

CARBON-14 AND CARBON-13 IN SOIL CO₂

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ABSTRACT. Carbon isotope measurements in soil CO₂ are presented and discussed. Soil CO₂ concentration and ¹³C profiles were measured using a new technique. A simple model describing the CO₂ transport from the soil to the atmosphere is derived. The finding that CO₂ in the soil is richer in ¹³C than the CO₂ leaving the soil is attributed to isotopic fractionation in molecular diffusion.

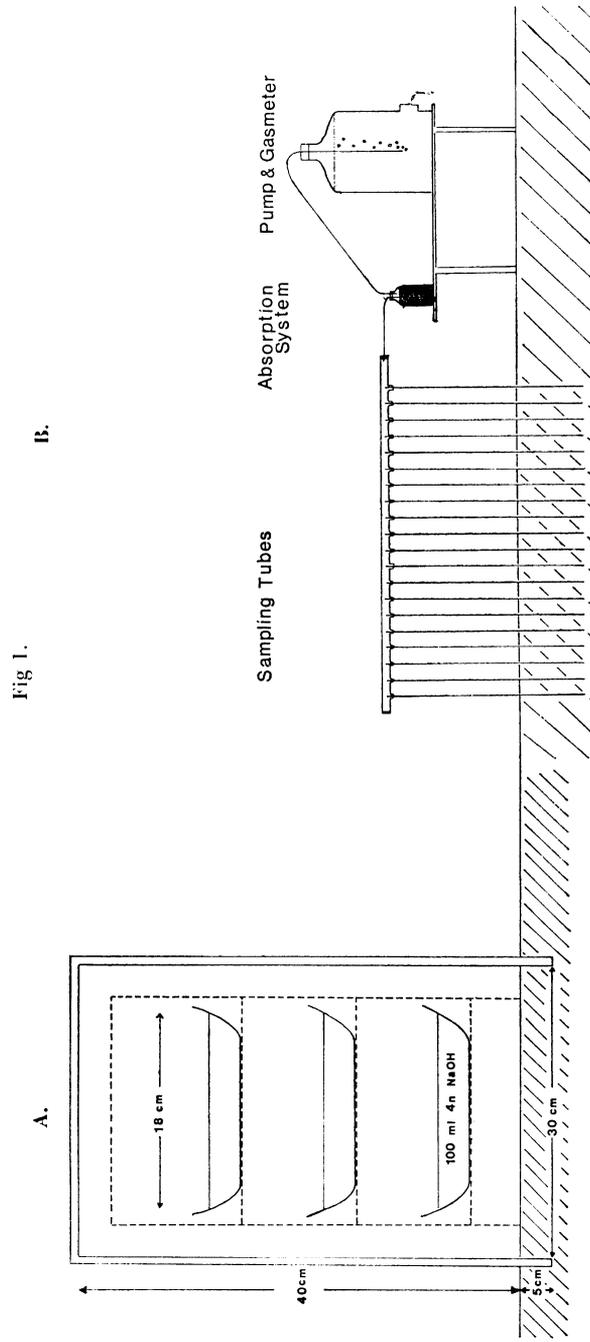
INTRODUCTION

In modeling local variations of the atmospheric $\frac{[^{14}\text{C}]}{[^{12}\text{C}]}$ ratio due to anthropogenic sources (Levin, Münnich, and Weiss, 1980) there is some doubt as to the precise value of this figure for soil respiration CO₂ which considerably influences the atmospheric level. Therefore, ¹⁴C soil respiration studies implemented years ago (Münnich, 1963; Münnich and Roether, 1963) have been resumed and are now being supplemented by CO₂ concentration and ¹³C profile measurements in the uppermost 60cm of the soil. The findings are relevant to the understanding of soil respiration mechanisms of atmospheric CO₂ balance as well as to the initial value in ¹⁴C groundwater dating (Münnich, 1968; Fontes and Garnier, 1979).

