Tellus (1998), 50B, 163–178
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TELLUS
ISSN 0280–6495

Oxygen isotopic equilibrium between carbon dioxide and water in soils

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(Manuscript received 23 January 1997; in final form 15 October 1997)

ABSTRACT

Exact mathematical solutions are presented for some simple cases of isotopic equilibration of oxygen-18 between carbon dioxide and water in soils, which is a major component of the ^{18}O isotopic balance of atmospheric CO_2. The soil-to-air exchange is made up of 2 components. First, respiratory CO_2 is produced in the soil and escapes to the atmosphere through diffusion. The lighter isotopic species escapes a little more rapidly, enriching the heavier isotopic species in the CO_2 left behind in the soil, which is then out of isotopic equilibrium with soil water. Therefore, simultaneously with the escape of gas, there is continuous re-equilibration of CO_2 with soil water. The second component of soil-to-air exchange is independent of the production of CO_2 in the soil: the invasion of atmospheric CO_2 into the soil, where it equilibrates isotopically with the soil moisture before diffusing back out. A consequence for atmospheric isotopic measurements is that, in general, for respired CO_2 a plot of the isotopic ratio versus the inverse of the concentration is curved, and that the slope in the vicinity of the ambient concentration may not point towards the isotopic ratio of the net CO_2 evolved from the soil.

1. Introduction

Carbon at the surface of the earth continually moves between the atmosphere, oceans, and biosphere. Our interest in this biogeochemical cycle has been heightened by concern about the emissions of carbon dioxide resulting from the burning of fossil fuels. The part of the additional CO_2 that remains in the atmosphere is the main contributor to the enhanced greenhouse effect that will effect global climate over the next decades, centuries and beyond. Uptake of CO_2 by the oceans, as well as the response of terrestrial ecosystems (plants and soils), needs to be quantified and understood before we can have faith in long-term predictions of the atmospheric CO_2 burden. Furthermore, once it has been generally accepted that we bear a responsibility for our environment, including the climate, one of the questions naturally becomes what we can do about climate forcing, and about the atmospheric CO_2 burden in particular. Because fossil fuel burning is at the heart of our energy economy, any action taken (or not taken) ought to be based on a quantitative understanding of the cycle of carbon between the atmosphere, oceans, and biosphere. Because the oceans, and even more so the terrestrial biosphere, appear to be "patchy" and complex with respect to carbon, it is advantageous to extract as much information as possible from the atmosphere. The latter is certainly the simplest with respect to measurements, and mixes on spatial and temporal scales suitable for setting observational limits on the carbon budgets of landscapes, regions, and large ocean areas, integrated over weeks to months.

The atmospheric monitoring of CO_2 started on Mauna Loa and the South Pole during the late

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1950's (Pales and Keeling, 1965), and the data were first used to set global, and then hemispheric, limits on the carbon cycle. During the late 1970's and early 1980's the continued monitoring of a second molecular species was added, $^{13}CO_2$, or rather the isotopic ratio of $^{13}CO_2$ to $^{12}CO_2$ (Mook et al., 1983; Francey et al., 1995) which allowed a distinction to be made between oceans and plants as absorbers or sources of atmospheric CO_2. In the mean time, many laboratories had started to measure CO_2, and in particular the Geophysical Monitoring for Climatic Change Laboratory (GMCC, now the Climate Monitoring and Diagnostics Laboratory, CMDL) made a concerted effort to improve observations of the spatial patterns of CO_2 (Komhyr et al., 1985) in order to obtain more information about the carbon cycle. The combined time series of CO_2 and its $^{13}C/^{12}C$ ratio appeared to indicate large shifts over the years between the oceans and the biosphere as sources/sinks of atmospheric CO_2 (Keeling et al., 1995), but there is considerable debate as to what extent these shift are real (Francey et al., 1995) because the two longest isotopic records do not agree sufficiently in all respects. The $^{13}C/^{12}C$ isotopic measurements need to be exquisitely precise. By the early 1990's many laboratories were measuring isotopic ratios of CO_2, improving its spatial definition. In this way the CMDL/INSTAAR (Institute for Arctic and Alpine Research, University of Colorado) isotopic data enabled the identification of an enormous terrestrial sink of CO_2 at mid-latitudes in the northern hemisphere (Ciais et al., 1995).

The measurement of the $^{18}O/^{16}O$ isotopic ratio ($^{18}O^{12}C^{16}O$, mass 46) has always been an integral part of the $^{13}C/^{12}C$ measurement (mass 45) because a correction needs to be made for the presence of ^{17}O in the mass 45 beam. The correction is (in almost all cases) proportional to the presence of ^{18}O (Craig, 1957). Initially, these ^{18}O data were not considered seriously for geochemical information because most air samples were collected as (moist) whole air samples, and it was realized that isotopic exchange of oxygen between H_2O and CO_2 during storage of the samples could easily destroy the original information embedded in the $^{18}OC^{16}O$. The artifact has been tested explicitly, and under what sampling conditions the ^{18}O signature of CO_2 is retained (Gemery et al., 1996).

For many years R. Francey had already been collecting dried samples via two different methods, and from those it became apparent that there are isotopic signals in $^{18}O/^{16}O$ of CO_2 that are an order of magnitude larger than the $^{13}C/^{12}C$ signals (Francey and Tans, 1987). Isotopic exchange with ground water and with leaf water, the latter being catalyzed by the enzyme carbonic anhydrase, were postulated as the explanation for the large observed asymmetric north-south gradient in the global atmosphere. The precipitation at high latitudes is depleted in heavy isotopic species (HDO, $H_2{}^{18}O$), and some of that signature is imparted to CO_2 through isotopic exchange reactions. Significant interannual variability in $\delta^{18}O$ of CO_2 was also observed. Together with the large north-south gradient, this suggested that very large exchange fluxes had to be involved, of the order of $20 \cdot 10^{15}$ mol per year. For comparison, the fossil fuel emissions of CO_2 into the atmosphere amounted to about $0.5 \cdot 10^{15}$ mol per year during the 1990s decade. At the same time Friedli et al. (1987) concluded from the isotopic analysis of aircraft samples over Switzerland that exchange with soil and leaf water must play an important role in setting the $^{18}O/^{16}O$ ratio of atmospheric CO_2. More recently, Farquhar et al. (1993) noted that different biomes can have markedly different effects on atmospheric $\delta^{18}O$, and confirmed that strong fluxes are involved. These findings open up the possibility of diagnosing terrestrial carbon exchange processes from atmospheric isotopic data.

We are particularly interested in exploring the possibility of assessing separately the magnitudes of the photosynthetic and the respiratory fluxes of carbon. Water in leaves is enriched in heavy isotopes with respect to groundwater through the process of evapotranspiration. The reason is that light isotopic water species evaporate slightly more rapidly than heavy species, and the latter are preferentially left behind in leaves. The CO_2 originating from root respiration and heterotrophic respiration has an isotopic signature determined by soil water, which is more depleted in heavy isotopes, whereas the CO_2 that has been inside a photosynthesizing leaf has an isotopic signature closer to leaf water, which is enriched. On average, one third of the CO_2 diffusing into stomates is assimilated. The two thirds that diffuses back out has isotopically equilibrated with leaf water. A full explanation of observed atmospheric isotopic pat-

terns requires much additional input, in general the coupling of the carbon cycle to the hydrologic cycle. We will need to know the isotopic values of the precipitation, soil water budgets including the isotopic profile of the water with depth, the relative humidity of the air, soil and leaf temperatures, evapotranspiration, whether plants have shallow or deep sources of water, etc. The first attempts to construct global models of ^{18}O in CO_2 have already been made (Farquhar et al., 1993; Ciais et al., 1997a,b). An exciting aspect is that possibly measurements of CO_2 isotopes can be used to provide constraints on evapotranspiration, and thereby on how the continental atmospheric energy balance is portrayed in climate models. But before launching into a full simulation of $\delta^{18}O$ of CO_2 in space and time, we can study in detail the effects of various isotopic processes in simple "schematic" cases, which aid in our understanding, and which can serve as benchmark tests for numerical simulations suitable for more general cases. I have developed a more general, time-dependent numerical model that allows variable diffusivity, temperature, water content, $\delta^{18}O$ of the water as a function of depth as well as catalysis of the hydration reaction, but that will be described elsewhere, together with measurements on soil systems. Especially in dry soils, there is often a very pronounced enrichment of isotopically heavy water near the surface (Barnes and Allison, 1983; Allison et al., 1983).

