Seasonal variations of concentration and $\delta^{13}C$ in soil air CO_2 and soil respired CO_2

Hiroshi Aoki Takahashi⁽¹⁾, Eiichi Konohira⁽²⁾, Tetsuya Hiyama⁽²⁾, Toshio Nakamura⁽³⁾ and Naohiro Yoshida⁽⁴⁾

ABSTRACT– Seasonal changes of δ^{13} C of soil respired CO₂ and vertical profiles of soil air CO₂ concentration and δ^{13} C are discussed at an urban deciduous forest in Nagoya City, central Japan. The δ^{13} C values of soil respired CO₂, which were obtained by the isotopic mass balance using the chamber method, showed seasonal fluctuations ranging from -31.0 to -24.5% with low values from summer to autumn and high ones from winter to spring. Seasonal variation in soil air CO₂ showed high concentration and low δ^{13} C value in summer, and low concentration and high δ^{13} C value in winter. They ranged from 0.1 to 3.4% (0.8-3.0% in vertically) in concentration and from -23.7 to -18.1% (0.3-4.6% in vertically) in δ^{13} C. CO₂ concentration in soil air increased gradually with depth, whereas the δ^{13} C value decreased suddenly at the depth from 10 to 20cm and remained relatively constant below 20cm. The seasonal δ^{13} C fluctuation of soil respired CO₂ was influenced by CO₂ production at a shallow depth in soil (<10cm). On the other hand, the vertical δ^{13} C profiles in soil organic matter increased *ca.* 2% from 10 to 60cm in depth. This δ^{13} C enrichment is much larger than the expected value from the isotopic fractionation during decomposition.

Introduction

Soil is a reservoir of particular importance to global carbon cycle. To qualitatively understand and predict changes in atmospheric CO₂, a detailed understanding on the behavior of major sources and sinks of atmospheric CO₂, including soil and the terrestrial biosphere, is necessary. Soil organic matter contains a large amount of carbon *ca.* 1500Gt, more than twice the size of atmospheric CO₂ in which carbon pool is *ca.* 720Gt (Schlesinger, 1997), and has the capacity to act as a carbon sink on decadal timescale (Bird *et al.*, 1996). Changes in size of the soil carbon pool therefore can significantly affect atmospheric CO₂ concentration.

CO₂ flux from soil surface was estimated by several methods such as the alkali-chamber (Lundegardh, 1927; Carlyle and Than 1988; Rout and Gupta 1989), static chamber (Dörr and Münnich, 1990; Crill, 1991; Dong *et al.*, 1998), air flow chamber (Reiners, 1968; Kucera and Kirkham, 1971; Edwards and Sollins, 1973) and ²²²Rn (Dörr and Münnich, 1990; Gaudry *et al.*, 1990; Uchida *et al.*, 1997) methods.

¹ Earth and Planetary Sci., Graduate School of Sci., Nagoya Univ. tak@nendai.nagoya-u.ac.jp

² Laboratory of Hydrological Processes, Inst. Hydrosphric-Atmospheric Sci., Nagoya Univ.

³ AMS facility Center for Chronological Research, Nagoya Univ.

⁴ Dept. Environ. Sci. and Tech., Titech., Japan, also with CREST Project JST

For isotopic analysis, soil air CO_2 (the CO_2 occupying soil pore space) and soil respired CO_2 (the flux CO_2 resulting from root respiration and microbial oxidation of soil organic matter) have been collected by different methods in the previous study mentioned above. Soil air CO_2 can be collected by a grab sampler, e.g., drawing air into an evacuated vessel, and this method was used in the present study. Soil respired CO_2 can be collected by capturing CO_2 as it exits on the soil over time, e.g., placing an alkali solution at the soil surface in a chamber to absorb CO_2 emitted. In the present study, the isotopic mass balance in CO_2 mixing between the ambient atmosphere and the soil respiration component (Keeling, 1958, 1961a, 1961b) was used in order to obtain the $\delta^{13}C$ value of soil respired CO_2 . Seasonal changes of $\delta^{13}C$ of soil respired CO_2 and vertical profiles of soil air CO_2 concentration and $\delta^{13}C$ are discussed to estimate contribution of soil respired CO_2 to the forest atmosphere and clarify carbon cycling and storage in soil.

