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Production and stable isotopic composition of CO_2 in a soil near Bern, Switzerland

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ABSTRACT

During a period of one year, we measured the concentration and the stable isotopic composition of CO_2 in weekly soil air samples from two depths in a grass-covered soil. The CO_2 production rate, as estimated from the diffusion equation and the observed concentration gradient, was 15 mmol m^{-2} h^{-1}, as an annual mean. During the cold season, the production rate varied with soil temperature, but no correlation existed with temperature above about 10°C. Concentrations and fluxes of N_2O in the soil were also determined. Observed $\delta^{13}C$ values were in the expected range, and $\delta^{18}O$ of soil CO_2 was found to be in isotopic equilibrium with the soil water. $\delta^{18}O$ of the CO_2 released to the atmosphere is expected to be lower by roughly 8 ‰ due to diffusive isotope fractionation; the precise value depends on the competition between CO_2 production, equilibrium with soil water and diffusion.

1. Introduction

Carbon dioxide production in soils is a significant source of CO_2 to the atmosphere. The production rate varies seasonally, and it has often been found to be well correlated with soil temperature and sometimes with soil moisture (e.g., Dörr and Münnich, 1987).

Being produced by the decomposition of organic matter and by root respiration, soil CO_2 carries the corresponding carbon isotope signal, having lower $\delta^{13}C$ values than atmospheric CO_2. Recently, the $^{18}O/^{16}O$ ratio of atmospheric CO_2 has received attention as a potential tracer (Francey and Tans, 1987; Friedli et al., 1987); however, the processes determining it are complex and have not been studied in detail. $\delta^{18}O$ of CO_2 in soils, one of the sources to the atmosphere, can be expected to be in equilibrium with $\delta^{18}O$ of the soil water, but no experimental data were available until now to test this assumption. We have analyzed air samples from a soil for about a year with respect to the concentration and isotopic composition of CO_2, and also the N_2O concentration. From the measured concentrations, we estimated the production rates of these gases. In order to test the hypothesis of oxygen isotopic equilibrium with soil water, we also performed $\delta^{18}O$ analyses on soil water.

The concentration of N_2O must be known, in order to correct the mass-spectrometric $\delta^{13}C$ and $\delta^{18}O$ analyses (Friedli and Siegenthaler, 1988). N_2O is produced by bacteria in the soil, but can be destroyed in the uppermost soil layer (Conrad et al., 1983).

2. Sampling site and experimental methods

On a weekly basis from September 1988 to September 1989, we collected soil air samples from two depths in a grass-covered soil in Liebefeld, near Bern. The uppermost soil layer down to 80 cm depth consists of humus, sand and loam with imbedded stones. Below this layer is moraine material. This soil type is typical for the regions of the Swiss pre-Alps. The groundwater level is at about 30 m below the surface (Schudel, 1982). The sampling area is not cultivated, but the grass is cut during summer time. On the same plot, the Swiss Meteorological Institute measures, amongst other parameters, air and soil temperatures.

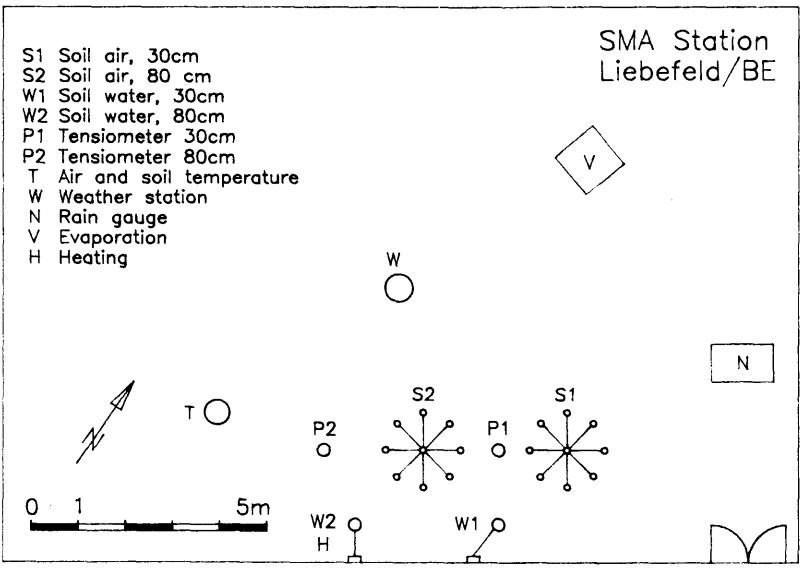

Fig. 1. The sampling site at Liebefeld near Bern.

