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Model analysis of the influence of gas diffusivity in soil on CO and H_2 uptake

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ABSTRACT

CO and H_2 uptake by soil was studied as a diffusion process. A diffusion model was used to determine how the surface fluxes (net deposition velocities) were controlled by in-situ microbial uptake rates and soil gas diffusivity calculated from the 3-phase system (solid, liquid, gas) in the soil. Analytical solutions of the diffusion model assuming vertical uniformity of soil properties showed that physical properties such as air-filled porosity and soil gas diffusivity were more important in the uptake process than in the emission process. To incorporate the distribution of in-situ microbial uptake, we used a 2-layer model incorporating "a microbiologically inactive layer and an active layer" as suggested from experimental results. By numerical simulation using the 2-layer model, we estimated the effect of several factors on deposition velocities. The variations in soil gas diffusivity due to physical properties, i.e., soil moisture and air-filled porosity, as well as to the depth of the inactive layer and in-situ microbial uptake, were found to be important in controlling deposition velocities. This result shows that the diffusion process in soil is critically important for CO and H_2 uptake by soil, at least in soils with higher in-situ uptake rates and/or with large variation in soil moisture. Similar uptake rates and the difference in deposition velocity between CO and H_2 may be attributable to differences in CO and H_2 molecular diffusivity. The inactive layer is resistant to diffusion and creates uptake limits in CO and H_2 by soil. The coupling of high temperature and a thick inactive layer, common in arid soils, markedly lowers net CO deposition velocity. The temperature for maximum uptake of CO changes with depth of the inactive layer.

1. Introduction

Carbon monoxide (CO) is a significant atmospheric pollutant and contributes to the formation of tropospheric ozone (Fishman and Crutzen, 1978). The background concentration of atmospheric hydrogen (CO) is about 150 ppbv in the northern and 50 ppbv in the southern hemisphere (Khalil and Rasmussen, 1994; Novelli et al., 1998). Global emission of CO is mainly attributed to biomass burning and anthropogenic sources such as automobile exhausts and production from methane and non-methane hydrocarbons by photochemical reaction in the atmosphere. In global inventories of CO, the biosphere acts both as a source and a sink (Seiler and Conrad, 1987; Khalil and Rasmussen, 1990). However, a large uncertainty exists in most estimates and in the mechanisms involved. Vegetation has been identified as a source of atmospheric CO (Seiler et al., 1978; Tarr et al., 1995). Soil acts as a net sink of CO at the global level (Seiler and Conrad, 1987; Potter et al., 1996). Bender and Conrad (1994) showed that CO is oxidized by various microorganisms, such as carboxydotrophs, methanotrophs, and nitrifiers. Conrad (1988) and Bender and Conrad (1994) mentioned that *Nitrosomonas*

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species are the actual oxidizers of CO at atmospheric concentrations.

The background concentration of atmospheric hydrogen (H_2) is 500–550 ppbv on average (Ehhalt et al., 1977; Schmidt, 1978; Novelli et al., 1999). Global emission of H_2 is mainly attributed to sources similar to those of CO (Conrad and Seiler, 1980a; Seiler and Conrad, 1987). Soil is considered to be the major sink of H_2 apart from its reaction with OH radicals in the atmosphere. Assessing the strength of the H_2 soil sink is important for estimating the balance of H_2 in the atmosphere. H_2 consumption by soil was thought to be due to extracellular enzymes in soil (Conrad et al., 1983).

In general, gases are absorbed by or emitted from soil depending on the net balance of its production and uptake in soil. Production obeys zero-order kinetics. Uptake obeys first-order kinetics. The compensation concentration of the gas in soil, C_{equiv}, is determined from the balance between in-situ uptake rate on a spatial basis $u_{\text{in situ}}$ (s^{-1}), in-situ production rate on a spatial basis $P_{\text{in situ}}$ (s^{-1}), and volume of gas per unit volume of soil (air-filled porosity) V_a, as follows:

$$C_{\text{equiv}} = \frac{P_{\text{in situ}}}{V_a u_{\text{in situ}}} \tag{1}$$

If $C_{\text{equiv}} > C_{\text{atmos}}$ (atmospheric concentration), the gas is emitted from soil; if $C_{\text{equiv}} < C_{\text{atmos}}$, the gas is absorbed by soil.

In case of CO, production is thought to be due to abiological production from organic matter (Conrad and Seiler, 1985b; Moxley and Smith, 1998b). The absolute value of the activation energy of CO production is higher than that of the uptake rate. Accordingly, when the temperature is higher, the compensation concentration of CO in soil is higher. In temperate or cool regions, CO is absorbed by soil (Liebl and Seiler, 1976; Conrad and Seiler, 1980b; Zepp et al., 1997; Sanhueza et al., 1998; Moxley and Smith, 1998a; Kuhlbusch et al., 1998; Yonemura et al., 1999). However, during daytime in tropical or arid regions (Conrad and Seiler, 1985a; Scharffe et al., 1990; Sanhueza et al., 1994; Zepp et al., 1996) where surface soil temperature is high and/or carbon content is high, the CO compensation concentration in surface soil becomes higher than the atmospheric concentration and CO is released into the atmosphere

In case of H_2, production is only known in the process of biological nitrogen fixation so far (Conrad and Seiler, 1980a). The compensation concentration of H_2 could be very low and aerated soils always act as sinks of atmospheric H_2.

Potter et al. (1996) estimated the global sink strength of soils for CO uptake by use of a diffusion model. However, the few studies that have focused on the diffusion process of CO and H_2 deposition onto soil have been quite limited, and our understanding of the soil CO and H_2 uptake processes remains poor. H_2 has a higher molecular diffusivity than CO due to the former's lower molecular weight. Knowledge of the difference in molecular diffusivity between CO and H_2 would be useful for understanding the soil uptake processes of these gases. In this paper, we attempt to clarify how the surface fluxes (net deposition velocity) are controlled by in situ microbial uptake rate and soil gas diffusivity calculated from the 3-phase system (solid, liquid, gas) in the soil.