Materials and methods

Study site

The study site was located about 8km east of central Nagoya, central Japan. Observation was carried out within a secondary forest growing on a gentle slope at Nagoya University (35° 08' 57" N, 136° 58' 28" E; 65m above sea level) from June in 1998 to August in 2000, but that for soil respired CO₂ was started from February in 1999. The forest is dominated by oak trees (*Quercus variabilis* and *Q. serrata*) with its canopy as high as *ca.* 18m. Broad-leaved evergreen plants (*Ilex pedunculosa, Vaccinium bracteatum, Eurya japonica, Ligustrum japonicum* and *Aucuba japonica*) dominate below 9.5m in height. There is little undergrowth at this forest.

Method for estimating $\delta^{13}C$ value of soil respired CO_2

A simple technique developed by Keeling (1958, 1961a, 1961b) can be used to determine the δ^{13} C of soil respired CO_2 based on changes in the concentration and δ^{13} C within the chamber (The chamber observation system is described in below). The δ^{13} C value of soil respired CO_2 , therefore, was estimated from the isotopic mass balance and their mixing relationship. The CO_2 mixing relationship between the ambient atmosphere and the soil respiration component can be expressed by following equation,

$$\delta_{Sa}C_{Sa} = \delta_{Amb}C_{Amb} + \delta_{Res}C_{Res} \tag{1}$$

where the δ refers δ^{13} C value and C is CO_2 concentration. The subscript Sa indicates a specific sample, Amb is ambient atmospheric CO_2 and Res is soil respired CO_2 . The equation 1 can be expressed by the relationship between C_{Sa} and δ_{Sa} as follow,

$$\delta_{Sa} = \frac{\left(\delta_{Amb} - \delta_{Res}\right)C_{Amb}}{C_{Sa}} + \delta_{Res} = \frac{M}{C_{Sa}} + \delta_{Res}$$
 (2)

where M is an arbitrary constant. The intercept represents the δ^{13} C value of soil respired CO₂ (δ_{Res}), and can be calculated using the least-square method.

Observation system

To determine $\delta^{13}C$ of soil respired CO_2 , a chamber style sampling system was deployed at the A chamber-style sampling system with a chaplet of 5 plastic bags (1-liter) was installed (Fig. 1). Observation system contains the chamber, NDIR, plastic bags and a mini pump. The chamber was made of polypropylene that was 40×20 cm² on base and 15cm in height without sun-light shields. Before the chamber was placed bottom upward on soil surface the air inside observation system was purged by in situ ambient air. Sample air inside the system was circulated at a rate of 2L·m-1 from the chamber, through the NDIR, the mini pump, a chaplet of bags, and then returned to the chamber (Fig. 1). The rim of the chamber was sealed by clay paste in order to isolate air in the chamber from atmosphere. To keep the volume of the observation system constant, a small vacuum box was used to distend the plastic bag. The increase of CO₂ concentration inside the sampling system was monitored continuously after the chamber was turned Three to five samples were collected to estimate the δ^{13} C of soil respired CO₂. The valves of entry ports of plastic bags were closed after several minutes to an hour the pump was turned on. After closing the valves of the respective sampling bags, the air inside the observation system flowed in bypass line (shaded part in Fig. 1).

Soil air samples were drawn from 10, 20, 40 and 80cm in depth through the air sampling tubes. These tubes had been buried for 3 months before starting the first sampling. CO₂ concentration was measured by a gas detector (GasTEC Co., Japan). Before measurement of CO₂ concentration, air in the sampling tube was aspirated using a syringe, and separated from sampling system using a 3-way valve (Fig. 2). For the isotopic analysis, soil air was sampled into a pre-evacuated glass flask (ca. 100ml) connected to the sampling tube (Fig. 2). Soil air sampling was carried out with interval over 2 or 3 hours from measurement of CO₂ concentration to solve vertical contamination by the soil air drawing. Before soil air sampling, air in the sampling tube was aspirated and separated by the similar procedure of CO₂ concentration measurement (Fig. 2). After 1 minute aspirating, the entry port valve of the glass vessel was opened for 1 minute to soil air sampling, in order to equilibrate isotopically between soil air CO₂ and sampled CO₂ in the vessel.