In order to take soil air samples, 8 stainless steel tubes (6 mm outer and 4 mm inner diameter) for each depth were driven into the soil in a circular arrangement of about 140 cm diameter, plus one tube in the center (cf. Fig. 1). An air inlet was formed through 10 holes at the side of each steel tube; the tube tips are closed. The set-up is similar to that used by Dörr and Münnich (1987). We took samples at 30 cm and at 80 cm depth.

Soil air samples were collected in well-dried glass flasks (usually two flasks of 250 ml in series for each sample). In order to prevent oxygen isotope exchange between CO_2 and a water film on the walls of the flasks, which may lead to erroneous results (Francey and Tans, 1987), the air was dried during collection by means of a magnesium perchlorate trap. This drying agent leads to a very low residual content of 0.06% relative humidity at 20°C (see also Bower, 1934). In the laboratory, the CO_2 was frozen out quantitatively in a glass U-tube at liquid nitrogen temperature at a constant flow rate. After extracting the CO_2, the U-tube was warmed up to -80°C, at which temperature CO_2 evaporates while any traces of water are held back. To measure the concentration, the amount of CO_2 was determined manometrically in a calibrated volume, with a relative precision of 0.3%. $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios were determined on a mass spectrometer MAT 250. All isotope results were corrected for the influence of N_2O. The N_2O concentration was measured by mass spectrometry as described by Friedli and Siegenthaler (1988).

Soil water samples for oxygen isotope analysis were taken through semipermeable ceramic tubes ("candles"), placed at 30 cm and 80 cm depth. An evacuated 2 liter glass flask was connected via a Teflon tube to each "candle" and replaced after a week. The pressure in the flasks increased from 200 to 300 mbar in one week, so that the pressure difference to the atmosphere was nearly constant and the water samples (100 ml maximum) should approximately correspond to weekly averages.

The soil water content influences the free porosity and thus the gas transport. It is correlated with the soil moisture tension (that is, the negative pressure) and can thus be determined by measuring the latter. In early June 1989, we placed tensiometers at both sampling depths (30 and 80 cm). The soil-specific relationship between soil moisture content and tension is known from earlier work at this site (Schudel, 1982), in which the dry porosity was also determined (46% and 48% by volume at 30 and 80 cm depths, respectively).

3. Gas concentrations and fluxes

Fig. 2 shows the measured CO_2 concentrations, which varied in the ranges 1–3.5% (% per volume) at 30 cm depth and 2.5–5.5% at 80 cm. From the concentrations, we can estimate the diffusive CO_2 flux from the soil to the atmosphere, as discussed below. Under the assumption of stationarity (i.e., $\partial c/\partial t = 0$), the flux to the atmosphere equals the instantaneous production rate. An order-of-magnitude calculation indicates that the time required for establishing a new stationary concentration profile after a change, e.g., in the production rate is less than 1 day in a soil column of 1 m depth. Thus the assumption of stationarity (i.e., production rate = flux) is fulfilled except for rather abrupt changes.

The diffusive flux $j(t)$ out of the soil into the atmosphere is given by (see e.g. Dörr and Münnich, 1987; Solomon and Cerling, 1987):

$$j = \varepsilon \kappa D \left.\frac{\mathrm{d}c}{\mathrm{d}z}\right|_{(z=0)}, \tag{1}$$

where c = concentration, z = depth (positive downward, while j is positive upward), ε = free porosity, $\varepsilon = \varepsilon_0 - \theta$ where ε_0 = dry porosity and θ = soil water content, κ = tortuosity (accounting for the fact that the transport paths in the soil are not straight and therefore longer) and D = diffusivity of CO_2 in air. We have used the following values (assumed to be constant): $\varepsilon_0 = 0.47$ (see Section 2), $\kappa = 0.66$, $D = 0.15\ \mathrm{cm^2\ s^{-1}}$.