2. Methods

2.1. Diffusion model

To understand the diffusion aspects of CO and H_2 uptake by soil, we used a diffusion equation with production and uptake terms on the assumption that mainly the molecular diffusion process drives the transport of CO and H_2 in soil. Fick's Law and the mass balance of gas per unit volume of soil are expressed as follows:

$$F = D_s \frac{\partial C_M}{\partial z}, \tag{2}$$

$$\frac{\partial C_M}{\partial t} = \frac{\partial}{\partial z}\left(D_s \frac{\partial C_M}{\partial z}\right) + \rho P_{\text{in situ}} - u_{\text{in situ}} C_M, \tag{3}$$

where F is the flux of the gas (ng cm^{-2} s^{-1}), ρ is the density of the pure gas (g cm^{-3}), C_M is the concentration as mass per unit volume of soil (g cm^{-3}), z is the soil depth (cm), and D_s is soil gas diffusivity (cm^2 s^{-1}). Note that z increases downwards whereas F is positive for upward fluxes. C_M is related to the concentration of air in the soil, C (ppbv), as follows:

$$C_M = \rho V_a C. \tag{4}$$

We assume vertical uniformity of D_s, ρ, and V_a. Fick's law and the mass balance equation are then

rewritten using C as follows:

$$F = \rho V_a D_s \frac{\partial C}{\partial z}, \tag{5}$$

$$\frac{\partial C}{\partial t} = \frac{D_s}{V_a}\frac{\partial^2 C}{\partial z^2} + \frac{P_{\text{in situ}}}{V_a} - u_{\text{in situ}} C. \tag{6}$$

The uptake term ($u_{\text{in situ}} C$) reflects microbial uptake and is first order; the production term ($P_{\text{in situ}}/V_a$) reflects abiological production of CO and is zero order, which is supported by previous studies (Conrad and Seiler, 1985a, b). The $u_{\text{in situ}}$ and $P_{\text{in situ}}$ are given by:

$$1 = V_s + V_a + V_l, \tag{7}$$

$$u_{\text{in situ}} = d_P V_s u_s, \tag{8}$$

$$P_{\text{in situ}} = d_P V_s P_s, \tag{9}$$

where d_p is the particle density of the soil (set at 2.67 g cm^{-3}), V_s ($m^3\ m^{-3}$) is the ratio of solids on a volume basis, V_l ($m^3\ m^{-3}$) is the ratio of liquids (water) on a volume basis, u_s ($cm^3\ g^{-1}\ s^{-1}$), and P_s ($cm^3\ g^{-1}\ s^{-1}$) are the in-situ uptake rate and the in-situ production rate, respectively, on the basis of mass of dry soil.

Soil gas diffusivity, D_s, was treated in terms of the 3-phase system (solid, liquid, and gas) of soil in view of previous gas diffusion studies (Millington and Quirk, 1961; Sallam et al., 1984).

$$D_s = D_A V_a^{3.1} (V_a + V_l)^{-2}, \tag{10}$$

$$D_A = D_0 \frac{1013.25}{P_{\text{atmos}}} \left(\frac{T + 273.15}{273.15}\right)^{\gamma}, \tag{11}$$

where D_A is molecular diffusivity ($cm^2\ s^{-1}$), P_{atmos} is the atmospheric pressure, set at 1013.25 hPa, and T is soil temperature (°C). Eq. (10) shows that decreases in air-filled porosity by water decrease diffusion more than do decreases in air-filled porosity by solids. CO and H_2 molecular diffusion constants, D_0 and γ (Table 1), were fitted from the data of Marrero and Mason (1972).

Surface net deposition velocity, v_{nd}, and gross deposition velocity, v_{gd}, are obtained by

$$v_{nd} = -\frac{F_0}{\rho C_{\text{atmos}}}, \tag{12}$$

$$v_{gd} = -\frac{F_0}{\rho (C_{\text{atmos}} - C_{\text{equiv}})}, \tag{13}$$

where F_0 (ng $cm^{-2}\ s^{-1}$) is the flux at the soil surface.

Table 1. *Molecular diffusion coefficients of CO and H_2*

Molecule	D_0 ($cm^2\ s^{-1}$)	γ
CO	0.186	1.70
H_2	0.611	1.75

The coefficients were fitted using an exponential relationship; the data are from Marrero and Mason (1972).

Based on eq. (6), we obtained analytical solutions assuming vertical uniformity of soil properties and using a differential equation for numerical simulation. Although Ball et al. (1997a) reported that D_s and V_a have the tendency to be smaller with soil depth, this assumption is enough to describe the essential understanding of CO and H_2 uptake process by soil using a simulation model. The soil layer was divided in 1-mm units to 1000 mm depth. The time step was set at 0.01 s. The ratio of solids on a volume basis, V_s, was set at 0.2, which corresponds to the case of a well-cultivated field and reflects a state of near surface soil. Atmospheric concentrations of CO and H_2 in the top layer of soil, as the upper boundary condition, were set to be 200 and 550 ppbv, respectively, throughout this study. These concentrations are in the typical range of the boundary layer in the northern hemisphere. We assumed that there would be no transport to soil deeper than the bottom (1000 mm). Iterative calculations were conducted until the soil concentration profile converged to a steady state.

We made a 2-layer model for the simple description of CO and H_2 uptake profiles that reflected the distribution of in-situ uptake rates (Fig. 1). The upper layer cannot absorb CO or H_2, but can produce CO because CO production is an abiological process; we hereinafter call this upper layer the inactive layer. The lower layer can uptake CO and H_2 and produce CO; we call this the active layer. We define d_i (cm) as the depth of the inactive layer.

We summarized abbreviations for some variables in Table 2.

2.2. *Analytical solutions for a mono-layered model*

To understand the basic difference between the uptake and emission processes by soil, we considered the steady state of eq. (6), assuming vertical

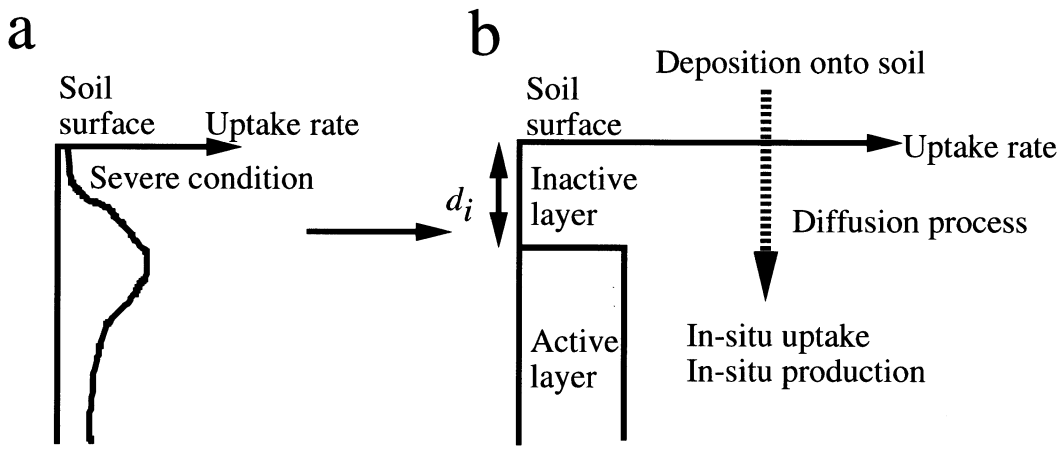

Fig. 1. Simplification of the uptake profile in soil from (a) a real image to (b) the 2-layer model. The variable d_i is the depth of the inactive layer and is considered to be an index of the distribution of in-situ uptake rates.