This paper will take a close look at two phenomena, described by the same differential equation: the isotopic signature of CO_2 respired from soils, and modification of atmospheric CO_2 because it invades soils. The respired CO_2 equilibrates with the soil moisture, but the light isotopic species diffuses from the soil more rapidly, thereby enriching the CO_2 left behind and bringing it out of isotopic equilibrium with the moisture. These two processes are in competition, and the escaping CO_2 is intermediate in its isotopic composition. The invasion is not associated with any net flux of CO_2 in or out of the soil, but is a purely isotopic process that always occurs, and that may interfere with the correct interpretation of isotopic flux measurements if not taken into account.

In Section 2 the differential equations describing the situation will be set up, and in Sections 3 to 5 the equations will be solved explicitly for 3 different cases in which certain simplifying assumptions are made. Each term in the solution has an explicit physical interpretation, thus providing insight. In Section 6 we will look at the consequences for atmospheric measurements of $\delta^{18}O$ of CO_2. As an aside, the term describing the invasion from the atmosphere could also be applied to the gas fluxes associated with several other chemical diffusive processes, such as the consumption of methane or hydrogen by soil bacteria, or the (extremely slow) equilibration of ^{18}O of CO_2 with ice particles in firn.

2. Equations for diffusion and equilibration in soils, and general method of solution

The rate of production of CO_2 as a function of depth z, through root respiration as well as heterotrophic processes, in $\mathrm{mol\,s^{-1}\,cm^{-3}}$ (of total soil volume) is described by the function $S(z)$. We assume that the transport of gas molecules takes place solely by diffusion, given by the molecular diffusivity of CO_2 in free air, D, equal to $0.14\ \mathrm{cm^2\,s^{-1}}$, times a tortuosity factor κ, in many situations equal to about 2/3 (Hillel, 1980), which accounts for the fact that the shortest path is often blocked by soil particles. The effect of pumping of soil air through pressure fluctuations is neglected. (It could be included by assuming that diffusive processes do not start at the surface, but at some finite depth, as has been done in firn modeling (Battle et al., 1996)). $C(z)$ is the air concentration of CO_2, and $\varepsilon_a(z)$ is the fraction of the total soil volume occupied by air (air porosity), typically 0.20 (Hillel, 1980). Then the diffusional CO_2 flux equals:

$$F = -\varepsilon_a \kappa D \,\mathrm{grad}\, C\,. \tag{1}$$

Advective mass flow, for instance from evaporating water, and thermal diffusion effects are neglected. The change in concentration as a function of time is

$$\frac{\partial(\varepsilon_t C)}{\partial t} = \frac{\partial}{\partial z}\left(\varepsilon_a k D \left(\frac{\partial C}{\partial z}\right)\right) + S\,. \tag{2}$$

The variable ε_t, which we will call the total CO_2 porosity, has been introduced here. It is equal to the sum $\varepsilon_a + B\varepsilon_w$. It takes into account both the CO_2 in the air-filled pores and the CO_2 dissolved in the finely dispersed water-filled pores (ε_w). B is the (dimensionless) Bunsen coefficient (Weiss,

1974), the molar density of the dissolved gas in water divided by the molar density in air, at equilibrium, and at the local temperature and pressure. The dissolved CO_2 contributes to the total CO_2 present in soil pores, but does not contribute to the diffusive transport. Because of the enormous air surface-to-volume ratio of liquid water in non-saturated soils dissolved and gaseous CO_2 are assumed to be in equilibrium at all times. For $S(z)$, ε_a, ε_t, and κ constant in time (or changing only very slowly) concentration gradients stabilize in one day over a distance of close to a meter, so we will limit ourselves to a consideration of the steady state concentration. If ε_a and κ are also independent of depth, eq. (2) becomes

$$0 = \varepsilon_a \kappa D \frac{d^2 C}{dz^2} + S. \tag{3}$$

Because eq. (3) is linear, the general solution for an arbitrary production function $S(z)$ can be obtained via the method of Green's functions (Butkov, 1968). The Green's function $G(z, z')$ is the solution to eq. (3) for a steady state production "spike" at depth z', and zero everywhere else, expressed by the Dirac delta function $\delta(z-z')$:

$$0 = \varepsilon_a \kappa D \frac{d^2 G(z, z')}{dz^2} + \delta(z - z'). \tag{4}$$

The Green functions for spikes at 2 different depths are shown in Fig. 1.

$$\begin{aligned} &\text{for} \quad 0 < z < z' \quad G(z, z') = z/\varepsilon_a \kappa D, \\ &\text{for} \quad z > z' \quad G(z, z') = z'/\varepsilon_a \kappa D, \end{aligned} \tag{5}$$

The solution for arbitrary $S(z)$ is obtained as a linear combination of the Green functions $G(z, z')$, each one weighted by the actual steady state

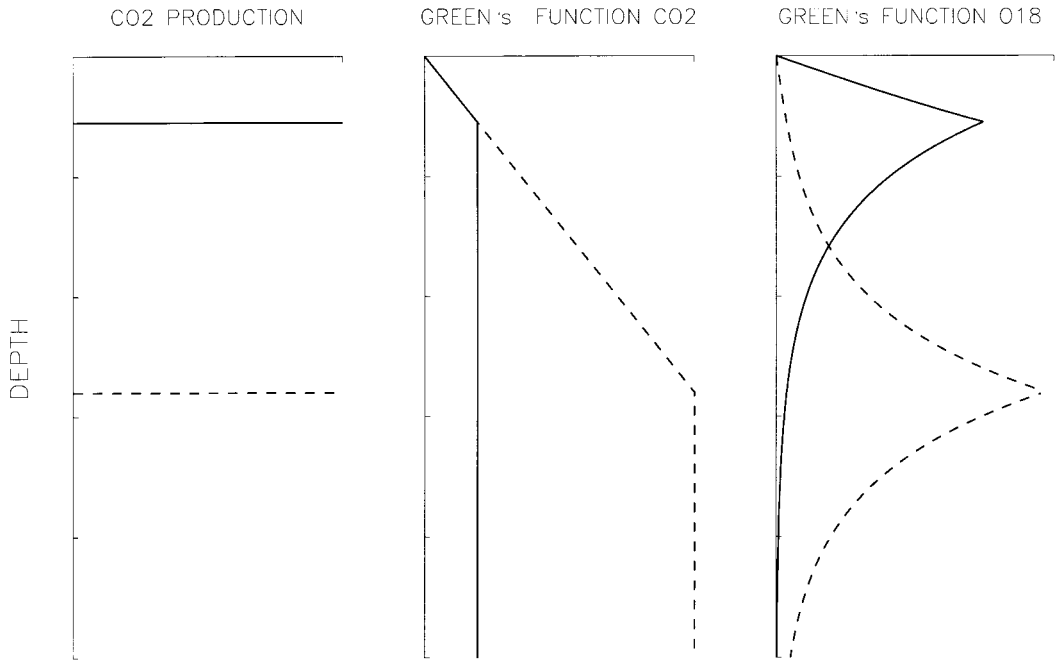

Fig. 1. Green's functions. Left panel: 2 cases of CO_2 production as a spike (δ-function) at different depths in the soil. Middle panel: CO_2 concentration responses to the two spikes, the dashed and solid lines corresponding to their respective spikes. The production is the same in both cases, so that the slopes are equal as a result of the assumption that the diffusivity is uniform with depth. The deeper spike leads to a higher concentration deep in the profile because it is more difficult for the gas to escape. Right panel: The curvature of the ^{18}O Green's functions is determined by z_1 [eq. (8)], the depth over which an ^{18}O-signature is preserved before it is erased by equilibration with water. In the isotopic case the peak of the Green's function is a little lower for a source close to the surface, and actually approaches zero as the location of the production spike approaches $z = 0$.

production rate $S(z')$ at depth z':

$$C(z) = \int_0^\infty \mathrm{d}z'\, G(z, z')S(z'). \tag{6}$$

In constructing the Green function, we choose the boundary value as $C(0)=0$, in other words zero atmospheric concentration, so that the flux is entirely out of the soil. To obtain the full solution, the effect of a finite atmospheric concentration C_a has to be added. The latter is the solution to eq. (4) with $S(z)=0$ everywhere and boundary condition $C(0)=C_a$, which is the trivial constant solution $C(z)=C_a$.

