0.627
11/20–11/21	−0.043	0.983	−0.141	0.802
12/25–12/26	−0.036	0.935	−0.074	0.908
1996/01/23–01/24	−0.045	0.972	−0.067	0.925
02/20–02/21	−0.042	0.762	−0.021	0.259
03/18–03/19	−0.038	0.847	−0.054	0.732
04/22–04/23	−0.048	0.993	−0.021	0.303
05/23–05/24	−0.049	0.706	−0.013	0.150
06/20–06/21	−0.046	0.994	−0.036	0.666

ature, e_a/e_i can therefore be regarded approximately as a measure of relative humidity in the atmosphere. By employing −8, 9 and −16‰ (in SMOW) for the respective summertime approximate values of δ_S, ε^* and δ_V at northern middle latitudes, together with ε_k of 26‰ (Hesterberg and Siegenthaler, 1991; Jacob and Sonntag, 1991; Farquhar et al., 1993; Farquhar and Lloyd, 1993), $\delta_S+\varepsilon_k+\varepsilon^*$ becomes positive constant (27‰) and $\delta_V-\delta_S-\varepsilon_k$ negative constant (−34‰). Therefore, δ_E increases during the day, i.e., leaf water becomes enriched in ^{18}O, since the atmospheric relative humidity decreases with increasing air temperature. During photosynthetic CO_2 fixation, a great quantity of CO_2 enters the leaf and then diffuses back to the atmosphere through stomata after achieving an equilibration with isotopically heavy oxygen in leaf water. This then leads to an atmospheric CO_2 enriched, during the day, in $\delta^{18}O$. During the nighttime, this effect is much reduced due to higher atmospheric humidity, and ^{18}O in leaf water tends to decrease toward that of water in plant body.

The oxygen isotopic discrimination during the diffusive transport of CO_2 from the atmosphere to the carboxylation sites in chloroplasts is another important factor governing the diurnal variation of $\delta^{18}O$ in atmospheric CO_2 (Farquhar et al., 1993). Atmospheric CO_2 with isotopically heavy oxygen reaches the carboxylation sites less readily than that with light oxygen. By this effect, $\delta^{18}O$ in atmospheric CO_2 is increased in the daytime when the gross flux of atmospheric CO_2 into the leaf increases. Farquhar et al. (1993) estimated this discrimination to be about 7.4‰.

As described above, biospheric activities near the sampling site affect the observed diurnal $\delta^{18}O$ variation significantly, especially in the warm season. It is therefore expected that the $\delta^{18}O$ value is also negatively correlated with the CO_2 concentration, in a similar way that $\delta^{13}C$ is negatively correlated with CO_2. Indeed, such a correlation is

clearly observed. The relationships between $\delta^{18}O$ and the CO_2 concentration on 24–25 August 1994 and 26–27 January, 1995 are shown in Fig. 4, as examples for the warm and cold seasons, respectively. The rates of change in $\delta^{18}O$ with respect to the CO_2 concentration for all measurements are also summarized in Table 2. The change rates obtained for the $\delta^{18}O$–CO_2 relationship are negative, but they are more variable than those of the $\delta^{13}C$–CO_2 relationship, probably implying that mechanisms and factors governing $\delta^{18}O$ in atmospheric CO_2 are more complicated and sensitive to weather conditions compared with those for $\delta^{13}C$. The negative correlation between $\delta^{18}O$ and the CO_2 concentration was also observed in the lowest part of the troposphere over East and West Siberia in the summer of 1993 and 1994, for which the rate of change in $\delta^{18}O$ with respect to the CO_2 concentration was estimated to be about -0.11‰/ppmv (Nakazawa et al., 1997b).

