# **Diurnal and Seasonal Changes in CO<sub>2</sub> Concentration** and Flux in an Andisol and Simulation Based on **Changes in CO<sub>2</sub> Production Rate and Gas Diffusivity**

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#### Abstract

Changes in the concentrations and fluxes of CO2 were monitored to a depth of 100 cm in an Andisol, under both fallow and soybean crop for a period of one year. Gas flux was calculated by the diffusion equation. Diurnal concentrations at depths less than 40 cm followed a sinusoidal pattern similar to that of the soil temperature, with the highest value being recorded in the daytime. Heavy rainfall which closes air voids open to the atmosphere resulted in a higher CO<sub>2</sub> concentration in the shallow soil layers. The subsequent decrease in the concentration in the shallow layers by the recovery of diffusion paths to the atmosphere was accompanied by an increase in concentrations in the deeper soil layers. CO2 concentration profile under soybean showed a peak at depths that increased gradually from 20 to 80 cm with the growth of the roots. Upward CO<sub>2</sub> fluxes decreased with depth in both fields, and the fluxes in the soil profile were high in summer and low in winter. CO<sub>2</sub> fluxes from the soil surface calculated by the diffusion equation and measured by the closed chamber method were fairly well correlated. Annual CO<sub>2</sub> fluxes were 3,522 g m<sup>-2</sup> under fallow and 4,975 g m<sup>-2</sup> under soybean. The CO<sub>2</sub> movement in soil was simulated by use of the diffusion first law combined with the mass conservation equation. This mechanistic model enabled to analyze phenomena occurring under field conditions, suggesting that soil aeration is controlled by gas diffusion.

Discipline: Soils, fertilizers and plant nutrition Additional key words: carbon dioxide, gas diffusion

# Introduction

Carbon dioxide (CO2), amounting to about 0.03% in the air, is referred to as "the greenhouse-effect gas" in the same way as methane, nitrous oxide, ozone, etc. because it absorbs infrared rays. Increase of the concentration of greenhouse-effect gases induces the warmingup of the earth which affects biological phenomena. According to the IPCC (Intergovernmental Panel on Climate Change) report, the contribution of CO2 to the warming-up of the earth is estimated at about half or more of the whole. CO2 concentration in the atmosphere

is controlled by exchange processes between the atmosphere, and the ocean and land biosphere. Therefore soils, which are the main habitat of land organisms, also play an important role in the changes in the CO2 dynamics.

Ouantitative analysis of CO2 movement in soil profiles is essential for analyzing the carbon circulation and CO2 emission from lands. De Jong and Schappert4) studied the CO2 flux and respiration rate at various depths in a soil by applying the diffusion equation combined with the mass conservation equation. They measured the CO2 concentration in a virgin prairie in Canada from May to

Experimental results of this report were partly reported9). Present address:

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November and recorded the highest surface  $CO_2$  flux in June (7.5×10<sup>-4</sup> g m<sup>-2</sup> s<sup>-1</sup>) and the lowest one in November (almost zero). They observed that the highest  $CO_2$  concentration shifted downward toward summer, and ascribed this phenomenon to the gradual increase in the soil temperature with depth as the season progressed, combined with a decrease in the moisture content due to evapotranspiration. Campbell and Frascarelli<sup>2</sup>) measured  $CO_2$  fluxes using sampling wells through which  $CO_2$  was trapped by an absorbent solution. They showed that the  $CO_2$  flux decreased with depth and increase throughout the profile about 2 weeks after the increase in the soil temperature.

However,  $CO_2$  concentration profiles on an hourly basis and after rainfall events are poorly documented, and more data on the  $CO_2$  flux from fallow and cultivated fields are needed for analyzing  $CO_2$  emission from agricultural lands.

The objectives of the present study are to investigate the diurnal changes, rain-induced changes, and seasonal changes in CO<sub>2</sub> concentrations and fluxes, and to confirm that soil aeration is controlled by gas diffusion through the simulation of the characteristics in CO<sub>2</sub> concentration changes using a model based on the gas diffusion law.

## Experimental procedures

#### 1) Field experiment

Field experiments to analyze the CO<sub>2</sub> behavior in an Andisol were conducted throughout a year from June 24, 1991 to June 25, 1992, in fields of the National Institute of Agro-Environmental Sciences (latitude 36° 01' N and longitude 140° 07' E). The soil was a Hydric Hapludand<sup>1</sup>, which extended over a 200 cm depth.

