Tellus (1999), 51B, 688–700
Printed in UK. All rights reserved

TELLUS
ISSN 0280–6509

Continuous measurements of CO and H_2 deposition velocities onto an andisol: uptake control by soil moisture

By S. YONEMURA*, S. KAWASHIMA and H. TSURUTA, *National Institute of Agro-Environmental Sciences, Kannondai 3-1-1, Tsukuba, Japan 305-8604*

(Manuscript received 15 December 1997; in final form 8 December 1998)

ABSTRACT

Carbon monoxide (CO) and hydrogen (H_2) net deposition velocities from the atmosphere onto soil and carbon dioxide (CO_2) effluxes to the atmosphere have been measured in an andisol field in Tsukuba, Japan by the open-flow chamber method. The deposition velocities of CO and H_2 were closely correlated ($R = 0.87$), with a ratio of 1.55, which was attributed to the difference in molecular diffusivities. However, the deposition velocities did not exhibit a direct relationship with the CO_2 efflux. Deposition velocities of CO and H_2 ranged from 0.00 to 0.06 cm s^{-1} and from 0.00 to 0.10 cm s^{-1}, respectively, and were closely related to the level of the surface soil moisture (0–5 cm) and were higher in plowed plots than in compacted plots. CO deposition velocity was slightly lower in the daytime due to higher production rates affected by the soil temperature. These findings indicate that microbial CO and H_2 consumption was limited by transport resistance in the soil and that the in situ CO and H_2 uptake rates may be limited by a higher soil moisture level. CO and H_2 deposition was estimated to be restricted to the surface soil (possibly only the top 2–3 cm). CH_4 and CO_2 gas profiles were also related to the variation of the soil moisture level.

1. Introduction

CO is an important constituent in the atmospheric chemistry of the troposphere and is closely related to the behavior of the greenhouse gases CH_4 and tropospheric O_3 (Fishman and Crutzen, 1978). The background level of CO is about 100 ppbv in the northern hemisphere (Khalil and Rasmussen, 1994; Novelli et al., 1994).

In the global budget of CO (Seiler and Conrad, 1987; Khalil and Rasmussen, 1990), there is a large uncertainty in most estimates. CO is emitted from biomass burning and anthropogenic activities as automobile exhaust, and is produced by photochemical reaction in the atmosphere from methane and non-methane hydrocarbons. Furthermore, photoproduction from plant matters may be a large source of atmospheric CO (Seiler et al., 1978; Tarr et al., 1995). Soils act as a net sink of CO, globally (Seiler and Conrad, 1987; Potter et al., 1996).

CO is oxidized in soil, as shown by radioactivity experiments (Bartholomew and Alexander, 1982; Duggin and Cataldo, 1985). Conrad (1988) concluded that especially *Nitrosomonas* species are the actual oxidizers of CO at atmospheric levels, and Bender and Conrad (1994) showed that CO was oxidized by various types of micro-organisms such as carboxydotrophs, methanotrophs, and nitrifiers.

CO is deposited onto or emitted from soil with a net balance of uptake and production in soil (Conrad and Seiler, 1985a, b; Conrad, 1988). Production rate follows a zero-order kinetics owing to the abiological production from organic matter. Uptake rate follows a first-order kinetics in CO. The compensation point concentration of

* Corresponding author.
e-mail: yone@niaes.affrc.go.jp

CO in soil, $[CO]_{equiv}$(ppbv) is determined by the balance of in situ uptake rate, $u_{in\,situ}(s^{-1})$ and in situ production rate, $P_{in\,situ}(s^{-1})$:

$$[CO]_{equiv} = \frac{P_{in\,situ}}{\theta u_{in\,situ}} \quad (1)$$

where θ is the gas-filled porosity (dimensionless).

If $[CO]_{equiv}$ exceeds the atmospheric concentration $[CO]_{atmos}$, CO is emitted from soil, and vice versa.

The absolute value of activation energy of CO production is higher than that of uptake rate. Therefore, when the temperature increases, the $[CO]_{equiv}$ is higher. In arid soils and subtropical soils under conditions of high soil temperature during daytime, CO was emitted from soil (Conrad and Seiler, 1982; Conrad and Seiler, 1985a; Scharffe et al., 1990; Sanhueza et al., 1994a; Sanhueza et al., 1994b). Soils in temperate environments generally showed CO uptake (Liebl and Seiler, 1976; Moxley and Smith, 1998).

The H_2 mixing ratio is about 550 ppbv at background sites (Ehhalt et al., 1977; Schmidt, 1978) and H_2 is emitted from sources similar to those of CO (Seiler and Conrad, 1987). Soil is considered to be the predominant sink of H_2 and the reaction with OH radicals in the atmosphere is less important (Conrad, 1988). Therefore, the estimation of the H_2 sink strength of soils is essential for understanding the behavior of H_2 in the atmosphere. H_2 consumption by soil is considered to be associated with the activity of the extracellular enzymes present in soil (Conrad et al., 1983).

Here, results of CO and H_2 deposition in an arable field under temperate conditions in Japan obtained by continuous measurements are reported to investigate the factors involved in these processes. Besides, CO_2 efflux was measured because it reflects the total activity of microorganisms in soil.

Four plots were set up in an arable field to study the effects of soil moisture, gas-filled porosity as an index of gas diffusivity in the soil, and the vegetation on the fluxes of the above gases. Soil concentration profiles of CO, CH_4, and CO_2 were also measured because these profiles reflect the gas diffusivity in soil.

In this study, the net deposition velocities were measured by the open-flow method. To estimate the deposition intensity onto soil, the flux value (Sanhueza et al., 1994a,b), net deposition velocity (Liebl and Seiler, 1976; Moxley and Smith, 1998), and gross deposition velocity and gross production rate (Conrad and Seiler, 1985a) were employed. If the net influx is expressed as F, (mol $cm^{-2}\,s^{-1}$) the gross deposition velocity v_g (cm s^{-1}) and the net deposition velocity v_n (cm s^{-1}) are written as follows:

$$v_s = \frac{F}{\rho(C_{atmos} - C_{equiv})}, \quad (2)$$

$$v_n = \frac{F}{\rho C_{atmos}}, \quad (3)$$

where C_{atmos} is the atmospheric concentration and C_{equiv} is the compensation point concentration in soil. The open-flow method measures the concentration difference through a chamber from which the net flux (F) between soil and the atmosphere was calculated. In this study, the net deposition velocities v_n (hereafter referred to as v instead of v_n for simplicity) were used to express the intensity of CO and H_2 deposition onto soil. Direct flux values were not employed because of the first order kinetics of CO and H_2 deposition and the rapid changes in CO and H_2 concentrations at Tsukuba, probably due to human activities.

2. Methods

2.1. Field site

Experiments were carried out in an upland experimental field of the National Institute of Agro-Environmental Sciences in Tsukuba Science City (36°01′N, 140°07′E), Ibaraki, about 60 km northeast of Tokyo, from 26 June 1995 which corresponds to the end of the rainy season until 26 August 1995 which corresponds to the end of summer. The rainy season in Tsukuba extends from about the beginning of June to the middle of July. Meteorological data such as precipitation were measured at a distance of several hundred meters from the measurement site.