Table 2. *Abbreviations for variables*

Variable	Unit	Meaning
C_M	g cm^{-3}	the concentration of the gas per mass per unit volume of soil
C	ppbv	the concentration of the gas in gas phase
C_{atmos}	ppbv	atmospheric concentration of the gas
C_{equiv}	ppbv	equilibrium (compensation) concentration of the gas
V_a		volume of gas per unit volume of soil (air-filled porosity)
V_s		volume of solids per unit volume of soil
V_l		volume of liquids (water) per unit volume of soil
d_p	g cm^{-3}	soil particle density
D_A	cm^2 s^{-1}	molecular diffusivity
D_s	cm^2 s^{-1}	diffusivity in soil driven by molecular diffusion (diffusion in soil is assumed to be driven by molecular diffusion)
u_s	cm^3 s^{-1} g^{-1}	in situ (microbial) uptake rate in soil based on unit mass of soil
P_s	cm^3 s^{-1} g^{-1}	in situ (abiological) production rate in soil based on unit mass of soil
$u_{in\ situ}$	s^{-1}	in situ (microbial) uptake rate in soil based on space
$P_{in\ situ}$	s^{-1}	in situ (abiological) production rate in soil based on space
v_n	cm s^{-1}	net deposition velocity at the soil surface
v_d	cm s^{-1}	(net) deposition velocity at the soil surface (in this study $v_d = v_{nd}$)
v_g	cm s^{-1}	gross deposition velocity at the soil surface
F	ng cm^{-2} s^{-1}	the flux of the gas
F_0	ng cm^{-2} s^{-1}	the flux of the gas at soil surface
d_i	cm	the depth of inactive layer

uniformity of soil properties. If the gas concentrations are controlled only by diffusion and production processes, eq. (6) can be written as:

$$\frac{D_s}{V_a}\frac{\partial^2 C}{\partial z^2} + \frac{P_{in\ situ}}{V_a} = 0, \tag{14}$$

and eq. (14) can be solved analytically. We define the thickness of the production layer as d (cm):

$$C = C_{atmos} + \frac{2P_{in\ situ}}{D_s d} z - \frac{P_{in\ situ}}{D_s} z^2, \tag{15}$$

$$F = \rho P_{in\ situ} d. \tag{16}$$

This formulation shows that the flux values cannot

be changed by physical properties of soil such as the soil gas diffusivity D_s or air-filled porosity V_a, although the gas concentration increases with soil depth (from the surface) and is high when soil gas diffusivity is low.

If the gas is absorbed by soil, eq. (6) can be written as:

$$\frac{D_s}{V_a}\frac{\partial^2 C}{\partial z^2} - u_{\text{in situ}}C + \frac{P_{\text{in situ}}}{V_a} = 0. \quad (17)$$

This can be also solved analytically as:

$$C = (C_{\text{atmos}} - C_{\text{equiv}}) \exp\left(- \sqrt{\frac{V_a u_{\text{in situ}}}{D_s}}\, z \right) + C_{\text{equiv}}, \quad (18)$$

$$F = -(C_{\text{atmos}} - C_{\text{equiv}})\sqrt{V_a D_s u_{\text{in situ}}}, \quad (19)$$

$$v_{\text{nd}} = \frac{C_{\text{atmos}} - C_{\text{equiv}}}{C_{\text{atmos}}}\sqrt{V_a D_s u_{\text{in situ}}}, \quad (20)$$

$$v_{\text{gd}} = \sqrt{V_a D_s u_{\text{in situ}}}, \quad (21)$$

where $C_{\text{equiv}} = P_{\text{in situ}}/V_a u_{\text{in situ}}$. Gas concentration decreases exponentially with soil depth from the surface, and deposition velocities increase with the square root of air-filled porosity V_a, soil gas diffusivity D_s, and in-situ soil uptake rate $u_{\text{in situ}}$.

3. Experimental

CO and H_2 in-situ uptake and production rates and their dependence on soil temperature used for the simulations were determined by experiments. Soil samples were taken from the mixture of soil in the plowed layer of an arable field in the National Institute of Agro-Environmental Sciences in Tsukuba (36°01′N,140°07′E), located about 60 km northeast of Tokyo, Japan. The soil type was Andisol Hydric Hapludands (United States Department of Agriculture, Soil Conservation Service 1994) named "Kuroboku" in Japan. It contained volcanic ash topsoil from Mt. Asama, Mt. Fuji, and Mt. Hakone with a pH (H_2O) of about 6.4. Carbon and nitrogen contents in the soil surface were approximately 4.5% dry matter and 0.4% dry matter, respectively. The density of solid particles in the plowed layer, d_p, was 2.67 g cm^{-3}. The distribution of soil particles in the AP1 layer was as follows: clay 55%; silt 26%; fine sand 15%; and coarse sand 4.4%. The soil samples were placed in a box for one week in laboratory conditions at temperatures of 15 to 25°C.

The closed-chamber technique was applied to determine in-situ soil uptake rates of CO and H_2 (Fig. 2). To obtain these rates with no loss from diffusional resistance in the soil, a small amount of wet soil (about 10 g) was thinly spread on the bottom of the chamber. We found that the experiments were free from loss in in-situ uptake rates due to the molecular diffusion resistance in soil sample when we used less than 50 g of sample soil. Gas samples were taken every 3 min for more than 12 min after enclosure. The temperature dependence of uptake rates was measured in triplicate with raising and lowering temperature.

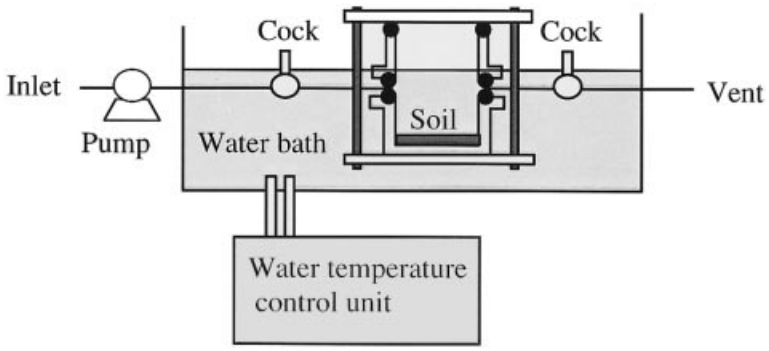

Fig. 2. Schematic diagram of the laboratory experiments. The chamber, of inner volume 695 cm^3, was made of Pyrex® glass and was gas-tight. The gaskets used for the chamber were made of Viton® rings. About 10 g of wet soil were spread on the bottom of the chamber, which was immersed in a temperature-controlled water bath. After the air in the chamber was flushed, soil net uptake rate was measured.