 CO_2 from respective bags and vessel were extracted using the vacuum system immediately after sampling and the $\delta^{13}C$ was measured on the IR-MS (MAT 252, Thermo Quest Inc., Germany) at the Center for Chronological Research, Nagoya University. The N_2O contamination effect (Craig and

Keeling, 1963) for the measured value of soil respired CO_2 was corrected on equal level with atmospheric sample, since the N_2O/CO_2 ratio for soil respired CO_2 seemed to be approximately equal to that for atmospheric CO_2 (Dong *et al.*, 1998). For the soil air CO_2 , that is not corrected, since CO_2 concentration in soil air seemed to be much larger than N_2O concentration (Dong *et al.*, 1998).

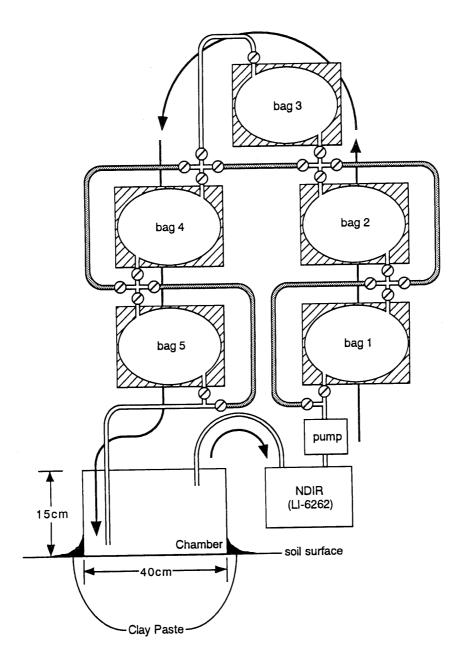


Fig. 1 The static chamber observation system. The chamber was placed bottom upward on soil surface with sealing by clay paste. The sampling bags distended by boxes under small vacuum condition (slanting part). The arrows indicate the gas flow direction. Air inside the system circulated from chamber, NDIR, pump and bags 1-5, and returned to the chamber. After closing the valves of the respective sampling bags, the air flowed in bypass line (shaded part).

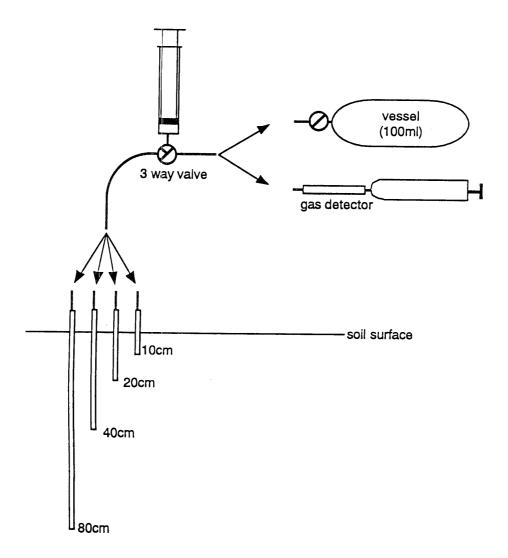


Fig. 2 Schematic diagram of soil air collection and CO_2 concentration measurement apparatus.

Litter on soil surface and soil at the depth of 10, 20, 40 and 60cm were sampled at the forest site to determine the δ^{13} C values of source materials of CO_2 . Litter samples were collected at 6 spots and soil at 3 spots on 4 July in 2000. Litter and soil samples were dried at 60°C for 48 hours. Soil samples were treated by HCl to remove carbonate after the filtration with 2mm mesh. Litter samples were milled. The δ^{13} C values were measured on an Elemental Analyzer-IRMS (NA2500: CE Instrument, Italy and MAT 252: Thermo Quest Inc., Germany) at the Institute for Hydrospheric and Atmospheric Sciences, Nagoya University, and standardized by CO_2 gas produced by Oztech Co. (USA). For the inter-machine reference check, the δ^{13} C values of the cellulose powder (reagent) are measured to be -25.31±0.05‰ on IRMS (MAT-252) at the Center for Chronological Research and -25.39 ±0.09‰ on EA-IRMS at the Institute for Hydrospheric and Atmospheric Sciences, showing no significant difference with each other.