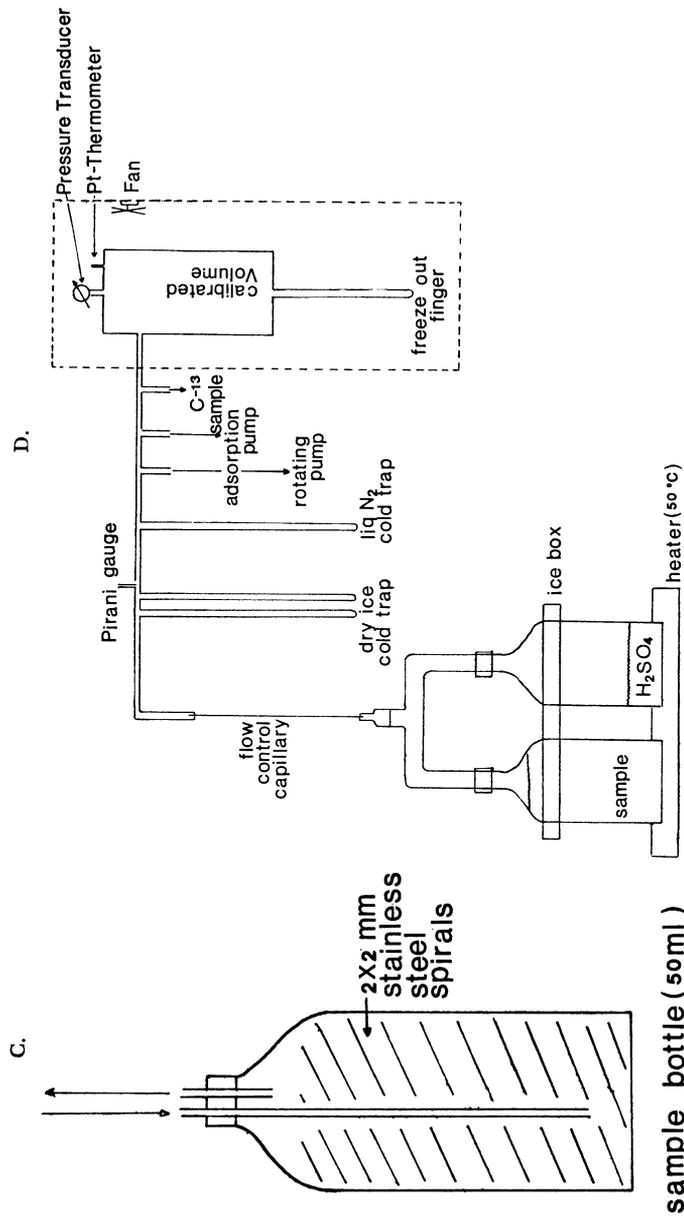
Theoretical considerations

Soil CO₂ is produced by respiration of plant roots and bacteria-oxidizing dead organic matter, and takes place primarily in the uppermost half-meter of the soil. If we denote CO₂ production per unit soil volume and time at depth z by $q(z)$ we find, for the horizontally homogeneous case in the steady state, $-(\partial j(z)/\partial z) + q(z) = 0$. Since, on the time average, practically all CO₂ produced leaves the soil surface at $z = 0$, the CO₂ flux density $j(z)$ has its maximum (negative) value at $z = 0$ and gradually goes to zero at greater depth z .

It is generally assumed (de Jong and Schappert, 1972) that gas transport in the soil is primarily by diffusion. It can, in fact, be shown that "pumping" by atmospheric pressure variations only occasionally plays a role where the groundwater table is at greater depth. Turbulent motion in the atmosphere above the soil surface usually is very effectively damped out in the soil because the average momentum relaxation time τ in the soil pores is $\tau \approx \frac{r^2}{8\nu}$ (Münnich, 1968) giving eg, $\tau \approx 20\mu\text{sec}$ for an average pore radius of $r = 50\mu$ and a kinematic viscosity $\nu = 0.15 \text{ cm}^2/\text{sec}$ for air. This means a relaxation length $\bar{x} = v \cdot \tau$ well below 1mm for outside air motion velocity v . It has been argued, however, (Kraner, Schroeder, and Evans, 1964) that micro-oscillation of atmospheric pressure (or rather the corresponding spatial wave pattern) might produce a kind of slight eddy diffusion in the uppermost soil layers.