The concentration of the rare isotopic species will be expressed as $R(z)\cdot C(z)$, in which R is the ratio of the rare isotopic species to the total concentration of the chemical species. As in the case of eq. (3) for the total chemical concentration we again assume steady state, and the equation for the isotopic species is:

$$0 = \frac{\partial(\varepsilon_t R\cdot C)}{\partial t} = S\cdot R_S + k_H B\varepsilon_w C(R_{eq} - R) + \frac{\partial}{\partial z}\left(\varepsilon_a \kappa D_{18}\frac{\partial(R\cdot C)}{\partial z}\right), \tag{7}$$

in which $R_{eq}(z)$ is the isotopic ratio of CO_2 in equilibrium with soil moisture at the local temperature, $k_H B\varepsilon_w$ is the rate of isotopic equilibration, which takes place in the dissolved phase only, and D_{18} is the free-air molecular diffusivity of $^{18}OC^{16}O$. B is again the Bunsen solubility coefficient. Mills and Urey (1940) found that isotopic exchange between H_2O and CO_2 takes place upon hydration of the dissolved CO_2 to carbonic acid (rate constant k_H), and that the hydration reaction is slow. The reaction rate is also strongly temperature dependent (Skirrow, 1975). In plants this reaction is catalyzed by the enzyme carbonic anhydrase (Reed and Graham, 1981), but it is uncertain if, or to what extent, catalysis may take place in soils and plant litter. We will assume it does not, and in that case k_H depends only on temperature. The equilibrium $R_{eq}(z)$ is in general a function of depth because the isotopic ratio of the water often varies with depth (Barnes and Allison, 1983; Allison et al., 1983), and the isotopic equilibrium fractionation depends on temperature as well. The actual total amount of the rare isotopic species of dissolved CO_2(aq) per volume of soil equals $B\varepsilon_w CR$, while in thermodynamic equilibrium it would be $B\varepsilon_w CR_{eq}$. The isotopic ratio of newly produced CO_2 is R_S, which we will assume to be in equilibrium with the local moisture (R_{eq}), although this is not at all a necessary simplification to reach a solution, as will be seen below. We neglect the isotopic effect on CO_2 caused by the net mass flux of water vapor out of the soil, against which other gases are diffusing back in (Severinghaus et al., 1996) because it can be estimated to be at most a few tenths of a permil. Likewise, thermal diffusion is neglected for the same reason. The thermal diffusion factor of CO_2 relative to O_2 and N_2 is small (Chapman and Cowling, 1970), and differences between heavy and light CO_2 relative to O_2 and N_2 can be estimated to be smaller still (Grew and Ibbs, 1952).

As in the case of eq. (3) we assume steady state, and simplify further by assuming ε_a, $B\varepsilon_w$, and κ, as well as k_H, to be independent of depth. We define z_1 as the isotopic equilibration distance by

$$z_1^2 = \frac{\varepsilon_a \kappa D_{18}}{B\varepsilon_w k_H}. \tag{8}$$

Then eq. (7) can be written as:

$$\left(1 - z_1^2\frac{\mathrm{d}^2}{\mathrm{d}z^2}\right)(R\cdot C) = \frac{S\cdot R_S}{B\varepsilon_w k_H} + C\cdot R_{eq}. \tag{9}$$

Eq. (9) is linear, and the Green function for a production spike at depth z' is defined by:

$$\left(1 - z_1^2\frac{\mathrm{d}^2}{\mathrm{d}z^2}\right)G(z, z') = \delta(z - z'). \tag{10}$$

In domain $(0, z')$ the general solution to eq. (10) is $A_1\exp(z/z') + B_1\exp(-z/z')$, and in domain (z', ∞) the solution is $A_2\exp(z/z') + B_2\exp(-z/z')$. Four conditions will specify the 4 constants A and B. As boundary conditions we take $G(0, z')=0$ because we will later handle separately the influence of the atmospheric boundary condition (therefore, in this part of the solution there is no back-diffusion of atmospheric $^{18}OC^{16}O$ into the soil), and $G(\infty, z')=0$ because the influence of a spike on the isotopic composition is local and does not extend to infinite depth. Furthermore, we require continuity at $z=z'$. The integral over a finite interval surrounding a delta function is unity, which leads to another condition on the solution, relating the derivatives on both sides of

$z = z'$:

$$\lim_{\delta \to 0} \int_{z'-\delta}^{z'+\delta} \left(1 - z_1^2 \frac{\mathrm{d}^2}{\mathrm{d}z^2}\right) G(z, z') = z_1^2 \left(\frac{\mathrm{d}G(z, z')}{\mathrm{d}z}\bigg|_{z'-\delta} - \frac{\mathrm{d}G(z, z')}{\mathrm{d}z}\bigg|_{z'+\delta} \right) = 1 .$$

As a result, we obtain for the Green function in the 2 intervals:

$$\begin{aligned} &\text{for} \quad 0 < z < z' \quad \frac{1}{2z_1} \mathrm{e}^{-z'/z_1} (\mathrm{e}^{z/z_1} - \mathrm{e}^{-z/z_1}), \\ &\text{for} \quad z > z' \quad \frac{1}{2z_1} \mathrm{e}^{-z/z_1} (\mathrm{e}^{z'/z_1} - \mathrm{e}^{-z'/z_1}). \end{aligned} \tag{11}$$

This Green's function is shown in the third panel of Fig. 1. The general steady state solution is the superposition of $G(z, z')$ properly weighted:

$$R(z)C(z) = \int_0^\infty \mathrm{d}z'\, G(z, z') \times \left[C(z')R_{\mathrm{eq}}(z') + \frac{S(z')R_{\mathrm{S}}(z')}{B\varepsilon_{\mathrm{w}} k_{\mathrm{H}}} \right]. \tag{12}$$

The influence of the atmosphere is taken into account by solving

$$\left(1 - z_1^2 \frac{\mathrm{d}^2}{\mathrm{d}z^2}\right) R(z)C(z) = R_{\mathrm{eq}}(z)C(z), \tag{13}$$

with $S(z) = 0$ everywhere, constant $C(z) = C_{\mathrm{a}}$, and $R(0) = R_{\mathrm{a}}$, the isotopic ratio in the atmosphere. Assuming that R_{eq} is independent of depth (not necessary, but it gives a simple solution), we obtain

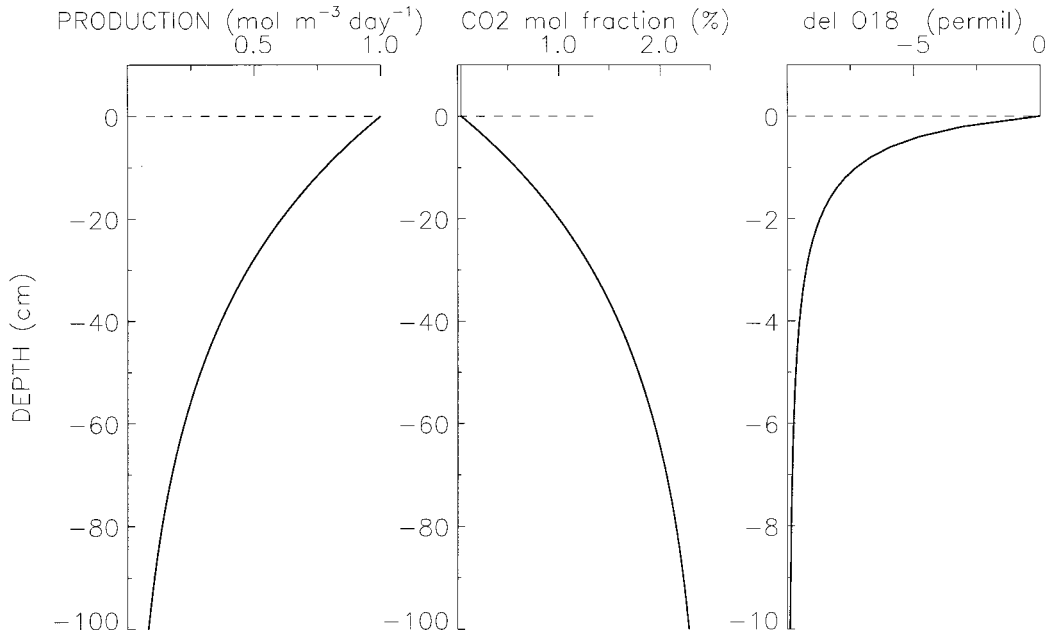

Fig. 2. Profiles in the soil of CO_2 production as a function of depth, the concentration, and the ^{18}O isotopic ratio. Assumptions: depth scale of exponential decrease of production 40 cm, depth-integrated production 0.4 mol m^{-2} day^{-1}, air-filled porosity equals 0.2, tortuosity equals 0.66, and $z_1 = 2.5$ cm. The CO_2 concentrations in the middle panel have been converted (approximately) from mol cm^{-3} to mol fractions in whole air for easier reading. The atmospheric CO_2 mixing ratio is nearly indistinguishable from zero on this scale. Because of the relatively short isotopic equilibration distance the z-axis of the right-hand panel has been expanded near the top of the profile. The assumptions about the isotopic values are that CO_2 completely equilibrated with the soil moisture is 10 permil lighter than atmospheric CO_2, which is assumed to be at 0 permil.

for the atmospheric contribution:

$$RC = C_a[R_{eq} + (R_a - R_{eq})e^{-z/z_1}], \tag{14}$$

which gives rise to a flux of isotopic CO_2 between the atmosphere and the soil because of isotopic equilibration taking place in the soil, even in the complete absence of any respiration. Expression (14) has to be added to eq. (12) in order to obtain the full solution with the correct atmospheric boundary values.