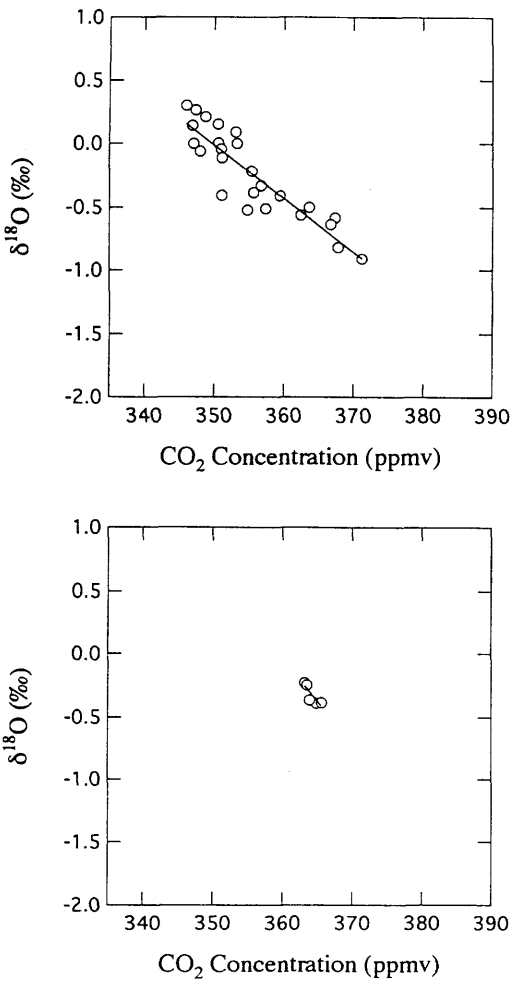

Fig. 4. Relationships between measured values of the CO_2 concentration and $\delta^{18}O$ at Takayama air sampling site on 24–25 August, 1994 (upper panel) and 26–27 January, 1995 (lower panel).

3.2. Seasonal variation

Averaged values of the CO_2 concentration, $\delta^{13}C$ and $\delta^{18}O$ for each month are shown in Fig. 5, together with monthly mean CO_2 concentrations obtained by the NIRE from their continuous measurements at a height of 18 m for the period June 1994 — June 1996. Our values of the CO_2 concentration are somewhat irregular due probably to discrete air sampling, but they agree fairly well with those obtained by the continuous measurements. The results of both measurements show a clear evidence of increasing trend and the seasonal variation in the CO_2 concentration. By applying a digital-filtering technique (Nakazawa et al., 1997c) to the present data set, an average CO_2 increase rate is estimated to be 2.2 ± 0.6 ppmv/year, which is colse to that from our aircraft measurements at a 0–2 km height interval over the Pacific Ocean off the coast of Sendai (38°N, 141°E), Japan for the same period (Tanaka et al., 1983b, 1987b; Nakazawa et al., 1993). The maximum and minimum concentrations of the seasonal CO_2 variation appear in spring (April to May) and summer (August to September), respectively, and the peak-to-peak amplitude is approximately 13 ppmv. This seasonal variation is close to those observed by using aircraft and ships in the lowest part of the troposphere near Japan (Tanaka et al., 1983b, 1987b, c; Nakazawa et al., 1992, 1993, 1997a).

It is seen from Fig. 5 that $\delta^{13}C$ is correlated well negatively with the CO_2 concentration. An increase rate in $\delta^{13}C$ during the study period is found to be -0.065 ± 0.026‰/year, which is apparently larger than those over Japan (about -0.035‰/year) from 1984 to 1990 (Nakazawa et al., 1993), from the western Pacific Ocean (-0.033‰/year) from 1984 to 1991 (Nakazawa et al., 1997a), at La Jolla, Cape Kumukahi, Fanning Island and the South Pole