The soil profile was divided into 6 layers, Ap1 (0 to 20 cm), Ap2 (20 to 37 cm), 2B1 (37 to 79 cm), 3B21 (79 to 108 cm), 4B22 (108 to 155 cm) and 5B23 (155 to 200 cm). The top 4 layers were used in this study. A fallow field and a field cultivated with soybean (*Glycine max* Merr. (cv. Tachinagaha)) were used for the experiments. They were adjacent and the area of each field was 150 m<sup>2</sup>. Soybean was sown on May 8, 1991, at a seed spacing of 15 cm on 65 cm rows and harvested on December 2. Plant residues above the ground were removed from the fields. Winter wheat (*Triticum aestivum* L. (cv. Norin No.61)) had been cultivated previously in both fields from the autumn of 1990 to the spring of 1991.

The soil profile and depths where measurements and samplings were performed are shown in Fig. 1. Triplicate soil air samples were withdrawn into 3 cm<sup>3</sup> vial bottles with a rubber cap *in vacuo* from gas-sampling tubes installed at depths of 2.5, 5, 17.5, 22.5, 34.5, 39.5, 55,



Fig. 1. Soil profile, measurements and sampling depths for air, water and temperature

76.5, 81.5 and 100 cm below the soil surface. The gas sampling tubes were installed in the fields at least at 30 cm intervals. In the soybean field, the sampling tubes were buried between rows. The tube consisted of a polyethylene filter (8 mm in diameter, 10 cm in length), a hollow needle, a capillary tube (0.5 mm in inside diameter) connecting the filter and the needle, and an acrylic tube (10 mm in outside diameter)9). The gas sampling tubes were inserted into holes bored in advance with a soil auger 21 mm in diameter, and the gap between the gas sampling tube and the wall of the hole was deliberately filled up by soils. The open end of the hollow needle was stuck into a rubber tap except at the time of the measurements. The air sample at 0-2 cm above the soil surface was drawn into the vial bottle through a hollow needle that pierced the rubber cap. Concentrations of CO2 in the vial bottles were analyzed within 1 h after sampling by injecting 0.3 cm<sup>3</sup> of sample air into a gas chromatograph (Hitachi gas analyzer, model 263-70, FID with Ni catalyst) using Porapack Q columns and N2 as a carrier.

#### 2) Gas diffusivity

The relative gas diffusion coefficient  $D/D_0$  was measured by the diffusion chamber method developed by Osozawa<sup>8</sup>. Undisturbed 100 cm<sup>3</sup> soil cores sampled from individual layers were used for the measurement.  $D/D_0$  was measured at several moisture contents adjusted by a pressure plate method. The diffusion coefficient of  $CO_2$  in air,  $D_0$  (cm<sup>2</sup> s<sup>-1</sup>), was calculated from the equation  $D_0 = 0.139 \times (T/273.2)^{1.75 \ 10)}$ , where T was the absolute temperature (K) of the soil that was measured in the fields with thermocouples.

When the soil gas was sampled, the soil moisture content in the profile was measured to determine the gas diffusion coefficients in each soil layer D, based on the  $D/D_0$ -air-filled porosity curves. Duplicate soil samples were taken to a depth of 100 cm using a thin steel tube with a tip 27.5 mm in diameter and 110 cm long, and the soil water content profile was measured by the oven-dry method.

## 3) CO<sub>2</sub> flux from the soil surface

 $CO_2$  fluxes from the soil surface were calculated by applying the diffusion equation (described in the next section) to the surface 0–2.5 cm layer.  $CO_2$  concentration at 0 to 2 cm above the soil surface was considered to be the  $CO_2$  concentration at the soil surface. The closed chamber method<sup>5,13</sup> was also applied to evaluate the  $CO_2$ flux from the soil surface.

The increase in the  $CO_2$  concentration in the chambers placed on the soil surface was measured every 2 min for 10 min. Duplicate measurements were carried out in each field. The measurement time was set at only 10 min to avoid large changes in temperature in the chamber and a gradient of  $CO_2$  concentration between soil and air in the chamber. Sunlight reaching directly the chamber was also avoided during the measurements. As a result, the temperature changes in the chamber during the sampling were less than 3°C.  $CO_2$  fluxes were corrected for the temperature in the chamber.

#### 4) Other experiments

Soil temperatures at 1, 5, 10, 20, 40 and 70 cm below the soil surface and atmospheric temperatures at 120 cm above the soil surface and in the closed chamber were measured with thermocouples.

After sampling on August 30, soybean roots were washed out from the duplicate soil blocks 15×10 cm in area to a depth of 80 cm. Root length was measured with a root scanner (Commonwealth Aircraft Co. Ltd.).