For the soil water content θ, we could use the measured values from June 1989 onwards. For the earlier period, we estimated θ based on a simple two-layer soil runoff model, using measured precipitation and evaporation as input. The model was calibrated by means of the measured soil moisture and $\delta^{18}O$ data. This method is only a rough approximation, but should be more realistic than the assumption of a porosity constant in time. The variability of the porosity is not of great influence on the calculated flux: for 30 cm depth, nearly 90% of the values for the effective porosity ($\varepsilon_0 - \theta$) lie in the range 0.11 to 0.16, and for 80 cm depth the variability is even smaller.

A first estimate for the concentration gradient at $z = 0$, needed for evaluating eq. (1), is given by the mean gradient between $z = 30$ cm and the surface ($z = 0$); we assume that the concentration at the surface equals that of the free atmosphere, $c_{atm} = 360$ ppm. Generally, the gradient at $z = 0$ will be larger, because the diffusion equation is (assuming depth-independent porosity):

$$\kappa D \frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{\mathrm{d}c}{\mathrm{d}z}\right) + \frac{P(z)}{\varepsilon} = 0. \tag{2}$$

The factor $1/\varepsilon$ arises because $c(z)$ is the concentration per unit volume of soil air, while $P(z)$ is the production rate per unit volume of bulk soil. Eq. (2) shows that, if the production of CO_2 is not zero, the gradient $\mathrm{d}c/\mathrm{d}z$ decreases downward (with larger z).

A second estimate is obtained by assuming that the production rate $P(z)$ decreases exponentially with depth, $P(z) = P_0 \exp(-z/z_0)$. Eq. (2) then yields:

$$c(z) = c_{atm} + c_1\,(1 - \exp(-z/z_0)), \tag{3}$$

with $c_1 = (P_0/\varepsilon)(z_0^2/\kappa D)$. c_1 and z_0 can be determined for each observation date from measured concentrations at 30 cm and 80 cm depths. Eq. (3) and (1) yield for the flux to the atmosphere

$$j = \varepsilon \kappa D c_1 / z_0. \tag{4}$$

Fig. 3 shows the calculated CO_2 production rates for the linear as well as for the exponential approach. For the exponential case, the calculated e-folding depth z_0 varies quite strongly within a short time, which is responsible for the stronger scatter of the production rate, compared to the linear approximation, but may not be realistic.

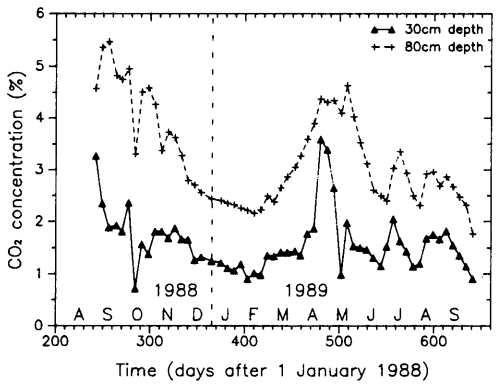

Fig. 2. CO_2 concentrations in the soil air, in % by volume.

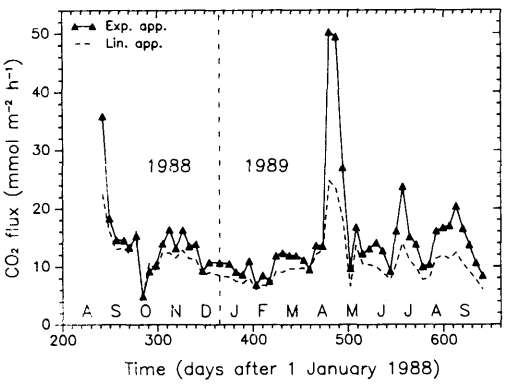

Fig. 3. Estimated CO_2 flux from the soil to the atmosphere. Triangles/solid line: calculated assuming an exponential depth dependence of the production rate; dashed line: calculated assuming a linear concentration profile between the surface and 30 cm depth.