Results and discussion

The $\delta^{13}C$ values of litter and soil organic matter and their vertical profile

The δ^{13} C values of litter samples (N=6) are identical among the different sampling spots within the forest site and the mean δ^{13} C value is -29.3±0.3‰. The average δ^{13} C of cellulose in oak trunks (*Q. serrata* and *Q. variabilis*) grown in the forest site was -26.0±0.8‰ (Aoki, 1997; Takahashi *et al.*, 1998). Generally, the δ^{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 depletion of 2‰ in leaves over stem cellulose. On the other hand, it is well known that the δ^{13} C values of tree cellulose show a seasonal fluctuation of 1-3‰ (Leavitt and Long, 1991; Kitagawa and Wada, 1993; Ogle and McCormac, 1994; Mole *et al.*, 1994; Takahashi *et al.*, 2001), and those of leaves within one species in single colony were reported to have a variation of 2-5‰ (Medina and Minchin, 1980; Ehleringer *et al.*, 1986; Medina *et al.*, 1991; Waring and Silvester, 1994; Hanba *et al.*, 1997). Therefore, the mean δ^{13} C value of land vegetation at the forest site seems to scatter considerably around -30‰ and the δ^{13} C values of soil organic matter and litter measured in the present study are reasonable.

The δ^{13} C values of soil organic matter range from -27.8 to -24.3‰. Vertical δ^{13} C profiles of soil organic matter and the δ^{13} C values of litter are shown in Fig. 3. The δ^{13} C profiles show an increasing trend varying ca. 2‰ from 10cm to 60cm in depth. This increasing trend is normally observed due to a negative carbon isotopic fractionation during decomposition of soil organic matter (Natelhoffer and Fry, 1988; Martin et al., 1992; Mary et al., 1992; Rao et al., 1994; Balesdent et al., 1993; Ågren et al., 1996; Bird and Pousai, 1997; Schüßler et al., 2000). This enrichment in 13 C of soil organic matter was caused by preferential use of 12 C for respiration by decomposers (Blair et al., 1985). Balesdent et al. (1993) proposed a simple formula to relate the δ^{13} C of soil organic matter to the δ^{13} C of tree leaves falling on the soil, which was derived from the observations that the further increment with increasing depth was similar in all soils they examined at the several sites of temperate forests in France,

$$\delta_{SOM} = \delta_L - 0.7 \log_{10} (Cc_{SOM}) \tag{3}$$

where δ refers δ^{13} C value and Cc is carbon contents (carbon in mass per unit mass). The subscript SOM indicates soil organic matter and L is litter. In order to explain the vertical δ^{13} C change of soil organic matter at the forest site using equation 3-3, it is necessary to obtain a vertical profile of carbon contents in soil at the same site. Carbon contents in soil at the forest site were measured to be $12.8 \text{mgC} \cdot \text{g}^{-1}$ at the depth between 0-10cm, $0.7 \text{mgC} \cdot \text{g}^{-1}$ between 10-20 cm, $0.5 \text{mgC} \cdot \text{g}^{-1}$ between 20-40 cm, $0.5 \text{mgC} \cdot \text{g}^{-1}$ between 40-60 cm and $0.3 \text{mgC} \cdot \text{g}^{-1}$ between 60-80 cm (Konohira, personal

communication). Thus, δ^{13} C enrichment is estimated to be 0.4% using equation 3. This estimated value is much smaller than that measured in the present study (1.7%).

The vegetation at the forest site was covered by pine trees (*Pinus densiflora*) for the past 20-30 years. The carbon isotopes of oak trees, which now dominates in the forest site, is ca. 2‰ depleted in 13 C relative to pine trees (Balesdent *et al.*, 1993; Aoki, 1997). This shift in the δ^{13} C value of litter provided to soil might influence the δ^{13} C enrichment of soil organic matter at the forest site.

