Systematic formulation of equations for trace-gas uptake by soil

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Abstract

We systematically and explicitly derived equations to estimate trace-gas uptake by soil using closed-chamber and flow-through-chamber techniques. We began from fundamental equations and reasonable assumptions, such as first-order kinetics and constant gas concentration in chambers for surface fluxes and laboratory bulk-soil experiments (emission and uptake). The important variables are deposition velocity, uptake rate in volume per unit mass of soil, and (relative) uptake rate in volume per unit of soil volume. Units of the uptake rate in volume per unit mass of soil and the (relative) uptake rate in volume per unit of soil volume are m³ kg⁻¹ s⁻¹ and s⁻¹ in MKS, respectively. We discuss the concept of deposition velocity with those of destruction velocity and uptake velocity. We also mention the relatively well-conserved mass balance of surface-soil chamber measurements of trace gas uptake.

Key words: Chamber, Deposition velocity, Field, Laboratory uptake rate.

1. Introduction

Because of current global-warming concerns, fluxes of trace gases in ecosystems have been studied intensively. Ecosystems have two important components: soil and plants. The exchange of trace gases between the soil and the atmosphere is measured by various techniques, such as micrometeorological, chamber, and diffusion techniques (see, for example, Matson and Harriss, 1995).

Chamber techniques, which are also called “enclosure-based measurements” (Hutchinson and Livingston, 1993; Matson and Harriss, 1995), include several sub-categories of techniques. The closed-chamber technique (see, for example, Nishimura et al., 2005; Rochette and Eriksen-Hamel, 2008) is also known as the static-chamber technique or nonsteady-state-chamber technique; in this technique, a volume of surface or bulk soil is enclosed and the gas-concentration fluctuations within this enclosed volume are measured, permitting emission or uptake rates to be calculated. In the flow-through-chamber technique, also called the open-through-chamber technique or dynamic-chamber technique, a volume of surface or bulk soil is again enclosed; however, in contrast to the previous technique, the volume is ventilated continuously by outside air. Gas concentrations are measured in the air entering and exiting the enclosed volume, and emission or uptake rates are thereby calculated. Measurements of gas exchange in surface soil are also done by collecting soil from fields, conditioning it, then incubating it in the laboratory, where the gas exchange is measured (see, e.g., Fang and Moncrieff, 2001; Tortoso and Hutchinson, 1990; Chen et al., 2010).

Direct and indirect greenhouse gases such as methane (CH₄), molecular hydrogen (H₂) (see Ehhalt and Rohrer, 2011), carbon monoxide (CO) (see Conrad, 1996; Yonemura et al., 2000a, b), and isoprene (C₅H₈) (see Cleveland and Yavitt, 1997), and gases important in the stratosphere such as methyl bromide (CH₃Br) (see Heines et al., 1998; Rhew et al., 2010), carbon disulfide (CS₂) (see Steinbacher et al., 2004), and carbonyl sulfide (OCS) (see, for example, Van Diest and Kesselmeier, 2008; Liu et al., 2010) are consumed biologically by soil. Each study used only

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equations to derive the magnitude of soil gas uptake. However, systematic formulations to derive the magnitude of soil gas uptake have not been done thus far. Here, we explicitly formulate equations describing soil gas uptake for the closed-chamber and flow-through-chamber techniques and for field and laboratory situations. Furthermore, the approximate deposition velocities of these gases, with the addition of pollutants, are summarized in Fig. 1.

**2. Basic equations**

The numerous variables appearing in this article are listed in Table 1. Two basic principles (the equation of state and the mass-balance equation) and two assumptions (first-order uptake kinetics and uniform chamber concentration) are used in the following derivations (Fig. 2).

The equation of state for an ideal gas is

\[ PV = nRT. \]  

The equation of state for the relevant gas is

\[ P_cV = n_cRT. \]  

Using Eq. (2.2), the concentration \( C \), and mixing ratio \( r \) (i.e., relative gas concentration) of the relevant gas are expressed as

\[ C = \frac{n_c}{V} = \frac{P_c}{RT}, \]  

\[ r = \frac{n_c}{n} = \frac{P_c}{P}. \]  

where the relevant gas was assumed to be an ideal gas. From Eqs. (2.3) and (2.4) \( C \) is obtained from \( r \) as follows:

\[ C = \frac{P_c}{RT} = \frac{rP}{RT}. \]  

