Tellus (2002), 54B, 97–109
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TELLUS
ISSN 0280–6509

Diurnal variation of CO_2 concentration, $\Delta^{14}C$ and $\delta^{13}C$ in an urban forest: estimate of the anthropogenic and biogenic CO_2 contributions

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(Manuscript received 13 June 2000; in final form 26 November 2001)

ABSTRACT

Diurnal variation in the atmospheric CO_2 concentration and the carbon isotopic composition ($\Delta^{14}C$ and $\delta^{13}C$) was measured in a forest in an urban area on 9 February 1999. The carbon isotope approach used in the present study differentiated between the quantitative contributions from anthropogenic and biogenic CO_2 sources in the urban atmosphere. The anthropogenic (fossil fuel) and biogenic (soil respiration) contributions was estimated, and they ranged from 1 to 16% and from 2 to 8% of the total atmospheric CO_2. The diurnal variation of the anthropogenic CO_2 was the major cause of the total atmospheric CO_2 variation, while the biogenic CO_2 remained relatively constant throughout the day. Estimating the contribution of soil respired CO_2 provided the mean residence time of soil respired CO_2 within the forest atmosphere.

1. Introduction

The concentration of atmospheric carbon dioxide (CO_2) has increased from ca. 280 ppm, the pre-Industrial Revolution level (e.g. Leuenberger et al., 1992), to over 370 ppm (e.g. Keeling et al., 1995; Penner et al., 1999). This increase has mainly been caused by CO_2 emissions from the burning of fossil fuels, such as coal and petroleum, and the cement production. The cumulative global total CO_2 emissions from fossil fuels were 250 GtC from 1751 to 1995 (Andres et al., 1999). The CO_2 emission due to the burning of fossil fuels and changes in land use keeps increasing. The influences of CO_2 fertilization and other human activities such as increasing nutrient status and enhanced temperature (a heat island effect) are strong, especially in an urban forest.

In urban areas, anthropogenic CO_2 emissions (e.g. car exhausts) mixes with the background and biogenic CO_2 components, which are influenced by photosynthesis and respiration. The anthropogenic and biogenic components have sources nearby or at the soil surface. Therefore, the relative contributions of the CO_2 derived from the respective components are expected to show a gradual change with increasing height. The carbon isotope composition and concentration of atmospheric CO_2 provide information about carbon pathways

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(e.g. Mook et al., 1983; Inoue and Sugimura, 1985; Sternberg et al., 1997). Radiocarbon is a powerful tool for estimating the contribution of anthropogenic CO_2 which is produced by burning of fossil fuels (e.g. Mook, 1980; Levin and Kromer, 1997; Zondervan and Meijer, 1996; Meijer et al., 1996; Kuc and Zimnoch, 1998; Zahn et al., 2000). In the present study, diurnal variation of concentration, carbon isotopic compositions in the atmospheric CO_2 are presented in order to estimate the proportions of CO_2 derived from anthropogenic and biogenic sources. For the diurnal analysis, concentration and carbon isotope levels of the background atmospheric CO_2 can be considered to remain constant within an observation day. The contribution of CO_2 supplied by soil respiration is compensated with that by photosynthesis, because the isotopic fractionation is opposite in the two processes. Furthermore, if plants use the respired CO_2 within a forest (CO_2 recycling), the isotopic composition of the atmospheric CO_2 within the forest will change (Sternberg, 1989). The present study was conducted in winter, when photosynthetic activity is quite low, so that the CO_2 sink or source related to biogenic activity is mainly the efflux from the soil surface. To compare contributions of anthropogenic and biogenic CO_2 just above the canopy of an urban forest and with that further above the canopy, air was sampled at two levels to measure CO_2 concentration, $\Delta^{14}C$ and $\delta^{13}C$. Within the forest, CO_2 concentration and $\delta^{13}C$ were measured at 6 different heights in order to clarify the behavior of CO_2 within the forest.

2. Materials and methods

2.1. Study sites

The study site was located about 8 km east of the center of Nagoya, Aichi Prefecture, central Japan (Fig. 1). Nagoya is surrounded by several big industrial cities, including Toyota City (automobile industry; ca. 20 km east-southeast) and Yokkaichi City (petroleum industry; ca. 35 km southwest). It is the fourth largest city in Japan, with a population of more than 2 million and an area of 330 km^2. Meteorological measurements and air sampling were made from towers within a secondary deciduous temperate forest at Nagoya University (35°8′57″N, 136°58′28″E) and a broadcasting tower (Chukyo TV Broadcasting Co. Ltd., 35°8′37″N, 136°58′15″E). These two sites are referred to as the forest site and the Chukyo TV site, respectively. The forest site was located 600 m east-northeast of the Chukyo TV site. Both tower bases are 66 m above sea level and near major roads that are heavily traveled in the morning and evening rush hours. The forest is dominated by oak trees (*Quercus variabilis* and *Q. serrata*) with its canopy as high as ca. 18 m. Broad-leaved evergreen plants (*Ilex pedunculosa*, *Vaccinium bracteatum*, *Eurya japonica*, *Ligustrum japonicum* and *Aucuba japonica*) dominate below 9.5 m in height. On the tower of the forest site, some meteorological instruments were installed both above and below the canopy to obtain wind speed, air temperature and relative humidity. Atmospheric stabiliy can be estimated using the Obukhov's length (L) to be represented as a non-dimensional parameter, z/L (e.g. Brutsaert, 1982), where z is the height on which the value of L is determined (i.e. 20.75 m). Positive and negative values of z/L indicate that the atmospheric stability is stable and unstable conditions, receptively. However, the atmosphere can be defined as a neutral condition when z/L ranges from -1 to 1. On the Chukyo TV site (85 m), the meteorological indices were obtained with an average of 10 min.