The soil type was an Andisol Hydric Hapludands (United States Department of Agriculture, Soil Conservation Service, 1994) which extended over a 200 cm depth with a volcanic ash topsoil with a pH (H_2O) of about 6.4. The soil is designated as "Kuroboku" in Japan and shows a very dark color with a fine granular structure; the soil particle density was 2.66 g cm^{-3}.

The distribution of the soil particles in the AP1 layer in terms of size was as follows: for clay, 55%; for silt, 26%; for fine sand, 15%; for coarse sand, 4.4%. The carbon and nitrogen contents in the top soil (0–5 cm) were analyzed with a MT-700 CN analyzer (Yanagimoto Co. Ltd., Japan) and were about 4.2% and 0.35% on a weight basis, respectively. In the winter season in 1995, wheat was growing in the field.

The field was divided into 2 main plots in the middle of May, and plowing and compaction were carried out using a plow and a roller. Soil three phases, solid, liquid, and gas and therefore gas diffusivities in the plots changed by these management practices. The depth of the plowed soil was about 15 cm. Each main plot was sub-divided into a sub-plot with vegetation cover vegetative (*Vicia villosa*) and a bare sub-plot. Each sub-plot measured 5 m × 3 m. Two chambers were installed in each sub-plot.

2.2. *Measurements*

Measurement instruments, data loggers and the flow control unit were set up in a temperature controlled cabin at the field site. A schematic diagram of the open-flow method applied is shown in Fig. 1.

The chambers used were made of poly vinyl chloride cylinders, 21 cm diameter cut to 15 cm length, of which 5 cm was inserted into the soil. During the measurements, a lid was loosely attached to the top of the chamber and a sun shade consisting of a white cone funnel was placed above the lid to avoid excessive temperature increase.

Air taken from the atmosphere was pumped through a large container acting as a buffer (> 200 l) with fans and introduced to the chamber to smooth the concentrations which display rapid changes. Two air inlets and outlets were connected to the middle of the cylinder wall to mix the airflow effectively. During the measurements, the air flow rate was controlled by mass flow meters with needle valves (Kojima Co. Ltd., Japan), and was set at values ranging between 3.0 and 3.3 l min^{-1} to match the high deposition rates of CO and H_2 onto the soil. The air samples were pumped from the inlet and outlet of the chamber to the RGA3 system and the CO_2 analyzer.

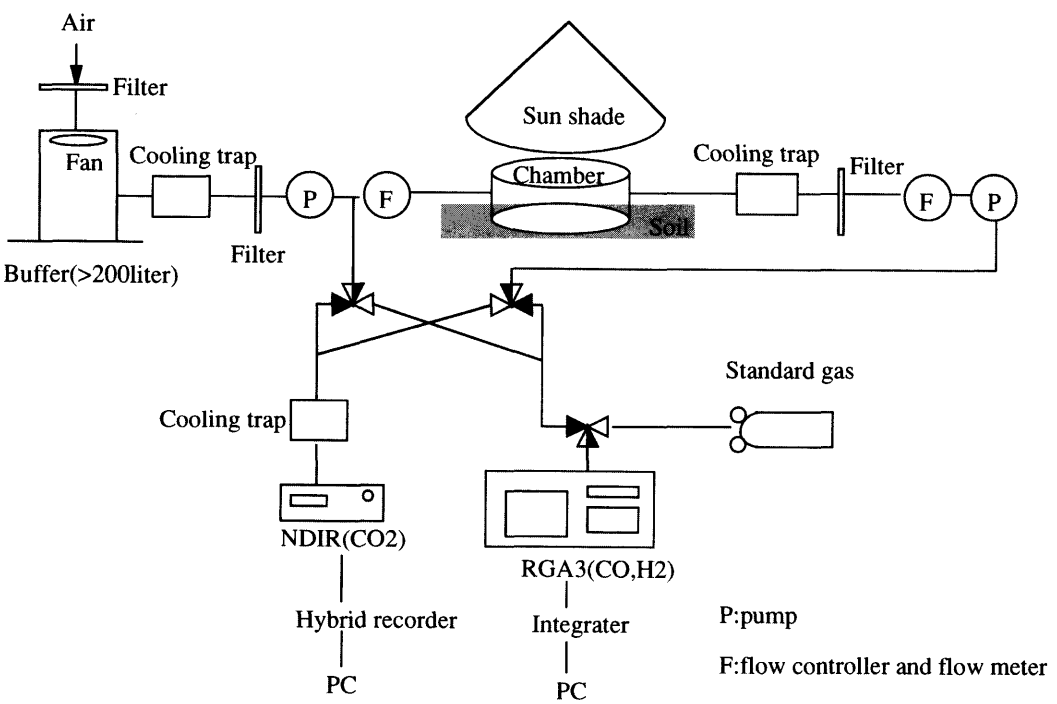


Fig. 1. Schematic diagram of the open chamber measurement system used.

The chromatographic data from the RGA3 system were downloaded to a CR5A integrator (Shimadzu Corporation, Japan) and gas concentrations were calculated. At the same time, the CR5A regulated the RGA3 and solenoid valves controlling the automatic sampling system. The soil temperature at a 5 cm depth under the chamber and soil temperature profiles in the plots were also measured.

The schedule of the measurements in the plots subjected to different treatments is shown in Table 1. The variations in deposition velocities were measured mainly in bare plots.

Soil core samples (100 ml) were taken from 0–5 cm surface soil in all the sub-plots and the soil moisture content was measured gravimetrically as an index of soil diffusivity. The sampling dates were 16, 17, 18, 19, 20, 22, 24, 25, 28, 31 July and 2, 22 August. During the other days, the soil moisture data were interpolated using the thermoconductivity data recorded on a datalogger (21X; Campbell Co. Ltd., California, USA). Soil thermoconductivities were measured in the field from 16 July to 21 August. The heat probe sensors were set at depths of 5 cm and 10 cm in each plot. The mean value of the two probes in each plot was correlated ($R = 0.78$) with the soil moisture values. Gas-filled porosity was calculated from the soil moisture content and the soil particle density.