For a flow-through chamber, mass balance with ventilation is expressed as

\[ \frac{dn_c}{dt} = S + f_{IN}C_{IN} - f_{OUT}C_{OUT}, \]  

where \( n_c \) is the amount of the relevant gas in the chamber and \( S \) is the soil source (or sink) term. The quantities \( f_{IN}, f_{OUT}, C_{IN}, \) and \( C_{OUT} \) are, respectively, the flow rates and concentrations of ventilations into and out of the chamber. From Eq. (2.6) \( S \) may be expressed as

\[ S = \frac{dn_c}{dt} = f_{IN}C_{IN} + f_{OUT}C_{OUT}. \]  

For the closed-chamber technique, \( f_{IN} = f_{OUT} = 0 \), in which case we have

\[ S = \frac{dn_c}{dt}. \]  

For the flow-through-chamber technique, normal measurements set \( f_{IN} = f_{OUT} \equiv f \) and assume the steady state \( (dn_c/ dt = 0) \):

\[ S = f(C_{OUT} \cdot C_{IN}). \]  

Furthermore, in the mass balances of the relevant gas

Fig. 1. Soil-gas deposition velocities.
(Eq. 2.8, Eq. 2.9), mixing ratios are usually used instead of concentrations. Assuming that the gas pressure and volume in the chamber are constant, we incorporate Eq. (2.5) into Eq. (2.8) and Eq. (2.9)

\[ S = \frac{dn_c}{dt} = \frac{PV}{RT} \frac{dr}{dt} \]  \hspace{1cm} (2.10)

where \( \frac{dr}{dt} \) can be determined from the time-series measurements of mixing ratios:

\[ S = f(C_{OUT} \cdot C_{IN}) = \frac{fP}{RT} \left( r_{OUT} \cdot r_{IN} \right) \]  \hspace{1cm} (2.11)

Based on the equations shown in this section, we shall introduce gas-exchange equations for closed-chamber and flow-through-chamber systems for both surface-soil experiments in the field and bulk-soil experiments in the laboratory.

The following two assumptions, which are widely

**Table 1.** Constant, variables, and parameters Most important obtained variables are stressed as bold characters.

<table>
<thead>
<tr>
<th>name</th>
<th>unit</th>
<th>meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R )</td>
<td>8.31 J K(^{-1}) mol(^{-1})</td>
<td>gas constant</td>
</tr>
<tr>
<td>Basic variables</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( t )</td>
<td>s</td>
<td>time</td>
</tr>
<tr>
<td>( P )</td>
<td>Pa</td>
<td>Pressure of air in chamber (=atmospheric pressure)</td>
</tr>
<tr>
<td>( P_c )</td>
<td>Pa</td>
<td>Partial pressure of the target gas</td>
</tr>
<tr>
<td>( V )</td>
<td>m(^3)</td>
<td>chamber volume</td>
</tr>
<tr>
<td>( A )</td>
<td>m(^2)</td>
<td>chamber area covering ground (soil) surface</td>
</tr>
<tr>
<td>( h )</td>
<td>m</td>
<td>chamber height</td>
</tr>
<tr>
<td>( T )</td>
<td>K</td>
<td>temperature of air in chamber</td>
</tr>
<tr>
<td>( n )</td>
<td>mol</td>
<td>amount of the air in chamber in mol</td>
</tr>
<tr>
<td>( n_c )</td>
<td>mol</td>
<td>amount of the target gas in chamber in mol</td>
</tr>
<tr>
<td>( C )</td>
<td>mol m(^{-3})</td>
<td>concentration of the target gas in chamber in mol per unit volume</td>
</tr>
<tr>
<td>( C_{IN} )</td>
<td>mol m(^{-3})</td>
<td>concentration of the target gas in the inlet air to chamber in mol per unit volume</td>
</tr>
<tr>
<td>( C_{OUT} )</td>
<td>mol m(^{-3})</td>
<td>concentration of the target gas in the outlet air from chamber in mol per unit volume</td>
</tr>
<tr>
<td>( r )</td>
<td>mol mol(^{-1})</td>
<td>mixing ratio (relative concentration) of the target gas in chamber in mol per mol</td>
</tr>
<tr>
<td>( r_{IN} )</td>
<td>mol mol(^{-1})</td>
<td>mixing ratio of the target gas in the inlet air to chamber in mol per mol</td>
</tr>
<tr>
<td>( r_{OUT} )</td>
<td>mol mol(^{-1})</td>
<td>mixing ratio of the target gas in the outlet air from chamber in mol per mol</td>
</tr>
<tr>
<td>( r_{eq} )</td>
<td>mol mol(^{-1})</td>
<td>equilibrated mixing ratio of the target gas in mol per mol</td>
</tr>
<tr>
<td>( m_s )</td>
<td>kg</td>
<td>(dry) weight of soil</td>
</tr>
<tr>
<td>( f )</td>
<td>m(^3) s(^{-1})</td>
<td>flow rate of the air in volume (flow-through-chamber technique)</td>
</tr>
<tr>
<td>( f_{IN} )</td>
<td>m(^3) s(^{-1})</td>
<td>flow rate of the inlet air to chamber in volume</td>
</tr>
<tr>
<td>( f_{OUT} )</td>
<td>m(^3) s(^{-1})</td>
<td>flow rate of the outlet air from chamber in volume</td>
</tr>
<tr>
<td>( \rho_s )</td>
<td>kg m(^{-3})</td>
<td>bulk density (soil weight per unit volume of soil)</td>
</tr>
</tbody>
</table>
recognized to describe well the dynamics of various types of trace gases, are used for the calculations:

1. The uptake rate simply follows first-order kinetics. Ambient gas concentrations are low at atmospheric concentration levels. Gas uptake is generally explained by Michaelis-Menten kinetics, which shows the activity of enzymes $V_{\text{enzyme}}$:

$$V_{\text{enzyme}} = \frac{V_{\text{max}} C_{\text{sub}}}{K_m + C_{\text{sub}}}$$

(2.12)

where $C_{\text{sub}}$ is the substrate concentration, $V_{\text{max}}$ is the maximum rate of the reaction at saturating substrate concentrations, and $K_m$ is the substrate concentration at which the reaction rate is half of $V_{\text{max}}$. The substrate is the relevant gas for the gas uptake ($C_{\text{sub}} = C$). Because $K_m \gg C$ at atmospheric concentration levels, the uptake rate simply follows first-order kinetics, which means it is proportional to the relevant-gas ambient concentration whose rate constant is given as $V_{\text{max}}/K_m$ (Bender and Conrad, 1993; Conrad, 1996; King, 1999).

2. The emission rate is independent of the relevant-gas ambient concentration. This assumption is supported by a general

<table>
<thead>
<tr>
<th>name</th>
<th>unit</th>
<th>meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
<td>flux (emission/uptake rate in mol per unit area)</td>
</tr>
<tr>
<td>$F^+$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
<td>gross flux (emission/uptake rate in mol per unit area)</td>
</tr>
<tr>
<td>$S$</td>
<td>mol s$^{-1}$</td>
<td>net emission/uptake rate (in the total system) in mol</td>
</tr>
<tr>
<td>$S_m$</td>
<td>mol kg$^{-1}$ s$^{-1}$</td>
<td>net emission/uptake rate in mol per unit mass of soil</td>
</tr>
<tr>
<td>$S_v$</td>
<td>mol m$^{-3}$ s$^{-1}$</td>
<td>net emission/uptake rate in mol per unit volume of soil</td>
</tr>
<tr>
<td>$S^+$</td>
<td>mol s$^{-1}$</td>
<td>gross emission rate (in the total system) in mol</td>
</tr>
<tr>
<td>$S_-$</td>
<td>mol s$^{-1}$</td>
<td>gross uptake rate (in the total system) in mol</td>
</tr>
<tr>
<td>$S_{m,+}$</td>
<td>mol kg$^{-1}$ s$^{-1}$</td>
<td>gross emission rate in mol per unit volume of soil</td>
</tr>
<tr>
<td>$S_{m,-}$</td>
<td>mol kg$^{-1}$ s$^{-1}$</td>
<td>gross uptake rate in mol per unit volume of soil</td>
</tr>
<tr>
<td>$v$</td>
<td>m s$^{-1}$</td>
<td>deposition velocity (apparent decreasing rate in volume per unit area)</td>
</tr>
<tr>
<td>$v_n$</td>
<td>m s$^{-1}$</td>
<td>net deposition velocity (apparent decreasing rate in volume per unit area)</td>
</tr>
<tr>
<td>$v_g$</td>
<td>m s$^{-1}$</td>
<td>gross deposition velocity (apparent decreasing rate in volume per unit area)</td>
</tr>
<tr>
<td>$u$</td>
<td>m$^3$ s$^{-1}$</td>
<td>uptake rate (in the total system) in volume</td>
</tr>
<tr>
<td>$u_m$</td>
<td>m$^3$ kg$^{-1}$ s$^{-1}$</td>
<td>uptake rate in volume per unit mass of soil</td>
</tr>
<tr>
<td>$u_v$</td>
<td>s$^{-3}$ or mol mol$^{-1}$ s$^{-4}$</td>
<td>(relative) uptake rate in volume per unit soil volume</td>
</tr>
<tr>
<td>$u_n$</td>
<td>m$^3$ s$^{-1}$</td>
<td>net uptake rate (in the total system) in volume</td>
</tr>
<tr>
<td>$u_g$</td>
<td>m$^3$ s$^{-1}$</td>
<td>gross uptake rate (in the total system) in volume</td>
</tr>
<tr>
<td>$u_{m,n}$</td>
<td>m$^3$ kg$^{-1}$ s$^{-3}$</td>
<td>net uptake rate in volume per unit mass of soil</td>
</tr>
<tr>
<td>$u_{m,g}$</td>
<td>m$^3$ kg$^{-1}$ s$^{-3}$</td>
<td>gross uptake rate in volume per unit mass of soil</td>
</tr>
</tbody>
</table>
recognition that the substrate concentration is almost constant (Eq. 2.12) during short-time measurements of gas emission/uptake.