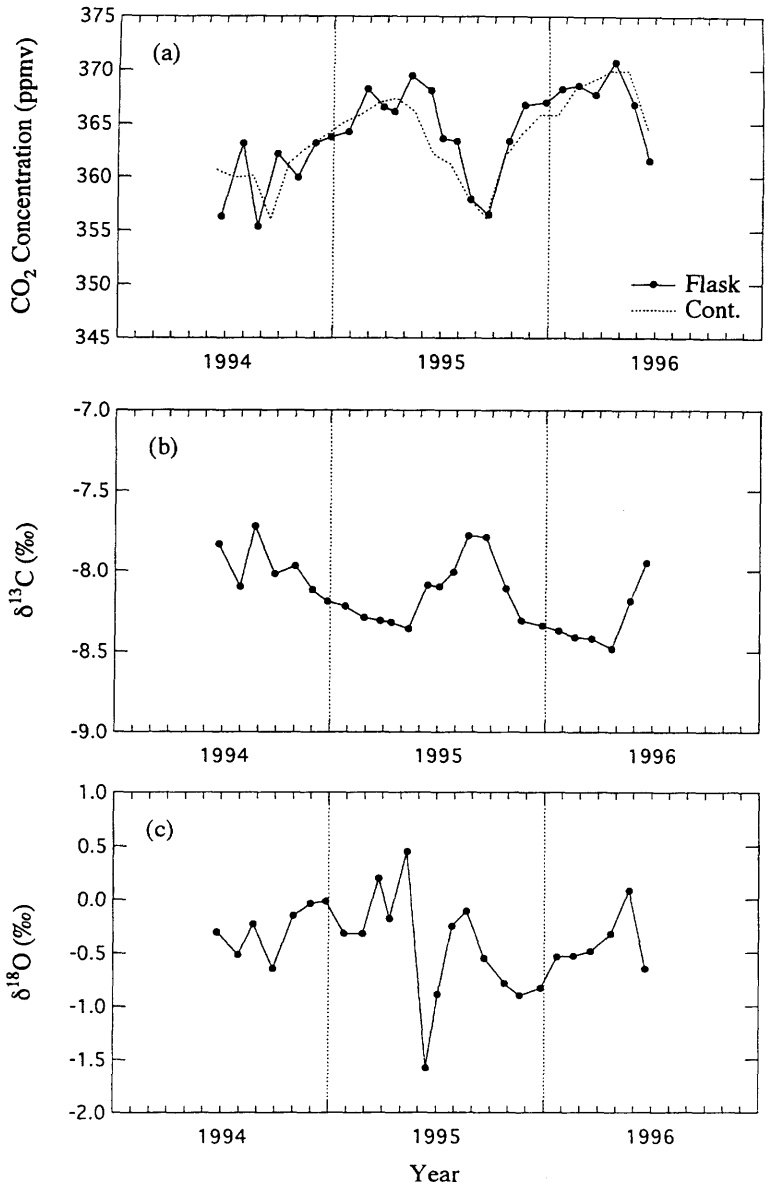

Fig. 5. Monthly mean values of the CO_2 concentration (a) and its $\delta^{13}C$ (b) and $\delta^{18}O$ (c) obtained at Takayama air sampling site during the period June 1994–June 1996. Monthly mean CO_2 concentrations obtained from continuous measurements by the NIRE were also plotted for reference.

(−0.027‰/year) around 1980 (Mook et al., 1983), at La Jolla, Mauna Loa, Fanning-Christmas Islands and the South Pole (−0.021‰/year) from 1978 or 1979 to 1986 (Keeling et al., 1989a) and at Cape Grim (−0.022‰/year) from 1982 to 1993 (Francey et al., 1995). Taking account of the fact that our measurements were made in a forest, the difference between the present and previous results is probably attributable to local effects near our sampling site, as well as to their different measure-

ment periods. It is well known that $\delta^{13}C$ of atmospheric CO_2 shows interannual variations with periods of a few to several years, associated mainly with climate change (Keeling et al., 1989a, 1995; Nakazawa et al., 1993, 1997a). From the observed values of −0.065‰/year and 2.2 ppmv/year, the rate of change in $\delta^{13}C$ with respect to the CO_2 concentration is calculated to be −0.030‰/ppmv. This rate is somewhat larger than approximate value of −0.02‰/ppmv obtained from systematic measurements in the background atmosphere (Mook et al., 1983; Nakazawa et al., 1993, 1997a). The value of $\delta^{13}C$ also varies seasonally; the minimum and maximum values appear in April to May and in August to September, respectively, with a peak-to-peak amplitude of about 0.6‰, and it is almost opposite in phase with the seasonal CO_2 variation. The seasonal $\delta^{13}C$ variation observed in this study is similar to those in the lowest part of the troposphere near Sendai and at northern middle latitudes in the western Pacific Ocean (Nakazawa et al., 1993, 1997a).

The relationship between the seasonal variations of the CO_2 concentration and $\delta^{13}C$ is approximated well with a linear function, as seen in Fig. 6. Such a correlation was also observed in the background atmosphere near Japan (Nakazawa et al., 1993, 1997a). By applying a least squares fitting technique to the data in Fig. 6, the rate in change of $\delta^{13}C$ with respect to the CO_2 concentration is estimated to be −0.053‰/ppmv, with a correlation coefficient of 0.957, which is very close to those for the diurnal variation discussed already. This implies that the seasonal CO_2 variation observed at our sampling site is produced mainly by seasonally-dependent metabolic processes of the biota.