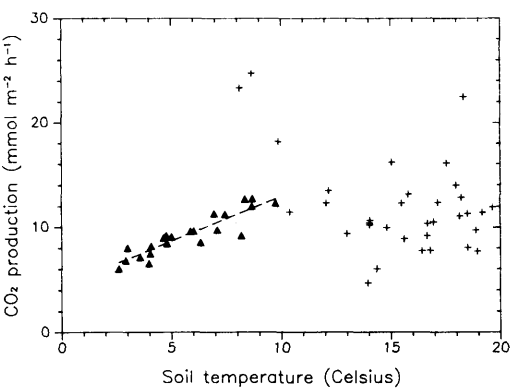

Fig. 4. Estimated CO_2 production rate (assuming a linear concentration profile 0–30 cm depth) against soil temperature. Full triangles: measurements used for the calculation of the Q_{10} value of 2.1.

The true values are probably between the two estimates.

There is an indication for a seasonal trend, with low values in winter. Fig. 4 is a plot of production rates (estimated with the 0–30 cm gradient) versus soil temperature (average of 30 cm and 80 cm depths).

A good correlation exists for temperatures below 10°C, with a Q_{10} value, between 4° and 14°C, of 2.1, which is in the range usually quoted for soil respiration. (The production rates calculated using an exponential profile would give a similar Q_{10} value.) At higher temperatures, however, the correlation breaks down for reasons that are not obvious. In May 1989, the CO_2 flux decreased nearly to winter values. This was a period of dryness; the grass suffered from water stress and showed brown spots. Thus, low soil moisture may have been responsible for the relatively small fluxes in summer 1989.

Two conspicuous events are seen in Fig. 3. In early October 1988, a drastically reduced CO_2 flux was observed after heavy rainfall (60 mm in 48 h). The reason might be either a perturbation of the CO_2 transport in the soil (e.g., dissolution of CO_2 in the infiltrating rainwater), or a reduction of the microbial activity. The fact that the production was still low during the two subsequent observation dates points to the latter explanation. Maximum values were observed in late April-early May 1989, possibly due to root respiration of grass which is often highest in spring during sprouting (Larcher, 1984).

Measured N_2O concentrations in the soil (Fig. 5) are significantly higher than in the atmosphere (presently 0.31 ppm), indicating that the soil is a source of N_2O. The flux (Fig. 6) was calculated as for CO_2, but taking the average of the concentration gradients 0–30 cm and 0–80 cm, because the two gradients were usually similar and that from 0 to 80 cm was in about 50% of all cases even larger than that from 0 to 30 cm. The fact that the concentration gradients 0–30 cm and 30–80 cm were often nearly equal indicates that the N_2O must have been produced at depths greater than 80 cm. The estimated production rate varied

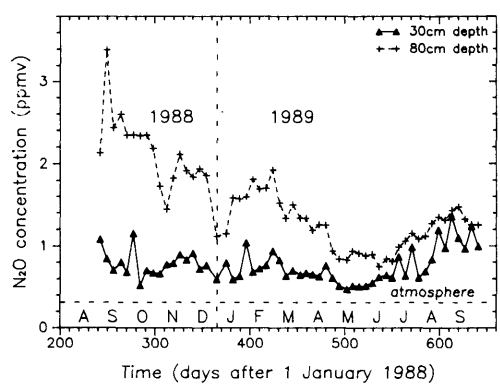

Fig. 5. N_2O concentrations in soil air. Dashed line: atmospheric value.