Soil pH (H<sub>2</sub>O) was measured using duplicate samples taken on July 4 from 12 depths for each field. Soil pH was measured after thorough stirring, with a soil: water ratio of 1 : 2.5.

Data about precipitation and evaporation were obtained from a weather station located at less than 500 m from the experimental fields.

Student's t test was conducted for testing the significance between data of CO<sub>2</sub> concentrations or CO<sub>2</sub> fluxes measured at different depths, fields, and times.

## Calculation of CO2 flux

Gas diffusion through soil water can be ignored

because the value of the gas diffusion coefficient in water is about 1/10,000 of that in air, and the gradient of CO<sub>2</sub> concentrations in soil water is of the same order as that in soil air, assuming that the vapor-liquid equilibrium is attained. Thus, gas diffusion in soils can be written as:

 $q = -D dC_a/dz$  .....(1) where:

 $q = flux of gas, g cm^{-2} s^{-1}$ ,

D = diffusion coefficient in soil, cm<sup>2</sup> s<sup>-1</sup>,

 $C_a =$  concentration of gas in soil air, g cm<sup>-3</sup>,

z = depth, cm.

The mass conservation of a gas in soil is written as:

dG/dt = -dq/dz + p .....(2) where:

 $G = amount of gas in soil, g cm^{-3}$ ,

t = time, s,

 $p = evolution rate of gas in soil, g cm^{-3} s^{-1}$ .

The amount of a particular gas in soil is expressed by the following equation:

 $G = C_a V_a + C_w V_w$  .....(3) where:

 $C_a =$ concentration of gas in soil air, g cm<sup>-3</sup>,

 $V_a = air-filled porosity in soil, cm^3 cm^{-3}$ ,

 $C_w =$  concentration of gas in soil water, g cm<sup>-3</sup>,

 $V_w$  = water-filled porosity in soil, cm<sup>3</sup> cm<sup>-3</sup>.

CO<sub>2</sub> concentration in soil water is linearly related to that in soil air when the soil water pH is constant.

where a is a constant.

Thus, Eq. (3) becomes:

 $G = C_a V_a + a C_a V_w = C_a (V_a + a V_w) \quad \dots \dots \dots (5)$ Substituting Eq. (5) for Eq. (2) gives,

 $dC_a/dt = 1/(V_a + a V_w) (-dq/dz + p)$  .....(6)

In these calculations, the soil profile was divided into 10 layers whose boundaries were the soil surface ( $z_0$ ) and the sampling depths of soil air ( $z_1, z_2, ..., z_{10}$ ) shown in Fig. 1. Gas flux in the nth layer, qn, is written as  $q_n = -D_n (C_n - C_{n-1})/(z_n - z_{n-1})$ , where  $D_n$  and  $C_n$  are the gas diffusion coefficient and CO<sub>2</sub> concentration in the nth layer, respectively.

#### Simulation model

A simulation for calculating flux and CO<sub>2</sub> concentration to analyze the above characteristics observed in the field experiments was carried out.

CO<sub>2</sub> concentration in water is identical with that in air, when the water pH is 5.81, on the assumption that vapor-liquid equilibrium is attained.

Then, Eq. (6) becomes:

 $dC_a/dt = 1/V_p(-dq/dz + p)$  .....(6') where:

Layer	Depth(cm)	Total-C(%)*	Color	Structure and pores
Apl	0-20	4.25	very dark	fine granular
Ap2	20-37	3.17	very dark	weakly fine granular
2B1	37-79	1.58	dark	weakly blocky cracks(<1 mm) and tubular pores
3B21	79–	1.16	dark	blocky cracks(<1 mm) and tubular pores

Table 1. Description of soil profile of the fields

\*Data quoted from National Institute of Agro-Environmental Sciences 1984<sup>6</sup>). Total-C was measured by CN corder (Yanagimoto Co., Ltd.).

 $V_p = porosity in soil, cm^3 cm^{-3}$ .

When the gas diffusion can be considered to be a steady-state process, i.e. C<sub>a</sub> is constant with time, Eq. (6') becomes :

dq/dz = p .....(7)

Eqs. (1), (6') and (7) were used to simulate the changes of  $CO_2$  concentrations in the soil profile. For simplification of these calculations, it was assumed that the soil pH was 5.81, and that the pore space was 0.75 throughout the profile. The assumptions were close to the field conditions as described later. The unit distance was 5 cm in vertical length, and the unit time was 10 min.

## **Results and discussion**

#### 1) Physical and chemical properties of soil

Total carbon content and profile descriptions of the fields are shown in Table 1.