Although the forest canopy consists of leafless oak trees in winter, there is a weak photosynthetic activity by evergreen plants, which grow below 9.5 m in height at the forest site. Sirisampan (1999) determined that the CO_2 flux, which was the balance between photosynthesis and plant respiration per unit area of the leaf surface, was from -0.0794 to 0.2131 $mgCO_2\,m^{-2}\,s^{-1}$ for the evergreen plants in the forest site, where a negative value indicated that respiration dominates. The average value of LAI (leaf area index) is 0.054 $m^2\,m^{-3}$ below the height of 9.5 m. Thus, CO_2 flux by evergreen plants is equivalent to the rate of CO_2 concentration change, i.e. from -2.2×10^{-3} to 5.8×10^{-3} ppm s^{-1}. We can assume that CO_2 movement around canopy height is rapid during daytime (we concluded that the residence times of CO_2 in the lowermost part of the atmosphere are several hours in the present study, but that time means the daily and spatial average one). The forest atmospheric CO_2 is 10^5 or 10^7 times as large compared with the CO_2 influenced by photosynthesis and respiration, since

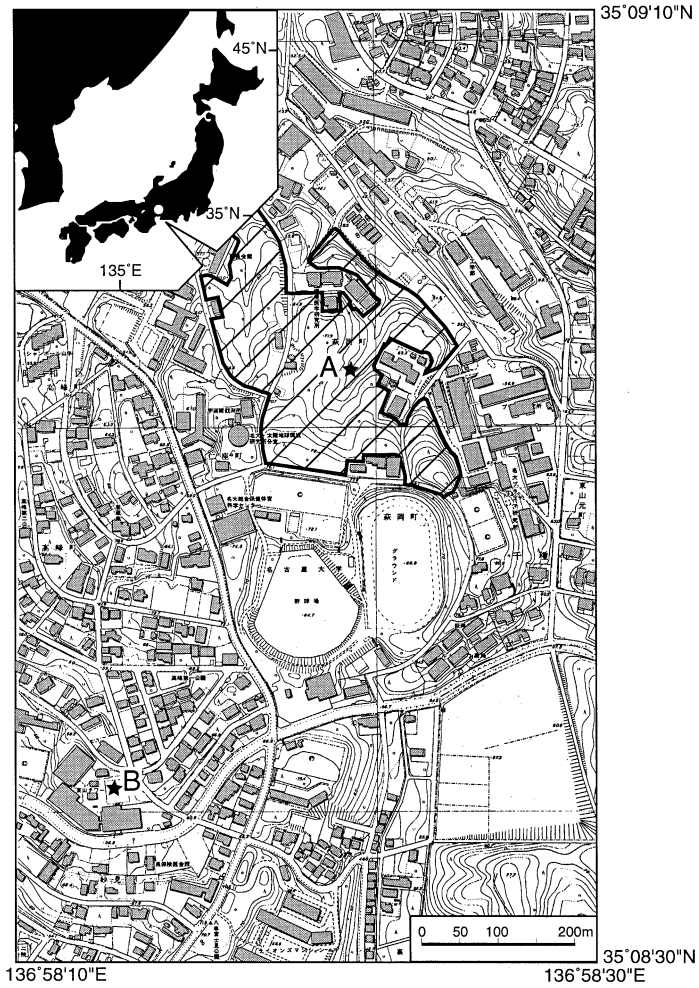

Fig. 1. The study sites in Nagoya City (open circle), central Japan, the forest site (asterisk A) and the Chukyo TV site (asterisk B). The area of slanting line indicates the forest, which was surrounded with residential buildings (shaded).

the CO_2 concentration of the forest atmosphere is ca. 400 ppm. Moreover, this estimated range of photosynthesis effect is almost identical with the CO_2 flux from the soil surface, which was almost remained constant for a whole day. Hence, the photosynthetic and respiratory effects are very small and may be ignored in the present study.

2.2. *Sampling and measuring CO_2 concentration*

Air sampling started at 0:00 and carried out at intervals of 3 h at night and 2 h in the daytime at the forest site, 6 h at night and 3 h in the daytime at the Chukyo TV site on 9 February 1999. The air sampling ports were set at 6 heights at the forest site (23.75, 19.00, 14.75, 9.10, 5.60 and 1.55 m in height) and one height at the Chukyo TV site (85 m). The sampling ports at 23.75 and 19.00 m were located above the forest canopy, while that at 14.75 m was located in the upper canopy, which at the time of observation consisted of leafless oak trees. The air was sampled into 10-L plastic bags (GL science, Japan) or an aluminized 20-L plastic bag (GL Sciences, Japan) through the mini-pump (NP-2N, Shibata Scientific Technology Ltd., Japan). Before sampling, the bag was filled and evacuated three times in order to substitute the

pre-existing gas with in situ air. To close the sample bag, PharMed tubes (Norton Performance Plastic Co., USA) which were connected to the sample bag ports were clamped. Air sampled into a 10-L plastic bag at the height of 23.75 m in the forest site was used for radiocarbon analysis in addition to $\delta^{13}C$ analysis. Air at the height of 85 m in the Chukyo TV site was collected into a 10-L plastic bag and a 20-L aluminized plastic bag: the plastic bag was used for CO_2 concentration and $\delta^{13}C$ measurements and the aluminized plastic bag was for ^{14}C. The CO_2 concentration of air in the each sampling bag, which was collected both at the forest site and the Chukyo TV site, was measured with a non-dispersive infrared absorption spectrometer (NDIR, LI-6262: LI-COR, USA) against two reference gases (248 and 444 ppm) as soon as the air sampling was finished.