### Table 1. (continued)

<table>
<thead>
<tr>
<th>name</th>
<th>unit</th>
<th>meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_0$</td>
<td>mol mol$^{-1}$</td>
<td>initial mixing ratio</td>
</tr>
<tr>
<td>$a_F$</td>
<td>ratio s$^{-1}$</td>
<td>estimated increasing/decreasing rate of the target gas mixing ratio for flux</td>
</tr>
<tr>
<td>$b_F$</td>
<td>ratio (dimensionless)</td>
<td>estimated initial mixing ratio for flux</td>
</tr>
<tr>
<td>$a_B$</td>
<td>ratio s$^{-1}$</td>
<td>estimated increasing/decreasing rate of the target gas mixing ratio for bulk-soil</td>
</tr>
<tr>
<td>$b_B$</td>
<td>ratio (dimensionless)</td>
<td>estimated initial mixing ratio for bulk-soil</td>
</tr>
<tr>
<td>$k_F$</td>
<td>s$^{-1}$</td>
<td>turnover rate (turnover ratio) for flux</td>
</tr>
<tr>
<td>$k_B$</td>
<td>s$^{-1}$</td>
<td>turnover rate (turnover ratio) for bulk-soil</td>
</tr>
</tbody>
</table>

Parameters for Michaelis-Menten kinetics

- $V_{enzyme}$: reaction velocity of enzyme
- $C_{sub}$: concentration of the substrate
- $V_{max}$: the maximum rate of the reaction at saturating substrate concentrations
- $K_m$: the substrate concentration at which the reaction rate is half of $V_{max}$

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**Fig. 2.** Assumptions used to calculate the soil emission and uptake rates for the chamber techniques.

3. Flux density

3.1 Surface-soil gas-exchange field measurements

It is essentially impossible to obtain mass balance in surface-soil gas exchange because the measurement...
itself changes the soil-air concentrations by emission or absorption, which is contrary to the assumption of mass balance. Thus, we must consider quasi-mass balance, which excludes the air space in the soil and considers only the above-soil chamber air. We assume a soil-surface emission or uptake rate (flux) of \( F \) \([\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]\). We assume a chamber height of \( h \) and a covered area \( A \), where \( h = V/A \).

3.1.1 Surface-soil gas exchange by closed-chamber technique

We begin with Eq. (2.10) and for emission, \( r \) is assumed to increase with time at a constant rate because the emission rate is independent of the relevant-gas ambient concentration. So \( r \) can be linearly regressed from the time-series measurements of the mixing ratios as

\[
r = a_F t + b_F, \tag{3.1}
\]

where \( a_F \) is the slope, namely, the degree of increase of gas concentration in the chamber, and \( b_F \) is the regression intercept, namely, the initial gas concentration in the chamber. Differentiating Eq. (3.1) with time \( t \) gives

\[
\frac{dr}{dt} = a_F, \tag{3.2}
\]

so Eq. (2.10) can be expressed as

\[
S = \frac{PV}{RT} a_F. \tag{3.3}
\]

\( S \) is divided by the surface area \( A \) of the covered chamber, and the ratio is labeled \( F \):

\[
F = \frac{S}{A} = \frac{PV}{RT} a_F. \tag{3.4}
\]

3.1.2 Surface-soil gas exchange by flow-through-chamber technique

We divide the total-system net emission \( S \) (Eq. 2.11) by the surface area \( A \) of the soil:

\[
F = \frac{S}{A} = \frac{fP}{RTA} \left( r_{\text{OUT}} - r_{\text{IN}} \right). \tag{3.5}
\]

3.2 Bulk-soil gas exchange

To clarify the response of soil to changes in various conditions such as temperature and soil moisture, or to the addition of nutrients, laboratory experiments are done to obtain the exchange ratios of the relevant gas for bulk soil. Usually, bulk soil is set in chambers in a thin layer to avoid the gas-diffusion limitation of soil itself. In contrast to surface-soil measurements, it is possible to obtain mass balance in bulk-soil gas exchange using well-designed experiments.