To obtain in-situ CO production rates of soil, we measured compensation CO concentrations equilibrated in the sample field. The surface of the soil was covered with a closed chamber continuously and the gas concentration in the chamber was measured. The measurements were made during 3 to 6 March and 19 to 22 July 1996. Based on the compensation concentrations and the in-situ uptake rates, the dependence of the in-situ production rates on temperature was obtained using eq. (1).

The difference in CO and H_2 uptake between the inactive layer and deeper soil was investigated using the stored soil samples. The water content was measured gravimetrically at the same time. The depth of the inactive layer was less than 1 cm.

CO concentrations in the soil were measured at 0, 1, and 2 cm soil depth by slowly (>1 min) extracting soil gas samples not to disturb the concentration profile using a gas-tight syringe fixed to a pole by a clamp. This extraction of soil gas samples is possible because CO and H_2 reaction is rapid.

CO and H_2 concentrations were analyzed by reduction gas analyzer (RGA3; Trace Analytical, Menlo Park, CA, USA) using the mercuric oxide technique (Seiler et al., 1980). The RGA3 was equipped with a 1 µl sample loop, a pre-cut column Unibeads 1S, and a main column molecular sieve 5A which was set at 105°C. The mercuric oxide bed was maintained at 265°C. Nitrogen was used as the carrier gas. The standard gases contained in aluminum and iron cylinders were 494 ppbv of CO and 537 ppbv of H_2, respectively, with nitrogen balance, and were commercially supplied (Takachiho Chemical Industry Co. LTD., Japan). The standard deviations of CO and H_2 were 1.5 and 4 ppbv for the standard gases, respectively ($n = 8$). The difference between the CO 494-ppbv standard and the NOAA/CMDL scale used by the Meteorological Research Institute of Japan (Matsueda et al., 1998) was less than 5%.

4. Results

4.1. Experimental results

In the laboratory experiments, CO concentrations measured at 0, 1, and 2 cm depth were >150, <50, and <15 ppbv, respectively. The CO and H_2 concentrations in soil decreased exponentially with soil depth. Surface soil (Case A) had smaller uptake rates than deeper dark soils (Case B) (Table 3). Soils in the shallower layer (Case B) had higher uptake rates than did the deeper layer (Case C) (Table 3), although there was little difference in water content between 1.5-cm (Case B) and 5-cm deep soil (Case C).

The dependence of in-situ uptake and production rate on soil temperature, obtained by laboratory experiments, is shown in Fig. 3. Gross in situ uptake rates in function with temperature were obtained by linear regression from the net in situ uptake rates in the lower temperature range ($\leqslant 20$°C for CO and $\leqslant 30$°C for H_2) because

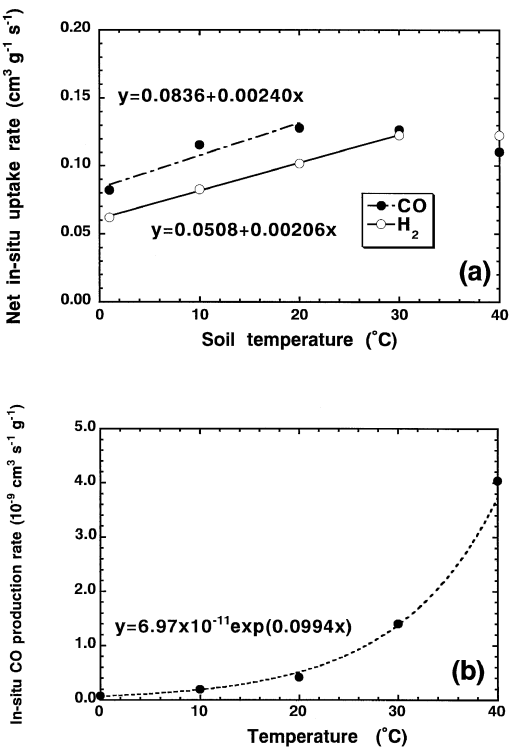

Fig. 3. Temperature dependence of (a) net in-situ uptake rates of CO and H_2 of mixed soil (0–5 cm) from laboratory experiments and (b) in-situ CO production rates calculated using (a) and the CO equilibrium concentration measured by field experiments. The data points in (a) were averages of 3 temperature-dependent curves. The regressions in the lower temperature range were regarded as approximating gross uptake rate curves. The data points in (b) were representative values of continuous measurements at 3-min intervals over several days in two different seasons.

Table 3. *CO and H_2 in situ uptake rates at different depths in the experimental soil*

Case	Net CO uptake rate ($cm^3\ s^{-1}\ g^{-1}$)	Net H_2 uptake rate ($cm^3\ s^{-1}\ g^{-1}$)	Water content mass basis
(A) surface soil (0–1 cm)			
1	0.028	0.12	0.17
2	0.021	0.09	0.21
3	0.003	0.01	0.17
average	0.017	0.07	0.18
(B) soil just below A (about 1.5 cm)			
1	0.143	0.16	0.42
2	0.194	0.19	0.40
3	0.180	0.20	0.40
average	0.172	0.18	0.41
(C) soil at about 5 cm depth			
1	0.042	0.11	0.46
2	0.087	0.11	0.44
3	0.094	0.12	0.45
average	0.074	0.11	0.45

In A, there was a low net uptake rate due to water stress. In B, there was a higher net uptake rate for both CO and H_2 than in C. This may be due to the CO (and H_2) fertilization effect (Smith et al., 1973; Spratt and Hubbard, 1981; Bender and Conrad, 1994).

relatively low production rates were expected at these temperatures (Fig. 3a). The calculated activation energies based on the Ahhrenius equation were -6.78 and $-6.95\ kJ\ mol^{-1}$ for CO ($\leqslant 20°C$) and H_2 ($\leqslant 30°C$), respectively. These values were in reasonable accordance with those of Conrad and Seiler (1985a). The CO in-situ production rate (Fig. 3b) was given by the combination of the gross CO in-situ uptake rate and the equivalent CO concentration value obtained from the closed chamber, using eq. (1). The activation energy of CO production was $65.3\ kJ\ mol^{-1}$, also in reasonable accordance with those of Conrad and Seiler (1985a, b) and Conrad (1988), taking into account the pH value.

4.2. *Calculations using experimental in-situ uptake and production rates.*

Fig. 4 shows the changes in net deposition velocity, which we call hereinafter simply v_d, with changes in air-filled porosity (i.e., soil gas diffusivity) and depth in the inactive layer, using in-situ uptake and production rates obtained experimentally. The increase in deposition velocity due to the increase in air-filled porosity is more nearly exponential than linear because the thickness of the uptake layer extended to deeper soil. The relationship is consistent with field measurements (Yonemura et al., 1999) and confirms the validity of our model's application to CO and H_2 uptake by soil. In Fig. 4, when $d_i = 0.2$ cm and $V_a = 0.6$, the v_d was lowered by about 14%, and when $d_i = 0.5$ cm and $V_a = 0.6$, the decrease was 29%. The effect of the inactive layer was stronger for CO than for H_2.