For estimating the $\delta^{13}C$ of soil-respired CO_2, a chamber-style sampling system with a chaplet of 4 plastic bags (1-L) was installed. The observation system contains the chamber, NDIR, plastic bags and a mini pump. The chamber was made of polypropylene that was $40 \times 20\ cm^2$ in base area and 15 cm in height, without sunlight shields (no grass in the chamber area). Before the chamber was placed bottom upward on the soil surface the air inside the observation system was purged by in situ ambient air. Sample air inside the system was circulated at a rate of $2\ L\ m^{-1}$ from the chamber, through the NDIR, the mini pump, a chaplet of bags, and then returned to the chamber. The rim of the chamber was sealed by clay paste in order to isolate air in the chamber from the atmosphere. To keep the volume of the observation system constant, a small vacuum box was used to distend the plastic bag. The increase of CO_2 concentration inside the sampling system was monitored continuously after the chamber was turned down. The valves of the entry ports of the plastic bags were closed 1, 10, 40 and 60 min after the chamber had been placed. After closing the valves of the respective sampling bags, the air inside the observation system flowed in the bypass line. From this observation, a relation between CO_2 concentration and $\delta^{13}C$ could be established.

2.3. *Collection and isotope analysis of carbon dioxide*

CO_2 was cryogenically separated in a vacuum from the sampled air within a few hours of collection. H_2O and CO_2 were condensed with dual ethanol slush traps (ca. $-95°C$) and liquid N_2 traps, and other gases, e.g. N_2, O_2, and Ar, were evacuated from the vacuum line. The CO_2 was purified by removing H_2O cryogenically under a vacuum and was sealed in a Pyrex tube for isotope analysis. The CO_2 was typically separated from a ca. 1.5-L air sample at STP, whereas the sample for radiocarbon analysis was ca. 10 L at STP. Although only a small part of each air sample was processed, isotopic fractionation between the extracted and residual CO_2 in the air bags was confirmed negligible; it was less than 0.03‰ for $\delta^{13}C$. Since the air storage in the plastic bags was less secure than in the aluminized ones (Takahashi, 2001), the plastic bags were processed first.

For radiocarbon analysis, the purified CO_2 gas was reduced to graphite on an iron powder catalyst with hydrogen gas (Kitagawa et al., 1993). Graphite targets prepared from the sample and a standard were used for ^{14}C analysis with a Tandetron Accelerator Mass Spectrometer (General Ionex Co., USA) at the Center for Chronological Research, Nagoya University, Japan (Nakamura et al., 1985). The atmospheric ^{14}C content is expressed as $\Delta^{14}C$, as defined by the Hox-II oxalic acid standard supplied by the National Institute of Standards and Technology (NIST). The measurement error was calculated using ^{14}C counting statistics, and ranged from 6 to 12‰ for the air samples in the present study.

In the present study, stable carbon isotopic compositions were measured on an isotope ratio mass spectrometry (IR-MS: MAT-252, Thermo Quest Inc., Germany) at the same laboratory. Carbon isotopic composition is expressed in per mil (‰) on VPDB-CO_2 scale, using the NBS-19 standard material as a reference. A working reference CO_2 gas was prepared from air sampled at the forest site on 8 September 1998. N_2O contamination of the reference and sample gases was not determined. A correction of 0.2‰ for N_2O contamination was applied to the $\delta^{13}C$ calculations for the reference gas (Mook and Jongsma, 1987). Repeated measurements of the same standard and sample estimated that the measurement error between the maximum and minimum analytical results was better than 0.04‰ for $\delta^{13}C$. For an inter-laboratory reference check, a specially prepared CO_2 gas called NACIS (NIES-Atmospheric CO_2 Isotope ratio Standard;

http://info.nies.go.jp:8092/~lnmukaih/english.htm) were measured. The measured value of NACIS in the present study was consistent with the recommended values.

2.4. *Methods for estimating contributions of anthropogenic and soil respiratory CO_2*

Atmospheric CO_2 in an urban area is a mixture of CO_2 emitted from anthropogenic and biogenic sources with CO_2 of the background atmosphere. Photosynthesis is neglected, since the observations were carried out in winter. Therefore, any increase in CO_2 concentration over the background level is considered to result from fossil-fuel burning and soil respiration. The transport of emitted CO_2 to the background atmosphere and the mixing of CO_2 from the two sources control the concentration and carbon isotope composition of the atmospheric CO_2. A mixing model for the three isotopically distinct gases is expressed by the following equations:

$$(1+{}^{14}\delta_i^S)T_i=(1+{}^{14}\delta_a^S)T_a+(1+{}^{14}\delta_f^S)T_f+(1+{}^{14}\delta_b^S)T_b \quad (1)$$

