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The relationship between soil CO_2 efflux and its carbon isotopic composition under non-steady-state conditions

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ABSTRACT

Soil CO_2 efflux and its carbon isotopic composition are undoubtedly important for estimating ecosystem carbon budgets and for partitioning respiration sources at various spatial and temporal scales. Under natural conditions, non-steady processes will strongly influence the diffusive fluxes of $^{13}CO_2$ and $^{12}CO_2$ between soil and the atmosphere, which results in variations of effluxed soil $\delta^{13}CO_2$ and will lead to bias in respiration source partitioning. In this study, we present a set of quantitative relationships between soil CO_2 efflux and its $\delta^{13}C$ by solving the diffusion equation. The results showed that the effluxed $\delta^{13}CO_2$ converged toward the respiratory $\delta^{13}CO_2$ with an increasing efflux rate but that the values greatly differed at low efflux rates. Both our own experiments and data from the literature verified this convergence pattern of the effluxed $\delta^{13}CO_2$, which implies that most of the variations in the $\delta^{13}C$ of soil effluxed CO_2 may derive from diffusive fractionation rather than from biological causes. Our results explain the isotopic flux patterns of CO_2 under natural environmental variations and are vitally important for isotope-based modeling of ecosystem carbon exchange under changing climatic regimes.

1. Introduction

Partitioning soil and ecosystem respiration (e.g., estimating the relative ratio of root respiration to soil microbial respiration) with isotopic fluxes of CO_2 is useful for quantifying terrestrial carbon budgets (Bowling et al., 2001; Baggs, 2006; Susan, 2006). In most early studies of the carbon cycle and budget, the measured soil CO_2 effluxes and their $\delta^{13}C$ values ($\delta^{13}CO_{2e}$) are normally taken for granted as the soil respiration rates and the $\delta^{13}C$ values of respiratory CO_2 ($\delta^{13}CO_{2r}$) (the respiratory CO_2 is defined as the CO_2 produced from the biochemical reactions that occur before emission). Therefore, the observed variations in $\delta^{13}CO_{2e}$ were usually attributed to the contributing ratio shifts of different CO_2-producing sources (Lin et al., 1999; Klumpp et al., 2005; Kodama et al., 2008; Zobitz et al., 2008; Marron et al., 2009; Unger et al., 2010a, 2012). However, soil CO_2 effluxes with different isotopic compositions are not only controlled by the CO_2 production rates but also affected by the diffusion conditions of the soil-atmosphere continuum (Jassal et al., 2005; Bowling et al., 2008; Bahn et al., 2009; Moyes et al., 2010a,b; Werner & Gessler, 2011; Rey, 2015; van Asperen et al., 2017). The equivalences between the soil efflux rate and the respiration rate as well as $\delta^{13}CO_{2e}$ and $\delta^{13}CO_{2r}$ could only apply to ideal steady-state conditions. Under natural conditions, non-steady states of the soil-atmosphere diffusion systems are actually inevitable due to (i) the variations in the concentration and $\delta^{13}C$ of atmospheric CO_2 (e.g., Broadmeadow et al., 1992 on diurnal variation; Flanagan & Ehleringer, 1998 on seasonal variation), (ii) the variation in the soil respiration rate and (iii) the changes in the soil diffusion condition. The changes of the relative concentration gradients of the different CO_2 isotopologues between the soil and atmosphere, together with the 4.4‰ difference between the diffusion coefficients of $^{12}CO_2$ and $^{13}CO_2$ ($^{12}CO_2$ diffuses more rapidly) (Craig, 1953), will lead to the difference between $\delta^{13}CO_{2e}$ and $\delta^{13}CO_{2r}$. Such 'diffusive fractionation' will complicate the isotopic partitioning of the contributing respiration sources (Moyes et al., 2010b).