2.3. *Analysis of CO, H_2, and CO_2*

Analysis of CO and H_2 was carried out using a RGA3 Reduction Gas Analyzer (Trace Analytical, California, USA). In this instrument, the mercuric oxide technique is applied to detect CO and H_2 as low as the atmospheric concentration level (Seiler et al., 1980). The detection limits of CO and H_2 were about 1 ppbv and 50 ppbv, respectively, and the averages of 10 standard deviations of CO and H_2 were 1.2 and 5 ppbv at about 500 ppbv, respectively (s.d. for $n = 20$). For the calibration of CO and H_2 concentrations, standard gases enclosed in aluminum and iron cylinders at 1 ppmv CO and 1.1 ppmv H_2 with N_2 balance, respectively, that were commercially supplied (Nihon Sanso Corporation, Japan) were used. The linearities of CO and H_2 concentration measurements by RGA3 in the range $\leqslant 1$ ppmv fell within a 5% precision level and within the precision of analysis, respectively. The CO_2 concentration was obtained using an infrared analyzer (LI6250; LI-COR Inc., Nebraska, USA) with a 396 ppmv CO_2 cylinder, commercially supplied (Takachiho Chemical Industry Co. Ltd., Japan). An autosampler was fitted to the system to allow the continuous automatic measurements necessary for the application of the open-flow method. The instruments were calibrated in the field. Data acquisition of CO_2 was conducted every 3 min to be synchronized with those of CO and H_2.

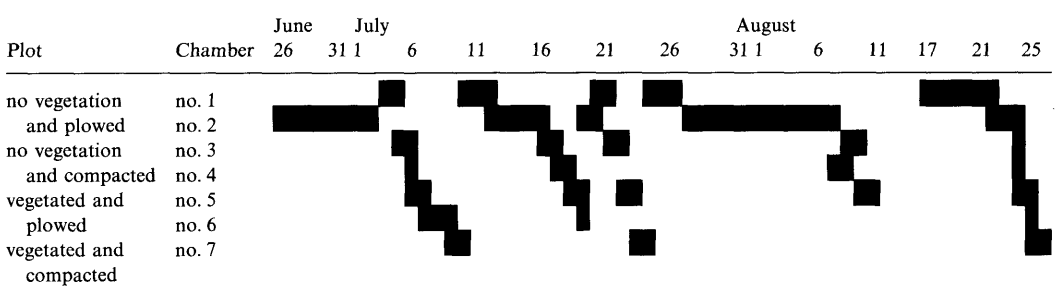
2.4. *Calculation of deposition velocities*

The mass balance of the target gas in the chamber can be written as:

$$\rho \frac{\mathrm{d}(VC_{\mathrm{ch}})}{\mathrm{d}t} = f\rho(C_{\mathrm{in}} - C_{\mathrm{out}}) - \rho A v C_{\mathrm{surface}} + P_{\mathrm{vinyl}}, \quad (4)$$

where t is time (s), C_{ch} is mean concentration in the chamber (ppbv), C_{in} is concentration at the inlet (ppbv), C_{out} is concentration at the outlet

Table 1. *Dates of open chamber measurements in the different treatment plots during the period from 26 June to 26 August 1995 in Tsukuba, Japan (indicated by shaded areas)*



(ppbv), $C_{surface}$ is concentration on the soil surface (ppbv), f is flow rate (l min^{-1}), A is soil surface area in the chamber (cm^2), V is volume of the chamber (cm^3) and P_{vinyl} is production from the vinyl chloride chamber (mol s^{-1}).

In our measurements, time series of C_{in} and C_{out} were analyzed in turn every 6 min. Interpolating these data, the values at 3 min intervals were calculated. From the advective term on the left hand side of eq. (1), the correction of the CO_2 efflux was $<1\%$, and the correction for CO and H_2 deposition velocities amounted to a maximum of several percentage points in our measurements due to the rapid changes of CO and H_2 concentrations in the air, although the concentrations were smoothed by the buffer. CO deposition velocities were corrected for temperature-dependent CO flux from the vinyl chloride chambers.

Here, we assumed as follows:

$$C_{ch} = C_{surface} = \frac{C_{in} + C_{out}}{2}. \quad (5)$$

The assumption that C_{ch} is the mean of C_{in} and C_{out} does not result in any large error because the chamber was ventilated at the high flow rate. On the other hand, the interpretation of $C_{surface}$ can lead to a bias of calculated deposition velocities. Finally, we calculated v as follows:

$$v = \frac{2f(C_{in} - C_{out}) - \frac{d}{dt}\{V(C_{in} + C_{out})\} + \frac{2}{\rho}P_{vinyl}}{A(C_{in} + C_{out})}. \quad (6)$$

2.5. *Measurement of gas profiles in soil*

Samples of the soil air were taken at depths of 0, 5, 10, 20, 30, 50 and 70 cm at 5 locations in the field using stainless steel tubes inserted into the soil. CO and H_2 concentrations were measured by immediately injecting 10 ml samples into the RGA3 analyzers using a gas-tight syringe. Further samples were injected into 5 ml or 10 ml evacuated vials for the analysis of CO_2 and CH_4 in the laboratory using a gas chromatography fitted with a thermoconductivity detector and a flame ionization detector, respectively (Shimadzu Corporation, Japan). CH_4 was measured because it was reported that it was oxidized by soil micro-organisms. Samples were collected on 26 June, 9, 12, 19, 26 July and 2, 24 August. The gas profiles were compared in relation to the moisture level.

3. Results

3.1. *Characteristics of the deposition velocities*

Fig. 2 shows the changes of (a) rainfall, soil moisture level, and temperature, (b) CO_2 efflux, (c) CO deposition, and (d) H_2 deposition velocity throughout the experiment. In 1995, since rainfall was above average and soil deposition of CO and H_2 was negligible due to the water cover until 26 June, the data prior to this date were not shown. The rainy season ended in the middle of July and afterwards the soil moisture level gradually decreased while the temperature increased (Fig. 2a). Similarly, CO and H_2 deposition velocities gradually increased during the measurement period (Fig. 2b,c). Deposition velocities of $0.00 \sim 0.06$ cm s^{-1} for CO and $0.00 \sim 0.10$ cm s^{-1} for H_2 in our measurements were in the same order as those reported previously (Liebl and Seiler, 1976; Moxley and Smith, 1998).

The CO_2 efflux (Fig. 2d) did not affect directly on CO and H_2 deposition velocities. Intermittent peaks of CO_2 effluxes which were observed in the beginning of July, coinciding with high rainfall (Fig. 2a), were not observed for CO and H_2 deposition velocities.

CO and H_2 deposition velocities were higher in the plowed plots. The effect of compaction or plowing on CO and H_2 deposition velocities was more conspicuous than that on CO_2 efflux. No striking differences in CO and H_2 deposition velocities between the measured deposition velocities in the vegetated and the bare sub-plots were observed.