Fluxes at the atmosphere-soil boundary are derived from

$$\begin{aligned} F &= -\varepsilon_a \kappa D \left.\frac{dC}{dz}\right|_{z=0}, \\ F_{18} &= -\varepsilon_a \kappa D_{18} \left.\frac{d(RC)}{dz}\right|_{z=0}, \end{aligned} \tag{15}$$

with a minus sign when directed out of the soil.

3. Case 1. Respiration as an exponential function of depth

3.1. The mathematical solution

We first work out the solution for the case where the CO_2 production decreases exponentially with depth, $S(z) = S_o \exp(-z/z_0)$, because it has been presented (without derivation) by Hesterberg and Siegenthaler (1991). The isotopic ratio of CO_2 in equilibrium with soil moisture is assumed to be independent of depth. Their equation and its solution are not entirely correct because they do not take account of the distinction between $B\varepsilon_w$ and ε_a. We will also group the terms somewhat differently, so that they correspond better to the separate physical processes occurring. For total CO_2 we find with the help of eqs. (5), (6):

$$\begin{aligned} C(z) &= \frac{1}{\varepsilon_a \kappa D}\left[\int_0^z dz'\, S(z')z' + z\int_z^\infty dz'\, S(z')\right] \\ &= \frac{S_o}{e_a \kappa D} z_0^2(1 - e^{-z/z_0}) + C_a. \end{aligned} \tag{16}$$

The flux into the atmosphere is, with the help of eq. (15), equal to $S_o z_0$, the total respiration integrated over depth.

In the same way we have for the isotopes, assuming R_S and R_{eq} to be independent of depth, and using (11), (12), and (16):

$$\begin{aligned} (R \cdot C)(z) = {} & \frac{1}{2z_1}\int_0^z dz' \left[\frac{S_o R_S}{B\varepsilon_w k_H} e^{-z'/z_0} + \frac{S_o z_0^2 R_{eq}}{\varepsilon_a \kappa D} \right. \\ & \left. \times (1 - e^{-z'/z_0})\right] e^{-z/z_1}(e^{z'/z_1} - e^{-z'/z_1}) \\ & + \frac{1}{2z_1}\int_z^\infty dz' \left[\frac{S_o R_S}{B\varepsilon_w k_H} e^{-z'/z_0} + \frac{S_o z_0^2 R_{eq}}{\varepsilon_a \kappa D} \right. \\ & \left. \times (1 - e^{-z'/z_0})\right] e^{-z'/z_1}(e^{z/z_1} - e^{-z/z_1}) \\ & + C_a[R_{eq} + (R_a - R_{eq})e^{-z/z_1}]. \end{aligned} \tag{17}$$

After straightforward, but tedious, algebra this equals

$$\begin{aligned} (R \cdot C)(z) = {} & \frac{S_o z_0^2 R_{eq}}{\varepsilon_a \kappa D}(1 - e^{-z/z_0}) \\ & + \left(\frac{S_o R_S z_0^2}{B\varepsilon_w k_H} - \frac{S_o z_0^2 R_{eq} z_1^2}{\varepsilon_a \kappa D}\right) \\ & \times \left(\frac{e^{-z/z_0} - e^{-z/z_1}}{z_0^2 - z_1^2}\right) \\ & + C_a[R_{eq} + (R_a - R_{eq})e^{-z/z_1}]. \end{aligned} \tag{18}$$

The reader may verify that eq. (18) solves the differential equation, eq. (9) above, and that the boundary condition $R(z) = R_a$ at $z = 0$ is satisfied.

The CO_2 production as a function of depth, and the solutions for $C(z)$ and $(R \cdot C)(z)$ are shown in Fig. 2, the latter expressed in the customary δ-notation (see below). The first term of eq. (18) is the CO_2 profile due to production in the soil completely isotopically equilibrated with the water. The second represents corrections to the state of complete equilibration due to kinetic effects. The third term is completely due to the invasion from the atmosphere. After rewriting $S_o/B\varepsilon_w k_H$ as follows,

$$\begin{aligned} \frac{S_o}{B\varepsilon_w k_H} &= \frac{S_o z_0^2}{\varepsilon_a \kappa D}\frac{\varepsilon_a \kappa D}{z_0^2 B\varepsilon_w k_H} \\ &= \frac{S_o z_0^2}{\varepsilon_a \kappa D}\frac{\varepsilon_a \kappa D_{18}}{B\varepsilon_w k_H}\frac{1}{z_0^2}\frac{D}{D_{18}} \\ &= \frac{S_o z_0^2}{\varepsilon_a \kappa D}\frac{z_1^2}{z_0^2}\frac{1}{\alpha_D}, \end{aligned} \tag{19}$$

in which the kinetic fractionation factor associated with diffusion is defined as $\alpha_D = D_{18}/D$, it can be seen that eq. (18) is equal to eq. (8) of Hesterberg and Siegenthaler (1991). Note, however, that our

definition of z_1 differs from theirs. The kinetic fractionation factor α_D has a magnitude slightly less than 1 because the heavier molecules diffuse more slowly.

3.2. The soil-to-air fluxes

For the $^{18}OC^{16}O$ flux at the soil-air boundary we obtain with eq. (15), assuming (for simplicity) that $R_S = R_{eq}$,

$$F_{18} = -\frac{\varepsilon_a \kappa D_{18}}{\varepsilon_a \kappa D} R_{eq} S_o z_0 \left[1 + \left(\frac{1}{\alpha_D} - 1\right)\frac{z_1}{(z_0 + z_1)}\right] + \frac{\varepsilon_a \kappa D_{18}}{z_1} C_a (R_a - R_{eq}). \quad (20)$$

Since the flux out of the soil has a negative sign with z increasing with depth, we will define $F_{sa} = -F(= +S_o z_0)$, for the soil to atmosphere flux with a positive sign, and $F_{sa,18} = -F_{18}$. With $\alpha_D = 1 + \varepsilon_D$, expression (20) simplifies further to:

$$F_{sa,18} = -F_{18} = R_{eq} F_{sa}\left(\alpha_D - \frac{\varepsilon_D}{1 + z_0/z_1}\right) + \sqrt{\varepsilon_a B \varepsilon_w k_H \kappa D_{18}}\, C_a (R_{eq} - R_a). \quad (21)$$

The factor $\sqrt{e_a B \varepsilon_w k_H \kappa D_{18}}$ has dimensions of velocity, and could, in analogy with air-sea exchange, be called a "piston" velocity or exchange velocity for atmosphere-soil exchange, the rate at which a column of air gets "pushed" into the soil. In yet other words, it gives us the equivalent column of air out of which all CO_2 exchanges its oxygen isotopes with soil water in a given amount of time. It will be seen that this piston velocity is greater in many cases than the mean piston velocity of CO_2 exchange between the air and the sea. The reason is that the surface area of water in the soil is enormous, which compensates for the fact that gas diffusion in a soil is relatively slow. The influence of $F_{sa,18}$ and F_{sa} on the isotopic composition in the atmosphere can be derived, completely analogous to an earlier derivation for ^{13}C (Tans, 1980), from:

$$HC_a \frac{dR_a}{dt} = F_{sa,18} - F_{sa} \cdot R_a .$$

H is the equivalent height of the atmospheric column in meters, when it is assumed that the atmosphere has the same (sea level) density everywhere. At sea level and 25° degrees centigrade and a CO_2 mole fraction in dry air of 350 μmol/mol^{-1}, C_a equals $14.3 \cdot 10^{-3}$ mol m^{-3}, neglecting dilution effects by water vapor. Changing to the customary δ-notation by dividing all isotopic ratios by R_{PDB}, the ratio of the isotopic standard PeeDee Bellemnite, and again writing the kinetic fractionation factor during diffusion α_D as $1 + \varepsilon_D$, we obtain, by approximating, where appropriate, R_{eq}/R_{PDB} as equal to 1:

$$HC_a \frac{d\delta_a}{dt} = F_{sa}\left(\delta_{eq} - \delta_a + \varepsilon_D \frac{z_0/z_1}{1 + z_0/z_1}\right) + \sqrt{\varepsilon_a B \varepsilon_w k_H \kappa D_{18}}\, C_a (\delta_{eq} - \delta_a). \quad (22)$$

In eq. (22), we can clearly see the effect of the competition between the lighter isotopic species leaving the soil more rapidly, and the isotopic exchange trying to prevent the soil CO_2 from becoming enriched as a result. When the equilibration is rapid, taking place over a distance much shorter than the zone of CO_2 production, $z_1 \ll z_0$, the respiratory flux leaving the soil is depleted by the full kinetic effect ε_D (−0.0087, or -8.7 permil). On the other hand, in cases where the equilibration is slow, or when all CO_2 production takes place right near the top of the profile in a zone much shallower than the isotopic equilibration distance, $z_0 \ll z_1$, the CO_2 becomes enriched, cancelling the kinetic effect.