The order of relative gas diffusion coefficient in the range of low air-filled porosities was inversely related to the total carbon content. This result was similar to that obtained in a former study. The gas diffusion coefficients of humic soils were smaller than those of soils with a blocky structure at the same level of air-filled porosity<sup>8</sup>.

Soil pH was not appreciably different with depths and fields. Soil pH throughout the profile was  $5.90 \pm 0.14$  under fallow and  $6.06 \pm 0.14$  under soybean.

## 2) CO2 movement in soil

(1) Diurnal changes in CO2 concentration and flux

 $CO_2$  concentration and soil temperature were measured 6 times on fine summer days from August 8 to 9, 1991. The mean atmospheric temperature was 24.2°C and 23.6°C for August 8 and 9, respectively. There had been a rainfall of 23 mm on August 7. At the beginning of the measurements, i.e. 11:00 a.m. on August 8, the airfilled porosities at the 6 cm depth were 0.30 (the soil matric potential was -13.5 kPa) under fallow and 0.29 (the soil matric potential was -11.6 kPa) under soybean.

Fig. 2. shows that the CO<sub>2</sub> concentrations at depths less than 40 cm tended to be high in the daytime and low

during the night.  $CO_2$  concentrations at 5 and 17.5 cm depths at 2:00 p.m. on August 8 were significantly (5% level) higher compared with those at 0:00 a.m. and 5:00 a.m. on August 9, based on Student's t test. Diurnal soil temperatures at 1 and 5 cm depths also followed a similar trend.  $CO_2$  concentrations at depths more than 40 cm were relatively stable throughout the day from August 8 to 9, presumably due to the stable soil temperatures. Thus, the fact that both the  $CO_2$  concentration and the temperature at shallower depths under fallow changed with time may be ascribed to the respiration of microorganisms, which is closely related to the soil temperature.

A similar trend was observed in the soil under soybean cultivation. However, the  $CO_2$  concentrations were less related to the soil temperatures than in the fallow field, presumably because the respiration of the roots also affected the  $CO_2$  concentrations.

Diurnal changes in CO<sub>2</sub> fluxes from the soil surface followed a sinusoidal pattern<sup>9)</sup>.

Comparison of the  $CO_2$  fluxes calculated by the diffusion equation method and those measured by the closed chamber method showed that both fluxes followed similar patterns. The difference between the fluxes measured by the 2 methods was not statistically significant (5% level) based on Student's t test. The calculation based on the mean fluxes determined by the diffusion method showed that the total fluxes for 24 h were 9.68 g m<sup>-2</sup> in soil under fallow, and 22.2 g m<sup>-2</sup> in soil under soybean, a value about twice that observed under fallow in the daytime from August 8 to 9, 1991.

(2) Turn-over time of CO2

To determine the turn-over time of CO<sub>2</sub> in soil during the 24 h period from August 8 to 9, 1991, the total amount of CO<sub>2</sub> in soil under fallow to 100 cm depth was calculated based on the data of CO<sub>2</sub> concentrations and water contents measured at 11:00 a.m. on August 8. The values of 1.65 g m<sup>-2</sup> in soil air, and 6.03 g m<sup>-2</sup> in soil water were obtained by assuming that the vapor-liquid equilibrium of CO<sub>2</sub> was attained and the soil water pH was 5.90, which was the average value of soil pH throughout the profile under fallow. The turn-over time,



Fig. 2. Diurnal changes in CO<sub>2</sub> concentration and soil temperature under fallow a: CO<sub>2</sub> concentration. b: soil temperature.

which is expressed as the total amount of  $CO_2$  within 100 cm depth divided by the  $CO_2$  flux from the soil surface was 0.57 day based on the  $CO_2$  flux calculated by the diffusion equation. Under ordinary field conditions,  $CO_2$  is considered to evolve rapidly into the atmosphere. (3) Changes in  $CO_2$  concentration after heavy rainfall

Heavy rainfall which intercepts the open-air void pathway to the atmosphere must affect significantly the  $CO_2$  movement in soil. Fig. 3 shows the changes in the  $CO_2$  concentration profile in soil under fallow and under soybean after heavy rainfall of 79 mm on August 20 and 30 mm on August 21. The  $CO_2$  peak under fallow appeared at 5 cm depth on August 22 but disappeared by August 23. However, the  $CO_2$  concentrations in the deeper layers on August 23 were higher than on the previous day. Thereafter, the CO<sub>2</sub> concentration decreased markedly at shallow depths.