Fig. 3 depicts typical variations of CO and H_2 deposition velocities and CO_2 efflux over a few sunny days. During that time, CO mixing ratios ranged from approximately 180 ppbv to 1 ppmv. However, this wide range of CO mixing ratios did not affect the velocities. Daytime deposition velocities for CO and H_2 were smaller than nighttime values, and the diurnal variation in CO deposition velocities in August (Fig. 3b) was larger than that in July. Fig. 3c shows the effect of the soil temperature (5 cm) on CO and H_2 deposition velocities and CO_2 efflux. The latter was positively correlated with the soil temperature, while CO deposition velocities showed a slight decrease at higher

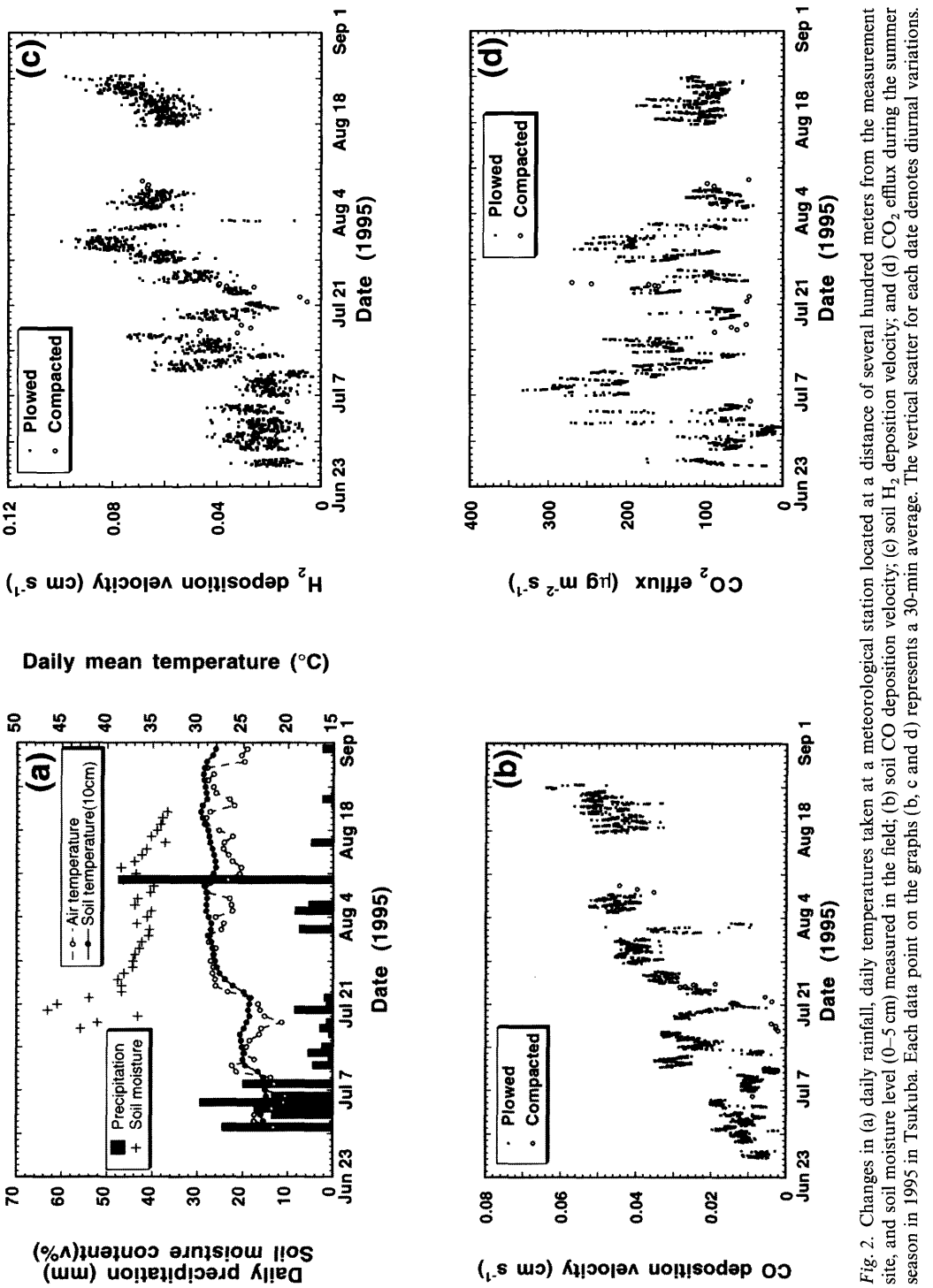


Fig. 2. Changes in (a) daily rainfall, daily temperatures taken at a meteorological station located at a distance of several hundred meters from the measurement site, and soil moisture level (0–5 cm) measured in the field; (b) soil CO deposition velocity; (c) soil H_2 deposition velocity; and (d) CO_2 efflux during the summer season in 1995 in Tsukuba. Each data point on the graphs (b, c and d) represents a 30-min average. The vertical scatter for each date denotes diurnal variations.