Estimates for typical magnitudes of the terms in eq. (22) are as follows. The respiratory flux in a mid-latitude forest during the summer can typically be 0.4 mol m^{-2} day^{-1}, whereas during the winter this value may drop to 0.1 mol m^{-2} day^{-1}. The annual total for the respiration may be 60 mol m^{-2} year^{-1} (Wofsy et al., 1993). Since the total amount of CO_2 in the entire atmospheric column is about 125 mol m^{-2}, respiration obviously has a major influence. The second term of eq. (22), CO_2 invasion into the soil, is smaller in many cases, but still important. The rate of hydration k_H equals $0.037 \exp(0.118(T-25))$ (T in degrees C; Skirrow, 1975), and B, the Bunsen solubility coefficient of CO_2, has been fitted to the solubility data of Weiss (1974) as follows: $B = 1.739 \exp(-0.0390T + 0.000236T^2)$. If we take for the air-filled pore fraction $\varepsilon_a = 0.20$, the water-filled pore fraction $\varepsilon_w = 0.3$, $B = 0.76$ (at 25 °C), $\kappa = 0.66$, $D = 0.14$ cm^2 s^{-1}, we find for $T = 25$ °C a piston velocity of 0.0125 cm s^{-1}, or 10.8 m day^{-1}, or 0.15 mol m^{-2} day^{-1}, assuming the CO_2 mole fraction in humid air to be $350 \cdot 10^{-6}$. For compar-

ison, a typical air-sea piston velocity (defined with respect to CO_2 dissolved in water) is 4 m day^{-1}. The equilibration depth in the soil (z_1) is 1.5 cm for the assumptions above. At $T=0°C$ we obtain 0.0043 cm s^{-1}, or 3.7 m day^{-1}, or 0.060 mol m^{-2} day^{-1}, while z_1 is 4.3 cm. The length scale for the CO_2 production rate (z_0) is typically tens of cm. The small equilibration depth (even without catalytic enhancement) implies that the kinetic diffusion effect will be strongly expressed, and furthermore, that only the isotopic composition and the temperature of the water in the uppermost 5–10 cm of the soil determine the isotopic signature of the outgoing CO_2 flux in most cases.

In areas of low biological productivity the invasion term may become the major influence on $\delta^{18}O$ of atmospheric CO_2. We will see later how much the invasion flux is diminished by first having to traverse a dry upper soil zone. The isotopic invasion flux slows down during the cold season mostly because the rate of hydration is strongly dependent on temperature. Based on the annual temperature variation in the top 10 cm of the soil in a forest in Wisconsin (P. Bakwin, personal communication), the estimated magnitude for the annual total invasion flux may be 20–30 mol m^{-2} in that case (CO_2 near the forest floor is considerably higher than the background value), which is about 20% of the atmospheric column. However, that number may still only be a lower bound for two reasons. Catalysis of the CO_2 hydration reaction may occur, either through the presence of the enzyme carbonic anhydrase, or directly on clay surfaces. Secondly, the diffusion in the upper layers of a soil is significantly greater than modeled here. Macropores and fissures in aggregated soils greatly enhance diffusivity in the top meter or so (Davidson and Trumbore, 1995), and the effect is especially pronounced in the top 5–10 cm of a drying soil, as was found by Matthieu and Bariac (1996a, b) from a study of the effect of water infiltration and evaporation on the soil water content and its isotopic ratio.

4. Case 2. Respiration constant as a function of depth

4.1. The mathematical solution

The next simple case for which we will obtain exact solutions is where the CO_2 production as a function of depth is constant, and equal to S_o from $z=0$ to $z=z_0$, and $S=0$ below z_0. Using the same method as for case 1, we find

$$\text{for} \quad 0<z<z_0 \quad C(z)=\frac{S_o}{\varepsilon_a \kappa D}(z_0 z-\tfrac{1}{2}z^2)+C_a,$$

$$\text{for} \quad z>z_0 \qquad C(z)=\frac{S_o z_0^2}{2\varepsilon_a \kappa D}+C_a. \tag{23}$$

The flux into the atmosphere is again equal to $S_o z_0$, the total CO_2 production integrated over depth in the soil. The production and concentration profiles are shown in Fig. 3. The concentration function and its first derivative are continuous at $z=z_0$, as they should.

Again after tedious algebra, we find for the isotopes, for $0<z<z_0$:

$$\begin{aligned}(R\cdot C)(z)=&\frac{S_o R_{eq}}{\varepsilon_a \kappa D}(z z_0-\tfrac{1}{2}z^2)\\&+C_a[R_{eq}+(R_a-R_{eq})e^{-z/z_1}]\\&+\left(\frac{S_o R_S}{B\varepsilon_w k_H}-\frac{S_o R_{eq} z_1^2}{\varepsilon_a \kappa D}\right)\\&\times[1-e^{-z/z_1}-\tfrac{1}{2}e^{-z_0/z_1}(e^{z/z_1}-e^{-z/z_1})]\end{aligned} \tag{24a}$$

and for $z>z_0$:

$$\begin{aligned}(R\cdot C)(z)=&\frac{S_o R_{eq} z_0^2}{2\varepsilon \kappa D}+C_a[R_{eq}+(R_a-R_{eq})e^{-z/z_1}\\&+\left(\frac{S_o R_S}{B\varepsilon_w k_H}-\frac{S_o R_{eq} z_1^2}{\varepsilon_a \kappa D}\right)\\&\times\tfrac{1}{2}e^{-z/z_1}(e^{z_0/z_1}+e^{-z_0/z_1}-2).\end{aligned} \tag{24b}$$

The reader may verify that (24) solves the differential equation, and that the solution and its derivative are continuous at $z=z_0$. It is shown in the right-hand panel of Fig. 3.

4.2. The soil-to-air fluxes

The flux at the soil-air boundary, using (15), and now assuming $R_S=R_{eq}$, equals:

$$\begin{aligned}F_{sa,18}=&-F_{18}=\alpha_D F_{sa} R_{eq}\\&+F_{sa}R_{eq}\frac{z_1}{z_0}(1-\alpha_D)(1-e^{-z_0/z_1})\\&+\sqrt{\varepsilon_a B\varepsilon_w k_H \kappa D_{18}}(R_{eq}-R_a)C_a.\end{aligned} \tag{25}$$