The v_d response to temperature at intervals of 5°C was investigated using the in-situ uptake and production rates obtained experimentally (Fig. 5). The increase in D_s is shown by the solid line in Fig. 5. The combination of the uptake rates and production rates leads to a maximum v_d for CO because CO uptake and production are first and zero-order reaction, respectively. With increasing d_i, the optimum temperature for CO uptake decreased. Without the inactive layer ($d_i = 0.0$ cm), the temperature that maximized the v_d was about 32°C; when $d_i = 0.5$ cm, the optimum temperature was about 26°C.

The difference between the presence and absence of production in the inactive layer is shown in Fig. 6. In the absence of CO production in the inactive layer, the soil always showed CO uptake. However, at temperatures $>20°C$ and assuming

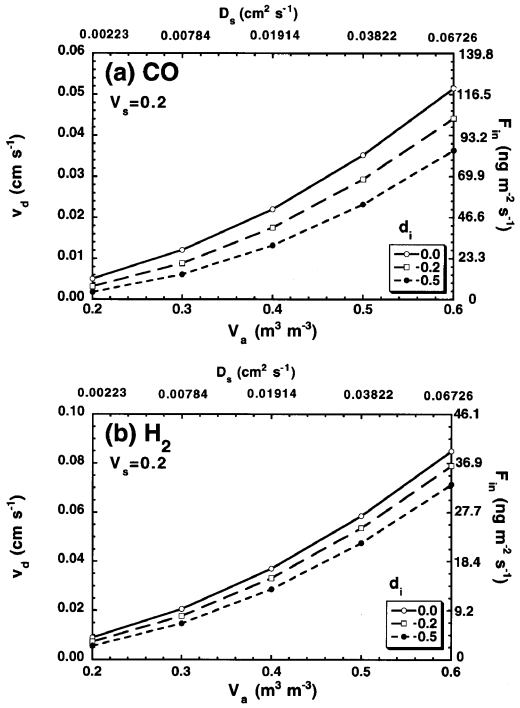

Fig. 4. Influence of air-filled porosity, V_a, on the net deposition velocity, v_d, for (a) CO and (b) H_2. Calculations were made under conditions of $V_s = 0.2$ and $T = 20°C$. Right *Y*-axis means net uptake by soils (ng m^{-2} s^{-1}), defined by $F_{in} = -10\,000F_0$.

5 cm of d_i, the soil was a net source of CO, and when $d_i \geqslant 2.0$ cm, as temperature increased, the v_d decreased. The maximum CO concentration was shown when CO was emitted from the soil surface (Fig. 7). Under this condition, CO produced in the inactive layer was transported upward to the atmosphere and downward to the lower active soil layer.

4.3. *Calculations incorporating changes in in-situ uptake rates*

The v_d was calculated without a production term by changing uptake rates of the active layer and with d_i at fixed diffusivity at 20°C (Fig. 8). The calculated v_d values were identical with gross deposition velocities. However, the v_d did not increase in proportion to the in-situ uptake rates, $u_{in\ situ}$, because soil uptake was restricted to the shallower zone when the $u_{in\ situ}$ was high (Fig. 9). In the active layer, gas concentration decreased exponentially with soil depth; in the inactive layer, concentration decreased linearly with soil depth. Under the same $u_{in\ situ}$, H_2 permeated deeper than CO due to the higher molecular diffusivity of H_2.

When $d_i = 0.0$ cm, the slope in Fig. 8 was 0.5, which means that v_d was increasing proportionally with the square root of $u_{in\ situ}$ as shown by eq. (21).

The d_i reduced v_d at higher $u_{in\ situ}$, when the curve approached a convergence value depending on the value of d_i.

When $u_{in\ situ}$ of CO was doubled from 0.1 s^{-1} to 0.2 s^{-1}, the increases in deposition velocities v_d were 41.4 and 22.9% for $d_i = 0.0$ and 0.5 cm, respectively; when $u_{in\ situ}$ of H_2 was doubled from 0.1 s^{-1} to 0.2 s^{-1}, the increases were 41.4 and 28.7% for $d_i = 0.0$ and 0.5 cm, respectively. The resistance to diffusion from the atmosphere to the active layer through the inactive layer was stronger for CO than for H_2, because H_2 has greater soil gas diffusivity, 0.126 cm^2 s^{-1}, than does CO, 0.0382 cm^2 s^{-1}.

4.4. *Analysis of the contribution of the various factors affecting CO and H_2 uptake by soil*

The effects of such factors as soil temperature, air-filled porosity V_a, and the depth of the inactive layer d_i, on deposition velocity v_d, are summarized in Table 4. The value of the contribution of each factor was obtained around the point where the ratio of solids in volume $V_s = 0.2$, $V_a = 0.4$, and $u_{in\ situ} = 0.2$ s^{-1}. The strength of deposition velocity dependence on each factor, within their ranges assumed in Table 4, was strongest in V_a. These trends are consistent with results of field measurement of Yonemura et al. (1999).

5. Discussion

5.1. *Diffusion control of CO and H_2 uptake by soil*

The analytical solutions (eqs. (20) and (21)) show that soil physical properties such as air-filled porosity V_a and soil gas diffusivity D_s are intrinsically more important for the uptake process than for the emission process. The numerical results show that the inactive layer causes resistance to diffusion from the atmosphere to the active layer and thus limits CO and H_2 uptake by soil in the higher range of $u_{in\ situ}$ (Fig. 8). The vertical distri-