$$T_i=T_a+T_f+T_b=T_a+(T_i-T_a)p+(T_i-T_a)(1-p) \quad (2)$$

where ${}^{14}\delta^S$ is the radiocarbon concentration and T is the concentration. The subscripts f, b, and a distinguish the fossil fuel and biogenic (soil respiration) components, and background atmosphere, respectively. The proportion of the fossil-fuel component to the increment of CO_2 concentration from the background level ($T_i - T_a$) is p, where $0 \leqq p \leqq 1$. This p was computed using eqs. (1) and (2). The radiocarbon concentration expressed in eq. (1) is re-evaluated to ${}^{14}\delta^S$ (Mook and van der Plicht, 1999) using $\delta^{13}C$ value of each sample, which corresponds $\delta^{14}C/1000$ in Stuiver and Polach (1977), since CO_2 behavior is given by the atmospheric mixing of CO_2 released from various sources. The CO_2 concentration of the background component was given as 374.54 ppm, data obtained at Kosan Station (33°17′27″N, 120°09′55″E: 72 m above sea level) in Cheju Island, Korea (Kim, personal communication). Since fossil fuel does not contain ^{14}C, ${}^{14}\delta_f^S$ is obviously equal to -1. The value of ${}^{14}\delta_a^S$ can be obtained from the report of $\Delta^{14}C$ and $\delta^{13}C$ by Levin and Kromer (1997), which were observed in Germany in the winter season of 1996 and 1997 to be 0.136 ± 0.003. ${}^{14}\delta_a^S$ declined during 2 yr, i.e. from 1997 to the observation year, i.e. 1999. Thus, ${}^{14}\delta_a^S$ was corrected to be 0.124 for the decline using the exponential curve reported by Levin and Kromer (1997). Although the present study area (Japan) is far from Germany, it is possible to use ${}^{14}\delta_a^S$ in eq. (1) for the following reason. CO_2 concentration and $\delta^{14}C$ values of the background atmosphere in each area, i.e. Japan and Germany, can be explained by the simple physical CO_2 mixing between global background and fossil-fuel components (the relation between CO_2 concentration and ${}^{14}\delta^S$), since the ${}^{14}\delta^S$ value of CO_2 derived from fossil fuels, which currently controls the discrepancies in CO_2 concentration and ${}^{14}\delta^S$ in the atmosphere from the global background, is always a constant of -1. Over and above, the background CO_2 concentration shows similar values at both areas, i.e. Germany and Korea (Uhse et al., 1998; Kim, personal communication). On the other hand, $\delta^{13}C$ for the background atmospheric CO_2 has been reported in several studies (e.g. Levin and Kromer, 1997; Keeling et al., 1995). In contrast to ${}^{14}\delta^S$, these values are not used in the present study owing to a potential $\delta^{13}C$ heterogeneity that is dependent on source materials, e.g. coal, petroleum and natural gas, and the localities of their productions. ${}^{14}\delta_b^S$ can be obtained from $\Delta^{14}C$ and $\delta^{13}C$ values of soil-respired CO_2, assuming that the $\Delta^{14}C$ values of soil-respired and background atmospheric CO_2 are equal.

3. Results

3.1. *Diurnal variation of CO_2 concentration and carbon isotopic composition*

The diurnal variations of CO_2 concentration, $\Delta^{14}C$ and $\delta^{13}C$, with the meteorological results, i.e. wind velocity (4 different heights) and atmospheric stability (z/L), are shown in Fig. 2. There are some missing $\delta^{13}C$ data from the forest site (all heights at 0:00; 23.75 m at 14:00 and 16:00; 14.75 m at 24:00). The CO_2 concentration of the urban atmosphere ranges from 383.8 to 427.0 ppm at a height of 85 m (Chukyo TV site) and 394.2 to 454.8 ppm at a height of 23.75 m (forest site). Carbon isotopic compositions range from -16 to 81‰ ($\Delta^{14}C$) and -10.8 to -8.5‰ ($\delta^{13}C$) at 85 m,