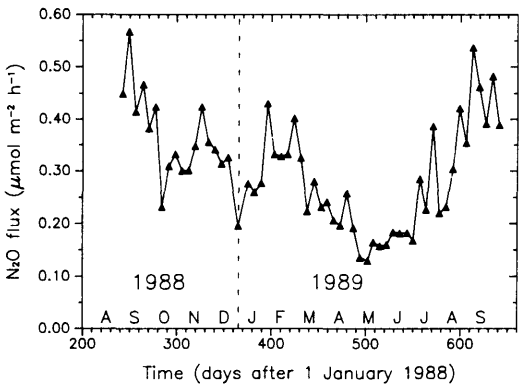

Fig. 6. N_2O flux in the soil, calculated assuming a linear N_2O concentration profile (see text).

roughly in the range 0.15–0.5 μmol m^{-2} h^{-1}, comparable to fluxes determined, e.g., by Seiler and Conrad (1981) for 3 different unfertilized soils in Germany. The latter authors concluded from their work that measured N_2O profiles in soils do not yield reliable values for the N_2O release to the atmosphere, because N_2O is apparently destroyed in the top soil layer. If this is the case, the results in Fig. 6 should not be interpreted as fluxes to the atmosphere.

The concentrations as well as the fluxes of N_2O vary in time, with minimum values in May 1989 (when CO_2 exhibits a maximum). Thus, temperature cannot be the factor governing the seasonal variation. For comparison, the N_2O concentrations measured in three different soils by Albrecht et al. (1970) do not show a clear seasonal pattern; in winter, high values were observed, as is also true for our results.

4. Stable isotopes in soil CO_2

Fig. 7 shows measured $\delta^{13}C$ data in soil CO_2. The values are in the range expected for carbon of biogenic origin. $\delta^{13}C$ is generally somewhat higher at 30 than at 80 cm depth. The difference between the two depths can partly be explained by the presence of a CO_2 component of atmospheric origin, with a concentration of approximately 350 ppm and $\delta^{13}C = -7.6\,‰$ (determined from analyses of air samples in Bern). This contribution has a larger influence at smaller soil CO_2 concentrations, leading to slightly higher $\delta^{13}C$ at the shallower depth. A simple two-component mixture calculation shows that the different relative amounts of air-CO_2 can account for a few tenths of a permil difference in $\delta^{13}C$ between 30 and 80 cm depths for the measured concentrations. This explains the observed difference on average, although not the details of its variation in time.

$\delta^{13}C$ of the soil CO_2 shows clear variations in time (Fig. 7). In late April 1989, minimum values were reached at both depths; they coincide with a maximum in CO_2 concentrations and production. After this, $\delta^{13}C$ rapidly increased, while the CO_2 production declined. $\delta^{13}C$ throughout the summer 1989 was higher than before; this shift is particularly clear at 80 cm depth. Furthermore, short-term changes, lasting a few weeks, also occurred. We do not know the reason for these variations, but we speculate that they may be related to different isotopic composition of the two sources of CO_2 in the soil: microbiological decomposition of organic soil matter and root respiration of plants (the latter with more negative $\delta^{13}C$). The $\delta^{13}C$ decrease in late April 1989 might then be due to intense root respiration during sprouting. Similarly, in early July and early September 1989, $\delta^{13}C$ decreased while the CO_2 production increased. The rapid isotopic increase in May and June 1989 might be the result of reduced root respiration in consequence of the dry period in late May-early June and late July. Our speculative hypothesis can, however, not explain why $\delta^{13}C$ remained high throughout the following summer. In order to really understand these variations, it would be necessary to carry out further studies, especially to separately determine the isotopic

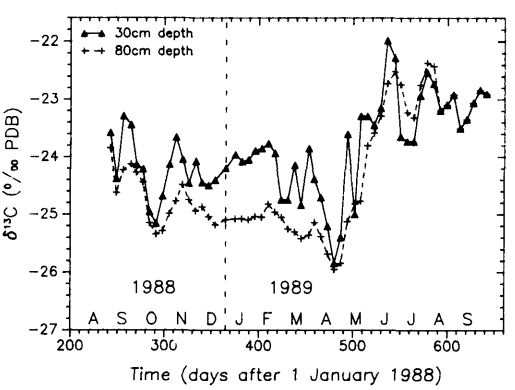

Fig. 7. $\delta^{13}C$ values (versus PDB) in soil CO_2.

composition of CO_2 produced by root respiration and by microbial activity.