As seen in Fig. 5, the variation of $\delta^{18}O$ in atmospheric CO_2 is quite different from those of the CO_2 concentration and $\delta^{13}C$. A visual inspection of the $\delta^{18}O$ data indicates no clear evidence for the seasonal variation. However, if one were to excluded the significantly low values in June and early July of 1995, there appears a visual sense of a seasonal cycle where the $\delta^{18}O$ value increases between the springs of 1994 and 1995, declines until the end of 1995 and then increases again. On the other hand, our aircraft measurements at a height interval 0–2 km near Sendai for the period 1984–1994 show an apparent seasonal

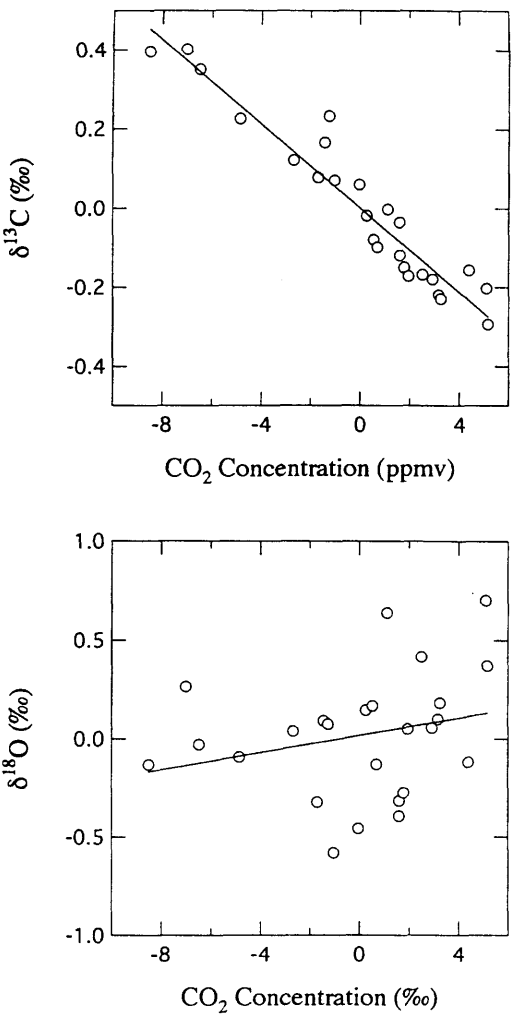

Fig. 6. Relationships between the monthly mean values of the CO_2 concentration and $\delta^{13}C$ (upper panel) and between those of the CO_2 concentration and $\delta^{18}O$ (lower panel), derived from the data at Takayama air sampling site during the period June 1994–June 1996.

variation of $\delta^{18}O$ where the maximum and minimum values appear in June and in October to November, respectively, with a peak-to-peak amplitude of about 1.0‰ (our unpublished data). A similar seasonal $\delta^{18}O$ variation was also reported by Francey et al. (1990) for Pt. Barrow and Mauna Loa. The difference between the seasonal variations obtained by this study and the aircraft measurements may be attributed to the

fact that aircraft sampling was made under fine weather conditions in the atmosphere which was fairly free from local effects, while the present air samples were collected under various weather conditions in the atmosphere with strong biospheric signals. As will be discussed later, $\delta^{18}O$ in atmospheric CO_2 is very sensitive to weather conditions.

The measured values of $\delta^{18}O$ are also plotted in Fig. 6 against their corresponding CO_2 concentration. The CO_2 concentration and $\delta^{18}O$ are not so strongly correlated with each other, when compared with the relationship between the CO_2 concentration and $\delta^{13}C$. However, a slightly positive correlation is found between both components, the rate in change of $\delta^{18}O$ with respect to the CO_2 concentration being 0.024‰/ppmv though a correlation coefficient is 0.270. This relationship is opposite to that for the diurnal variations of $\delta^{18}O$ and the CO_2 concentration in the warm season. The cause is probably attributable to the fact that high values of the CO_2 concentration and $\delta^{18}O$ were observed simultaneously during the period from spring to early summer.