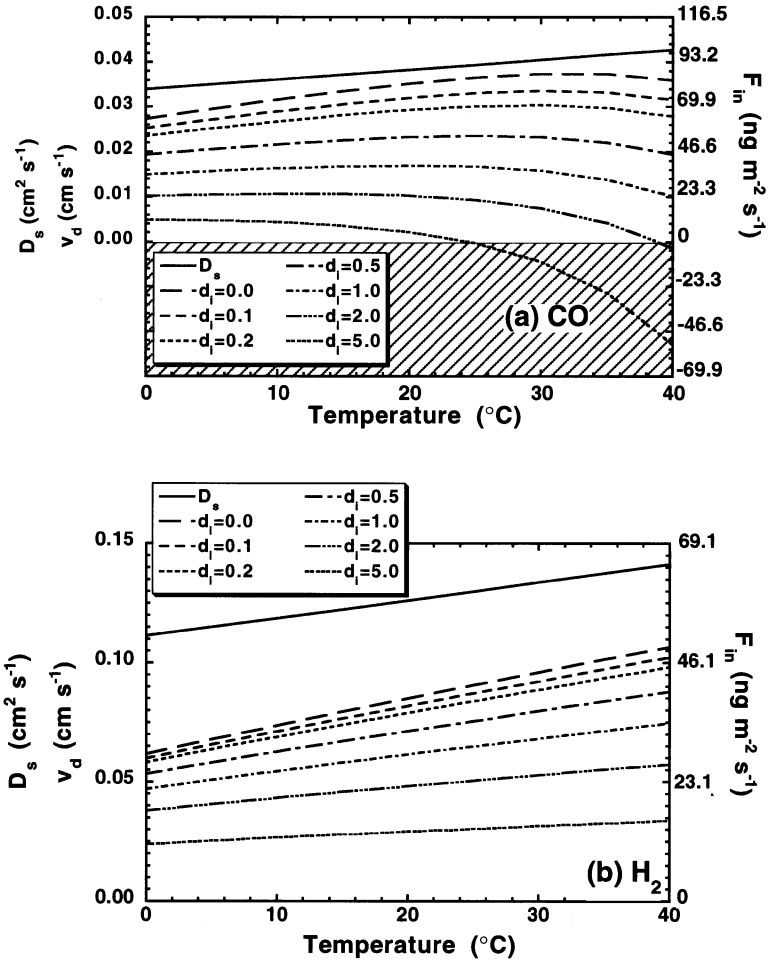

Fig. 5. Temperature dependence of v_d calculated for the experimental soil for (a) CO and (b) H_2. Solid lines are curves of soil gas diffusivity. CO is emitted from soil in the shaded area. Calculations were made under conditions of $V_s = 0.2$ and $V_a = 0.5$. For CO, the optimum temperature to maximize the v_d varied with d_i.

bution of uptake rates in near-surface (mm scale) soil is very important in controlling CO and H_2 deposition onto soil. This is analogous to diffusion resistance of the leaf layer in temperate forests, where net CO deposition is accelerated by clearing this layer (Sanhueza et al., 1998).

Our simulation results (Figs. 8, 9) show that soil gas diffusivity is very important in control of deposition velocities; properties of the soil in the top few millimeters below the surface are very important. Our simulation results (Table 4) also show that gas diffusion is the major factor controlling CO and H_2 uptake in the arable field that we sampled in the temperate climate of Japan, where high uptake rates were observed. This result is also consistent with field measurements (Yonemura et al., 1999). Both CO and H_2 deposition velocities increased as air-filled porosity and soil gas diffusivity became higher because the soil became drier. However, this increase could be suppressed by the inactive layer, which is thought to deepen due to water stress under dry conditions. Thus, diffusion is the rate-determining process for CO and H_2 uptake by soil when $u_{\text{in situ}}$ are large.

Estimation of the range of $u_{\text{in situ}}$ is needed to determine which factor controls deposition velocit-

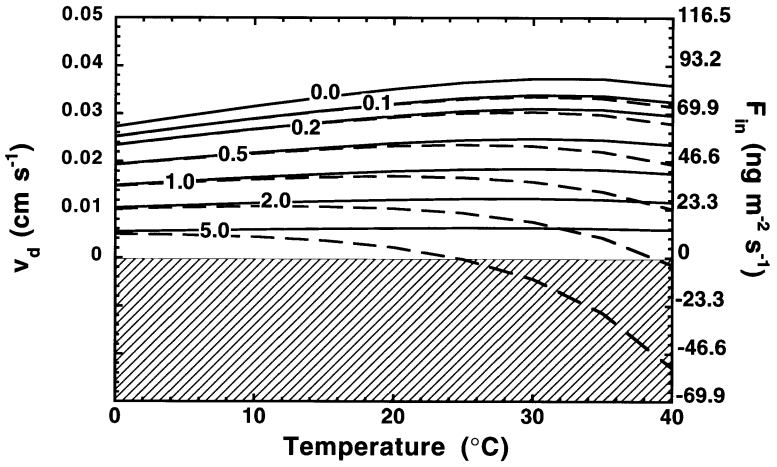

Fig. 6. Impact of the CO source in the inactive layer on v_d. Numerals on lines are depths of the inactive layer d_i. Solid lines represent calculations assuming no production in the inactive layer; wavy lines show production taking into account the inactive layer. CO is emitted from soil in the shaded area. Calculations were made under conditions of $V_s = 0.2$ and $V_a = 0.6$.

ies: D_s or $u_{in\ situ}$. Moxley and Smith (1998a) measured the initial CO utilization rates of samples of Scottish soils. If we regard the initial utilization rates in Table 2 of Moxley and Smith (1998a) as being the same as $u_{in\ situ}$, the range of their data corresponds to approximately 0.0036 to 0.038 s^{-1} for 41 sites, apart from the lowest rates of 2 sites. These $u_{in\ situ}$ are lower than those of our experiments. If this range of values from Moxley and Smith (1998a) is applied to Fig. 8, the uptake rates are roughly proportional to the square-root of deposition velocities (eqs. (20) and (21)), and the deposition velocity varied by a factor of <3.3. This range of deposition velocities at various sites is roughly comparable to the changes expected due to the variation in air-filled porosity (Table 4).

5.2. *Factors affecting CO and H_2 uptake by soil*

In situ uptake reflects the activity of microorganisms/enzymes in oxidizing CO/H_2, a process that is influenced in a complex manner by various environmental factors such as soil moisture, soil temperature, carbon and nitrogen content, oxygen concentration, and CO concentration.

Among the environmental factors, Moxley and Smith (1998a) found good correlation between deposition velocities and total organic carbon in Scottish soils. However, high carbon content, as in forest floor soils, not only enhances in-situ CO uptake rate, it also results in exponentially increasing production of CO with increasing soil temperature. Correlation of in-situ CO uptake rate with carbon content is often masked by production, especially at higher temperatures.

Soil temperature is a basic and very important factor that influences all other factors that affect deposition velocity. Our simulation results (Figs. 5 and 6) showed that the optimum temperature to maximize v_d depended not only on the quantitative balance between uptake and production functions but also on d_i (Fig. 5). Thus, the optimum temperature for soil uptake of CO cannot be determined only by the optimum temperature of in-situ soil CO uptake by microorganisms, but also by the distribution of oxidizing activity as denoted by d_i.

Atmospheric concentrations of CO and H_2 influence the v_d and the temperatures that maximize them. Under high atmospheric concentration of CO, eq. (20) shows that the contribution of $C_{equiv,}$, which increases with temperature (Fig. 3b), is lessened and v_d increases toward v_{gd}. As the atmospheric CO concentration increases, the apparent optimum temperature is lowered because production is a zero-order reaction.