3.2.1 Bulk-soil gas exchange by closed-chamber technique

The emission from a unit mass of bulk soil, \( S_m \) \([\text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}]\), is obtained from Eq. (3.3) by dividing by the soil mass, \( m_s \):

\[
S_m = \frac{S}{m_s} = \frac{PV a_B}{RT m_s}, \tag{3.6}
\]

where a different parameter of regression is used for bulk soil as \( a_B \). Moreover, using the bulk density (i.e., the soil mass of a unit volume of soil) \( \rho_s \), the emission can be expressed as an emission per unit volume of soil, \( S_m \) \([\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]\):

\[
S_m = \frac{S}{m_s \rho_s} = \frac{PV a_B \rho_s}{RT m_s}. \tag{3.7}
\]

3.2.2 Bulk-soil gas exchange by flow-through-chamber technique

Dividing Eq. (2.11) by soil mass gives the per-unit-soil expression:

\[
S_m = \frac{fP}{RT m_s} \left( r_{\text{OUT}} - r_{\text{IN}} \right). \tag{3.8}
\]

Then, \( S_v \) can be expressed as:

\[
S_v = S_m \rho_s \frac{fP \rho_s}{RT m_s} \left( r_{\text{OUT}} - r_{\text{IN}} \right). \tag{3.9}
\]

4. Deposition velocity

4.1 Deposition velocity for closed-chamber technique

In Eq. (2.10), the rate \( dr/dt \) for gases absorbed by the soil is a function of time. As the concentrations of relevant trace gases are low in most environmental studies, we can assume that the uptake obeys first-order kinetics, which means that the uptake is proportional to the concentration of the relevant gas (Fig. 1). This constitutes our first assumption and means that the relevant-gas concentration in the chamber decreases exponentially. With this assumption, the relevant-gas concentration can be expressed as

\[
r = r_0 e^{-k_F t}, \tag{4.1}
\]

Differentiating Eq. (4.1) with time \( t \) gives
After $S$ is obtained by Eq. (2.10), $F$ is given by dividing $S$ by $A$:

$$F = \frac{S}{A} = \frac{dn_s}{dt} \left( - \frac{PV}{RTA} r = - \frac{Phk_r}{RT} = -hk_F C \right).$$

As seen from Eq. (4.3), the total-system flux $F$ is linearly dependent on the relevant-gas concentration. Note that the relevant-gas concentration changes not only with time but also with atmospheric concentrations. For this reason, an expression for $S$ that is negative is not appropriate for soil studies. Then, we define the deposition (i.e., uptake) velocity $v$ [m s$^{-1}$] (McMahon and Denison, 1979) as:

$$v = \frac{-F}{C} = hk_F.$$

Furthermore, for simultaneous emission and uptake in the soil, emission and net and gross deposition velocities, $F_+$, $v_n$, and $v_g$, can be defined as

$$F_+ = \frac{S_+}{A} = \frac{hk_F Pr_{eq}}{RT},$$

$$v_n = \frac{u_n}{A} = hk_F \left( 1 - \frac{r_{eq}}{r} \right),$$

$$v_g = \frac{u_g}{A} = hk_F.$$

### 4.2 Deposition velocity for flow-through-chamber technique

Deposition velocity was obtained by dividing $S$ by $A$ and $C$:

$$v = \frac{-F}{C} = -\frac{S}{AC} = \frac{f (r_{IN} - r_{OUT})}{A} \frac{1}{r}.$$