A more typical trend of  $CO_2$  concentration profiles was observed under soybean crop. The  $CO_2$  concentration at depths more than 55 cm was the highest on August 26, 5 days after the rainfall, although the  $CO_2$  concentrations in the shallower layers had started to decrease.

Soil matric potential in the surface layer (6 cm in depth) increased to -1 to -2 kPa by rainfall on August 20, and such conditions persisted for almost 1 day. During this period, air-filled porosity in the surface layer estimated from the soil water characteristic curve was about 10%, at which the D/D<sub>0</sub> value was 0 based on laboratory experiments<sup>9</sup>.

Based on the above facts, the changes in the CO<sub>2</sub>



Fig. 3. Changes in CO<sub>2</sub> concentration after heavy rainfall

concentration with time and depth after heavy rainfall may be ascribed to the following process. First, the  $CO_2$ concentration increased in the shallow layers because of the lack of a continuous air-void pathway to the atmosphere. Second, with the progression of the drying process (drainage and evapotranspiration),  $CO_2$  in the shallow layers started to diffuse both upwards and downwards, resulting in a decrease of the  $CO_2$  concentration in the shallow layers and an increase in the deeper layers. Thereafter, the  $CO_2$  concentration throughout the soil profile decreased almost in the same way as under the initial conditions.

(4) Rapid vapor-liquid equilibrium of CO<sub>2</sub> in the subsoil after heavy rainfall

The increase of the CO<sub>2</sub> concentration in the subsoil by downward diffusion which appeared after heavy rainfall was investigated on the basis of the vapor-liquid equilibrium of CO<sub>2</sub> in soil. The soil layer studied extended from the center of the 7th layer to that of the 10th layer, i.e. the depth between 47 and 91 cm under soybean, and gas fluxes in this layer were calculated from 12:00 a.m. on August 22 to 12:00 a.m. on August 23. The values of the 7th flux q<sub>7</sub> and the 10th flux q<sub>10</sub>, which were the average values on August 22 and 23 corresponded to downward fluxes of 1.066 × 10<sup>-5</sup> g m<sup>-2</sup> s<sup>-1</sup> and 2.42 × 10<sup>-6</sup> g m<sup>-2</sup> s<sup>-1</sup>, respectively. The value of the flux

obtained by subtracting the value of q10 from the value of  $q_7 \text{ was } 8.24 \times 10^{-6} \text{g m}^{-2} \text{ s}^{-1} (1.88 \times 10^{-7} \text{ mol} \text{ m}^{-2} \text{ s}^{-1})$ which must have contributed to the increase of the CO2 concentration both in the gaseous and liquid phases of the soil. The values of air and water volumes through the depth of 47 to 91 cm per 1 cm<sup>2</sup> cross-section were 4.6 cm<sup>3</sup> and 30.1 cm<sup>3</sup>, respectively on an average between August 22 and 23. Thus, the amount of downward CO2 flux for 24 h must have increased the CO2 concentration in the air phase by 0.091% (3.81 × 10<sup>-5</sup> M) and in the dissolved state (H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>) by  $4.80 \times 10^{-5}$ M. In addition to the vapor-liquid equilibrium, the above calculations were conducted on the assumption that the soil temperature was 20°C and that the soil water pH was 6.06, which corresponded to the average value of the soil pH throughout the profile under soybean.

Measured values showed that the  $CO_2$  concentration in the air phase increased by 0.089% on an average in the 47 to 91 cm layer during the 24 h period from August 22 to 23. Thus, the calculation fitted well to the increase of the  $CO_2$  concentration observed in the field.

If the second term on the right side of Eq. (3) is not considered, the increase in the CO<sub>2</sub> concentration in the soil air phase becomes 0.84%, which is much larger than the value observed in the experiment. Thus, the results suggested that CO<sub>2</sub> which flowed into a specific layer



Fig. 4. Seasonal changes in CO<sub>2</sub> concentration

through the gaseous phase was distributed rapidly into both the gaseous and liquid phases. Based on Eq. (6), the increase in the  $CO_2$  concentration in the subsoil layers after heavy rainfall could be mainly attributed to the downward flux rather than to the increase in the evolution rate in the subsoil.

## (5) Seasonal changes in CO2 concentration

Seasonal changes in the  $CO_2$  concentration were measured once a month, except in the summer, in 1991. Only the data collected between 11:00 a.m. and 2:00 p.m. on the days with negligible rain effect were used.