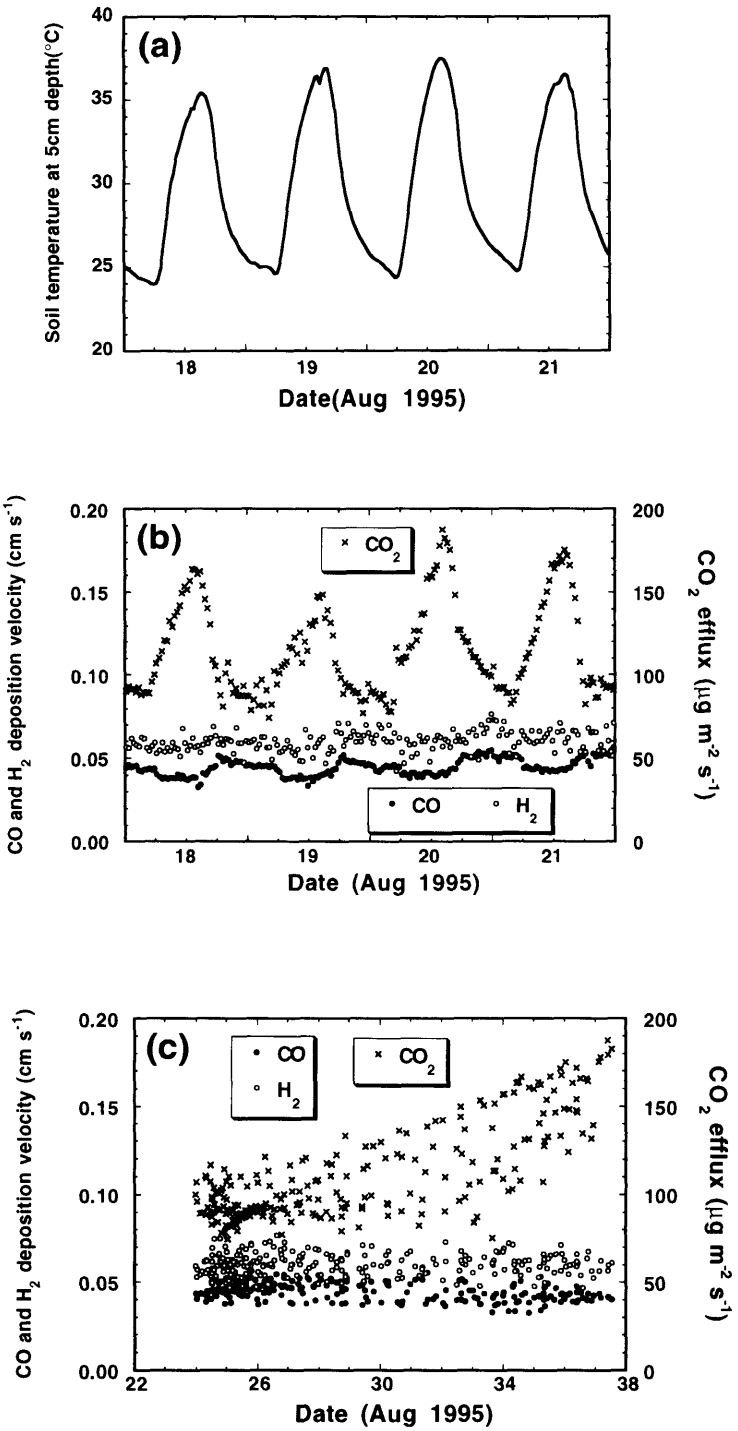


Fig. 3. Changes in (a) soil temperature, (b) CO and H_2 deposition velocities, and CO_2 efflux during 4 sunny days between 18 and 21 August in 1995 and (c) relationship between the soil temperature and deposition velocities and flux rates of CO, H_2 and CO_2 during the same period. Date and time are JST.

temperatures. The daily averaged deposition velocities were higher when the surface soil was drier and gas-filled porosity in the surface soil had increased. Daily averaged CO and H_2 deposition velocities increased approximately by 2% per day as the soil became drier (Fig. 3b).

Generally, the patterns of CO and H_2 deposition velocities were similar. The relationship between CO and H_2 deposition velocities measured in all the plots is shown in Fig. 4. The relationship appeared to be linear and the value of the ratio was similar to that reported by Liebl and Seiler (1976).

The relationship between the moisture content of the surface soil (0–5 cm) and CO and H_2 deposition velocities is shown in Fig. 5, and the relationship between the surface gas-filled porosity (0–5 cm) and CO and H_2 deposition velocities is shown in Fig. 6. Good correlations were found in the data shown in Figs. 5 and 6. In Fig. 5, in the lower range of CO and H_2 deposition velocities, there was a difference between plowed and compacted plots. On the other hand, in Fig. 6, in the higher range of CO and H_2 deposition velocities, there was a difference between plowed and compacted plots.

3.2. *Characteristics of the gas profiles in the soil*

H_2 concentrations in soil were below the detection limit, probably due to the strong oxidizing activity of micro-organisms and the lack of any production in soil (Conrad and Seiler, 1985a).

Fig. 7 shows profile data of the CO, CH_4, and CO_2 concentrations. Concentrations of CO in soil decreased rapidly from atmospheric concentrations on the soil surface to <10 ppbv at 10 cm indicating the presence of a strong CO oxidation (Fig. 7a). Therefore, the oxidation of CO occurred mainly on the surface soil (<5 cm). The CH_4 concentration decreased with increasing soil depth, but the rate of decrease was lower than that for CO, indicating that the oxidation rates of CH_4 in soil were lower (Fig. 7b). In contrast, the concentration of CO_2 in soil increased with the soil depth (Fig. 7c).

During the rainy season (9 and 12 July), CH_4 concentrations near the soil surface were low whereas those of CO_2 were high, suggesting that at that time the precipitated water acted as a barrier near the soil surface and limited the gas exchange between the atmosphere and soil.

4. Discussion

The soil was aerobic throughout the measurement period because CH_4 was deposited onto soil due to the negative gradients of the CH_4 concentration with the soil depth even in the beginning

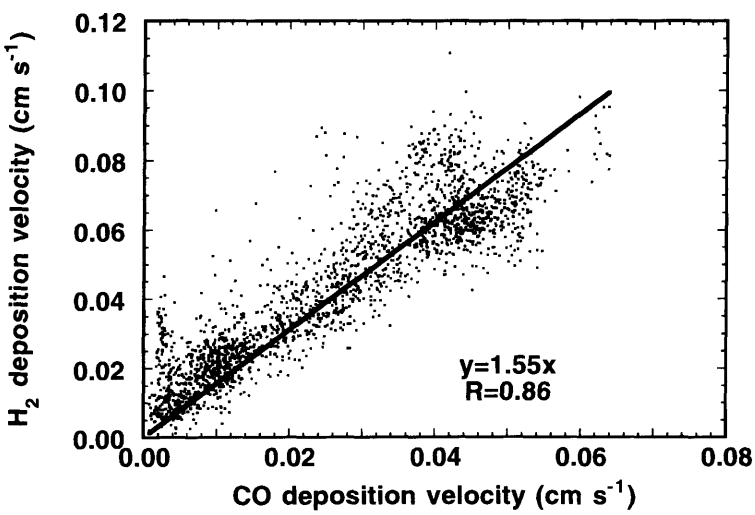


Fig. 4. Relationship between CO and H_2 deposition velocities. Each point represents a 30-min average.

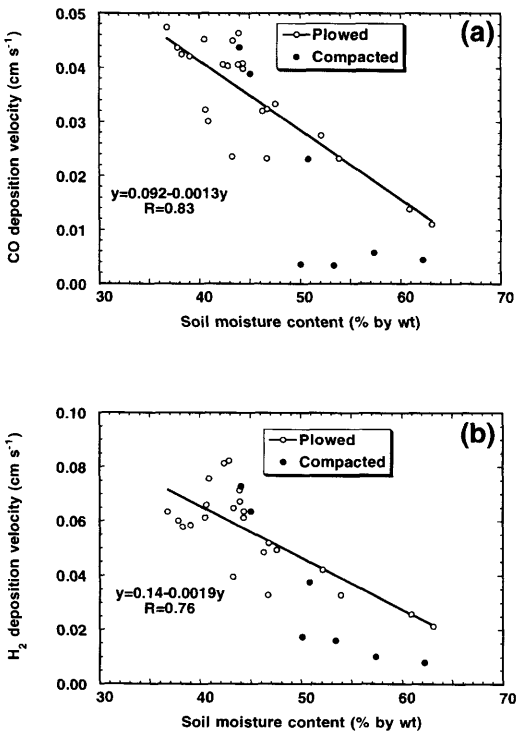


Fig. 5. Relationship between soil moisture content (0–5 cm) and the deposition velocities of (a) CO and (b) H_2: the data points represent 12- or 24-h averages to eliminate diurnal variation. Regressions were calculated for plowed plots.