For a chamber in which a fan stirs the air, the following assumption is possible:

$$r = r_{OUT}.$$

Incorporating this assumption in Eq. (4.8) gives

$$v = \frac{f}{A} \left( \frac{r_{IN}}{r_{OUT}} - 1 \right).$$

Furthermore, in the case of the presence of both emission and uptake processes in soil, we set emission and uptake terms for $F$ as:

$$F = F_+ - Cv_g.$$

If much different types of upstream concentrations can be controlled, $F_+$ and $v_g$ can be simultaneously estimated. If two sets of concentrations were $r_{IN1}$, $r_{OUT1}$, $r_{IN2}$, and $r_{OUT2}$, $v_g$ and $F_+$ are:

$$v_g = \frac{f}{A} \left( \frac{r_{IN2} - r_{IN1}}{r_{OUT2} - r_{OUT1}} - 1 \right),$$

$$F_+ = \frac{fP}{RT} \frac{r_{IN2}r_{OUT1} - r_{IN1}r_{OUT2}}{r_{OUT2} - r_{OUT1}}.$$

$F$ or $v_n$ can be expressed as Eq. (4.10), but $v_n$ depends on the atmospheric concentration of the gas.

### 5. Gas uptake by bulk soil

#### 5.1 Soil gas uptake by closed-chamber technique

As the concentrations of relevant trace gases are low in most environmental studies, we can again assume that the uptake obeys first-order kinetics, which means that the uptake is proportional to the concentration of the relevant gas (Fig. 1). With this assumption, the relevant-gas concentration can be expressed exponentially as:

$$r = r_0 e^{-kt}.$$

Differentiating Eq. (5.1) with time $t$ gives

$$\frac{dr}{dt} = -kr_0 e^{-kt} = -kB r.$$

which is inserted into Eq. (2.10) to give

$$S = \frac{dn_s}{dt} = \frac{PV}{RT} (-kB r) = -kB C.$$

As seen from Eq. (5.3), the total-system uptake $S$ is linearly dependent on the relevant-gas concentration. Note that the relevant-gas concentration changes not only with time but also with atmospheric concentrations. For this reason, an expression for $S$ that is negative is not appropriate for soil studies. Therefore, we define the total-system volume uptake rate $u$ [m$^3$ s$^{-1}$] in a manner similar to that in Eq. (4.4)

$$u = S/C.$$

Inserting Eq. (5.3) into Eq. (5.4) gives
which shows that $u$ is given by simply multiplying the chamber volume by the concentration-rate constant $k$. This equation should be further transformed by dividing by the soil mass, which is usually the dry soil mass. Thus, we define $u_m \text{ [m}^3\text{s}^{-1}\text{kg}^{-1}]$ as

$$u_m = \frac{u}{m_s}. \quad (5.6)$$

From Eqs. (5.5) and (5.6), we find

$$u_m = \frac{VK}{m_s}. \quad (5.7)$$

In physical terms, Eqs. (5.5) and (5.7) give the air volume, where the relevant gas can be absorbed around the soil. Furthermore, using the bulk density $\rho_s$, we convert this to an uptake rate $u_v \text{ [s}^{-1}]$ in terms of volume of relevant gas absorbed per unit soil volume as

$$u_v = u_m \rho_s \frac{VK}{m_s}. \quad (5.8)$$

The physical meaning of $u_v \text{ [s}^{-1}]$ is the ratio of the relevant gas that is absorbed by the soil per unit of time.

For gases that are simultaneously emitted and absorbed by the soil, $r(t)$ is regressed in time by

$$r = r_0 e^{-k_s t} + r_{eq}, \quad (5.9)$$

where the concentration of the relevant gas increases or decreases exponentially towards a constant equilibrium concentration. The equilibrium volume-mixing ratio $r_{eq}$ is determined by balancing emission and uptake in soil. From Eq. (5.9), we have

$$\frac{dr}{dt} = -k_B r_0 e^{-k_s t} = -k_B (r - r_{eq}). \quad (5.10)$$

Inserting Eq. (5.10) into Eq. (2.10), we have

$$S = \frac{PV}{RT} \frac{dr}{dt} = \frac{PV}{RT} k_B r_{eq} - \frac{PV}{RT} k_B r = \text{emission - uptake}. \quad (5.11)$$

Explicitly, the emission and uptake terms are

Emission term: $S_+ = \frac{PV}{RT} k_B r_{eq}$, \quad (5.12)

Uptake term: $S_- = \frac{PV}{RT} k_B r$.

The net uptake rate $u_n$, can be calculated by dividing $S$ by the concentration:

$$u_n = -\frac{S}{C} = \frac{VK}{B} \left(1 - \frac{r_{eq}}{r}\right), \quad (5.13)$$

The net volume uptake rate (in the total system) depends on $r$, which can be changed easily and is not a standardized parameter for soil gas-uptake studies under changing atmospheric concentrations. Only when $r$ is large or almost constant may $u_{c,net}$ be used.