The seasonal changes in the  $CO_2$  concentration are shown in Fig. 4. At the beginning of the experiment on June 24, 1991, the  $CO_2$  concentration profiles under fallow and soybean were statistically nonsignificant (5% level) based on Student's t test. The  $CO_2$  concentrations under fallow increased with depth throughout the year, and showed maximum values toward the end of July. Thereafter, the  $CO_2$  concentration began to decrease. On the other hand, the  $CO_2$  concentrations under soybean showed maximum values at depths that shifted downward gradually with soybean growth from 20 to 40 cm on July 11 to 40 to 80 cm on August 30, suggesting the effect of root elongation. CO<sub>2</sub> concentrations from the end of autumn to winter again increased with depth. The CO<sub>2</sub> concentrations under soybean were significantly (5% or 1% level) higher than those under fallow, except on June 24, 1991, based on Student's t test.

Although the root length density decreased with depth, some roots reached 80 cm depth on August 30, 1991. The main factor influencing the difference in the  $CO_2$  concentrations between fields under fallow and those under soybean may be the respiration of roots and the microbial activity in the rhizosphere.

(6) Changes in CO<sub>2</sub> concentration in the subsoil layer and determining factors

CO<sub>2</sub> concentrations at the depth of 79 cm (the average of CO<sub>2</sub> concentrations at 76.5 cm and 81.5 cm depths) including those after rainfall, and daily-mean soil temperatures at depths of 10 cm and 70 cm are shown in Fig. 5. Total precipitation during one year was 1,977 mm and 51% of it occurred from late August to October.

CO<sub>2</sub> concentrations at 79 cm depth under fallow seemed to coincide well with the temperatures at 10 cm depth compared with those at 70 cm depth. This phenomenon may be explained as follows. The CO<sub>2</sub> increase



in the surface layers by enhanced microorganism respiration associated with the increase in the temperature suppressed the  $CO_2$  upward flux from the deeper layers due to the decrease in the concentration gradient between the surface and deeper layers. As a result, the  $CO_2$  concentration at 79 cm depth increased when the soil temperature at 10 cm depth was high. The decrease in the surface temperature resulted in an inverse effect on the  $CO_2$  concentration at 79 cm depth. This assumption is based on the fact that most of the microorganisms are distributed in the surface layer where the seasonal changes in temperature are highly conspicuous<sup>12</sup>.



Fig. 6. Seasonal changes in CO2 flux profiles

On the other hand,  $CO_2$  concentrations under soybean increased until the middle of September when the temperature was lower than the maximum. Root respiration in addition to microorganism respiration is likely to influence the  $CO_2$  concentration at 79 cm depth.  $CO_2$ concentrations under soybean were higher than those under fallow, and the difference became more pronounced until October and still persisted until June of the following year.

Heavy rainfall clearly reflected the increase in the  $CO_2$  concentration during 1–2 days after rainfall, even though only 3 measurements in August and September supported this assumption.

#### (7) Seasonal changes in CO2 flux

The seasonal changes in upward CO<sub>2</sub> fluxes in each layer are shown in Fig. 6. Fluxes decreased with depth in both fields. Fluxes in the upper to middle parts of the profile were higher under soybean than under fallow. Fluxes increased until the end of July and then decreased in both fields. However, fluxes under soybean in August were still high compared with those under fallow.

The  $CO_2$  fluxes at depths deeper than that at which the  $CO_2$  peak was observed from July 11 to August 30 under soybean (cf. Fig. 4) showed negative values. The negative values were smaller by 2 to 3 orders compared with those of the fluxes in shallow layers because the diffusion coefficient decreased with depth.

The seasonal changes in the  $CO_2$  flux from the soil surface calculated by the diffusion equation are shown in Fig. 7. Data for a few days after heavy rainfall exceeding 100 mm on August 22 and 23 were not included, because the  $CO_2$  concentration changed so much after heavy rainfall in comparison with the seasonal changes that the  $CO_2$ concentrations on such days were not suitable for following the seasonal changes. The values of the fluxes were high in summer and low in winter, and  $CO_2$  fluxes under soybean were higher than those under fallow, especially during the growing season. Even after harvest, the difference in the values of the  $CO_2$  flux under fallow and under soybean was statistically significant (5% level) based on Student's t test, presumably because of the increase in the microbial activity in the rhizosphere.  $CO_2$  fluxes from the surface in summer were about 10 times higher than those in winter in both fields. The characteristics of the seasonal changes and amplitude of the  $CO_2$  fluxes from the surface were similar to those previously reported<sup>2,4)</sup>.  $CO_2$  fluxes from the surface under soybean were about 2 times higher than those under fallow in summer.