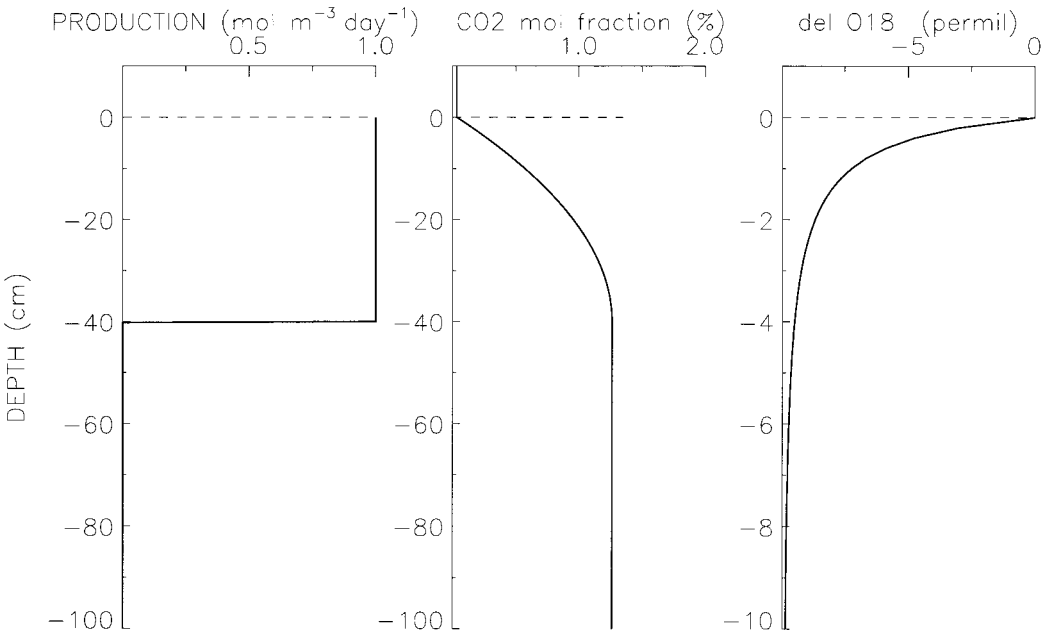

Fig. 3. Soil profiles as in Fig. 2, but assuming that the same total amount of productivity is uniformly distributed over the first 40 cm. The deep soil CO_2 is lower than in Fig. 2 because all production takes place relatively close to the surface where there is less resistance to escape toward the atmosphere.

After changing to the customary δ-notation, we have for the change in the atmosphere, to a very good approximation:

$$HC_a \frac{d\delta_a}{dt} = F_{sa}\left[\delta_{eq} - \delta_a + \varepsilon_D\left(1 - \frac{z_1}{z_0}(1 - e^{-z_0/z_1})\right)\right] + \sqrt{\varepsilon_a B \varepsilon_w k_H \kappa D_{18}}\, C_a(\delta_{eq} - \delta_a). \quad (26)$$

The form of this equation is a little different from (22), but the result is nearly identical. For $z_0 \ll z_1$, the CO_2 is isotopically enriched near the surface, nullifying the kinetic depletion, because the equilibration with water is too slow (large z_1). This is expressed by the fact that the factor multiplying ε_D is near zero. At the other extreme, $z_1 \ll z_0$, the full kinetic effect is experienced because the factor multiplying ε_D is near 1.

5. Case 3. A zone of constant production underneath an inert surface layer

5.1. *Total CO_2*

The next case is a generalization of the previous one. In desert areas the upper layer can be completely dry, but there is moisture deeper down in the profile, with which oxygen isotopic exchange takes place. The same can happen under a layer of snow on the surface. We will assume that some CO_2 production occurs in the moist zone as well, so that our simple picture comprises a zone of constant production of thickness z_0 from depth d_1 to d_2, with air-filled porosity ε_2, tortuosity κ_2, rate of oxygen equilibration k_H, overlain by a dry layer of thickness d_1, (greater) porosity ε_1, tortuosity κ_1, and no oxygen exchange. We assume no production below d_2, but constant ε_2, κ_2. Total production is then $S_o z_0$. The Green function for total CO_2 is shown in Fig. 4, and given

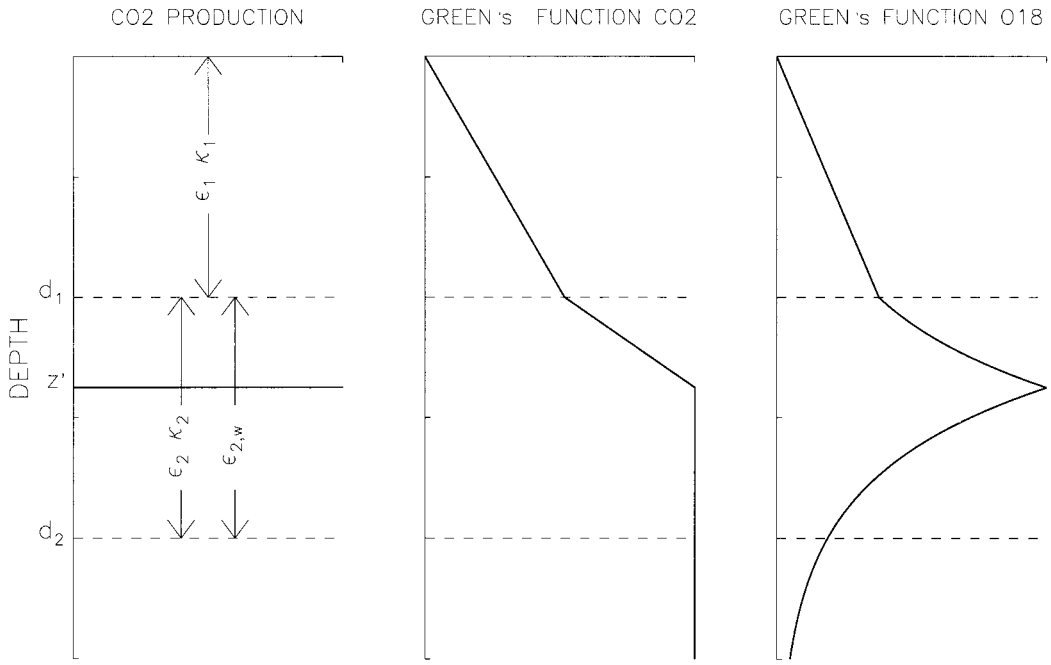

Fig. 4. Green's functions for a soil with no water and no CO_2 production from $z=0$ to $z=d_1$, and moisture and productivity between d_1 and d_2. The air porosity (ε_1) is larger in the dry zone than in the moist zone (ε_2) so that the diffusional flux requires a lower concentration gradient.

here:

$$\begin{aligned} z<d_1 \qquad & G(z,z')=\frac{z}{\varepsilon_1\kappa_1 D},\\ d_1<z<z' \qquad & G(z,z')=\frac{d_1}{\varepsilon_1\kappa_1 D}+\frac{z-d_1}{\varepsilon_2\kappa_2 D}, \qquad (27)\\ z>z' \qquad & G(z,z')=\frac{d_1}{\varepsilon_1\kappa_1 D}+\frac{z'-d_1}{\varepsilon_2\kappa_2 D}. \end{aligned}$$

The concentration profile is calculated from

$$C(z)=\int_{d_1}^{d_2} \mathrm{d}z'\, S(z')G(z,z'),$$

because $S(z)=0$ outside the interval (d_1, d_2). The resulting profile, including the effect of the atmospheric boundary condition, is

$$\begin{aligned} z<d_1 \qquad & C(z)=\frac{S_o z_0}{\varepsilon_1\kappa_1 D}\,z+C_a,\\ d_1<z<d_2 \qquad & C(z)=\frac{S_o z_0}{\varepsilon_1\kappa_1 D}\,d_1+\frac{S_o}{2\varepsilon_2\kappa_2 D} \qquad (28)\\ & \qquad \times[z_0^2-(z-d_2)^2]+C_a,\\ z>d_2 \qquad & C(z)=\frac{S_o z_0 d_1}{\varepsilon_1\kappa_1 D}+\frac{S_o z_0^2}{2\varepsilon_2\kappa_2 D}+C_a. \end{aligned}$$

It is seen from (28), with (15), that the flux of total CO_2 out of the soil is not affected, in steady state, by a layer of inert porous material on top of the producing layer, as expected.