As noted by Dörr and Münnich (1980), ^{13}C is enriched in soil CO_2 compared to produced CO_2, because $^{13}CO_2$ diffuses out into the atmosphere at a slower rate than the lighter $^{12}CO_2$ molecule. The ratio of the diffusivities is 1.0042, as measured by Lehmann (1987), so that the $\delta^{13}C$ value of soil CO_2 is about $4\,‰$ higher than in the source material. Thus, the $\delta^{13}C$ values of the CO_2 produced in the soil are $4\,‰$ lower than shown in Fig. 7, or about -29 to $-27\,‰$; and so is also $\delta^{13}C$ of the CO_2 escaping to the atmosphere, since the isotopic composition of the flux leaving the soil must (in a steady state) be equal to that of the CO_2 produced in the soil. These conclusions are confirmed by a detailed mathematical treatment (see Section 5).

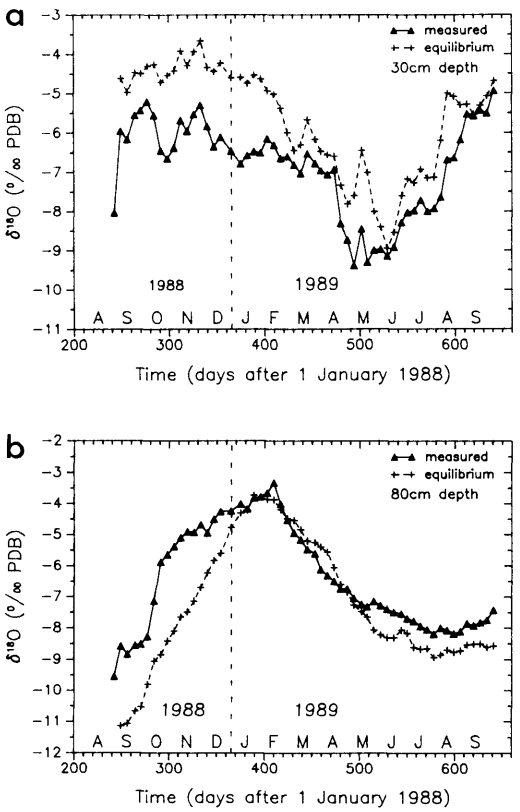

Fig. 8. $\delta^{18}O$ (versus PDB) measured on soil CO_2 (triangles/solid line) and calculated for CO_2 isotopically equilibrated with soil water (+/dashed line): (a) 30 cm depth, (b) 80 cm depth.

Fig. 8 shows the $\delta^{18}O$ values measured on soil CO_2 (full triangles). It can be expected that these values are determined by an isotopic equilibrium with the soil water. This equilibrium is achieved at a rapid rate, given by the rate constant k for hydration of CO_2 to H_2CO_3 with a corresponding characteristic time k^{-1} of about 6 min at 0°C and 50 s at 20° (Kern, 1960). Thus, local isotopic equilibrium between CO_2 and soil water should prevail. For the equilibrium isotope fractionation factor between H_2O and CO_2, we took the expression by O'Neil and Adami (1969):

$$\ln \alpha = 16.60\, T^{-1} - 1.519 \cdot 10^{-2} \qquad (5)$$

(T = absolute temperature in K). As we express our $\delta^{18}O$ values in the PDB scale for CO_2, but in the SMOW scale for water, a conversion between the two scales is necessary (Friedman and O'Neil, 1977), so that the isotopic composition of CO_2 in equilibrium with water has the δ value:

$$\delta_{\mathrm{eq.,PDB}}(CO_2) = (1.04142)^{-1}\,\alpha[1 + \delta_{\mathrm{SMOW}}(H_2O)] - 1. \qquad (6)$$

The measured $\delta^{18}O$ values of soil water (Fig. 9) reflect the seasonal isotope variations in precipitation, but delayed (by about 6 months at 80 cm depth) and slightly damped. The $\delta^{18}O$ values of CO_2 equilibrated with the soil water, as calculated