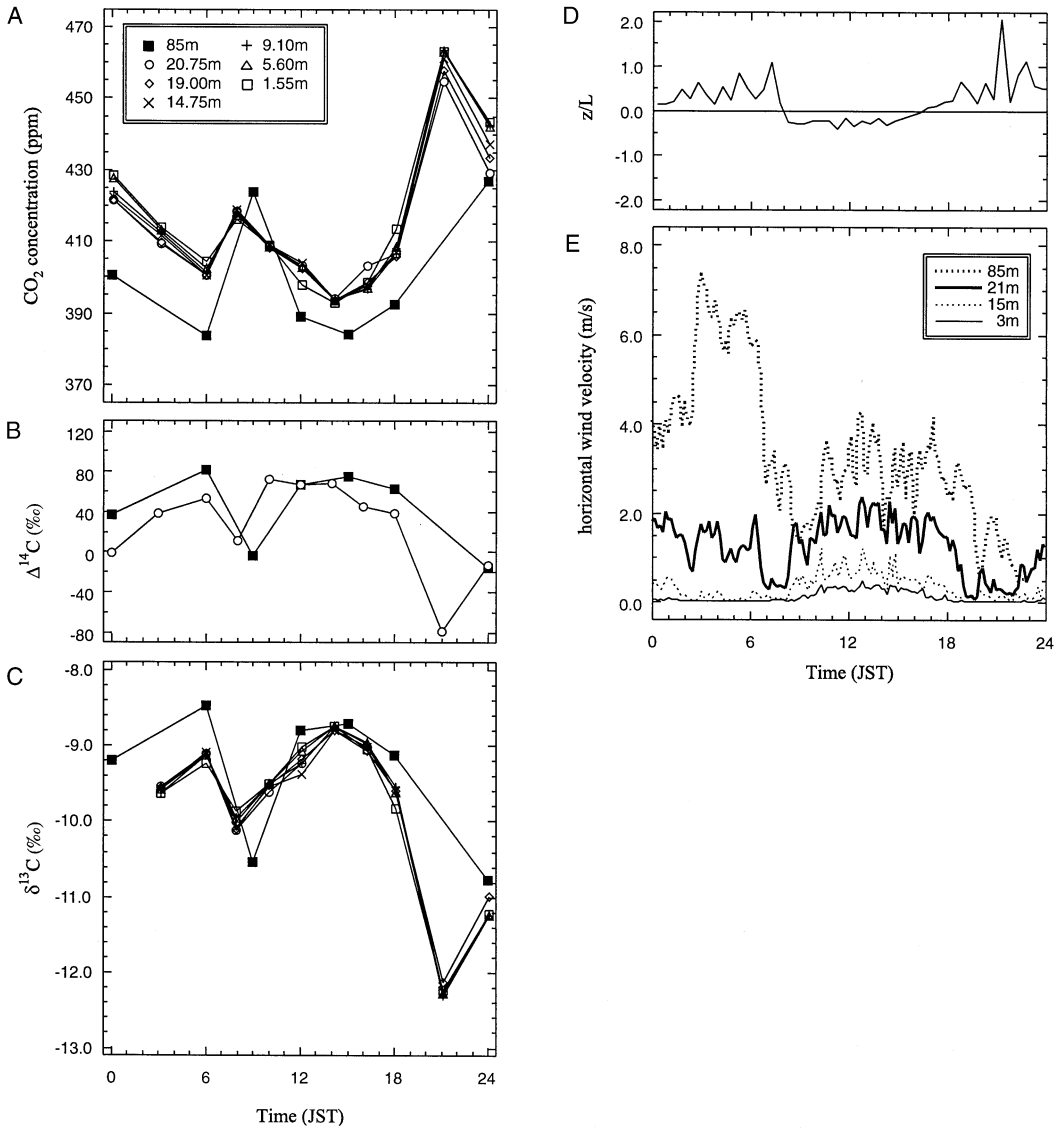

Fig. 2. Diurnal variations of CO_2 concentration (A), $\Delta^{14}C$ (B), $\delta^{13}C$ (C), atmospheric stability (D) and wind velocity (E) at the forest and Chukyo TV sites. The data for a height of 85 m are for the Chukyo TV site and those for the other heights are for the forest site.

and −79 to 72‰ ($\Delta^{14}C$) and −12.0 to −9.0‰ ($\delta^{13}C$) at 23.75 m, respectively. The concentration exceeds the global background level (ca. 370 ppm) throughout the day. Both $\Delta^{14}C$ and $\delta^{13}C$ show a negative relationship to the diurnal variation in CO_2 concentration and are lower than the global background levels. The CO_2 concentration is generally low during the daytime and high at night. This trend is similar to that observed all year round in the present study area, but the diurnal variations of CO_2 concentration observed in the present study have remarkable peaks in the morning and evening. The variations of carbon isotopic compositions have a large depletion at the corre-

sponding time of CO_2 concentration peaks observed. The diurnal variation in the CO_2 concentration observed in the present study was similar to that reported in previous studies (e.g. Inoue and Sugimura, 1984; Aikawa et al., 1995). The atmosphere is almost under neutral conditions ($-1 < z/L < 1$) throughout the day. Hence, the atmospheric stability seems to have no influence on the diurnal variations in CO_2 concentration. The wind velocity shows a gradual increase vertically and is higher in daytime.

3.2. *Carbon isotope composition of soil respiratory CO_2 measured by chamber-style observation*

When two isotopically different CO_2 sources are mixed, the relationship between the concentration and $\delta^{13}C$ of the ambient CO_2 follows a simple mixing model (Keeling, 1958), which is given by

$$\delta^{13}C_i = \frac{M}{T_i} + I(^{13}C) \quad (3)$$

where M is a constant and $I(^{13}C)$ is the $\delta^{13}C$ value of CO_2 added as end member of mixing to the initial air. The ambient atmosphere corresponds to the initial air and soil respiratory CO_2 is the end member component added in the flux chamber observation. Using the least-squares method, the $\delta^{13}C$ value of soil-respired CO_2 was calculated to be $-27.3 \pm 0.3‰$ ($n = 4$, $r = 1.00$) from the interception in eq. (3) (Fig. 3). The average $\delta^{13}C$ value of cellulose in oak tree trunks (*Q. serrata* and *Q. variabilis*) was $-26.0 \pm 0.8‰$ ($n = 5$: Aoki, 1997; Takahashi et al., 1998); these two species are dominant in the forest site. Generally, the $\delta^{13}C$ of leaves, which contain most of the original soil organic matter, is lower than that of stem cellulose. Leavitt and Long (1982) reported an average isotopic decrease of 2‰ in leaves over stem cellulose. Therefore, the $\delta^{13}C$ value of soil-respired CO_2 as found in this flux chamber study is reasonable.

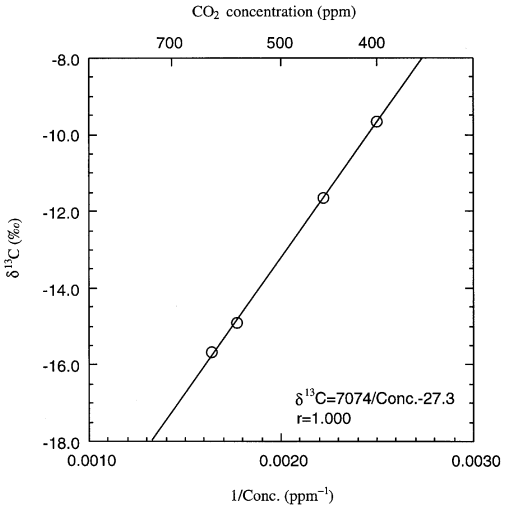

Fig. 3. There was a linear relationship between the $\delta^{13}C$ and increase in CO_2 concentration with the addition of soil respiratory CO_2 to the atmosphere. The solid line was calculated using the least-squares method.

4. Discussion

4.1. *Estimating diurnal variation in the anthropogenic and biogenic CO_2*

The contributions of the fossil-fuel and soil respiration components to the background just above the forest canopy (23.75 m) and at 85 m were computed using eqs. (1) and (2). Diurnal variations in CO_2 for the fossil-fuel and soil respiration components from the respective sampling sites are shown in Fig. 4. CO_2 concentration of fossil-fuel component (its percentage to total atmospheric CO_2) ranges from 2 to 70 ppm (0.4–15.5%) at 23.75 m, and from 1 to 41 ppm (0.2–9.5%) at 85 m. Its error (σ) ranges from 2.6 to 5.5 ppm (0.7–1.4%) for the respective components. This estimated range includes the value measured in the industrial region of Krakow (Poland), where it was reported to be ca. 27 ppm in February on an average between 1983–94 by Kuc and Zimnoch (1998). Zondervan and Meijer (1996) reported that the vertical different in fossil fuel component ranged from 0 to 36 ppm. The CO_2 concentration of the respective components at 85 m is lower than that at 23.75 m in the present study. The mean values of the vertical difference from 23.75 to 85 m at the same sampling time were 7.4 ppm in the fossil-fuel component and 6.2 ppm in soil respiration component. This stratification is consistent with the fact that CO_2 was released near or from the ground surface.

