

## **A comparison of field methods for measuring soil carbon dioxide evolution: Experiments and simulation**

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### **Abstract**

Three widely used methods for measuring total soil CO<sub>2</sub> evolution are evaluated, including the dynamic CO<sub>2</sub> absorption method, the static CO<sub>2</sub> absorption method and the closed chamber method. The study covers laboratory experiments, numerical experiments with a simulation model and field measurements. The results are used to perform an error analysis. The aim of this error analysis is to indicate the impact of each method on the CO<sub>2</sub> dynamics during the measurement, and to select the most suitable method for frequent field usage.

Laboratory experiments and simulation results show that the dynamic CO<sub>2</sub> absorption method has the potential to absorb all CO<sub>2</sub> evolving at the soil surface. The results also prove that the method has only a minor impact on the CO<sub>2</sub> concentration-depth gradient and the CO<sub>2</sub> efflux. The static CO<sub>2</sub> absorption method underestimates the soil CO<sub>2</sub> evolution, because the absorption velocity is too low, due to slow diffusion processes. Measurements with the closed-chamber method are based on an increasing concentration with time under a closed cover. However, the accumulation of gas alters the concentration gradient in the soil profile and thus causes a rapidly decreasing efflux during the measurement. A commonly used mathematical procedure, which corrects for the altered concentration gradient, does not yield the exact surface efflux, because the effect of increasing storage in the soil profile is not incorporated. Field measurements of CO<sub>2</sub> evolution, using the closed-chamber method and the dynamic CO<sub>2</sub> absorption method confirm the trends that have been predicted by the simulation model. The results of this study indicate that the dynamic CO<sub>2</sub> absorption method is accurate. As it is cheap and simple, it is suitable for the study of temporal and spatial dynamics of CO<sub>2</sub> evolution from the soil.

### **Introduction**

Soil carbon dynamics is an important topic in research on decomposition of organic matter (Witkamp, 1966a) and soil acidification (Bouten et al., 1984). The concern over increasing CO<sub>2</sub> levels in the atmosphere has stimulated efforts to quantify both storage and changes in the soil carbon pool (Edwards and Ross-Todd, 1983). Most field studies of soil CO<sub>2</sub> budgets evaluate

CO<sub>2</sub> effluxes at the surface and CO<sub>2</sub> concentrations within the soil. Especially, the determination of CO<sub>2</sub> effluxes gives a clear view of CO<sub>2</sub> production in the soil. One of the methods which is applied to determine the CO<sub>2</sub> efflux is based on the use of Fick's law with independent measurements of the soil-gas diffusivity and the concentration gradient (De Jong and Schappert, 1972). This indirect method has some major disadvantages that are associated with the spatial

variability of concentration measurements and uncertainties concerning the diffusion coefficient (Rolston, 1986).

For frequent field measurement of the CO<sub>2</sub> efflux, an inexpensive and reliable direct method is desirable. Most direct measurement techniques use an inverted box that is driven into the soil to trap the evolved CO<sub>2</sub>. The installation of such a chamber always causes mechanical disturbance, which may affect the diffusion coefficient of the soil, and possibly stimulates microbial activity. Matthias et al. (1980) reported that inserting the chamber into the soil resulted in a higher N<sub>2</sub>O efflux compared to placing the chamber on the soil surface without soil disturbance. Jury et al. (1982) stressed the importance of the dynamics of production and subsequent diffusion of gas when surface effluxes are measured. Gas dynamics should be taken into account when quantifying a relationship between gas production and efflux. This also holds for the interpretation of measured effluxes when a chamber is used to capture gas. A new artificial boundary condition is then imposed upon the soil profile, which may affect gas dynamics. The bias thus introduced depends on the measuring device.

For the direct measurement of CO<sub>2</sub> effluxes, three types of methods can be distinguished: Firstly, the flow-through chamber method concerns an open system (Witkamp and Frank, 1969; Garret and Cox, 1973; Rolston, 1986). Ambient air is continuously drawn through the chamber space, and its CO<sub>2</sub> enrichment is measured by means of a differential infra-red gas analyser. The flow-through chamber method was not used in this study. Although results presented by Witkamp and Frank (1969) and Garret and Cox (1973) are promising, high expenses (field installation of an infra-red gas analyser) make it less attractive for the study of field variability of soil CO<sub>2</sub> evolution. Secondly, the closed-chamber method, as discussed by Rolston (1986), whereby carbon dioxide is trapped under a closed chamber, and the efflux is computed from the concentration increase in the chamber. Finally a third type of method can be distinguished based on the absorption of CO<sub>2</sub> evolving from the soil in a caustic solution: the CO<sub>2</sub> absorption method (Anderson, 1982). In the past 30 years, several versions of this method have

been described. Carbon dioxide is either absorbed in a caustic solution by diffusion (static approach; Witkamp, 1966b) or pumped through this solution (dynamic approach; Witkamp and Van der Drift, 1961).