A. Static collection of soil respiration CO_2 by alkali absorption under Lundgardh's cup.
 B. Sampling technique for CO_2 concentration and ^{13}C depth distribution measurements.



C. CO₂ absorption bottle used with technique b; the air inlet tube stays in the bottle during acidification and CO₂ recovery.

D. CO₂ recovery system for technique b; volumetric measurement of CO₂ amount sampled.

Diffusion transport of a substance through any medium is defined by its permeability¹ $P = S \cdot D$ where S is the solubility, *ie*, the equilibrium partition factor of the substance between the medium in question and a reference medium; D is the diffusion constant. In our specific case the obvious reference medium is air which makes $S = \epsilon$, the air filled fraction of the total soil volume (porosity). The available (air-filled) porosity ϵ and the volumetric fraction of soil moisture, F , add up to the total porosity $\epsilon_0 = \epsilon + F$ of the soil. The diffusion constant, D , on the other hand, would be identical to D_0 , the diffusion constant of CO_2 in air, only if the soil consisted of a bundle of straight capillary tubes pointing in the direction of the concentration gradient. In reality, however, we have $D = \beta \cdot D_0$ with a factor $\beta \leq 1$, considering the fact that the reduction of available diffusion cross-section, only on the *average*, is given by the available porosity, ϵ . Microscopically, this cross-section fluctuates around the average value, larger voids alternate with bottlenecks where the soil grains touch each other. It can easily be shown, from the extreme example of very narrow bottlenecks, that the larger than average cross-section between the two bottlenecks do not compensate their impedence to diffusion. With reference to a similar mechanism, assuming that the diffusing substance cannot travel the direct route, the factor, $k = 1/\beta$, is often called the tortuosity factor (see, eg, Penman, 1940; Zimmermann, Münnich, and Roether, 1967).

EXPERIMENTAL METHOD

Figure 1A shows static collection by Lundgardh's inverted cup. The CO_2 diffusing out of the soil surface is collected under a tin container and absorbed quantitatively in three ceramic dishes containing a total of 300ml 4 normal sodium-hydroxide-solution. The average sampling time is two weeks. With this method, soil respiration rate, ^{13}C , and ^{14}C content of respiration CO_2 are measured.

Figure 1B shows CO_2 and ^{13}C depth profile measurement. Twenty thin brass tubes, 70cm long, of 2mm outer diameter, carrying 12 inlet holes of 0.5mm diameter just behind the cone tip are driven to a preset depth into the soil. All probes are connected in parallel and are attached to a 5L Mariotte bottle serving as an air pump and as a gas meter, simultaneously. Soil CO_2 contained in the air stream is absorbed quantitatively in a 50ml glass bottle. This absorption bottle contains a packing of stainless steel spirals $2 \times 2\text{mm}$ in diameter (Vereinigte Füllkörper-Fabriken, D-5412 Baumbach) which holds 4ml of a 4 normal NaOH solution like a sponge exposing a very large absorption surface to the passing air (fig 1C). Total air flow rate is about 10L/hr (or 500cc/hr per individual probe). At this flow rate, the natural diffusion steady state in the soil cannot be disturbed. We show this by assuming that a sphere of radius, r , around the suction tip had been flushed free from CO_2 by

¹The permeability P , is often incorrectly called a diffusion constant (see eg, Kraner, Schroeder, and Evans, 1964: "bulk diffusion constant"). This notation is tolerable only if a single and homogeneous medium is to be described (see Stiller and Carmi, 1975 for the treatment of the general case).

injecting CO₂-free air into the soil. Relaxation time, which restores the natural situation by diffusion, can be estimated from the lowest order relaxation time, τ_1 , of the corresponding eigenfunction representation of the problem (Carslaw and Jaeger, 1959). We find $\tau_1 = r^2/(\pi^2 D) \approx r^2/60$ [min], which means that the disturbance produced by injection of 1/2L of air (with $\epsilon = 0.25$ this gives $r = 7.8$ cm) decays with a relaxation time in the order of one min.