The CO_2 concentration of the soil respiration component (its percentage of the total atmospheric CO_2) ranges from 11 to 33 ppm (2.4–8.2%) at 23.75 m at the forest site; and from 7 to 16 ppm

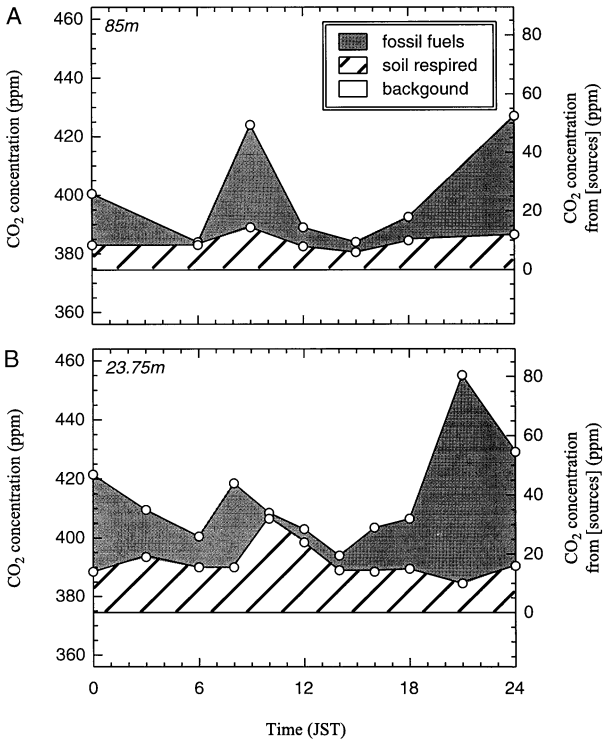

Fig. 4. Diurnal variations of CO_2 concentration from fossil-fuel burning and soil respiration, at the Chukyo TV (A) and forest (B) sites.

(1.9–3.7%) at 85 m at the Chukyo TV site. The contribution of CO_2 derived from soil respiration remained relatively constant throughout the day, ca. 15 ppm (23.75 m) and 10 ppm (85 m), whereas there was a large fluctuation in the fossil-fuel component. The constant contribution of soil respiration component is reflected by a constant CO_2 flux from the soil. According to the CO_2 flux measurement using a chamber observation (not estimated from the soil temperature), the range of its diurnal variation is only 0.0120 $mgCO_2\ m^{-2}\ s^{-1}$ with a daily average value of 0.0320 $mgCO_2\ m^{-2}\ s^{-1}$ at the forest site (Oguri, 2001). This average value of CO_2 flux from the soil surface would correspond to 2.7 ppm h^{-1}, if the respired CO_2 were distributed equally within the forest atmosphere of 23.75 m height. Thus the mean residence time of soil-respired CO_2 may be considered to be several hours on a daily average. A meteorological analysis cannot be used to assess whether this residence time is reasonable or not, since the rate of transportation of each component in the forest atmosphere cannot be obtained.

4.2. *Diurnal variations of CO_2 concentration and meteorological conditions*

Air transportation from ambient to background atmosphere, which is mainly controlled by the atmospheric stability and wind velocity, causes the diurnal variations of CO_2 concentration. Atmospheric stability seems to have no influence on the diurnal variations in CO_2 concentration on the day of observation in the present study, since it is almost under neutral conditions ($-1 < z/L < 1$) throughout the day (Fig. 2). If the wind velocity were low, vertical atmospheric mixing would not occur easily. Hence, the CO_2 concentration in an urban atmosphere cannot return to the background level, since CO_2 that evolves on the land surface is not transported to

the background atmosphere, especially within the forest.

The CO_2 concentration of the respective components, i.e. ambient atmosphere, soil respiration and fossil-fuel components (Fig. 4), was compared with the wind velocity (Fig. 2). The wind velocity shows a negative correlation against both the CO_2 concentration of the total atmosphere ($r = -0.80$) and that of the fossil-fuel component ($r = -0.76$), with almost identical coefficients. The CO_2 concentration of the soil respiration component at the Chukyo TV site shows a negative correlation with the horizontal wind velocity ($r = -0.61$), whereas that at the forest site shows no distinct correlation ($r = 0.28$). The negative correlation of the CO_2 concentration of the ambient atmosphere and fossil-fuel components with the wind velocity indicates that air transportation controls the diurnal variation. On the contrary, the soil respiration component shows another trend. At the forest site, the CO_2 from soil respiration is directly supplied from the nearby forest floor; therefore, the diurnal variation of the soil respiration component below the forest canopy is not affected by wind velocity at the canopy height. The CO_2 concentration of the soil respiration component at the forest site increases when a light wind starts blowing at a height of 3 m (Fig. 2). Probably, CO_2 from soil respiration at the forest site has accumulated just on the soil surface (e.g. below 0.3 m in Buchmann et al., 1997) until the breeze starts. This accumulation may be associated with a long mean residence time of biogenic CO_2, i.e. several hours. At the Chukyo TV site, the CO_2 from soil respiration is supplied from a wider urban area. Therefore, it seems that the behavior of CO_2 from soil respiration at a height of 85 m in the atmosphere is almost identical with that of CO_2 from fossil-fuel and total atmospheric components.

In the study area, large CO_2 emissions by automobiles may contribute to the increase of CO_2 concentration in the ambient atmosphere. However, it is very difficult to evaluate quantitatively its diurnal effect on the change in CO_2 concentration, since we do not have a tool to separate the contribution of automobiles from the fossil-fuel component in the present study. We can only discuss circumstantial evidence. Our estimated results that the contribution of the fossil-fuel component is large in the rush hours indicate the influence of automobiles on the urban atmosphere. Aikawa et al. (1995) also monitored two shoulders in the diurnal trend of atmospheric CO_2 concentration, which appeared around both rush hours in the same urban area. The CO_2 emission from human activities can be considered to be the principal contributor to the CO_2 increase in the urban atmosphere.