This paper discusses the errors that occur with the closed-chamber method and three versions of the CO<sub>2</sub> absorption method. Laboratory experiments were carried out in order to optimise the design of the measurement procedure of the CO<sub>2</sub> absorption method. A simulation model was used to determine the potential accuracy of the closed-chamber method and the dynamic CO<sub>2</sub> absorption method. Finally, field measurements were performed in the study area, in order to verify the simulation results.

## Materials

### *The measurement techniques*

The closed-chamber method (Hutchinson and Mosier, 1981) was originally designed to determine N<sub>2</sub>O surface effluxes. However, the measuring procedure can also be applied to other gases (Rolston, 1986). Cylinders made of stainless steel are installed in the soil. For a measuring period of one hour air samples of the enclosed air are periodically withdrawn through a needle connection in the cover. They are transported to the laboratory in vacutainers and are then analysed by means of gas chromatography. The efflux is computed from the increase of CO<sub>2</sub> concentration under the cover as set out against time.

Hutchinson and Mosier (1981) proposed an analytically derived mathematical correction procedure for decreasing gradients resulting from increasing concentrations under the cover. This procedure is based on the solution of the differential equation that describes the accumulation of gas at the soil surface:

$$f = \frac{V}{A} \cdot \frac{\partial C}{\partial t} = D_s \cdot \frac{\partial C}{\partial z}, \quad z = 0 \quad (1)$$

Where

$$\begin{aligned} f &= \text{efflux [kg m}^{-2} \text{ d}^{-1}] \\ V &= \text{internal volume of the cover [m}^3] \end{aligned}$$

- $A$  = cross sectional area of the cover [ $\text{m}^2$ ]  
 $\partial C/\partial t$  = increase in head-space concentration with time [ $\text{kg m}^{-3} \text{d}^{-1}$ ]  
 $\partial C/\partial z$  = change of concentration with depth [ $\text{kg m}^{-3} \text{m}^{-1}$ ]  
 $D_s$  = coefficient of  $\text{CO}_2$  diffusion in the soil [ $\text{m}^2 \text{d}^{-1}$ ]  
 $z$  = depth [m]  
 $t$  = time [d]

Hutchinson and Mosier (1981) state that this equation can be integrated and transformed to:

$$f = \frac{V(C_1 - C_0)^2}{At_1(2C_1 - C_2 - C_0)} \cdot \text{Ln} \left[ \frac{C_1 - C_0}{C_2 - C_1} \right] \quad (2)$$

if

$$\frac{C_1 - C_0}{C_2 - C_1} > 1$$

with

$$t_0 = 0 \quad \text{and} \quad t_2 = 2t_1$$

in which

$$t_j = \text{time [d]}$$

$$C_j = \text{gas concentration under the cover at time } t_j \text{ [kg m}^{-3}\text{]}$$

The following assumptions should then be valid: (a) The concentration at  $t = 0$  under the cover equals the concentration at the surface; (b) At some depth there is a plane of constant concentration that is not influenced by the presence of the cover; (c) The soil profile is relatively uniform; (d) The concentration increases linearly with depth. This equation provides an estimate of the efflux for the measurement interval, calculated from the concentration increase under the cover.

Rates of  $\text{CO}_2$  evolution from the soil can also be measured, using the  $\text{CO}_2$  absorption method (Anderson, 1982). This method concerns the absorption of  $\text{CO}_2$  by a caustic solution, aiming to keep the  $\text{CO}_2$  concentration under the cover to approximately the level of the free atmosphere. Several versions of this method have been described.

A static absorption method is proposed by Witkamp (1966b). Carbon dioxide is absorbed by a KOH solution in a dish under a cover. Reinke et al. (1981) apply a NaOH solution instead of a KOH solutions. After the measurement, an excess of a  $\text{BaCl}_2$  solution is added to stabilise the NaOH solution. Solutions are titrated with HCl. The amount of  $\text{CO}_2$  that is trapped can be calculated from the amount of HCl that has been added during the titration. Edwards and Ross-Todd (1983) use a different technique, in which a dish filled with soda lime is placed under a cover to absorb  $\text{CO}_2$ . Carbon dioxide evolution is then calculated from the weight change of the soda lime during the measuring period.

An alternative approach for the static method is given by Witkamp and van der Drift (1961). Ambient air is pumped at a fixed rate through the cover and then through the caustic solution. The contact between the air and the solution is thus improved. However, a flow-through system can introduce an error resulting from pressure differences between the chamber and the soil gas phase. Even small pressure differences may cause convective flow, which seriously affects the  $\text{CO}_2$  efflux. Instead of a flow-through system, Bouten et al. (1984) therefore use an air-circulating system, in which the air is returned to the head space after stripping the  $\text{CO}_2$  (Fig. 1).