Absorbed CO₂ is recovered by adding 5ml of 5 normal sulfuric acid to the sampling bottle (fig 1D). The sample and acid bottles are heated from the bottom and cooled from the top. The stainless steel spiral packing, thus, is continuously flushed with water vapor enhancing the degassing of the system. The whole system is cleaned of air beforehand in the same way. The transfer of CO₂ to the vacuum line is again by water vapor (flux controlled by the capillary) condensing in the first cold trap while the CO₂ is being collected in the second. The crucial point of our absorption and recovering technique (a continuation and simplification of the technique used by Esser, ms, for atmospheric ¹³C work) is that there is absolutely no loss of absorbing solution, and the CO₂ is recovered quantitatively afterwards. The amount of CO₂ is measured volumetrically in a calibrated metal container with precision temperature and pressure meters. Using a Na₂CO₃ standard solution, the measurement of the CO₂ amount sampled is reproducible to $\pm 1.2\%$ STD. The system allows for checking of degassing of the absorbing solution to better than 0.1% of the CO₂ amount processed. The ¹³C measurements are reproducible to $\pm 0.03\%$. For ¹⁴C measurement setup, see Schoch and others (1980).

RESULTS AND DISCUSSION

CO₂ soil respiration flux and temperature

From our measurements the flux density of soil respiration CO₂ supplied to the atmosphere is determined independently by two different techniques. Figure 2 shows both sets of data: the dots give the rates calculated from the concentration versus depth profiles of figure 4 as $j = -P(dc/dz)$, while the histogram shows the amount of CO₂ collected under the inverted cup divided by the collection time and the soil area covered by the cup. Figure 3 nicely shows how the flux depends on soil temperature, apparently being approximately doubled by each 5°C temperature increase. The flux density is calculated from the profiles with $P = \epsilon\beta D_0 = .042$ cm²/sec, assuming the free porosity to be $\epsilon = .20$, and the tortuosity reduction factor, β , by which the gas diffusion constant, $D_0 = .15$ cm²/sec, is to be multiplied to be $\beta = 2/3$ (Penman, 1940; Zimmermann, Münnich, and Roether, 1967a). In view of the uncertainty of the factors ϵ and β , the agreement between the two data sets is quite acceptable. The soil CO₂ profiles have been fitted by a parabolic curve that occurs if constant CO₂ production is assumed between 0 and 60cm depth. Inspection shows, however, that, eg, an exponential fit, assuming exponential decrease of source strength with depth at a scale height $\bar{z} \approx 60$ cm, would be, likewise, possible.

Note that the flux variation histogram derived from CO_2 absorbed under the inverted cup crosses the other curve and gives comparatively lower fluxes at high respiration intensity. This is to be expected if absorption in the alkali solution is not fast enough: the total absorbing alkali surface in our case is just about equal to the soil surface area covered by the inverted cup. Thus, if CO_2 absorption were at its maximum rate (piston velocity $w_a = 700\text{cm/hr}$, see Münnich, 1963) the steady state CO_2 concentration under the cup would always be below atmospheric CO_2 level, and the system would gain CO_2 from the atmosphere. Ideally, the concentration under the cup should always be identical with the atmospheric concentration to avoid gain or loss due to diffusion

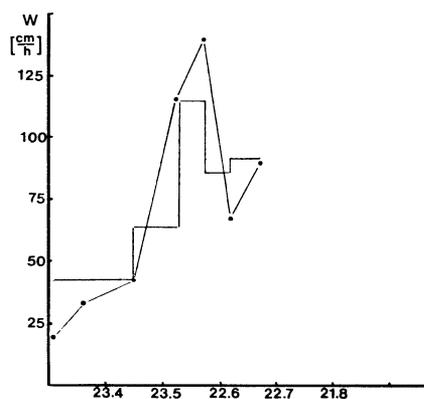


Fig 2. Soil respiration CO_2 flux density j vs date (1979) presented as the production velocity $w = j/c_A$ with standard atmospheric concentration $c_A = 330\text{ppm}$.