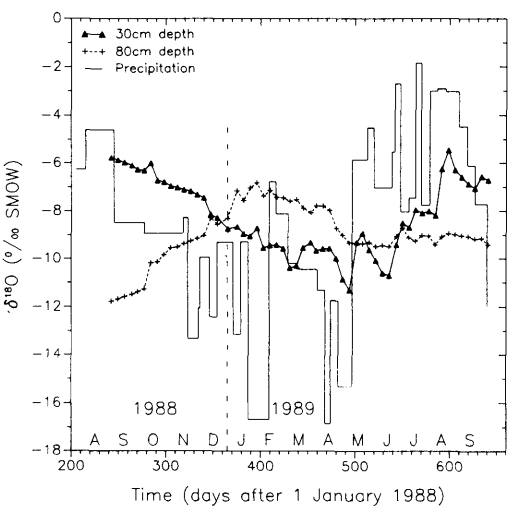

Fig. 9. $\delta^{18}O$ values (versus SMOW) in soil water and in precipitation from Bern.

using eq. (6), are shown in Fig. 8 (crosses, dashed line). The measured values agree reasonably well with those expected, and they show in particular the same patterns of variation with time. We conclude that $\delta^{18}O$ of soil CO_2 is indeed in local equilibrium with the soil water. The measured values deviate, however, systematically by about $1\,‰$ from the expected ones, being more negative at 30 and more positive at 80 cm depth. We explain this by the fact that the water samples could not be taken at precisely the same place as the soil air samples (cf. Fig. 1), and that the isotopic profiles of the soil water must have been slightly different at those places.

5. Isotopic composition of the CO_2 flux from soil to atmosphere

As mentioned above, $\delta^{13}C$ of the CO_2 flowing from the soil into the atmosphere is not the same as that of CO_2 in the soil, because $^{12}CO_2$ diffuses faster out of the soil than $^{13}CO_2$. The same is basically true for $\delta^{18}O$, but here the situation is more complicated, because production, isotopic equilibration with soil water and diffusion compete with each other.

The transport equation for $C^{16}O^{18}O$ in the soil is given by:

$$\frac{\partial}{\partial t}(R\cdot c)=\frac{1}{\varepsilon}P(z)\,R_p+\kappa D_{18}\frac{\partial^2}{\partial z^2}(R\cdot c)+k\cdot c(R_{eq}-R), \tag{7}$$

where

$R = {}^{18}O/{}^{16}O$ ratio of soil CO_2,

$R_p = {}^{18}O/{}^{16}O$ ratio of produced CO_2,

$R_{eq} = {}^{18}O/{}^{16}O$ ratio of CO_2 equilibrated with soil water,

D_{18} = diffusion coefficient of $^{12}C^{16}O^{18}O$ in air,

k = hydration rate constant of CO_2.

We assume that the CO_2 production rate varies with depth as $P(z)=P_0\exp(-z/z_0)$. The stationary solution of eq. (7), obtained after some calculations, is (assuming R_{eq} independent of z):

$$R(z)\cdot c(z)=R_{atm}c_{atm}e^{-z/z_1}+(c_{atm}+c_1)\,R_{eq}(1-e^{-z/z_1})+c_1(\alpha_D R_p-(z_0/z_1)^2\,R_{eq})\frac{e^{-z/z_0}-e^{-z/z_1}}{(z_0/z_1)^2-1}, \tag{8}$$

where

$z_1=\sqrt{D_{18}\cdot\kappa/k}$,

$c_1=(P_0/\varepsilon)(z_0^2/\kappa D)$ (see Section 3),

$\alpha_D=D/D_{18}=1.0088$ (Lehmann, 1987).

z_1 can be interpreted as the depth where oxygen isotopic equilibration of CO_2 by hydration and diffusive escape to the atmosphere are equally important, while above this depth, isotopic equilibration is incomplete.

Incidentally, the $^{13}C/^{12}C$ profile is obtained from (8) by setting $k=0$ and $z_1=\infty$ (no exchange with water). This yields, using eq. (3) for c:

$${}^{13}R(z)=\frac{c_{atm}\cdot R'_{atm}+c_1\alpha'_D R'_p(1-e^{-z/z_0})}{c_{atm}+c_1(1-e^{-z/z_0})}, \tag{9}$$

where in this case $\alpha'_D=D/D_{13}=1.0042$, D_{13} = diffusion coefficient of $^{13}C^{16}O_2$ in air and R'_{atm} and R'_p refer to $^{13}C/^{12}C$ ratios. For $c_1\gg c_{atm}$ and z not too small, eq. (9) becomes ${}^{13}R(z)\cong\alpha'_D R'_p$.