5.2. *The isotopic species*

For the isotopes, we need to construct the Green function solving eq. (10) in the interval (d_1, ∞), and, since there is only diffusion and no isotopic equilibration above d_1, the Green function needs to solve $\varepsilon_1\kappa_1 D_{18}\,\mathrm{d}^2G(z,z')/\mathrm{d}^2z=0$ in the interval $(0, d_1)$. $G(z,z')$ is set to zero at $z=0$ because the atmospheric boundary condition is handled separately.

$$\begin{aligned} z<d_1 \qquad & G(z,z')=Az,\\ d_1<z<z' \qquad & G(z,z')=B_+\mathrm{e}^{z/z_1}+B_-\mathrm{e}^{-z/z_1},\\ z>z' \qquad & G(z,z')=D\mathrm{e}^{-z/z_1}. \end{aligned} \qquad (29)$$

Already, use has been made of the boundary conditions $G(0,z')=0$ and $G(\infty,z')=0$. We demand continuity, as well as continuity of the

flux, at $z=d_1$. Two more conditions on the coefficients follow from continuity at $z=z'$, and from the relation between the derivatives on both sides of $z=z'$, as in the discussion following eq. (10). From these conditions, we find

$$A=\frac{1}{z_1}(e^{(d_1-z')/z_1})\frac{1}{d_1+z_1(\varepsilon_1\kappa_1/\varepsilon_2\kappa_2)}$$

and

$$B_+=\frac{1}{2z_1}e^{-z'/z_1}$$

$$B_-=\frac{1}{2z_1}(e^{(2d_1-z')/z_1})\frac{d_1-z_1(\varepsilon_1\kappa_1/\varepsilon_2\kappa_2)}{d_1+z_1(\varepsilon_1\kappa_1/\varepsilon_2\kappa_2)}$$

and

$$D=\frac{1}{2z_1}(e^{(2d_1-z')/z_1})\frac{d_1-z_1(\varepsilon_1\kappa_1/\varepsilon_2\kappa_2)}{d_1+z_1(\varepsilon_1\kappa_1/\varepsilon_2\kappa_2)}+\frac{1}{2z_1}e^{z'/z_1}.$$

The same definition [eq. (8)] for the equilibration distance, $z_1^2=\varepsilon_2\kappa_2 D_{18}/(B\varepsilon_{2,w}k_H)$, has been employed. $\varepsilon_{2,w}$ is the water-filled porosity between d_1 and d_2. This Green function is shown in Fig. 4. This time we will not calculate the entire solution before deriving the soil-to-air flux. We employ a shortcut by obtaining the contribution to the flux from $G(z,z')$ as

$$G_F(z')=-\varepsilon_1\kappa_1 D_{18}\left.\frac{dG(z,z')}{dz}\right|_{z=0}$$
$$=-B\varepsilon_{2,w}k_H(e^{(d_1-z')/z_1})\frac{1}{1+(d_1/z_1)\varepsilon_2\kappa_2/\varepsilon_1\kappa_1}, \quad (30)$$

and the integrated flux as

$$F_{18}=\int_{d_1}^{\infty}dz'\,G_F(z')\left(\frac{S(z')R_{eq}}{B\varepsilon_{2,w}k_H}+C(z')R_{eq}\right). \quad (31)$$

The integration extends from d_1 to infinity because there is no isotopic equilibration for $z<d_1$, and therefore no isotopic source term for $z<d_1$. Using the relation $F_{sa}=S_o z_0$ for the total CO_2 flux from the soil, we obtain from (31)

$$F_{sa,18}=-F_{18}=\alpha_D F_{sa}R_{eq}$$
$$+\frac{F_{sa}R_{eq}}{1+(d_1/z_1)(\varepsilon_2\kappa_2/\varepsilon_1\kappa_1)z_1/z_0}$$
$$\times(1-\alpha_D)(1-e^{-z_0/z_1}). \quad (32)$$

Expression (32) is identical to the applicable part of (25) in the limit $d_1\to 0$ (no inert layer on top of the profile).

The contribution to the isotopic flux from the invasion of atmospheric CO_2 is again obtained from the boundary conditions $C(0)=C_a$ and $R(0)=R_a$. In the two separate regions, the contributions to the solution $R(z)C(z)$ are

$0<z<d_1$

$$C_aR(z)=C_a\left(R_a+\frac{R_{eq}-R_a}{d_1+z_1(\varepsilon_1\kappa_1/\varepsilon_2\kappa_2)}z\right),$$

$z>d_1$

$$C_aR(z)=$$
$$C_a\left(R_{eq}-\frac{(R_{eq}-R_a)z_1(\varepsilon_1\kappa_1/\varepsilon_2\kappa_2)}{d_1+z_1(\varepsilon_1\kappa_1/\varepsilon_2\kappa_2)}e^{(d_1-z)/z_1}\right). \quad (33)$$

Thus we obtain for the contribution to the flux from CO_2 invasion

$$F_{sa,18}=-F_{18}=\sqrt{\varepsilon_2 B\varepsilon_{2,w}k_H\kappa_2 D_{18}}$$
$$\times C_a\frac{R_{eq}-R_a}{1+(d_1/z_1)\varepsilon_2\kappa_2/\varepsilon_1\kappa_1}, \quad (34)$$

and for the total change in atmospheric $\delta^{18}O$ resulting from the total soil-to-air flux:

$$HC_a\frac{d\delta_a}{dt}=F_{sa}\left[\delta_{eq}-\delta_a\right.$$
$$\left.+\varepsilon_D\left(1-\frac{z_1}{z_0}\frac{(1-e^{-z_0/z_1})}{1+(d_1/z_1)\varepsilon_2\kappa_2/\varepsilon_1\kappa_1}\right)\right]$$
$$+\sqrt{\varepsilon_2 B\varepsilon_{2,w}k_H\kappa_2 D_{18}}$$
$$\times\frac{C_a(\delta_{eq}-\delta_a)}{1+(d_1/z_1)\varepsilon_2\kappa_2/\varepsilon_1\kappa_1}. \quad (35)$$

Expression (35) is equal to the earlier expression (26) in the limit $d_1\to 0$.

We will look at two extreme cases to appreciate the effect on isotopic fluxes of the layer of inert porous material above the region of isotopic exchange. In the case $z_1\ll z_0$ (rapid exchange), the full effect of kinetic isotope fractionation during diffusion is felt (ε_D times ≈ 1). This is no different from the case without the inert layer (expression (26)). In the case $z_0\ll z_1$ (slow isotopic exchange) the kinetic effect is approximately equal to $\varepsilon_D[(d_1\varepsilon_2\kappa_2+z_0\varepsilon_1\kappa_1/2)/(d_1\varepsilon_2\kappa_2+z_1\varepsilon_1\kappa_1)]$, which means that it could be almost fully restored (if $d_1\varepsilon_2\kappa_2\gg z_1\varepsilon_1\kappa_1$) compared to the case without an

inert top layer. The reason is that the average residence time of the CO_2 produced in the soil increases, allowing more time for equilibration to occur. The concentration in the soil will build up to a higher level also. If there is no equilibration at all (corresponding to $z_1 =$ infinite), the kinetic effect is zero because in that case "all that comes in must go out". At the same time, the magnitude of the invasion flux is diminished by the factor $[z_1\varepsilon_1\kappa_1/(z_1\varepsilon_1\kappa_1 + d_1\varepsilon_2\kappa_2)]$, which depends most strongly on the ratio of the thickness of the inert layer (d_1) and the equilibration distance (z_1).

Let us estimate the invasion flux for an example of a dry soil. Assume that there is a completely dry layer, with air porosity of 0.5, of 10 cm thickness above a soil at 25°C, with water-filled pore fraction $\varepsilon_{2,w} = 0.3$, air-filled pore fraction $\varepsilon_2 = 0.2$, $\kappa = 0.66$. The equilibration depth z_1 equals then 1.5 cm. In the example following eq. (22) the invasion flux into such a soil would have been 10.8 m day^{-1}. The 10 cm thick dry top layer lowers the invasion flux by a factor of 3.7, making it 2.9 m day^{-1}.

6. Effect on atmospheric observations

Explicit analytical solutions have been presented for some simplified cases of CO_2 flux and isotopic equilibration in soils. Each term of the solutions has a physical interpretation, allowing a quantitative comparison of the competing effects of kinetic isotope fractionation during diffusion and isotopic re-equilibration, as well as allowing a quantitative assessment of the isotopic invasion flux. A more general time-dependent numerical simulation model, incorporating arbitrary profiles of CO_2 production, temperature, water content, water isotopic ratio, and diffusivity will be described elsewhere, together with experiments on soil columns.

In most cases only the upper 5–10 cm of the soil is important for the isotopic composition of the outgoing flux. Important questions to be addressed by experiments are (1a) what the effective average soil depth is where equilibration takes place, (1b) whether, and to what extent, catalysis may be taking place, (2a) how the effective air diffusivity changes as a function of depth near the surface, (2b) whether there is a significant amount of air-soil exchange through pumping by pressure fluctuations, and (3) how much isotopic enrichment of the soil water occurs near the surface in different environments. Hopefully, the soil water isotopic profile can be reliably modeled from the isotopic ratio of the precipitation, the surface energy balance (sensible versus latent heat loss) and the state of the vegetation (evapotranspiration through plants versus direct evaporation from the soil).