Further, CO enhances CO in-situ uptake itself (Smith et al., 1973; Spratt and Hubbard, 1981;

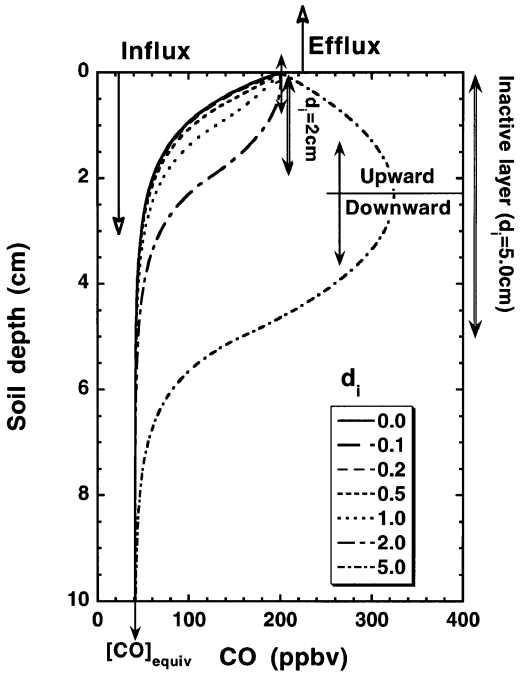

Fig. 7. CO concentration profiles calculated for the experimental soil at 40°C. Calculations were made under conditions of $V_s = 0.2$ and $V_a = 0.5$. When $d_i = 2.0$ and 5.0 cm, CO is transported to the atmosphere and to deeper soil layers from the inactive layer. In conditions of high soil temperature together with a thick d_i, the deposition velocity of CO is markedly lowered or CO is emitted from soil.

Bender and Conrad, 1994), which we call as "fertilization effect". This was observed in the difference not only in CO but also in H_2 uptake rate between cases B and C in Table 3, although the soil moisture content was similar. This effect may cause higher uptake rates in surface soil. Because the response time of this fertilization effect may be as fast as a week, under conditions of high soil gas diffusivity accompanied by low soil moisture, the v_d could be enhanced by this effect. The fertilization effect could also lead to a greater diffusional control of CO and H_2 uptake by soil.

Heichel (1973) and Moxley and Smith (1998a) reported that there is an optimum water content for CO oxidation. Both higher and lower moisture may reduce the in-situ uptake rates. Soil moisture is very important for controlling in-situ uptake rates because water is essential for microbial growth. Under low soil moisture as in desert or arid soils, the presence of the inactive layer was considered to be crucially important, as is also shown in case A in Table 3. When soil temperature in arid soils during daytime was high, net emission was observed (Conrad and Seiler, 1985a; Sanhueza et al., 1994). In these soils, the inactive layer is possibly thick due to the decrease in microbial activity resulting from water and thermal stresses. Furthermore, Moxley and Smith (1998b) showed that CO production is enhanced under very dry conditions. Previous studies (Conrad and Seiler, 1985a; Scharffe et al., 1990) mentioned that moisture supply activated CO uptake in arid soil, which suggests the presence of a thick d_i. The combination of a thick d_i and high temperature could crucially reduce net CO deposition onto soil (Fig. 7).

5.3. *Relationship between deposition velocities of different gas species*

Trace gases known to be absorbed by soil in addition to CO and H_2 are sulfur dioxide, nitrous oxide, nitrogen oxide, ammonia, and methane. Unlike CO, H_2 and methane, which are utilized biologically, the sulfur and nitrogen compounds have high deposition velocities, >0.1 cm s^{-1}, onto soil due to the physical process of dry deposition (McMahon and Denison, 1979). Biological deposition of gases other than CO and H_2 on soil might be limited, i.e., <0.1 cm s^{-1} (Fig. 8), if d_i is <0.2 cm.

In the case of methane, Dörr et al. (1993) and Ball et al. (1997a, b) concluded, from records of the methane uptake by differently aerated soils in Europe, that methane consumption in aerated soils is mainly influenced by the gas transport properties of sub-surface soil. Long-term CO- and H_2-uptake measurements and mechanical core studies at various sites are needed in order to determine the applicability of this finding to the process of CO and H_2 uptake by soil.

Our experimental results show that CO in-situ uptake rates were similar to those of H_2 (Fig. 3, Table 3), which may be attributed to their solubility in a matrix of microorganisms or enzymes as mentioned by Conrad (1988); water solubility of CO and H_2 is 0.023 and 0.018 on a volumetric basis at 20°C, respectively (National Astronomical Observatory, 1994). The ratio of H_2 deposition velocities to those of CO is in the range 1.54 to

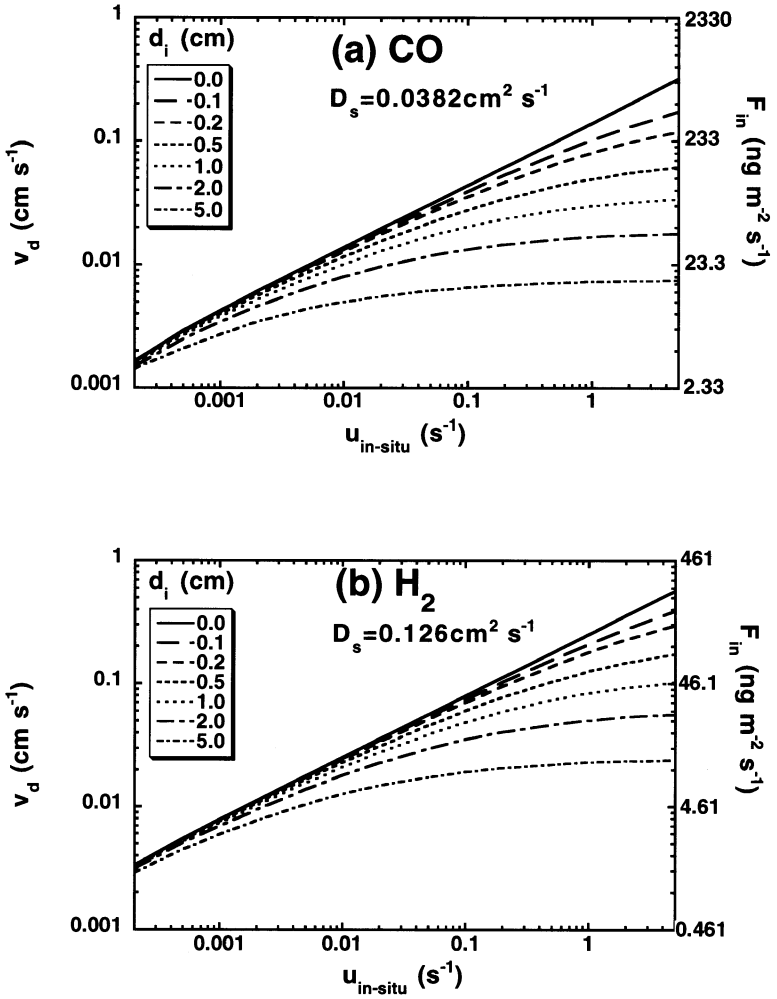

Fig. 8. Relationship between in-situ uptake rate $u_{\text{in situ}}$, and v_d for (a) CO and (b) H_2. Calculations were made under conditions of $T = 20°C$, $V_s = 0.2$, $V_a = 0.5$, and with no CO production in the soil. Flux values to the right of the graph were those at STP and $T = 20°C$. D_s is the soil gas diffusivity.