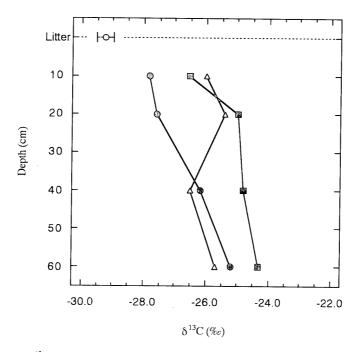


Fig. 3 The vertical $\delta^{13}C$ profiles of soil organic matter and the $\delta^{13}C$ value of litter with 1σ error bar (n=6).

Seasonal changes of concentration and $\delta^{13}C$ of soil air CO,

Seasonal changes of CO_2 concentration and $\delta^{13}C$ in soil air are shown in Fig. 4. CO_2 concentration and $\delta^{13}C$ at the depth of 40cm could not be obtained after 14 September 1999, since the sampling tube at that depth was clogged or cut. The CO_2 concentration and $\delta^{13}C$ range from 0.1 to 3.4% and from -23.7 to -18.1%, respectively. The ranges of the vertical changes are 0.8-3.0% in concentration and 0.3-4.6% in $\delta^{13}C$. There are many investigations reporting the $\delta^{13}C$ differences of CO_2 sampled from soil air relative to soil organic matter (*e.g.*, Cerling *et al.*, 1991; Davidson 1995), and both the theoretical and observed $\delta^{13}C$ difference were represented to be *ca.* 4.4%. In the present study, this difference is measured to be *ca.* 4-6% (Figs. 3 and 4), which is larger than the theoretical value. The $\delta^{13}C$ increment at the depth of 10cm causes this discrepancy between observed value in the present study and theoretical one, and suggests the CO_2 infiltrating

from the atmosphere to the soil air. There are seasonal variations in depth profiles of CO_2 concentration and $\delta^{13}C$ in soil air. The gradients of vertical profiles are steep in summer. This is, probably, caused by a high production rate of CO_2 in soil. The vertical trend of CO_2 concentration is slightly different from that of $\delta^{13}C$, and shows gradual change with depth, whereas the $\delta^{13}C$ trend suddenly changes at the depth between 10 and 20cm and remains relatively constant below 20cm.

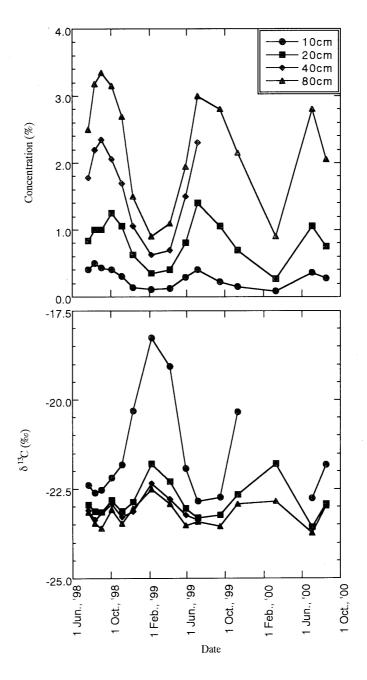


Fig. 4 The seasonal variations of CO_2 concentration and $\delta^{13}C$ in soil air at 10cm (circle). 20cm (square), 40cm (diamond) and 80cm (triangle) in depth from soil surface.

Seasonal 8¹³C change of soil respired CO₂

The δ^{13} C values of soil respired CO₂, which was estimated using equation 2, show seasonal fluctuations ranging from -31.0 to -24.5% with low from summer to autumn and high from winter to spring, and vary proportionally with the δ^{13} C values of soil air CO₂ collected at the depth of 10cm and have a negative correlation with CO₂ flux from soil surface to the atmosphere (Fig. 5). Flanagan *et al.* (1996) also observed the variation of δ^{13} C of soil respired CO₂, ranging from -28.0 to -25.9%. They reported the similar seasonal trend in Aspen forest with that of the present study.