The dots are derived from measured CO_2 concentration profiles (fig 4) with $\epsilon = 0.2$; $\beta = 2/3$; $D_o = 0.15\text{ cm}^2/\text{sec}$.

The histogram represents average flux density values for the time intervals indicated, measured directly by the amount of CO_2 collected under an inverted cup.

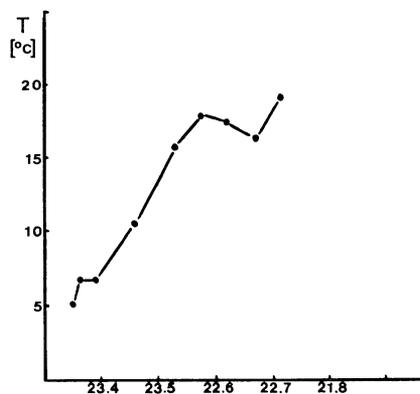


Fig 3. Soil temperature versus date (1979) at depth, 10cm, measured by a platinum thermometer.

around the rim of the cup. From the data in figure 2, we might estimate that the real absorption piston velocity is about 50cm/hr instead of 700. Statistically, there is a stagnant molecular diffusion layer of air over the absorber of about 10cm thickness. In the future, we shall try adjusting absorption velocity by an internal fan in order to force the cup concentration to approximately atmospheric level.

¹⁴C. One of us measured soil respiration CO₂ under an inverted cup during the period, 1958 to 1962 (Münnich, 1963; Münnich and Roether, 1963) finding that the ¹⁴C level in soil respiration seemed to follow the increasing atmospheric level with a time lag of about 2 to 3 years. The present data (table 1) shows no significant difference in ¹⁴C level of soil