Tans et al. (1985) and Francey and Tans (1987) suggested that oxygen isotope exchange of CO_2 with leaf water during photosynthesis, and release of CO_2 equilibrated with plant body water and soil water through plant respiration and soil respiration are responsible for the seasonal variation of $\delta^{18}O$ in atmospheric CO_2. This mechanism is essentially the same as that discussed for the diurnal $\delta^{18}O$ variation. If this is the case, it is expected that $\delta^{18}O$ increases in the warm season and decreases in the cold season. However, the expected variation differs from the observational fact. As mentioned above, both leaf water and soil water (equivalently, plant body water) originate in precipitation. From the oxygen isotope data from the global IAEA (International Atomic Energy Agency) network, Dansgaard (1964) and Yursever and Gat (1981) found that $\delta^{18}O$ in precipitation varies seasonally with air temperature and amount of precipitation (rainfall) and spatially with geographical factors such as latitude and altitude. Therefore, we calculated $\delta^{18}O$ in CO_2 equilibrated with precipitation, to examine various causes of the seasonal variation of $\delta^{18}O$ in atmospheric CO_2 observed in this study.

We first derived $\delta^{18}O$ in precipitation expected for our observation site, using the following multiple regression equations by Yursever and Gat (1981):

$$\delta^{18}O = -11.78 + 0.418 \times T - 0.0084 \times P, \qquad (6)$$

where T is the monthly-averaged air temperature (°C) and P is the monthly precipitation (mm). The values of $\delta^{18}O$ calculated by using this equation are expressed in SMOW. In this calculation, temperature data at our observation site were used, and the amounts of precipitation were taken from the data at a meteorological station in Takayama City. We found an average of the calculated monthly values of $\delta^{18}O$ to be -10.1‰. On the other hand, Mizota and Kusakabe (1994) reported from their measurements that $\delta^{18}O$ values of surface and shallow ground waters were approximately -11‰ near our observation site. Waseda and Nakai (1983) also observed a similar value for the surface water at a 1500 m height in the central part of the main island of Japan. Therefore, the calculated monthly $\delta^{18}O$ values were shifted down by 0.9‰, on the basis of these observational evidence. The results, thus obtained, are shown in Fig. 7, together with the observed values of air temperature and precipitation. Then, $\delta^{18}O$ values of CO_2 equilibrated with precipitation, $\delta^{18}O_{PDB}(CO_2)$, were calculated from those in precipitation obtained above, $\delta^{18}O_{SMOW}(H_2O)$, according to Friedman and O'Neil (1977),

$$\delta^{18}O_{PDB}(CO_2) = \left(\frac{1}{1.0415} \times \alpha(T) \times \left(1 + \frac{\delta^{18}O_{SMOW}(H_2O)}{1000}\right) - 1\right) \times 10^3, \qquad (7)$$

where

$$\alpha(T) = \frac{(^{18}O/^{16}O)_{CO_2}}{(^{18}O/^{16}O)_{H_2O}}, \qquad (8)$$

is the temperature-dependent equilibrium fractionation factor of oxygen isotopes between H_2O and CO_2. In this study, α was calculated by the equation determined experimentally by Bottinga and Craig (1969),

$$\left(\frac{\alpha(T)}{\alpha_{25}} - 1\right) \times 10^3 = 5.112 - 0.214T + 0.00041T^2, \qquad (9)$$

where T is temperature (°C) and α_{25} is 1.0412. In this regard, the value of 1.0412 for α_{25}, as well as