Although the influences of diffusion processes on soil CO_2 effluxes and carbon isotope fractionation have attracted wide attention in recent studies, most conclusions have been based on observations, qualitative analyses, and numerical model simulations because it is difficult to analytically solve the diffusion equation (Camarda et al., 2007; Nickerson and Risk, 2009b; Moyes et al., 2010b; Liang et al., 2016; van

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$$R_e(t) = \frac{F_e^{13}(t)}{F_e^{12}(t)} = \frac{D_s^{13}\left(e^{-\frac{D_s^{13}}{\Delta z^2}t}R_r\int\phi^{12}(t)e^{\frac{D_s^{13}}{\Delta z^2}t}dt + \left(\frac{D_s^{13}}{\Delta z^2}e^{-\frac{D_s^{13}}{\Delta z^2}t}\int R_{atm}(t)C_{atm}^{12}(t)e^{\frac{D_s^{13}}{\Delta z^2}t}dt - R_{atm}(t)C_{atm}^{12}(t)\right) + e^{-\frac{D_s^{13}}{\Delta z^2}t}C_I^{13}\right)}{D_s^{12}\left(e^{-\frac{D_s^{12}}{\Delta z^2}t}\int\phi^{12}(t)e^{\frac{D_s^{12}}{\Delta z^2}t}dt + \left(\frac{D_s^{12}}{\Delta z^2}e^{-\frac{D_s^{12}}{\Delta z^2}t}\int C_{atm}^{12}(t)e^{\frac{D_s^{12}}{\Delta z^2}t}dt - C_{atm}^{12}(t)\right) + e^{-\frac{D_s^{12}}{\Delta z^2}t}C_I^{12}\right)} \tag{6}$$

Asperen et al., 2017). They cannot give an explicit description to the patterns and ranges of $\delta^{13}CO_{2e}$ variation caused by diffusion. This makes it difficult to distinguish the biological and non-biological effects on carbon isotope fractionation during soil respiration, which has led to debate regarding the main cause of $\delta^{13}CO_{2e}$ variation (Werner and Gessler, 2011; Bowling et al., 2015). It is also difficult to derive the actual $\delta^{13}CO_{2r}$ from the varied $\delta^{13}CO_{2e}$ under non-steady-state conditions and then partition respiration sources. In this context, we provided a general analytical description of the isotopic fluxes of soil CO_2 under natural non-steady-state conditions by solving the diffusion equation. To make sure that our theoretical results are reliable and applicable in practice, we also designed a controlled experiment for verification.

2. Theoretical basis

2.1. Fick's diffusion law and mass balance model

Previous works on soil CO_2 efflux, soil CO_2 concentration and its carbon isotopic composition were generally based on the partial differential diffusion equation (PDE). Under steady-state conditions, the distribution of soil CO_2 concentration and isotopic composition with soil depth can be easily obtained by solving the PDE with ideal equilibrium assumptions (Cerling, 1984, Cerling et al., 1991). However, it is mathematically difficult to obtain a general solution to the PDE under non-steady-state conditions (Quarteroni and Valli, 1996). Since our main concern is the CO_2 flux between the soil and the atmosphere, we neglect the diffusion processes among different soil layers and consider the soil profile as a single entity. Then, the variations of the CO_2 concentration with time can be described by a simple mass balance equation:

$$V\frac{dC(t)}{dt} = V\phi(t) - SF_e(t) \tag{1}$$

where $C(t)$ is the soil CO_2 concentration ($\mu mol\,m^{-3}$); t is the time (s); $\phi(t)$ is the CO_2 production rate ($\mu mol\,m^{-3}\,s^{-1}$); and V (m^3) and S (m^2) are the volume and surface area of the soil, respectively.

According to Fick's first law,

$$F_e(t) = D_s\frac{C(t) - C_{atm}(t)}{\Delta z} \tag{2}$$

where Δz is the diffusion distance (m); D_s is the diffusion coefficient ($m^2\,s^{-1}$); and $C_{atm}(t)$ is the atmospheric CO_2 concentration, so that:

$$\frac{dC(t)}{dt} = \phi(t) - \frac{S}{V}D_s\frac{C(t) - C_{atm}(t)}{\Delta z}$$

where $\frac{S}{V} = \frac{1}{\Delta z}$ for a regular cylinder and

$$\frac{dC(t)}{dt} = \phi(t) - D_s\frac{C(t) - C_{atm}(t)}{\Delta z^2} \tag{3}$$

2.2. General solution

By using the method of variation of constants (Chicone, 2006), the general solution for Eq. (3) can be written as:

$$C(t) = e^{-\frac{D_s}{\Delta z^2}t}\int\phi(t)e^{\frac{D_s}{\Delta z^2}t}dt + \frac{D_s}{\Delta z^2}e^{-\frac{D_s}{\Delta z^2}t}\int C_{atm}(t)e^{\frac{D_s}{\Delta z^2}t}dt + e^{-\frac{D_s}{\Delta z^2}t}C_I \tag{4}$$

where C_I is a constant that depends on the initial state of the system.