 ${
m CO_2}$ concentration measured on the NDIR in the chamber observation system may show a slightly larger value than that of sampled air in the respective plastic bags, since the circulated air inside the observation system reached first the NDIR, and then move to the sampling bags. Hence, there is an offset between the ${
m CO_2}$ concentration measured at the observation site and those in the sampling bags due to the buffer effect based on the bag volume (1-liter) and gas flow rate ($2L \cdot m^{-1}$). The amplitude of this offset seems to be maximum at summer, since ${
m CO_2}$ flux from soil surface, *i.e.*, rate of ${
m CO_2}$ increase in the chamber, was highest during this season. However, this buffer effect was found to be negligible. For example, the $\delta^{13}{
m C}$ values of soil respired ${
m CO_2}$ on 6 July in 1999 was computed to be -28.3±0.7‰ by using ${
m CO_2}$ concentration measured on the NDIR at the sampling, which was consistent with the value of -27.7±0.6‰ computed by using an offset value

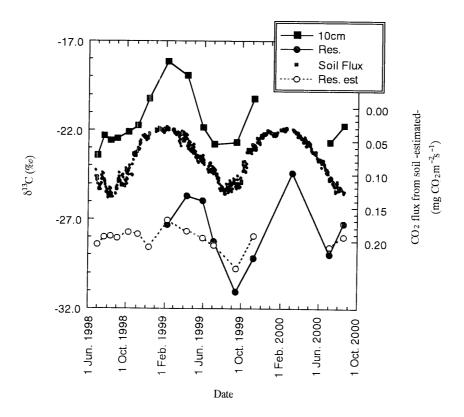


Fig. 5 Seasonal variations of the $\delta^{13}C$ values of soil respired (closed circle) and soil air CO_2 at the depth of 10cm (closed square), and the estimated values of $\delta^{13}C$ of soil respired CO_2 (open circle) and CO_2 flux from soil surface (dotted).

for CO₂ concentration. The offset value was computed using CO₂ concentration measured on NDIR 1 minute before closing the valves of the sampling bags: this time (1min) was twice the mean residence time of air in 1-liter plastic bag.

CO₂ flux from soil surface, shown in Fig. 5, was estimated using soil temperature, which controlled CO₂ production in soil. The regression equation was represented by Takahashi (1999) using observation data of soil temperature and CO₂ flux from soil surface measured at the forest site, give as

$$F_{Res} = 0.0877 \times 2^{(T-20)/10}$$
 $(r^2 = 0.98)$ (4)

where F_{Res} and T are CO_2 flux from soil surface (mg CO_2 ·m⁻²·s⁻¹) and soil temperature (°C) at the depth of 3cm, respectively. The correlation shown in Fig. 4 suggests that seasonal $\delta^{13}C$ variation of soil respired and soil air CO_2 resulted from fluctuation of CO_2 flux from soil surface.

It is possible to consider several hypotheses to explain the observed δ^{13} C fluctuation of soil respired CO_2 . These include, (1): infiltrating atmospheric CO_2 , (2): seasonal change of CO_2 source, (3): seasonal change of isotopic fractionation during CO_2 diffusion in soil. According to the first hypothesis, CO_2 infiltrating due to turbulent air flow from aboveground induces change in δ^{13} C value of soil respired CO_2 . Wind blowing to land surface introduces the turbulence flow inside soil (Kobayashi, 1993), but the depth of 10cm is too deep to be affected. However, vertical profiles of soil air CO_2 concentration and δ^{13} C suggested atmospheric CO_2 mixing. Thus, the fluctuations can not be explained with this hypothesis only.

The second hypothesis has two categories: isotope change of source materials due to isotopic fractionation during decomposition, and mixing of isotopically different components. During the initial stages (soon after defoliation, mostly beginning of winter) of decomposition, the soil respired CO_2 will have low $\delta^{13}C$ value. This will preferentially use ^{12}C and lates on enrich the ^{13}C in soil respired CO_2 . This prediction of $\delta^{13}C$ change is not consistent with the observed results. Second category requires the isotopically different CO2 sources in soil respired CO2, mainly plant root respiration and microbial oxidation (decomposition) of soil organic matter and litter. The δ^{13} C value of CO₂ derived from plant root respiration would be identical with that of decomposition of soil organic matter and slightly heavier than that of litter. Assuming that contribution of litter decomposition was large in summer, the seasonal δ¹³C fluctuation of soil respired CO₂ showed lower value in summer than that in winter. This assumption will be consistent with the fact that the contribution of root respiration at the shallow depth may not be prominent because of no undergrowth at the forest site. This model can partially explain the seasonal δ^{13} C fluctuation of soil respired CO2. However, it is difficult to separate root and soil microbial contributions to soil respiration using δ^{13} C analysis, since these two emissions have similar δ^{13} C values (Hanson et al., 2000)