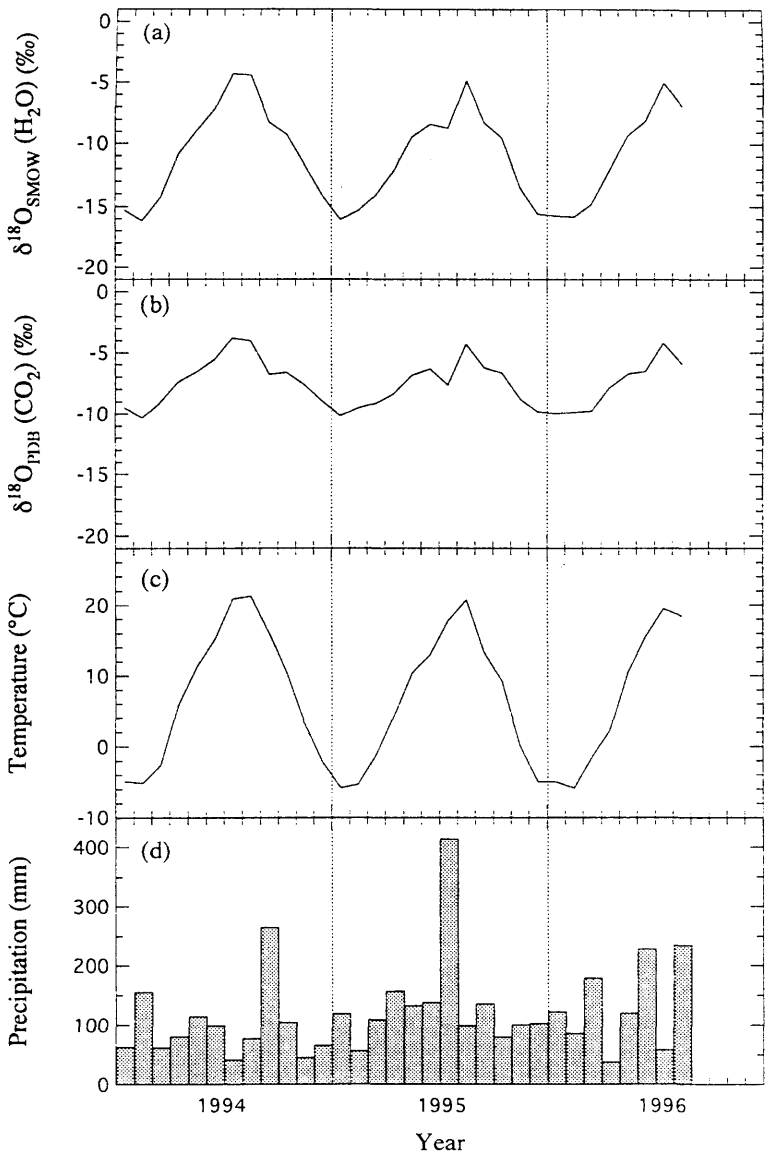

Fig. 7. Calculated values of $\delta^{18}O$ in precipitation (SMOW) (a) and those of CO_2 equilibrated with precipitation (PDB) (b) at Takayama air sampling site for each month from January 1994 to August 1996. Monthly averaged air temperatures at the site (c) and monthly amounts of precipitation (d) at Takayama Meteorological Station are also plotted.

the constant of 1.0415 in eq. (11), was taken from IAEA (1995). The calculated values of $\delta^{18}O$ in CO_2 equilibrated with precipitation are shown in Fig. 7.

As seen from Fig. 7, the calculated values of $\delta^{18}O$ in precipitation show an apparent seasonal variation with a maximum in summer and a minimum in winter. A similar behavior is also found in the calculated values of $\delta^{18}O$ in CO_2 equilibrated with precipitation, but the peak-to-

peak amplitudes are much reduced compared with those for $\delta^{18}O$ in precipitation, reflecting the fact that low values in winter are shifted up by the temperature-dependent isotopic fractionation. Also, the impact of precipitation on $\delta^{18}O$ is more evident in summer than in winter, and in 1995 than in 1994. Such an influence is characteristically seen in July 1995; it rained heavily on 3 and 4 July and the amount of precipitation during these 2 days reached 40% of the total amount for this month which was over 130% of a normal year value.

By comparing the observed values of $\delta^{18}O$ in atmospheric CO_2 (Fig. 5) with the calculated values of $\delta^{18}O$ in CO_2 equilibrated with precipitation (Fig. 7), the winter minimum expected from the calculation is clearly found in the observational results in cold months from 1995 to 1996. An increase of $\delta^{18}O$ from winter to spring is found in the observation. However, the variation of $\delta^{18}O$ in atmospheric CO_2 expected from the calculated results is not in agreement with the observation as a whole (e.g., winter of 1994/95). This suggests that the intra-annual variation of $\delta^{18}O$ in atmospheric CO_2 observed in this study does not directly reflect seasonally-dependent $\delta^{18}O$ in source water only. In order to evidence a full interpretation of the observed $\delta^{18}O$ variation, we need to consider other factors such as (1) the delay of the seasonal variation of $\delta^{18}O$ in soil water relative to precipitation, (2) seasonally-varying fluxes of CO_2 diffused back to the atmosphere from leaf and released into the atmosphere from plant and soil through respiration, (3) seasonality of $\delta^{18}O$ in leaf water, (4) seasonally-dependent gross CO_2 flux from the atmosphere into the leaf, and (5) short-time scale variations of $\delta^{18}O$ in leaf water due to weather conditions.