Then, the soil CO_2 efflux $F_e(t)$ and its carbon isotope ratio $R_e(t)$ can be expressed as:

$$F_e(t) = \frac{D_s}{\Delta z}\left(e^{-\frac{D_s}{\Delta z^2}t}\int\phi(t)e^{\frac{D_s}{\Delta z^2}t}dt + \left(\frac{D_s}{\Delta z^2}e^{-\frac{D_s}{\Delta z^2}t}\int C_{atm}(t)e^{\frac{D_s}{\Delta z^2}t}dt - C_{atm}(t)\right) + e^{-\frac{D_s}{\Delta z^2}t}C_I\right) \tag{5}$$

where R_{atm} and R_r are the carbon isotope ratios of atmospheric CO_2 and respiratory CO_2, respectively; and the superscripts '12' and '13' are for the parameters of $^{12}CO_2$ and $^{13}CO_2$, respectively. The $\delta^{13}C$ value can be calculated using equation $\delta^{13}C = (R/R_{std} - 1) \times 1000$, where $R_{std} = R_{PDB} = 0.011237$ (Craig, 1957).

To analyze the difference between $R_e(t)$ and R_r, we change the form of $R_e(t)$ to be:

$$R_e(t) = (F_e^{13}(t) - R_rF_e^{12}(t))\frac{1}{F_e^{12}(t)} + R_r \tag{7}$$

In most cases, the term $F^{13}(t) - R_rF^{12}(t)$ will be independent of $\phi(t)$ because $\phi^{13}(t) - R_r\phi^{12}(t) = 0$. In addition, since $F_e^{12}(t)$ is a major contributor of $F_e(t)$, $1/F_e^{12}(t)$ can be approximately replaced with $1/F_e(t)$.

Obviously, as shown by the above equations, the soil CO_2 concentration, CO_2 efflux and R_e under non-steady-state conditions are all influenced by the following five major factors: soil initial states (C_I), variation of respiration rates ($\phi(t)$), variation of atmospheric CO_2 ($C_{atm}(t)$ and $R_{atm}(t)$), diffusion coefficients (D_s) and diffusion distances (Δz). To quantify the effects of these factors and the range of the difference between $\delta^{13}CO_{2e}$ and $\delta^{13}CO_{2r}$, we will make a respective analysis in the following sections.

2.3. Effects of the initial state

Here, we assume that the respiration rate and atmospheric CO_2 remain relatively stable, which means that $\phi(t)$ and $C_{atm}(t)$ are both constants; then, $C(t)$, $F_e(t)$ and $R_e(t)$ can be simplified as:

$$C(t) = \frac{\Delta z^2}{D_s}\phi + C_{atm} + e^{-\frac{D_s}{\Delta z^2}t}C_I \tag{8}$$

$$F_e(t) = \Delta z\phi + \frac{D_s}{\Delta z}e^{-\frac{D_s}{\Delta z^2}t}C_I \tag{9}$$

$$R_e(t) = \left(\frac{D_s^{13}}{\Delta z}e^{-\frac{D_s^{13}}{\Delta z^2}t}C_I^{13} - R_r\frac{D_s^{12}}{\Delta z}e^{-\frac{D_s^{12}}{\Delta z^2}t}C_I^{12}\right)\frac{1}{F_e(t)} + R_r \tag{10}$$

When $t = 0$, $C = \frac{\Delta z^2}{D_s}\phi + C_{atm} + C_I = C_0$, where C_0 stands for the initial soil CO_2 concentration. Therefore, C_I can be written as:

$$C_I = C_0 - \frac{\Delta z^2}{D_s}\phi - C_{atm} \tag{11}$$

By entering Eq. (11) into Eq. (10), $R_e(t)$ can be transformed as:

$$R_e(t) = \left(\frac{D_s^{13}}{\Delta z}e^{-\frac{D_s^{13}}{\Delta z^2}t}(R_0C_0^{12} - R_{atm}C_{atm}^{12}) - R_r\frac{D_s^{12}}{\Delta z}e^{-\frac{D_s^{12}}{\Delta z^2}t}(C_0^{12} - C_{atm}^{12})\right)\frac{1}{F_e(t)} + R_r \tag{12}$$

where R_0 stands for the initial carbon isotope ratio of soil CO_2. As the difference between D_s^{12} and D_s^{13} is quite small, its effect on the slope of $R_e(t)$ should be less important than the effects of the initial state C_0. For