CO<sub>2</sub> fluxes from the soil surface measured by the closed chamber method (X) and calculated by the diffusion equation (Y) were expressed by the equation for a straight line that coincides with the origin: Y (g m<sup>-2</sup> d<sup>-1</sup>)=0.894 X (R=0.893, n=58), except for the fluxes after heavy rainfall. The correlation coefficient (R) between fluxes calculated by the diffusion equation (Y) and fluxes estimated by the equation (Y'): Y'=1 X was 0.888 (n=58). Therefore, the fluxes calculated by the chamber method and the diffusion method coincided relatively well. (8) Estimation of annual respiration

Total CO<sub>2</sub> fluxes from the surface estimated from measurements throughout a year were 3,522 g m<sup>-2</sup> y<sup>-1</sup> under fallow and 4,975 g m<sup>-2</sup> y<sup>-1</sup> under soybean. De Jong and Schappert<sup>4</sup>) estimated that 2,300 g m<sup>-2</sup> of CO<sub>2</sub> was emitted during the growing season from a virgin prairie in Canada. Tulaphitak et al.<sup>11</sup>) estimated that 5,170 g m<sup>-2</sup> of CO<sub>2</sub> was emitted during a year from an upland cultivation field in Thailand. Our values were comparable to the published data.



Fig. 7. Seasonal changes in CO2 flux from soil surface calculated by the diffusion equation

# Simulation model

#### 1)Simulation of diurnal changes in CO2 concentrations

In the field experiments,  $CO_2$  concentrations at depths less than 40 cm from the soil surface followed a sinusoidal trend with the highest values observed in the daytime.

Simulation was conducted to analyze the diurnal changes in  $CO_2$  concentrations. The initial conditions of  $CO_2$  distribution and the diffusion coefficient in the profile were set to be approximatly those recorded on August 8, 1991 as follows:

$$\begin{split} C_a &= 8.0 \cdot 10^{-6} + 2.7 \cdot 10^{-7} \cdot Z - 8.6 \cdot 10^{-9} \cdot Z^2 + 2.6 \cdot 10^{-10} \cdot Z^3 \\ &- 3.2 \cdot 10^{-12} \cdot Z^4 + 1.3 \cdot 10^{-14} \cdot Z^5, \end{split}$$

 $D = 0.024 e^{-0.042 x} + 0.0012$ 

where  $C_a = CO_2$  concentration, g cm<sup>-3</sup> of air, Z = depth, cm, D = CO<sub>2</sub> diffusion coefficient in soil, cm<sup>2</sup> s<sup>-1</sup>. The CO<sub>2</sub> evolution in the steady-state was calculated from the initial conditions.

 $CO_2$  evolution from soils has been reported to be 3 times as high with an increase of about 10°C in the soil temperature between 15–40 °C<sup>3,7)</sup>. A simulation for the  $CO_2$  diurnal changes was conducted based on the dependency of  $CO_2$  evolution on the soil temperature, as shown in Fig. 8.  $CO_2$  concentration at a depth less than about 40 cm from the soil surface increased in the daytime and decreased in the night time, reflecting the characteristics of  $CO_2$  changes in the field.

# Simulation of changes in CO<sub>2</sub> concentrations induced by rain

In the field experiments, heavy rains (August 20– 21) generated a CO<sub>2</sub> peak in the shallow layer at both sites. The peak gradually shifted downward with a decreasing magnitude accompanied with CO<sub>2</sub> accumulation in deeper layers. Soil matric potential in the surface layer (6 cm in depth) increased up to  $-1 \sim -2$  kPa by rainfall. The value remained constant for almost 1 day. During this period, air-filled porosity in the surface layer estimated from the water retention curve was 10%, and the D/D<sub>0</sub> value obtained from the curve of D/D<sub>0</sub> – airfilled porosity was almost 0.

To reproduce the changes in the CO<sub>2</sub> distribution obtained in the field experiments, the simulation was carried out on the following assumptions: (1) The initial dis-



Fig. 8. Simulation for CO2 diurnal changes based on the dependency of CO2 evolution on the soil temperature



Fig. 9. Simulation for CO<sub>2</sub> changes after heavy rain based on the decrease and recovery of the diffusivity in the surface soil layer

ini. : initial condition. d : day. + : time after gas diffusion occurred.

tribution of the  $CO_2$  concentration and the gas diffusion coefficient were the same as those on August 8 (the nearest measurement day before August 20), (2) The gas diffusion coefficient of the surface layer was assumed to be 0 during the first day, namely the continuity of the airfilled porosity in the surface layer was intercepted by abundant water. Thereafter, the gas diffusivity was assumed to recover gradually for 2 days to the previous level.