The $^{18}O/^{16}O$ ratio in the CO_2 flux out of the soil is given by the ratio of the fluxes of $C^{16}O^{18}O$ and of $C^{16}O_2$:

$$R_j=\frac{j_{18}}{j_{16}}=\frac{\varepsilon\kappa D_{18}}{j_{16}}\left.\frac{d(R\cdot c)}{dz}\right|_{(z=0)},$$

$$R_j=\frac{z_0 c_{atm}}{\alpha_D z_1 c_1}(R_{eq}-R_{atm})+\frac{1}{1+z_0/z_1}R_p+\frac{z_0/z_1}{\alpha_D(1+z_0/z_1)}R_{eq}.$$

In delta notation, using $R_i=(1+\delta_i)\,R_{standard}$:

$$\delta_j=\frac{z_0 c_{atm}}{\alpha_D z_1 c_1}(\delta_{eq}-\delta_{atm})+\frac{1}{1+z_0/z_1}\delta_p+\frac{z_0/z_1}{\alpha_D(1+z_0/z_1)}[\delta_{eq}-(\alpha_D-1)]. \tag{10}$$

This can be simplified by setting $\alpha_D=1$ in the denominators. For the $^{18}O/^{16}O$ ratio, we make the

plausible assumption that the CO_2 produced by root respiration or by decomposition of soil organic matter is in isotopic equilibrium with soil water, $\delta_p = \delta_{eq}$. Then, eq. (10) becomes:

$$\delta_j = \delta_{eq} - \frac{z_0/z_1}{1 + z_0/z_1}(\alpha_D - 1)$$

$$+ \frac{z_0 c_{atm}}{z_1 c_1}(\delta_{eq} - \delta_{atm}). \quad (11)$$

For our concentration profiles, a typical value for the e-folding depth is $z_0 = 80$ cm, and $c_{atm}/c_1 \leqslant 0.01$. With $k = 6.9 \cdot 10^{-3}\,s^{-1}$ at 10°C (Kern, 1960), $z_1 = 3.8$ cm and $z_0/z_1 = 21$. Thus, eq. (11) is approximated by

$$\delta_j \cong \delta_{eq} - (\alpha_D - 1) = \delta_{eq} - 8.8\,‰. \quad (12)$$

For a typical value $\delta_{eq} = -6\,‰$ (cf. Fig. 8), we thus obtain for the isotopic composition of the CO_2 flux from the soil to the atmosphere, $\delta_j \cong -15\,‰$, that is considerably more negative than δ_{atm}.

Eq. (12) is a good approximation as long as $z_0 \gg z_1$. If the production of CO_2 occurs mainly near the surface (small z_0), then the influence of the diffusive fractionation becomes less important and the negative shift smaller than 8.8‰. On the other hand, if the soil concentration c_1 is not much larger than c_{atm}, then the last term in eq. (11) must be considered, too.

6. Conclusions

We have found that the CO_2 production rates in a loamy grass-covered soil were correlated to temperature only at temperatures below 10°C, while they varied in a way not easily explained during the warm season. The N_2O concentrations and production rates in the soil showed significant variations with time, which were not related to temperature.

$\delta^{18}O$ of soil CO_2 is in equilibrium with the isotopic composition of the surrounding soil water. As already noted by Dörr and Münnich (1980), the heavy isotopes in the CO_2 flux from soil to atmosphere are depleted compared to their concentrations in the soil CO_2 due to diffusional fractionation, that is by about 4.2‰ for $^{13}C/^{12}C$ and 8.8‰ for $^{18}O/^{16}O$. The $\delta^{18}O$ value of the CO_2 released to the atmosphere is actually also controlled by the rate of equilibration with soil water: if the CO_2 production is concentrated in the uppermost soil layers (small value of z_0), then this $\delta^{18}O$ value is determined by a competition between production, isotopic equilibrium and diffusion.

7. Acknowledgements

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