4.3. *Estimating $\delta^{13}C$ of CO_2 derived from fossil fuels*

In the present study, any increase in CO_2 concentration over the background level is considered to result from fossil-fuel burning and soil respiration. The $\delta^{13}C$ values of fossil-fuel and background atmosphere components for the study area are estimated from the isotopic mass balance and the mixing relationship between the fossil-fuel and background atmospheric components. The relationship between background and fossil-fuel components can be expressed as

$$T_{(a+f)} = T_i - T_a \tag{4}$$

$$[\delta^{13}C \cdot T]_{(a+f)} = [\delta^{13}C \cdot T]_a + [\delta^{13}C \cdot T]_f = [\delta^{13}C \cdot T]_i - [\delta^{13}C \cdot T]_b \tag{5}$$

where the subscript (a + f) indicates a mixture of the background and fossil-fuel components. T_b is estimated using eqs. (1) and (2). $\delta^{13}C_b$ is already known (-27.3 ± 0.3‰), but we cannot use this value for estimation at a height of 85 m. This value might be not exact for that height, since the CO_2 from soil respiration at the 85 m tower is supplied from the wider urban area, as mentioned above. Therefore, the concentration–$\delta^{13}C$ relation between the background and fossil-fuel components can be obtained only for the height of the canopy at the forest site (Fig. 5) according to eq. (3), and $\delta^{13}C_f$ can be calculated using the least-squares method ($n = 8$, $r = 0.996$) to be -32.3 ± 1.0‰. This estimated $\delta^{13}C$ value is lower than $\delta^{13}C_b$ from the chamber observation. Petroleum and natural gas are the main fossil fuels burnt in the study area. Approximately 10 times more CO_2 is derived from petroleum than from natural gas (data from the Ministry of International Trade and Industry, Japan and TOHO GAS Co. Ltd.). Schoell (1984) reported that the $\delta^{13}C$ of kerogens of terrestrial origin ranged from -27 to -30‰. Moriizumi et al. (1998) reported that the $\delta^{13}C$ value of natural gas

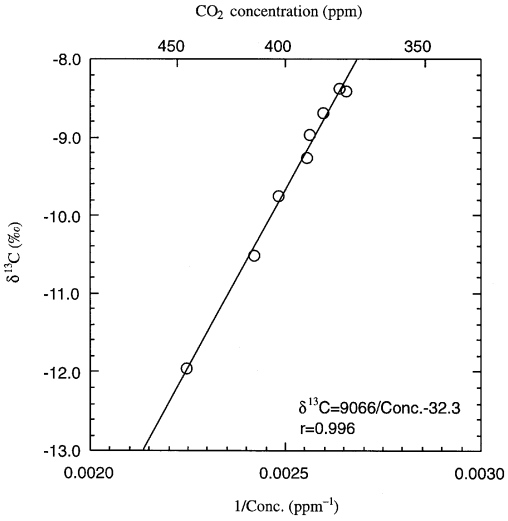

Fig. 5. The relationship between CO_2 concentration and $\delta^{13}C$ with change in the CO_2 mixing ratio between the fossil-fuel component and the background atmosphere at a height of 23.75 m in the forest site. The solid line was calculated by using the least-squares method.

(fossil CH_4) supplied to the Nagoya City area was -40.8 ± 3.0‰. Using these values in the isotopic mass balance equation, the $\delta^{13}C$ value of CO_2 from fossil-fuel burning is estimated to be from -28 to -32‰, which is consistent with the $\delta^{13}C$ of the fossil-fuel component estimated in the present study.

On the other hand, $\delta^{13}C_a$ is estimated to be -7.8 ± 0.1‰ by substituting the value of 374.54 ppm (Kim, personal communication) for $T_{(a+f)}$ in eq. (3). Using the $\delta^{13}C$ values of end-members estimated in the present study, the vertical contributions of the fossil-fuel and soil respiration components within the forest can be obtained from the isotopic mass balance. The diurnal changes in the vertical profiles of the fossil-fuel and soil respiration components are shown in Fig. 6. However, the estimated results have a large error (6–23 ppm) and uncertainty for the following reasons: two CO_2 sources, i.e. fossil fuel and soil respiration, have a similar $\delta^{13}C$ value, and the $\delta^{13}C$ value of the background component estimated in the present study is higher than that obtained from previous reports (Levin and Kromer, 1997; Zondervan and Meijer, 1996). Therefore, we can only obtain the vertical trend in diurnal variation. Although the total CO_2 concentration of the forest atmosphere was constant vertically, the CO_2 concentration for the soil respiration component had a vertical gradient within the forest. The CO_2 concentration was higher nearer the ground, especially at midnight. During the night, the gradient of the soil respiration component is larger than that of the fossil-fuel component.

5. Conclusions

The diurnal variations in the anthropogenic and biogenic contributions to the total atmospheric CO_2 in an urban area in winter were estimated using the carbon isotopic ratio and concentration of atmospheric CO_2. The respective contributions of fossil-fuel burning and soil respiration to the total atmospheric CO_2 ranged from 0.4 to 15.5% (2–70 ppm) and from 2.4 to 8.2% (13–32 ppm) at 23.75 m (just above the forest canopy) and from 0.2 to 9.5% (1–41 ppm) and from 1.9 to 3.7% (7–16 ppm) at 85 m. The diurnal variation in the atmospheric CO_2 concentration, which is low during the daytime and high at night, was controlled mainly by wind velocity, and was influenced by the amount of CO_2 emitted from fossil-fuel burning. At the forest, however, the diurnal variation of the soil respiration component below the forest canopy is not affected by wind velocity at the canopy height. CO_2 from soil respiration at the forest site has accumulated on the soil surface until the breeze starts at the bottom of the forest.