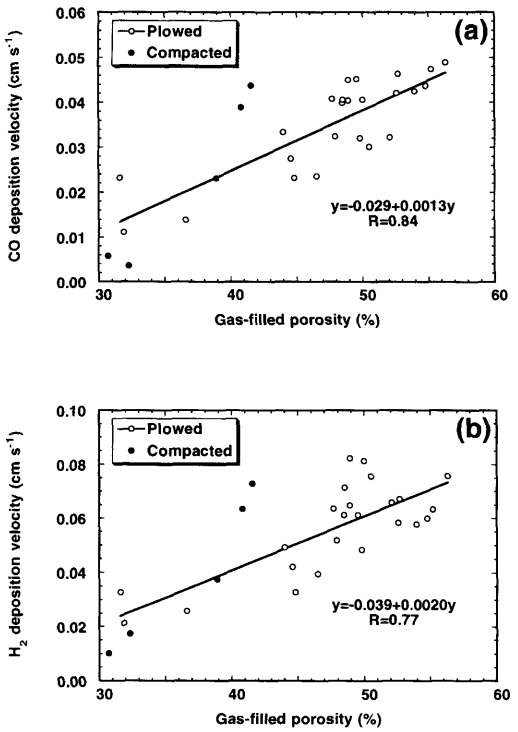


Fig. 6. Relationship between gas-filled porosity (0–5 cm) and the deposition velocities of (a) CO and (b) H_2: the data points represent 12- or 24-h averages to eliminate diurnal variation. Regressions were calculated for plowed plots.

of July which corresponded to the end of the rainy season in 1995 (Fig. 7b).

CO_2 efflux was less affected by the soil moisture content (Fig. 2a and Fig. 2d). CO_2 once produced in soil was eventually emitted from soil unless it was dissolved in water and transported downward into deeper layers. Hence, higher CO_2 concentrations (Fig. 7c) and intermittent high CO_2 effluxes (Fig. 2d) were observed in the beginning of July, regardless of the lower production rate under lower temperature conditions (Fig. 2a). The CH_4 profiles (Fig. 7b) indicate that the CH_4 concentrations were lower in the beginning of July. CH_4 deposition was lower when the soil moisture level was higher because the diffusivity in soil was hindered and CH_4 oxidation occurred only in the top soil layer.

In contrast to the CO_2 efflux and in the same way as CH_4 deposition, CO and H_2 deposition velocities were strongly controlled by the soil moisture content which predominantly controlled the gas-filled porosity (Fig. 2b,c, Fig. 5, and Fig. 6). Hence, the gas transport from the atmosphere to soil was considered to be more important for the gases deposited onto soil.

Through plowing and compaction, soils showed the same moisture content but higher and lower gas-filled porosity, respectively. The differences in the CO and H_2 deposition velocities between plowed and compacted soils (Fig. 5 and Fig. 6) are consistent with the measurements of Rust et al. (1957) who suggested that the decrease in the gas-filled porosity by water affects diffusion more than the decrease in gas-filled porosity by solids, i.e. due to compaction. Gas diffusivities in soil were controlled not only by the gas-filled porosity but also by the soil moisture content. Therefore, to explain the details of CO and H_2 sorption, not only gas-

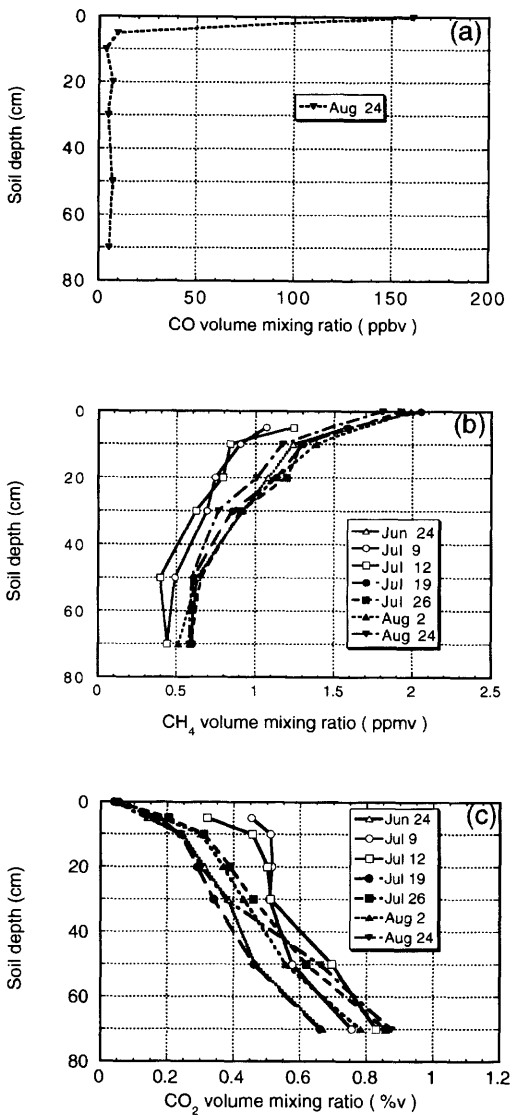


Fig. 7. Changes in soil air concentrations of (a) CO, (b) CH_4, and (c) CO_2 with soil depth on different dates during the period from 25 June to 24 August 1995 in Tsukuba. Only the 24 August measurements are shown for CO due to sample contamination.

filled porosity but also liquid to solid ratio should be considered in the diffusion calculation.

To illustrate our data of CO and H_2 deposition velocities from the diffusional point of view, firstly the mass flux of the gas can be determined by a generalization of Fick's first law that describes ordinary gaseous diffusion through porous unsaturated media as follows:

$$F = \rho D\theta\tau \frac{\partial C}{\partial z}, \tag{7}$$

$$\rho\theta \frac{\partial C}{\partial t} = \rho D\theta\tau \frac{\partial^2 C}{\partial z^2} - \rho C\theta u_{\text{in situ}} + \rho P_{\text{in situ}}, \tag{8}$$

where F = vertical gas flux (mol cm^{-2} s^{-1}); r = density of a gas (mol cm^{-3}); D = molecular diffusion constant for CO: 0.22 cm^2 s^{-1} and for H_2: 0.73 cm^2 s^{-1} at 30°C (Marrero and Mason, 1972); t = tortuosity coefficient for adjustment to increased resistance to diffusion caused by the soil structure (dimensionless); C = concentration of gas (ppbv); z = soil depth (cm). The multiplier value of in the diffusion term is different from that in eq. (3) of Potter et al. (1996) who used a soil aggregation model. Since the soil air concentrations of CO and H_2 are low compared with atmospheric levels, we assumed stationary conditions and $\partial C/\partial t = 0$ and $P_{\text{in situ}} = 0$, and we obtained:

$$\rho D\tau \frac{\mathrm{d}^2 C}{\mathrm{d}z^2} = \rho C u_{\text{in situ}}. \tag{9}$$

Assuming the uniformity of $u_{\text{in situ}}$, θ and τ, the solution to this equation is

$$C = C_1 \exp\left(\sqrt{\frac{u_{\text{in situ}}}{D\tau}}\, z\right) + C_2 \exp\left(-\sqrt{\frac{u_{\text{in situ}}}{D\tau}}\, z\right) \tag{10}$$

where C_1 and C_2 are integral constants.