The results of the simulation are shown in Fig. 9. The  $CO_2$  peak in the upper layer continued to increase along with the accumulation of  $CO_2$  in deeper layers during 1 day while the continuity of the air pores was kept for interception. After the recovery of the continuity of air-filled pores, the  $CO_2$  concentration in the upper layer began to decrease. On the other hand, the  $CO_2$  concentration in the subsoil layers at 90 to 100 cm depths continued to increase from 1 day to about 4 days after the rain in spite of the disappearance of the maximum peak.

These simulations reproduced the typical characteristics of the changes in CO<sub>2</sub> concentration after a large amount of rain.

3) Simulation of seasonal changes in CO2 concentrations

 $CO_2$  concentrations throughout the profiles in the fallow and soybean fields increased toward mid-summer and decreased toward winter.  $CO_2$  distribution in the fallow field showed an almost monotonic increase with depth throughout the year, while that of the soybean site showed a distinct peak during the growing season from 20 to 80 cm depths.

Simulation was conducted to analyze the seasonal changes in  $CO_2$  concentrations toward summer (from June 24 to July 31, 1991) by using the gas diffusion law. The initial conditions of  $CO_2$  distribution and the diffusion coefficient in the profile corresponded approximately to those on June 24, 1991.

CO<sub>2</sub> evolution rates in the steady-state were calculated from the initial conditions. They were assumed to increase at constants rates corresponding to the changes in daily mean temperatures between June 24 and July 31, 1991. The changes in the CO<sub>2</sub> distribution based on these



Fig. 10. Simulation for CO<sub>2</sub> seasonal changes toward summer based on the dependency of CO<sub>2</sub> evolution on the soil temperature

ini. : initial condition. d : day.

assumptions are shown in Fig. 10.

The increase of the  $CO_2$  concentration from shallow layers to deeper layers was attributed to the following factors: 1) Increase in the rates of  $CO_2$  concentration in the upper layers was larger than that in the subsoil layers. 2) The upward  $CO_2$  flux was suppressed by the decrease in the concentration gradient between the shallower layers and the deeper layers, and incidentally  $CO_2$  accumulated in the deeper layers.

## Conclusions

The objective of this study was to investigate the factors that determine the  $CO_2$  distribution in the soil profile by using a simulation model based on the calculation of the  $CO_2$  flux by the gas diffusion equation. To achieve this objective, diurnal, rain-induced, and seasonal changes in  $CO_2$  concentration were monitored along with the soil moisture content and soil temperature under fallow and soybean cultivation. The results were as follows.

Diel concentrations of  $CO_2$  at depths less than 40 cm followed a sinusoidal pattern similar to that of the soil temperature, with the highest value being recorded in the daytime.

Heavy rainfall interrupted the continuity of the air pathway to the atmosphere, which resulted in a high CO<sub>2</sub> concentration in shallow layers at first, and a decrease in the concentration from shallow depths accompanied by an increase in the concentration in deeper layers with the progression of drying for a few days.

 $CO_2$  concentration throughout the profile was high in summer and low in winter.  $CO_2$  concentration under soybean increased from shallow to deeper layers with the increase of the rooting depth.

CO<sub>2</sub> fluxes from the soil surface based on calculations from the diffusion equation corresponded relatively well to those measured by the chamber method.

CO<sub>2</sub> gas was found to move rapidly through airfilled pores and to be swiftly equilibrated between the air phase and liquid phase. A model was devised for calculating the  $CO_2$  flux and  $CO_2$  concentration to analyze the  $CO_2$  changes observed in field experiments.  $CO_2$  flux was calculated by the diffusion equation combined with the equation of continuity.  $CO_2$  concentration in the air phase in each layer was assumed to change by  $CO_2$  evolution and/or dissolution from/into the liquid phase as well as by  $CO_2$ influx and efflux through the air phase and by  $CO_2$  production.

In the model, the CO2 production rate changed with the soil temperature, and the diffusivity changed with the soil water content. The model enabled to analyze the changes in the CO<sub>2</sub> concentrations observed in the field experiments fairly well in the absence of root respiration. However, if the root respiration for each layer could be measured with time, and the data could be introduced into the model, it would be possible to analyze the CO2 concentration changes under vegetation. These results indicated that the changes in the CO2 concentrations in soil were significantly influenced by the following 2 factors: (1) microorganism respiration, which is closely related to the soil temperature, and root respiration, which is closely related to the stage of crop growth, (2) soil moisture, which mainly affects the gas diffusivity in soil.

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