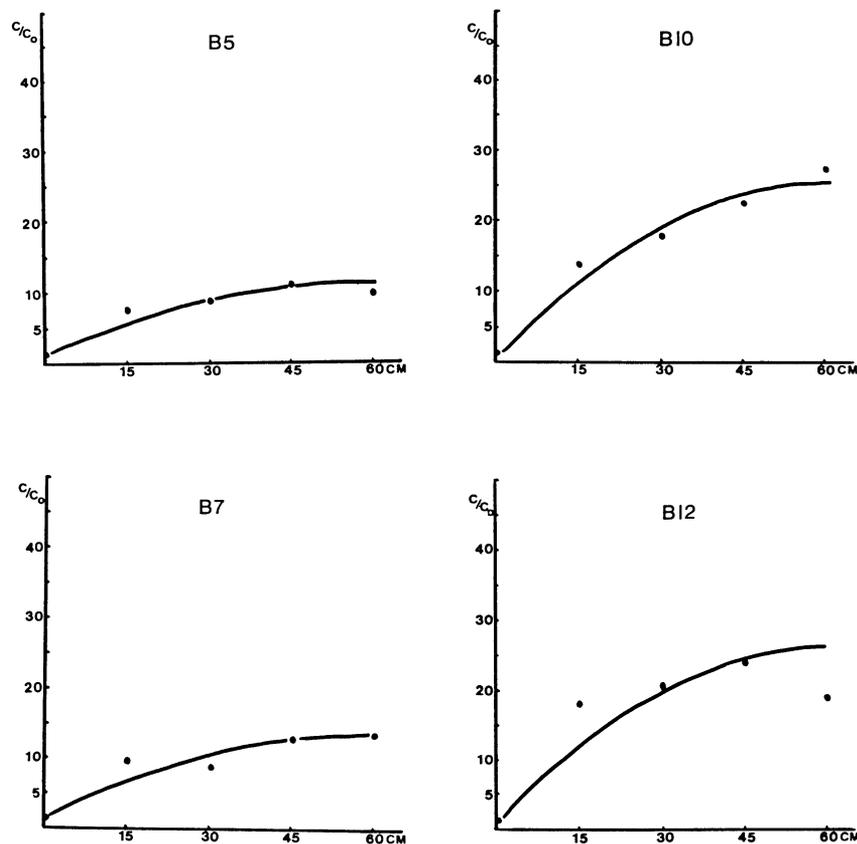


Fig 4. CO₂ concentration versus depth profiles taken at the sample location of table 1. The parabolic fit to data points assumes constant CO₂ production between 0 and 60cm depth (see text). With this assumption and the values of fig 2 for ϵ , β , D_0 , one obtains the following CO₂ source densities q :

B5: 10 April 79;	$q = 24 \text{mmoles CO}_2/\text{m}^3 \text{hr}$
B7: 9 May 79;	29
B10: 26 June 79;	59
B12: 11 July 79;	59

CO₂ if compared with contemporary atmospheric levels. Although the lowermost 100m of the atmosphere are strongly influenced by soil respiration CO₂ (Levin, Münnich, and Weiss, 1980) the ¹⁴C level in the atmospheric CO₂ is obviously altered very little by this. This greatly simplifies the interpretation of man-made ¹⁴C variations (Levin, Münnich, and Weiss, 1980).

¹³C. If the biospheric system under investigation is basically in a steady state, respiration CO₂ derived from organic matter with $\delta^{13}\text{C} = -25\text{‰}$ must, on the average, have $\delta^{13}\text{C} = -25\text{‰}$, as well. This, of course, does not exclude time variations around the average value. Both our flux and profile data show such variations with time. However, particularly during the time of high respiration flux, *ie*, after mid-May, CO₂ in the soil is richer in ¹³C than CO₂ leaving the soil by about 3.5‰. This is to be expected if transport is, as generally assumed, primarily by molecular diffusion: Craig (1954) notes that the diffusion constant of ¹³CO₂ should be by 4‰ smaller than the one of ¹²CO₂. As in evaporation from a tree leaf (Zimmermann, Ehalt, and Münnich, 1967b), making water in the leaf heavier than water passing through it and being transpired to the atmosphere, we should find CO₂ in the soil 4‰ heavier than that in the flux leaving the soil. No variation of the isotopic composition with depth should occur despite the strong increase of CO₂ concentration with depth. This is easily verified by Fick's law, and it seems to be exactly what we observe (fig 5). This behavior has been noticed before (Fontes and Garnier, 1979), but, to our knowledge, has not been explained according to our methods.

CONCLUSION

The data presented shows that the technique used yields reliable information on soil respiration fluxes and isotopic composition. We

TABLE 1

Sampling time	$\Delta^{14}\text{C}$ (‰) atm CO ₂ HD	$\Delta^{14}\text{C}$ (‰) soil respiration CO ₂ HD	$\delta^{13}\text{C}$ (‰) soil respiration CO ₂
16.3 – 30.3.79	278 ± 5		
24.3 – 10.4.79		287 ± 6	– 20.2
2.4 – 12.4.79	284 ± 6		
12.4 – 19.4.79	293 ± 6		
19.4 – 25.4.79	281 ± 5		
27.4 – 4.5.79	285 ± 5		
4.5 – 14.5.79	286 ± 5		
10.4 – 9.5.79		289 ± 5	– 24.6
14.5 – 25.5.79	311 ± 5		
9.5 – 30.5.79		293 ± 5	– 25.8
1.6 – 8.6.79	288 ± 5		
30.5 – 13.6.79		282 ± 5	– 25.9
8.6 – 15.6.79	318 ± 4		
13.6 – 26.6.79		296 ± 5	– 25.4
26.6 – 11.7.79		286 ± 5	– 24.8

¹⁴C and ¹³C data on soil CO₂ collected by alkali absorption under an inverted cup (sample location on uncultivated sandy soil with loess loam admixtures 15km south of Heidelberg). ¹⁴C data on atmospheric CO₂ samples collected in Heidelberg are also given for comparison.