Considering boundary conditions, $C = C_{\text{atmos}}$ at $z = 0$, $F = -\rho v C_{\text{atmos}}$ at $z = 0$, and $C = 0 z = -\infty$, we obtain an exponentially decreasing concentration profile:

$$C = C_{\text{atmos}} \exp\left(-\frac{vz}{D\theta\tau}\right), \tag{11}$$

and

$$u_{\text{in situ}} = \frac{v^2}{D\theta^2\tau}. \tag{12}$$

Hereafter the skin depth of deposition is defined as d:

$$d \equiv \frac{D\theta\tau}{v}. \tag{13}$$

From this definition, about 63% of the gas is

absorbed within the topsoil $< d$. The tortuosity coefficient can be expressed as follows (Striegl, 1993):

$$\theta^{2/3} \leqslant \tau \leqslant 0^{1/3} \tag{14}$$

so that

$$\frac{\theta^{5/3}D}{v} \leqslant d \leqslant \frac{\theta^{4/3}D}{v}, \qquad \frac{v^2}{D\theta^{8/3}} \geqslant u_{\text{in situ}} \geqslant \frac{v^2}{D\theta^{7/3}}. \tag{15}$$

From our experimental data (Fig. 6), substituting $\theta = 55\%$ (dry condition):

for CO ($v = 0.045$ cm s^{-1})

$$1.8 \text{ cm} \leqslant d \leqslant 2.2 \text{ cm}$$
$$0.045 \text{ s}^{-1} \geqslant u_{\text{in situ}} \geqslant 0.036 \text{ s}^{-1}; \tag{16}$$

for H_2 ($v = 0.071$ cm s^{-1})

$$3.8 \text{ cm} \leqslant d \leqslant 4.7 \text{ cm}$$
$$0.034 \text{ s}^{-1} \geqslant u_{\text{in situ}} \geqslant 0.027 \text{ s}^{-1}. \tag{17}$$

If $\theta = 30\%$ (Fig. 6) is substituted:

for CO ($v = 0.011$ cm s^{-1})

$$2.6 \text{ cm} \leqslant d \leqslant 4.0 \text{ cm}$$
$$0.014 \text{ s}^{-1} \geqslant u_{\text{in situ}} \geqslant 0.0094 \text{ s}^{-1}; \tag{18}$$

for H_2 ($v = 0.021$ cm s^{-1})

$$4.7 \text{ cm} \leqslant d \leqslant 7.1 \text{ cm}$$
$$0.015 \text{ s}^{-1} \geqslant u_{\text{in situ}} \geqslant 0.0098 \text{ s}^{-1}. \tag{19}$$

The results of CO skin depth < 4.0 cm (eqs. (16), (18)) and < 5 cm of CO soil profile (Fig. 7a) are in agreement with the measurements reported by other authors (Leibl and Seiler, 1976; Conrad, 1988) and with the value used by Potter et al. (1996) who estimated that the topsoil CO gradient was 26 ppbv cm^{-1} at 130 ppbv in the northern hemisphere on the assumption that the concentration gradient of CO in soils is linear.

A distinct difference in the skin depth between CO and H_2 was observed but no clear difference of in situ uptake rates was detected. These findings suggest that H_2 can move deeper into the soil than CO due to its larger diffusivity. Therefore, the ratio of the deposition velocity of H_2 to that of CO (Fig. 4) could be attributed to the difference in molecular diffusivities. Hence, the skin depth d of the CO and H_2 deposition layer may decrease with increasing soil moisture. The similarity of CO and H_2 in situ uptake rates (eqs. (16), (17) and eqs. (18), (19)) may be attributed to the similarity of solubilities in water at which microorganisms must utilize CO and H_2 (Conrad, 1988); the solubilities were 0.023 ml for CO and 0.018 ml for H_2 to 1 ml volume of water at 20°C and 1013.25 hPa (National Astronomical Observatory, 1994).

If $u_{\text{in situ}}$ values are the same in relation to θ, the difference in the skin depth when $\theta = 55\%$ (eqs. (16), (17)) and when $\theta = 30\%$ (eqs. (18), (19)) is apparently not compatible with the diffusion effect used by Potter et al. (1996) who employed a water balance model. However, the in situ uptake rates, $u_{\text{in situ}}$ were about 3 times lower in relation to θ which suggests that at the end of the rainy season, $u_{\text{in situ}}$ values were reduced due to higher moisture level in addition to the lower temperature. This deduction is supported by the previous results obtained by several authors (Heichel, 1973; Conrad and Seiler, 1980; Moxley and Smith, 1997) who showed that there is an optimum moisture level for microbiological CO uptake in soils. In moist and temperate regions such as Japan, since the soil moisture level is higher than or similar to the optimum soil moisture level, the high level of soil moisture can reduce the CO and H_2 in situ uptake between the atmosphere and the soil.

The temperature dependency of CO and H_2 deposition velocities depicted in Fig. 3c supports the data presented in Fig. 6 by Liebl and Seiler (1976). In Fig. 3b, only a slight decrease of deposition velocities was detected even during the days when the soil temperature was higher (Fig. 3a) and the abiological CO production from organic matter was highest. High deposition velocities were not only recorded in the night but also during the day and may be explained as follows: Firstly, the microbial activity of CO and H_2 uptake could have been accelerated by the CO fertilization effect (Smith et al., 1973; Spratt and Hubbard, 1981, Bender and Conrad, 1994) because the CO and H_2 concentrations in Tsukuba were very high (> 180 ppbv in the relevant period for CO). Secondly, nitrogen application to the arable soil may have stimulated the microbial uptake ability of CO and H_2, as reported in previous studies (Conrad, 1988; Bender and Conrad, 1994) who addressed nitrifiers as the most effective CO oxidizers in soils. Soil temperature as well as moisture

conditions were optimal for nitrification in the study area.

Although Liebl and Seiler (1976) suggested that vegetation enhances deposition velocities, this was not reflected in our study, since no appreciable any striking differences between the measured CO and H_2 deposition velocities in the vegetated and the bare sub-plots were observed. The lack of striking differences in the CO and H_2 deposition velocities between vegetated and plowed plots may be due to the low vegetation density, and also due to the fact that the duration of the experiment was too short to detect differences. Further studies should be carried out on the rôle of vegetation.

5. Conclusions

CO and H_2 deposition velocities and CO_2 efflux were measured by the open-flow method during the summer of 1995. The deposition velocities which were very low during the rainy season, gradually increased as the soil surface became drier. The gas profiles in the soil also reflected the moisture conditions. Deposition velocities in the plowed plots were higher than those in the compacted plots. The ratio of the deposition velocity of H_2 to that of CO could be attributed to the difference in molecular diffusivity. The deposition velocities were not directly correlated to the CO_2 efflux. The changes in the gas diffusivity resulting from the soil moisture content played a more important rôle in the deposition velocities than CO_2 effluxes.

Soil moisture level may limit the exchanges of CO and H_2 between the atmosphere and soil in temperate and moist climates such as Japan by two mechanisms. The first one is related to gas transport; higher soil moisture leads to lower gas diffusivity. The other is associated with the microbial uptake activity of CO and H_2 which decreases under the optimum moisture level for the oxidizers.

In addition, microbial biomass, soil carbon and soil physical characteristics may directly affect the deposition velocities and should be taken into account in future studies. Furthermore, the rôle of management practices such as fertilization and tillage should be investigated for the control of CO and H_2 uptake in arable soils.