For $S$, the gross uptake flow rate $u_g$ is given by

$$u_g = -\frac{S}{C} = \frac{VK}{B}. \quad (5.14)$$

Dividing Eq. (5.14) by soil mass gives the per-soil-unit expression:

$$S_m = -\frac{PV}{RT m_s} k_B = (r - r_{eq}), \quad (5.15)$$

$$S_{m, +} = -\frac{PV}{RT m_s} k_B r_{eq}, \quad (5.16)$$

$$S_{m, -} = -\frac{PV}{RT m_s} k_B r, \quad (5.17)$$

$$u_{m,n} = -\frac{k_B (r - r_{eq}) PV}{m_s (r P/RT)} = \frac{VK}{m_s} \left(1 - \frac{r_{eq}}{r}\right), \quad (5.18)$$

where $S_{m, +}$ and $u_{m,g}$ are normally used (and sometimes $u_{m,n}$).

### 5.2 Soil-gas uptake by flow-through-chamber technique

As in Sec. 3.1 for the closed-chamber technique, gas uptake for the flow-through-chamber technique depends on gas concentration, so we divide $S$ by $C$ to obtain the total-system bulk-soil uptake rate $u$:

$$u_n = -\frac{S}{C} = f \left(\frac{r_{IN}}{r_{OUT}} - 1\right). \quad (5.19)$$

For a chamber in which a fan stirs the air, the assumption in Eq. (4.9) is possible. Incorporating the Eq. (4.9) assumption into Eq. (5.19) gives

$$u = f \left(\frac{r_{IN}}{r_{OUT}} - 1\right). \quad (5.20)$$
Equation (5.20) shows that only the ratio of relevant-gas concentrations (or volume-mixing ratios) entering and leaving the chambers is necessary. In other words, although the absolute relevant-gas concentrations are unknown prior to calibration, the uptake can still be estimated. The per-soil-unit expression is

\[ u_m = \frac{f}{m_s} \left( \frac{n_N}{\eta_{OUT}} - 1 \right) \]  \hspace{1cm} (5.21)

Similar to Eq. (5.8), \( u_r \) is:

\[ u_r = u_m \rho_s \left( \frac{n_N}{\eta_{OUT}} - 1 \right) \]  \hspace{1cm} (5.22)

In the case of gases simultaneously emitted and absorbed by soil, we set emission and uptake terms for \( S \):

\[ S = S_+ - C u_g \]  \hspace{1cm} (5.23)

If much different types of upstream concentrations can be controlled, \( F \) and \( v_g \) can be simultaneously estimated. If two sets of concentrations were \( n_{IN1}, r_{OUT1}, r_{IN2}, r_{OUT2}, u_g \) and \( S_+ \) are:

\[ u_g = f \left( \frac{n_N - n_{IN1}}{r_{OUT2} - r_{OUT1}} - 1 \right) \]  \hspace{1cm} (5.24)

\[ S_+ = \frac{f \rho_r}{RT} \frac{n_{IN2}r_{OUT1} - n_{IN1}r_{OUT2}}{r_{OUT2} - r_{OUT1}} \]  \hspace{1cm} (5.25)

\( S \) or \( v_g \) can expressed as Eq. (5.20), but \( u_n \) depends on the ambient concentration of the gas. It is recommended, however, that the two concentrations be markedly different.

6. Notifications and cautions to apply to equations to soil-gas uptake

6.1 General discussion

This study is the first to systematically derive equations to calculate gas uptake by soil that are valid for both field and laboratory chamber experiments. The basic conversion can be summarized for surface uptake (Sec. 4) and bulk-soil uptake (Sec. 5) with normalization by concentration (Table 2). The important traditional and introduced variables to show the strength of trace-gas soil uptake at atmospheric concentration levels are the deposition velocity \( v \) [m s\(^{-1}\)] for the surface soil flux (Eqs. 4.4, 4.8) and the uptake rate in volume per unit mass of soil \( u_m \) [m\(^3\) kg\(^{-1}\) s\(^{-1}\)] for bulk-soil experiments in the laboratory (Eqs. 5.7, 5.21). The (relative) uptake rate in volume-per-unit soil volume \( u_v \) [s\(^{-1}\)] (Eqs. 5.8, 5.22) is, furthermore, important to show the strength of the underground vertical soil-uptake rate. The dimensions of these variables are not the absolute intake amount of the trace gas, namely, the flux, but the uptake ratio in the air space surrounding soil, reflecting the first-order kinetics. To those who engage in trace-gas uptake by soil, it is recommended that these variables be employed rather than the flux density. However, under higher concentrations (\( C > K_m \)) in laboratory experiments, we must return to the Michaelis-Menten kinetics (Eq. 2.12). Furthermore, applying the equations to actual measurements requires translating between systems of units because unit systems vary between different experiments. In the present article, we give all equations in MKS units.