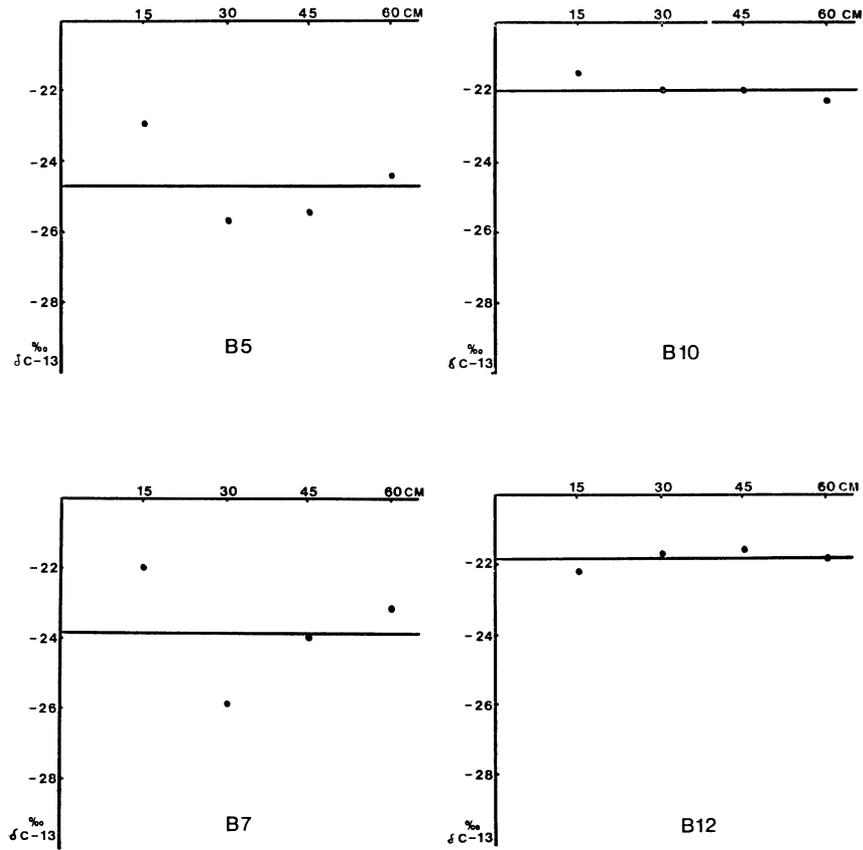


Fig 5. Soil δ¹³C profiles measured; see fig 4 for sampling dates.

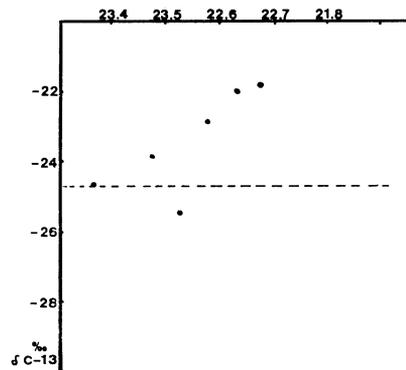


Fig 6. δ¹³C in soil CO₂ versus date of sampling (average values for individual profiles). Broken line shows average isotopic composition of CO₂ leaving the soil (table 1). Note that after mid-May the standing crop in the soil is heavier isotopically than CO₂ in the soil respiration flux.

shall continue these measurements in combination with radon-222 measurements in the soil using the detector designed by Roether and Kromer, (1978). Some tentative results have already been obtained (Volpp, personal commun, 1979). One of the aims of this combined study is to provide better flux data for soil-born gases to calibrate a regional atmospheric model. This will be developed to connect atmospheric concentrations with fluxes to and from the earth's surface by using meteorologic data such as atmospheric stability (Levin, Münnich, and Weiss, 1980). The study also relates to the question of initial ^{14}C content in groundwater.

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