Hesterberg and Siegenthaler (1991) reported, from their isotope measurements in a grass-covered soil in Switzerland, that $\delta^{18}O$ in soil water shows a prominent seasonal variation, and that the seasonal variation at 30-cm depth is almost in phase with that of precipitation, but is delayed by about 6 months at 80-cm depth due probably to a long penetration time of precipitation into the ground. If the biota around our observation site uses soil water at a depth where the seasonal $\delta^{18}O$ variation is opposite in phase with that of precipitation, $\delta^{18}O$ in atmospheric CO_2 would be higher in winter and lower in summer, compared with the results shown in Fig. 7. It could be that soil waters at various depths participate in biospheric activities near our site through photosynthesis and respiration. Such a situation would make the seasonal variation of $\delta^{18}O$ in atmospheric CO_2 complicated.

As already mentioned above, CO_2 diffused back to the atmosphere from a leaf is rich in ^{18}O, reflecting the exchange of isotopically heavy oxygen with the leaf water. Its influence on $\delta^{18}O$ in atmospheric CO_2 would be enhanced especially in the warm season, because the CO_2 exchange between the atmosphere and the leaf is increased and evapotraspiration is much activated. In addition, although CO_2 is always released into the atmosphere from soil and plant through respiration throughout the year, their fluxes also increase in the warm season. The gross flux of atmospheric CO_2 into the leaf is increased in the warm season. Therefore, the isotopic discrimination during the diffusive transport of CO_2 from the atmosphere to the carboxylation sites in chloroplasts affects $\delta^{18}O$ in atmospheric CO_2 in this season. Taking this into account, $\delta^{18}O$ in atmospheric CO_2 may also be dependent on the seasonality of (1) $\delta^{18}O$ in the leaf water produced by evapotranspiration, (2) flux of CO_2 return to the atmosphere through stomata, (3) CO_2 release into the atmosphere by soil respiration and plant respiration, and (4) gross CO_2 flux from the atmosphere into the leaf.

As can be seen in Fig. 5, the measured values of $\delta^{18}O$ in June and early July 1995, and possibly in June 1996, are much lower than contiguous data. Photosynthesis and respiration are already active in these months, and the collection of air samples were made under rainy condition. Since atmospheric relative humidity is very close to 100% under rainy a condition, e_a/e_i becomes equal to 1.0. Substituting the previous values of ε^* and δ_V into $\varepsilon^*+\delta_V$ in eq. (5), we now obtain $\delta_E = -7‰$. White and Gedzelman (1984) also reported that when atmospheric relative humidity increases, δ_V approaches $\delta^{18}O$ of water vapor originated in soil water, which implies $\delta_V = \delta_S - \varepsilon^*$. Taking this into account, it is possible that δ_E reflects $\delta^{18}O$ in soil water (equivalently, plant body water and precipitation) under rainy conditions. Indeed, the calculated value of δ_E is in agreement with -5 to $-9‰$ which were obtained by Hesterberg and Siegenthaler (1991) for $\delta^{18}O$ in soil water and precipitation near Bern, Switzerland. A similar

value was also obtained from the calculated values of $\delta^{18}O$ in precipitation given in Fig. 7. Under such conditions, CO_2 returned to the atmosphere after exchanging oxygen with leaf water, as well as that released by soil respiration and plant respiration, could in principle diminish $\delta^{18}O$ in atmospheric CO_2.