In order to examine the third hypothesis, the δ^{13} C differences between soil air CO_2 and soil respired CO_2 have to be explained. Davidson (1995) suggested that the δ^{13} C change during the diffusion from soil air to soil respired CO_2 was influenced by concentration as well as δ^{13} C of soil air CO_2 , and the relation between the δ^{13} C of soil air CO_2 (δ_{Soil}) and soil respired CO_2 (δ_{Res}) under the steady state condition can be expressed using the following equation,

$$\delta_{Soil} \cong 1.0044 \delta_{Res} + \frac{C_{Air}}{C_{Soil}} (\delta_{Air} - 1.0044 \delta_{Res} - 4.4) + 4.4$$
 (5)

where the δ refers δ^{13} C value and C is CO_2 concentration. The subscript *Soil* indicates soil air CO_2 , *Air* is atmospheric CO_2 and *Res* is soil respired CO_2 . Thus, the δ^{13} C values of soil respired CO_2 can be computed from the available data of soil air CO_2 using equation 5. For the calculation of δ^{13} C of soil respired CO_2 , concentration and δ^{13} C value in the atmospheric CO_2 were used to be 400ppm and -10‰, respectively. The results of δ^{13} C estimation using the soil air data of respective depths (10, 20, 40 and 80cm) are identical and only those from 10cm are shown in Fig. 4. The estimated results are not consistent with observed results exactly, having a smaller seasonal variation. Davidson (1995) derived equation 5 by assuming that δ^{13} C of soil respired CO_2 was identical with that of soil organic matter and soil was considered to be single component. It will be necessary to discuss without these assumptions in order to understand the processes fully. However, this estimation suggests that the seasonal δ^{13} C fluctuation of soil respired CO_2 is influenced by CO_2 at shallower depth in soil.

Conclusion

The $\delta^{13}C$ values of soil respired CO_2 , which were obtained by the static chamber method, showed seasonal fluctuations ranging from -31.0 to -24.5‰ with low values from summer to autumn and high ones from winter to spring. The $\delta^{13}C$ value of soil respired CO_2 varied proportional to that of soil air CO_2 , but was negatively correlated with CO_2 flux from soil surface to atmosphere. The CO_2 concentration and $\delta^{13}C$ in soil air ranged from 0.1 to 3.4% and from -23.7 to -18.1‰, respectively, and showed a seasonal variation with high concentration and low $\delta^{13}C$ value in summer, and low concentration and high $\delta^{13}C$ value in winter. The seasonal $\delta^{13}C$ fluctuation of soil respired CO_2 was influenced by CO_2 production at a shallow depth in soil (<10cm), since the $\delta^{13}C$ values of soil respired CO_2 were estimated to have no seasonal variation by applying diffusion theory to the available data of CO_2 concentration and $\delta^{13}C$ in soil air at the depth between 10 and 80cm.

The range of vertical variation of CO_2 concentration and $\delta^{13}C$ in soil air on each observation day were from 0.8 to 3.0% and from 0.3 to 4.6‰, respectively. CO_2 concentration in soil air increased gradually with depth, whereas the $\delta^{13}C$ value decreased suddenly at the depth from 10 to 20cm and remained relatively constant below 20cm. The gradients of vertical profiles of CO_2 concentration and $\delta^{13}C$ in soil air were steep in summer, owing to a high production rate of CO_2 in soil. On the other hand, the vertical $\delta^{13}C$ profiles in soil organic matter increased ca. 2‰ from 10 to 60cm in depth. This $\delta^{13}C$ enrichment is much larger than the expected value from the isotopic fractionation during decomposition. The ancient vegetation at the forest should be considered to explain the high $\delta^{13}C$ value of soil organic matter at the forest.

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