Atmospheric observations of isotopic ratios are often plotted against the inverse of the CO_2 concentration (Keeling, 1961) to derive the isotopic ratio characteristic of a source or sink. That procedure is fine for ^{13}C, but could lead to significant error for ^{18}O because of isotopic exchange independent of any sources. To illustrate the possible effect on the interpretation of atmospheric measurements, we can write for the isotopic flux entering the atmosphere and for the change in the atmospheric concentration and isotopic ratio, based on eqs. (21), (25), and (32):

$$H\frac{\mathrm{d}(RC)}{\mathrm{d}t} = F(1+\varepsilon_D f)R_{eq} + v_{ex}C(R_{eq} - R),$$
$$H\frac{\mathrm{d}C}{\mathrm{d}t} = F, \tag{36}$$

in which H is the height of a well mixed atmospheric layer adjacent to the surface, the factor $(1+\varepsilon_D f)$ takes into account the kinetic isotope effect arising from molecular diffusion, v_{ex} is the piston velocity or exchange velocity for isotopic exchange, equal to $\sqrt{e_a B e_w k_H \kappa D_{18}}$, and the subscript "eq" denotes isotopic equilibrium between CO_2 and soil water. The factor f expresses the effect that the kinetic fractionation $\varepsilon_D = -8.7$ permil is not fully expressed in the flux emanating from the soil. In the case of equations (21) and (22), f would be equal to $(z_0/z_1)/(1+z_0/z_1)$. The factor f is less than one, but is in most cases fairly close to 1.

The air parcel is in contact with the soil for an amount of time Δt, after which we have

$$\int \frac{\mathrm{d}(RC)}{\mathrm{d}t}\,\mathrm{d}t = \frac{F}{H}(1+\varepsilon_D f)R_{eq}\Delta t + \frac{v_{ex}R_{eq}}{H}\int C\,\mathrm{d}t - \frac{v_{ex}}{H}\int (RC)\,\mathrm{d}t,$$
$$\int \frac{\mathrm{d}C}{\mathrm{d}t}\,\mathrm{d}t = C - C_o = \frac{F\Delta t}{H},$$

which is equal to

$$RC - R_o C_o = (C - C_o)R_S + \frac{v_{ex}\Delta t}{H}(\overline{C}R_{eq} - \overline{RC}).$$

The subscript $_o$ stands for background or original concentration or isotopic ratio. R_S has replaced $(1+\varepsilon_D f)R_{eq}$, the isotopic ratio of the net flux leaving the ground. The overbars denote the mean value over the time interval of integration. We will assume that $\overline{C}$ equals $(C+C_o)/2$ and $\overline{RC}$ equals $(RC+R_oC_o)/2$. Further manipulation then leads to

$$\left\{1+\frac{A}{2}\left(1-\frac{C_o}{C}\right)\right\}\delta = \delta_S + (\delta_o - \delta_S)\frac{C_o}{C} + \frac{A}{2}\left\{\delta_{eq}\left(1-\frac{C_0^2}{C^2}\right) - \delta_o\frac{C_o}{C}\left(1-\frac{C_o}{C}\right)\right\}, \quad (37)$$

in which we have defined A as the total amount of exchanged CO_2 divided by the net CO_2 added from the soil,

$$A = \frac{v_{ex}\Delta t}{H}\frac{C}{C-C_o}. \quad (38)$$

In the example after eq. (16), the respiratory flux was 0.4 mol day^{-1}, and the exchange flux 0.15 mol day^{-1}, so that the factor A would be 0.375. In principle it could also be larger than 1, especially if the respiratory flux is low. Note that the classical "Keeling plot" is recovered in the case of $A=0$ (no isotopic exchange). For $A \gg 1$ (vigorous isotopic exchange combined with a low rate of respiration) the atmospheric isotopic ratio δ approaches δ_{eq}. In soil moisture there is often a significant isotopic gradient as a function of depth (Allison et al., 1983), so that the value of δ_{eq} of CO_2 represents a weighted equilibrium of CO_2 with the moisture in the upper 10 cm or so, depending on the isotopic equilibration distance z_1 [eq. (8)], which itself can vary with depth.

The atmospheric δ has been plotted as a function of C_o/C according to eq. (37) for various values of the parameter A in Fig. 5. A classical Keeling plot (see for instance, Flanagan et al., 1997) could easily give the wrong answer for the isotopic value of the respired CO_2. Over a fairly small range of C_o/C, noise in the data will usually prevent the detection of anything more than a linear trend. If the correlation between the isotopic values and C_o/C is tight and they cover a sufficient range, curvature may be detectable in the plot. In that case we can recover information on A and on δ_S and δ_{eq} in the following way. We fit a quadratic curve to δ in the vicinity of $C_o/C=1$, $\delta = \delta_o + a_1(C_o/C-1) + a_2(C_o/C-1)^2$, and use a relationship between the coefficients a_1, a_2, and A and δ_S. We find the relationship by using eq. (37) to write a Taylor expansion for δ in the vicinity

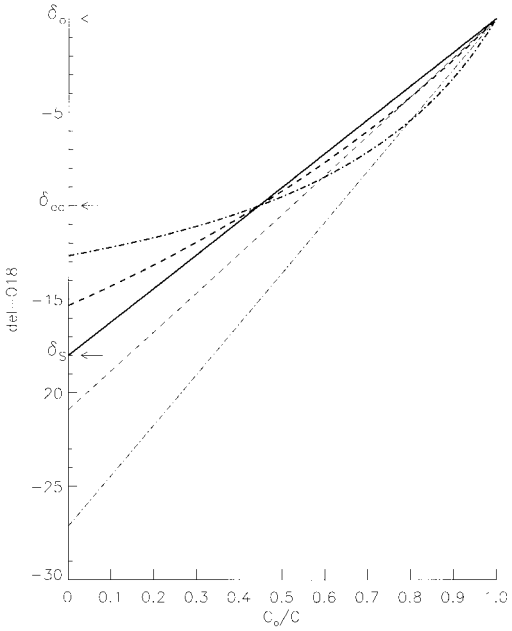

Fig. 5. $\delta^{18}O$ of atmospheric CO_2 as a function of the CO_2 concentration in air that is affected by both respiration and isotopic exchange, plotted as a function of the "background" concentration (C_o) divided by the concentration (C). The points marked by arrows, δ_o at 0, δ_{eq} at -10, and δ_S at -18 are the assumed isotopic delta values of background CO_2, CO_2 equilibrated with the upper soil water, and respired CO_2 entering the atmosphere, respectively. Three cases of A, the ratio of the amount of exchanged CO_2 to the amount of respired CO_2, are plotted. $A=0$, solid line, $A=0.5$, dashed line; $A=2$, dot-dash line. The thin straight lines are "Keeling plots" to hypothetical data between $C_o/C=0.8$ and 1.0, leading to apparent isotopic ratios of the respired CO_2 of -21 and -27 permil for $A=0.5$ and $A=2$ respectively.

of $C_o/C=1$, writing C_o/C as Y:

$$\delta = \delta_o + (Y-1)\left.\frac{d\delta}{dY}\right|_{Y=1} + \frac{(Y-1)^2}{2}\left.\frac{d^2\delta}{dY^2}\right|_{Y=1} + \dots .$$

We find

$$\begin{aligned} a_1 &= -(\delta_S - \delta_o) - A(\delta_{eq} - \delta_o), \\ 2a_2 &= -A(\delta_S + \delta_{eq} - 2\delta_o) - A^2(\delta_{eq} - \delta_o). \end{aligned} \quad (39)$$

Since $\delta_S = \delta_{eq} + \varepsilon_D f$, and $\varepsilon_D f$ can typically be estimated to about a permil or so, we have two equations with two unknowns, A and δ_{eq}. The equations are nonlinear, however, and A and δ_{eq} have to be found by iteration. If the δ versus C_o/C slope is assumed to be linear, as in the "Keeling plot", the error in the derived isotopic signature of the source equals $A(\delta_{eq}-\delta_o)$. In the example of Fig. 5 the extrapolation of the initial tangents in the neighborhood of C_o/C would lead to apparent source signatures of -23 and -38 permil for $A=0.5$ and $A=2$ respectively, whereas the correct isotopic signature is $\delta_S=-18$ permil. The straight dashed lines in Fig. 5 were drawn as the average linear slopes between $C_o/C=0.8$ and 1.0, so that the apparent source signatures were -21 and -27 permil, respectively. Mixing of air parcels with different values of C_o/C will tend to fill in the curvature depicted in Fig. 5.

7. Acknowledgements

Discussions with Dan Yakir during his stay at our laboratory are gratefully acknowledged. This work has been partially supported by the Ocean-Atmosphere Carbon Exchange Study and the Atmospheric Chemistry programs of the Office of Global Programs of the US National Oceanic and Atmospheric Administration.

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