To interpret the variation of $\delta^{18}O$ observed in this study, we have discussed some possible causal processes. These processes are easily affected by meteorological factors such as air temperature, humidity and precipitation. In addition, the present measurement was conducted in a forest with many sources which influence $\delta^{18}O$ in atmospheric CO_2 significantly. These environmental conditions could have made variations of $\delta^{18}O$ in atmospheric CO_2 complicated. In order to verify the speculative hypothesis discussed above, simultaneous measurements of $\delta^{18}O$ in atmospheric CO_2, those in soil water, leaf water and atmospheric H_2O, and CO_2 fluxes between the atmosphere and the biosphere during photosynthesis and respiration are needed. Also, simple models are needed to quantitatively assess and discriminate the importance of various processes in producing the observed variation of $\delta^{18}O$ in atmospheric CO_2 at Takayama, Japan.

4. Conclusions

In order to examine the rôle of the biosphere in temporal variations of the atmospheric CO_2 concentration and its $\delta^{13}C$ and $\delta^{18}O$, air samples were collected in a forest near Takayama in the central part of Japan, and then analyzed for the respective components for the period from June 1994 to June 1996. The diurnal variation is clearly observed for the CO_2 concentration, $\delta^{13}C$ and $\delta^{18}O$ in the warm season from May to September, but barely in the remaining months of the year. In the warm season, the diurnal CO_2 variation reaches a maximum early in the morning and a minimum in the afternoon, while $\delta^{13}C$ varies diurnally in opposite phase. The rate in change of $\delta^{13}C$ with respect to the CO_2 concentration is estimated to be approximately -0.048‰/ppmv from the observed data. This implies that the diurnal CO_2 variation is produced by the CO_2 exchange between the atmosphere and the biosphere, i.e., photosynthesis in the daytime and respiration in the nighttime. The measured values of $\delta^{18}O$ also show the diurnal variation similar to $\delta^{13}C$, due probably to isotopically heavy CO_2 diffused back to the atmosphere from leaf through stomata and the isotopic discrimination during the diffusive transport of atmospheric CO_2 to the carboxylation sites in chloroplasts in the daytime, as well as to isotopically light CO_2 released into the atmosphere from plant and soil through respiration in the nighttime.

The measured values of the CO_2 concentration and $\delta^{13}C$ vary seasonally. The maximum and minimum concentrations of the seasonal CO_2 variation appear in April to May and August to September, respectively, with the peak-to-peak amplitude of 13 ppmv. The seasonal $\delta^{13}C$ variation is almost opposite in phase with that of CO_2, and the peak-to-peak amplitude is about 0.6‰. The rate in change of $\delta^{13}C$ relative to the CO_2 concentration is found to be about -0.053‰/ppmv, which suggests that the seasonally-dependent CO_2 exchange between the atmosphere and the biosphere is primarily responsible for the observed seasonal CO_2 variation.

Monthly values of $\delta^{18}O$ are rather irregular, and they do not show a clear seasonal variation, being different from the CO_2 concentration and $\delta^{13}C$. Isotopically light CO_2 released into the atmosphere from soil and plant through respiration, as well as CO_2 diffused back to the atmosphere from leaf after equilibrating isotopically with leaf water rich in ^{18}O, is thought to be important for the observed $\delta^{18}O$ variation. However, to interpret the observed variation of $\delta^{18}O$ completely, it is necessary to include other factors such as the depth-dependent seasonal variation of $\delta^{18}O$ in soil water, the seasonally-varying fluxes of CO_2 diffused back to the atmosphere from leaf and released into the atmosphere by plant respiration and soil respiration, the seasonality of $\delta^{18}O$ in leaf water, the seasonal variation of the gross flux of atmospheric CO_2 into the leaf, and short-time scale variations of $\delta^{18}O$ in leaf water due to weather conditions.

The data from simultaneous measurements of the atmospheric CO_2 concentration and its $\delta^{13}C$ and $\delta^{18}O$ would be very useful for a better understanding of the global carbon cycle; the $\delta^{13}C$ data are indispensable for separating the CO_2 exchange between the atmosphere and the oceans from that between the atmosphere and the terrestrial bio-

sphere, and those of $\delta^{18}O$ are expected to contribute to elucidating the role of the terrestrial biosphere in the carbon cycle. However, measurements, especially of $\delta^{13}C$ and $\delta^{18}O$, are extremely sparse and their data are still insufficient. To obtain valuable information about the global carbon cycle from those data, systematic measurements are needed for a comprehensive study not only in the background atmosphere but also in forest regions with strong biospheric signals.

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