Although the total CO_2 concentration of the forest atmosphere was constant vertically, the CO_2 concentration for the soil respiration component had a vertical gradient within the forest. The CO_2 concentration was higher nearer the ground, especially at midnight. During the night, the gradient of the soil respiration component is larger than that of the fossil-fuel component.

Estimating the contribution of soil-respired CO_2 in the forest atmosphere from an isotopic analysis in the present study provided the mean residence time of soil-respired CO_2 within the urban forest to be several hours. The $\delta^{13}C$ of CO_2 derived from fossil fuels was calculated using the isotopic mass balance to be -32.3 ± 1.0‰. This estimated value is lower than that of the soil-respiration component obtained from a chamber observation.

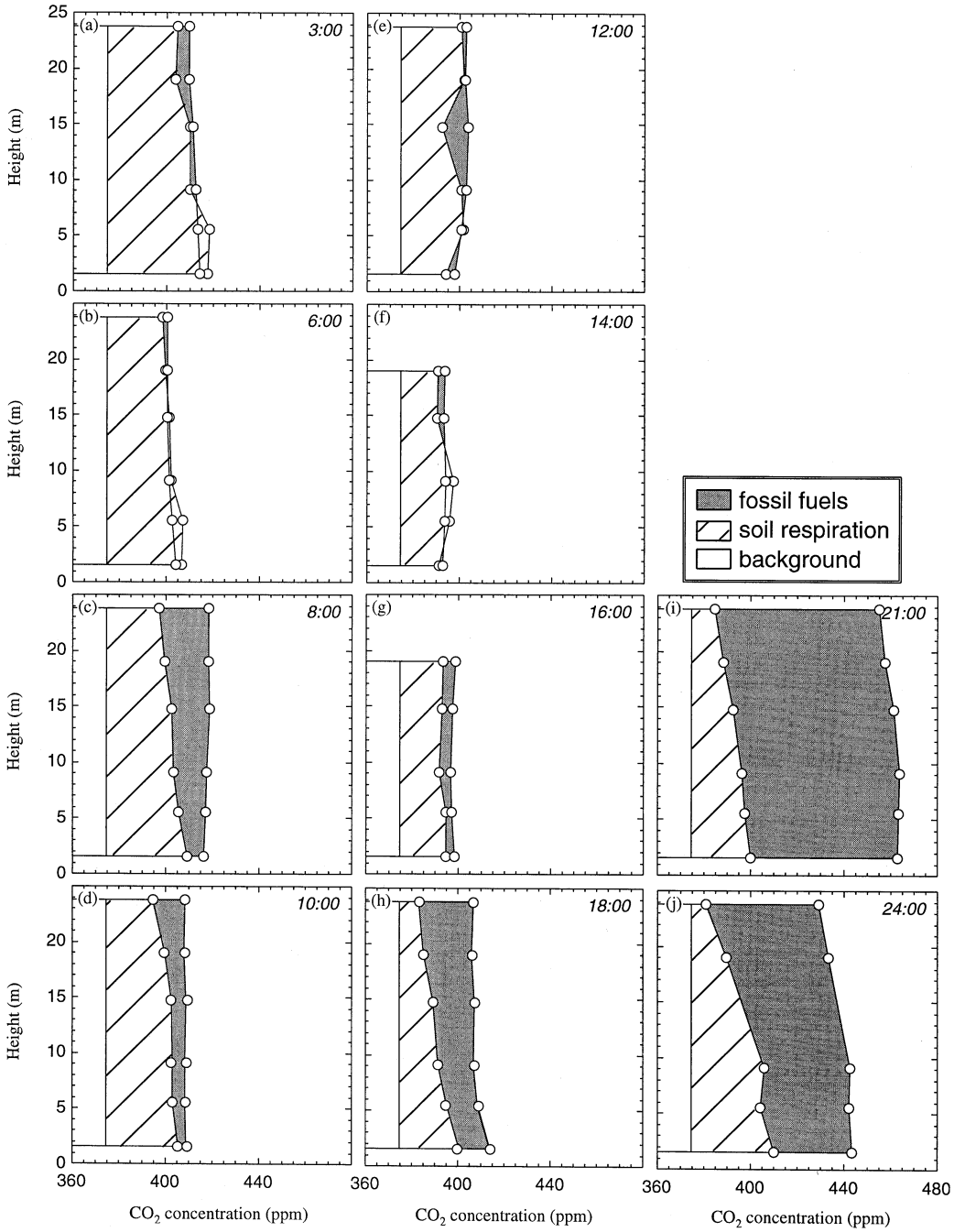

Fig. 6. The diurnal variations in vertical profiles of CO_2 concentration derived from fossil-fuel burning and soil respiration, at 3:00 (a), 6:00 (b), 8:00 (c), 10:00 (d), 12:00 (e), 14:00 (f), 16:00 (g), 18:00 (h), 21:00 (i) and 24:00 (j).

6. Acknowledgments

We are grateful to Dr. Atsuko Sugimoto of Kyoto University for her advice and encouragement and to Mr. Atsuhiro Takahashi and Mr. Hideyuki Oguri of Nagoya University for their help with the air sampling. We also thank the Chukyo TV Broadcasting Co. Ltd. for the kind permission to use their broadcasting tower for air sampling. We also thank Professor Dr. Kyung-Ryul Kim of Seoul National University for the special provision of data at the Kosan Station and Dr. Hitoshi Mukai of the National Institute for Environmental Studies for providing the NACIS standard. This work was financially supported by grants from the Ministry of Education, Science, Sports and Culture, Japan (Nos. 11213209, 11480103 and 10144103), and a Sasakawa Scientific Research Grant from the Japan Science Society (No. 10-258K).

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