Fans are crucially important for measurements in gas-uptake experiments because trace-gas uptake at atmospheric concentration levels obeys first-order kinetics and because they ensure that the trace-gas concentrations in the ambient air near the soil are the same as the trace-gas concentrations in the air exiting the chamber to be measured downstream by gas analyzers. The use of fans, in other words, makes it possible to ignore boundary layer resistance. However,
to avoid drying the soil, the fan speed should not be set excessively high or, in field experiments, to avoid modifying gas-diffusion rates in the soil driven by molecular diffusion.

Formulations under simultaneous emission and uptake were shown in Eqs. (4.5)–(4.7) and Eqs. (4.12) and (4.13) in Sec. 4 and in Eqs. (5.12), (5.14), and Eqs. (5.24) and (5.25) in Sec. 5. Examples of simultaneous emission and uptake are as follows: (1) CH₄: soil microbial uptake and emission from termites in tropics; (2) CO: soil microbial uptake and abiotic production from soil organic matter; (3) NO: NO is produced and consumed as an intermediate product in the nitrification processes. In experiments using the flow-through-chamber technique, when two upstream concentrations are set, it is recommended that the two concentrations be markedly different; it is further recommended that one of the concentrations be set at zero. If much different types of upstream concentrations can be controlled, more-reliable regression methods will also be available.

To date, the intensity of gas uptake (deposition or consumption) by surface soil has been conventionally described by deposition velocities (in some cases, destruction velocity), regardless of the differences of the mechanisms involved (Fig. 1). Historically, deposition of pollutants such as NOₓ, SO₂, NH₃, and particles were studied first (McMahon and Denison, 1979; Wesely and Hicks, 2000). Deposition velocity has dimensions of velocity and indicates how much of the above-soil layer is deposited onto/into the soil (see Sec. 4). The concept has also been applied to other gases that are consumed by soil, such as H₂ and CO. However, the mechanisms by which each trace gas disappears are different. NOₓ, SO₂, NH₃, and particles are rapidly deposited physico-chemically onto soil and are not directly used by the soil microorganisms. However, for gases such as H₂, CO, CH₄, CO, and CH₃Br that are biologically used (consumed) by the soil, the terminology “uptake velocity” or “consumption velocity” may be used. Furthermore, O₃ is physically destroyed at the soil surface. Thus, strict terminology must be used to differentiate between uptake velocity (e.g., for H₂, CO, CH₄, CH₃Br, CO, and CH₃Br) and destruction velocity (for O₃) and between new-deposition velocity (for NOₓ, SO₂, particles) and original-deposition velocity. The deposition velocity is not suitable terminology for biological trace-gas uptake by soil but can be used in order to eliminate confusion with previous studies.

6.2 Mass balance in soil-gas uptake in the field

In well-designed laboratory experiments, mass balance may essentially be guaranteed. On the contrary, in field experiments, mass balance cannot be closed because relevant-gas concentrations in the soil air situated beneath the chamber can change. However, in contrast to gas emission, soil-air consumed-gas concentrations cannot be changed markedly because the gas concentration cannot be less than zero. This is in contrast to the case for gas emission, for which the increase in the soil-air relevant-gas concentration is limited only by diffusion. For gas emission, therefore, corrections based on well-designed procedures are now found to be necessary to correct the flux density (Venterea and Parkin, 2012). Thus, measurements of soil-gas uptake are less sensitive to chamber effects than are measurements of soil-gas emission. Further, the effect upon gas-uptake data obtained with the flow-through-chamber technique is diminished with respect to those obtained with the closed-chamber technique. In addition, the use of fans is critically important for soil-uptake measurements done using the flow-through-chamber technique.

Note that for gases absorbed in deeper soil layers (i.e., CH₄, C₃H₈), mass-balance closure is more difficult to achieve than for gases absorbed in shallower soil layers (i.e., H₂, CO, COS, CH₃Br), and that, with the use of chambers, budgets for gases such as H₂, CO, CS₂, COS, CH₃Br can be more prone to artifacts caused by surface-soil temperature increases than those for gases such as CH₄ and C₃H₈ because surface soil is the main location for gas uptake for these gases.

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