3.5 for both the present simulation when $d_i =$ 0.0 cm and measurements in soils near Mainz (Liebl and Seiler, 1976). In view of the similarity in CO and H_2 uptake rates, the difference in their deposition velocities may be attributable to the difference in their molecular diffusivity.

6. Conclusions

The CO and H_2 diffusion process in soil, which is connected with in-situ soil uptake and deposition onto soil, was investigated with a diffusion model. Our calculations showed that soil physical properties as soil gas diffusivity and air-filled porosity are a very important factor in the control of deposition velocities; the properties of the near-surface soil are also very important. The difference in deposition velocity between CO and H_2 could be attributed to the difference in their molecular diffusivity because similar uptake rates were observed. The depth of the inactive layer, or the thickness of the microbiologically inactive layer, as well as the in-situ microbial uptake rate of CO

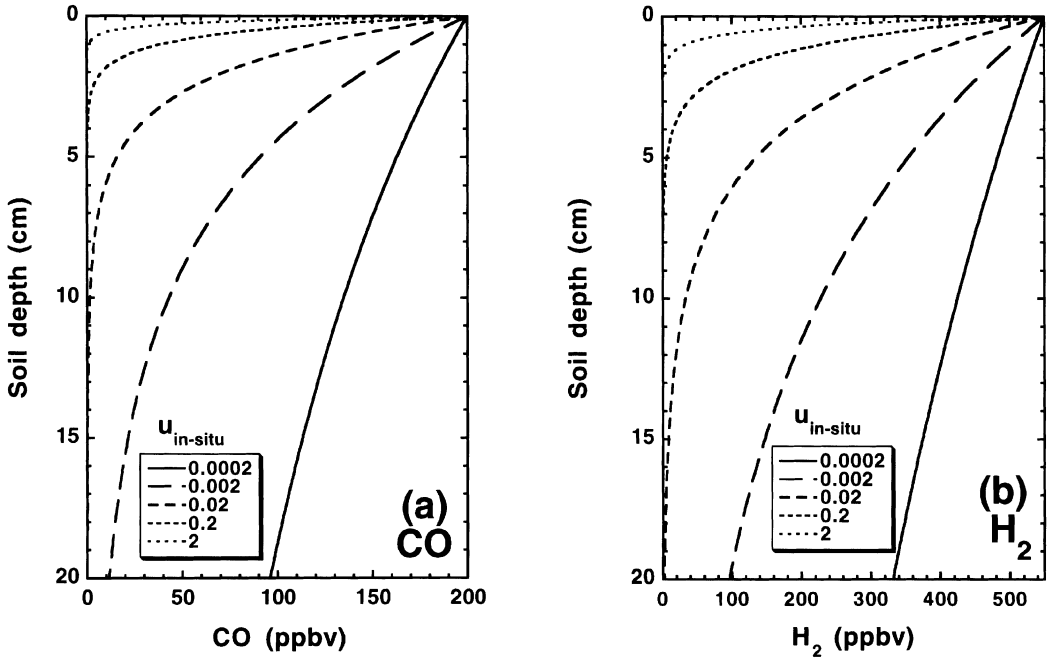

Fig. 9. Concentration profiles of (a) CO and (b) H_2 from Fig. 8. Values in the insets are in-situ uptake rates. As the in situ uptake rate increases, the depth of the oxidation layer becomes shallower. H_2 can permeate deeper than CO due to its higher molecular diffusivity.

Table 4. *Effects of soil temperature, air-filled porosity V_a, and the depth of inactive layer d_i on v_d*

Condition	Control factor	Range		Intermediate control factor	Changes in v_d (cm s^{-1})	Ratio in v_d
no CO production in soil	temperature	0–40°C		u_s (cm^3 s^{-1} g^{-1})		
			CO	0.8–0.18	0.0160–0.0234	1.47
			H_2	0.5–0.13	0.0247–0.0380	1.54
				D_s (cm^2 s^{-1})		
			CO	0.0170–0.0214	0.0189–0.0212	1.12
			H_2	0.0558–0.0708	0.0301–0.0340	1.13
				D_s (cm^2 s^{-1})		
	V_a	0.2–0.6	CO	0.00223–0.0673	0.0069–0.0376	5.46
	(air filled porosity)		H_2	0.00736–0.222	0.0110–0.0601	5.49
	d_i	0.0–1.0 cm	CO		0.0201–0.0098	0.49
	(the inactive layer)		H_2		0.0321–0.0213	0.66
CO production in soil	coupling of temp. and d_i					
	$d_i = 0.0$ cm	0–40°C	CO		0.0172–0.0212	1.23
	$d_i = 1.0$ cm	0–40°C	CO		0.0084–0.0020	0.24

The calculations were based on the experimental soil at $T = 20$°C, $V_a = 0.4$, and $d_i = 0.0$ cm. For example, when the temperature changed from 0 to 40°C, the in-situ microbial uptake rate of CO ranged from 0.8 to 0.18 cm^3 g^{-1} s^{-1} and the surface deposition velocity of CO increased by 47%. In the absence of production in soil, and within the range of controlling factors, their relative impact on deposition velocities was in the order air-filled porosity $V_a > d_i > u_{in\ situ}(u_s)$ change due to temperature change > molecular diffusivity change due to temperature change. When there was no CO production in the soil, the controlling factors acted in a similar manner on both CO and H_2. In the presence of CO production in the soil, the coupling effect of d_i and temperature-induced high production caused a large decrease in v_d.

and H_2, could be important factors in CO and H_2 consumption by soil, especially by arid soils. The presence of an inactive layer results in limited soil uptake of CO and H_2.

CO and H_2 uptake by soil, and their in-situ uptake rates and distribution, are controlled by environmental factors mentioned earlier that influence the microbial oxidizers of CO and H_2. However, there are few reports on this topic to date. The factors that control deposition velocities are thought to be different in different land-use types, soil types and climates, and further extensive investigations are therefore needed.

The 2-layered model that we proposed was found to be useful to depict the features of CO and H_2 fluxes in soil that have been reported in previous works. However, the model is tentative at this stage and there are many aspects needing improvement; in particular, the water transport process in near-surface soil should be incorporated into the model. Also, note that gas exchange in near-surface soil may be driven not only by molecular diffusion but also by the mixing due to wind (Ishihara et al., 1992).

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