6. Acknowledgments

We are indebted to Dr. K. Kita, the University of Tokyo for the improvement of RGA3 system and to Dr. Iain McTaggart, the Scottish Agricultural College who checked this manuscript. We are much obliged to anonymous reviewers who offered us several suggestions.

REFERENCES

Bartholomew, G. W. and Alexander, M. 1982. Microorganisms responsible for the oxidation of carbon monoxide in soil. *Environ. Sci. Technol.* **16**, 300–301.

Bender, M. and Conrad, R. 1994. Microbial oxidation of methane, ammonium and carbon monoxide, and turnover of nitrous oxide and nitric oxide in soils. *Biogeochemistry* **27**, 97–112.

Conrad, R. and Seiler, W. 1980. Role of microorganisms in the consumption and production of atmospheric carbon monoxide by soil. *Appl. Environ. Microbiol.* **40**, 437–445.

Conrad, R. and Seiler, W. 1982. Arid soils as a source of atmospheric carbon monoxide. *Geophys. Res. Lett.* **9**, 1353–1356.

Conrad, R., Weber, M. and Seiler, W. 1983. Kinetics and electron transport of soil hydrogenases catalyzing the oxidation of atmospheric hydrogen. *Soil Boil. Biochem.* **15**, 167–173.

Conrad, R. and Seiler, W. 1984. Destruction and production rates of carbon monoxide in arid soils under field conditions. In: *Planetary ecology* (eds. Caldwell, D. E., Brieler, C. L and Brierley, J. A.). Van Nostrand Reinhold, 112–119.

Conrad, R. and Seiler, W. 1985a. Influence of temperature, moisture, and organic carbon on the flux of H_2 and CO between soil and atmosphere: field studies in subtropical regions. *J. Geophys. Res.* **90**, 5699–5709.

Conrad, R. and Seiler, W. 1985b. Characteristics of abiological carbon monoxide formation from soil organic matter, humic acids, and phenolic compounds. *Envir. Sci. Technol.* **19**, 1165–1169.

Conrad, R. 1988. Biogeochemistry and ecophysiology of atmospheric CO and H_2. *Adv. Microb. Ecol.* **10**, 231–283.

Duggin, J. A. and Cataldo, D. A. 1985. The rapid oxidation of atmospheric CO to CO_2 by soils. *Soil. Biol. Biochem.* **17**, 469–474.

Ehhalt, D. H. and Schmidt, U. 1977. Vertical profiles of molecular hydrogen in the troposphere and stratosphere. *J. Geophys. Res.* **82**, 5907–5911.

Fishman, J. and Crutzen, P. J. 1978. The origin of ozone in the troposphere. *Nature* **274**, 855–858.

Heichel, G. H. 1973. Removal of carbon monoxide by field and forest soils. *Environ. Qual.* **2**, 419–423.

Khalil, M. A. K. and Rasmussen, R. A. 1990. The global cycle of carbon monoxide: trends and mass balance. *Chemosphere* **20**, 227–242.

Khalil, M. A. K. and Rasmussen, R. A. 1994. Global decrease in atmospheric carbon monoxide concentration. *Nature* **370**, 639–641.

Liebl, K. H. and Seiler, W. 1976. CO and H_2 destruction at the soil surface. In: *Microbial production and utilization of gases* (eds. Schlegel, H. G., Gottschalk, G. and Pfenning, N.). Akademie der Wissenschaften, Göttingen, 215–229.

Marrero, T. R. and Mason, E. A. 1972. Gaseous diffusion coefficients. *J. Phys. Chem. Ref. Data* **1**, 3–118.

Moxley, J. M. and Smith, K. A. 1998. Factors affecting utilisation of atmospheric CO by soils. *Soil Biol. Biochem.* **30**, 65–79

National Astronomical Observatory 1994. *Science table.* Maruzen, Tokyo, 454 pp. (in Japanese)

Novelli, P. C., Masarie, K. A., Tans, P. P. and Land, P. M. 1994. Recent changes in atmospheric carbon monoxide. *Science* **263**, 1587–1590.

Potter, C. S., Klooster, S. A. and Chatfield, R. B. 1996. Consumption and production of carbon monoxide in soils: a global model analysis of spatial and seasonal variation. *Chemosphere* **33**, 1175–1193.

Rust, R. H., Klute, A. and Gieseking, J. E. 1957. Diffusion-porosity measurements using a non-steady state system. *Soil Sci.* **84**, 453–463.

Sanhueza, E., Donoso, L., Scarffe, D. and Crutzen, P. J. 1994a. Carbon monoxide fluxes from natural, managed, or cultivated savannah grasslands. *J. Geophys. Res.* **99**, 16,4–16,427.

Sanhueza, E., Cardenas, L., Donoso, L. and Santana, M. 1994b. Effect of plowing on CO_2, CO, CH_4, and NO fluxes from tropical savannah soils. *J. Geophys. Res.* **99**, 16,429–16,434.

Scharffe, D., Hao, W. M., Donoso, L., Crutzen, P. J. and Sanhueza, E. 1990. Soil fluxes and atmospheric concentration of CO and CH_4 in the northern part of the guayana shield, Venezuela. *J. Geophys. Res.* **95**, 22,475–22,480.

Schmidt, U. 1978. The latitudinal and vertical distribution of molecular hydrogen in the troposphere. *J. Geophys. Res.* **83**, 941–946.

Seiler, W., Giehl, H. and Bunse, G. 1978. The influence of plants on atmospheric carbon monoxide. *Pageoph.* **116**, 439–451.

Seiler, W. and Conrad, R. 1987. Contribution of tropical ecosystems to the global budget of trace gases, especially CH_4, H_2, CO and N_2O. In: *The geophysiology of Amazonia* (ed. Dickinson, R. E.). John Wiley and Sons, New York, 133–162.

Seiler, W., Giehl, H. and Roggendorf, P. 1980. Detection of carbon monoxide and hydrogen by conversion of mercury oxide to mercury vapor. *Atmos. Technol.* **12**, 40–45.

Smith, K. A., Bremner, J. M. and Tabatabai, M. A. 1973. Sorption of gaseous atmospheric pollutants by soils. *Soil Sci.* **116**, 313–319.

Spratt, H. G. and Hubbard, J. S. 1981. Carbon monoxide metabolism in roadside soils. *Appl. Environ. Microbiol.* **41**, 1192–1201.

Striegl, R. G. 1993. Diffusional limits to the consumption of atmospheric methane by soils. *Chemosphere* **26**, 715–720.

Tarr, M. A., Miller, W. L. and Zepp, R. G. 1995. Direct carbon monoxide photoproduction from plant matter. *J. Geophys. Res.* **100**, 11,403–11,413.

United States Department of Agriculture, Soil Conservation Service 1994. *Keys to Soil Taxonomy*, 6th edition. Pocahontas, Blacksburg, Virginia.