### Simulation model

The potential accuracy of the various methods has been evaluated by using a simulation model. The model is a numerical finite difference model describing one-dimensional  $\text{CO}_2$  diffusion in a layered soil (Bouten et al., 1984), according to the equation:

$$\frac{\Delta C_i}{\Delta t} = \frac{D_{s,i}}{\varepsilon_{g,i}} \cdot \frac{\Delta^2 C_i}{\Delta z_i^2} + \frac{\alpha_i}{\varepsilon_{g,i}} \quad (3)$$

where

$$\varepsilon_g = \text{air-filled pore space [m}^3 \text{ of air m}^{-3} \text{ of soil]}$$

$$\alpha = \text{CO}_2 \text{ production rate [kg CO}_2 \text{ m}^{-3} \text{ of soil d}^{-1}\text{]}$$

$$i = \text{Layer index}$$

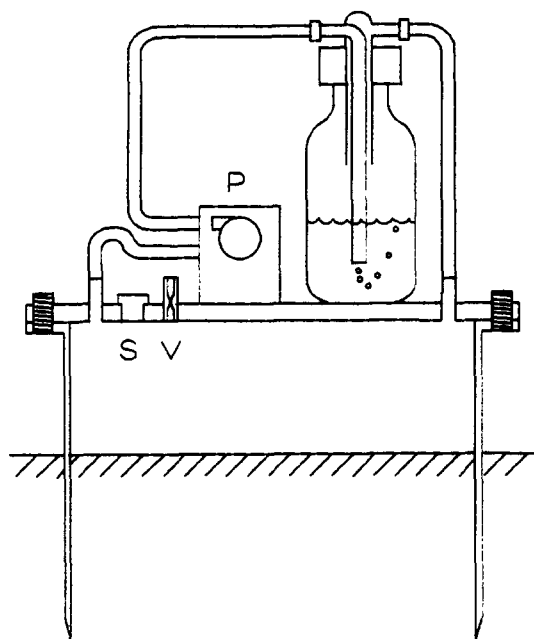


Fig. 1. Diagram of the dynamic CO<sub>2</sub> absorption method for measuring CO<sub>2</sub> effluxes at the soil surface (P: battery-operated air pump; V: vent; S: septum).

The lower boundary condition (flux = 0 kg m<sup>-2</sup> d<sup>-1</sup>) is defined at the groundwater level or at an impermeable layer. Three versions of the upper boundary condition have been used in order to simulate the impact of the measuring techniques on the CO<sub>2</sub> evolution from the soil. The first version concerns an undisturbed reference situation, in which the concentration at the surface is set to 5.9.10<sup>-4</sup> kg m<sup>-3</sup> (0.03% of volume), which corresponds to the concentration of the free atmosphere. In the second version the situation with the closed chamber is simulated (height = 0.05 m). The concentration at the surface in-

creases with time, corresponding to the dimensions of the chamber and the amount of CO<sub>2</sub> that is trapped. The last version contains a boundary condition that reflects the impact of the dynamic CO<sub>2</sub> absorption method. In this version the concentration at the surface is set to zero. This boundary condition simulates the worst case situation in which the pumping capacity is infinitely high, causing all CO<sub>2</sub> evolving from the soil to be immediately absorbed in the caustic solution.

## Methods

### Laboratory experiments

Before starting measurements under field conditions, the versions of the CO<sub>2</sub> absorption method discussed were evaluated by means of four laboratory experiments (Table 1). Each experiment reflects a different technique of CO<sub>2</sub> absorption and of detection of the amount of absorbed CO<sub>2</sub>. Carbon dioxide evolution from the soil under a cover was simulated by injecting CO<sub>2</sub> in closed jars (volume 0.001 to 0.016 m<sup>3</sup>) made of glass. For each experiment, known amounts (volumes of 30 to 100 mL) of 100% CO<sub>2</sub> were injected every thirty minutes during a maximum period of 150 minutes. Each new volume of CO<sub>2</sub> was thoroughly mixed with the atmosphere of the jar during the injection. Carbon dioxide concentrations in the jar were monitored by withdrawing 200-μL gas samples from the jar every ten minutes. The injection point and the sampling point were positioned on top of the jar (septa). The samples were analysed by gas chromato-

Table 1. Absorption of CO<sub>2</sub> in a caustic solution using four different experimental procedures

Reference	Caustic solution	Pumping system	Determination procedure	n <sup>a</sup>	Mass balance error (%)	Absorbed CO <sub>2</sub> (%)
Witkamp (1966b)	KOH 0.2 M	—	Titration	2	-4.5	30.8
Edwards and Ross-Todd (1983)	NaOH on carrier	—	Weight change	2	-33.6	77.7
Bouten et al. (1984)	KOH 0.2 M	+	Titration	3	9.1	99.3
Witkamp and van der Drift (1961)	NaOH 0.2 M and BaCl <sub>2</sub> 0.1 M	+	Titration	12	-0.6	99.6

<sup>a</sup> n = number of experiments.

graphy. The gas chromatograph used was a Carlo Erba 4200, equipped with a Spectra Physics SP4400 integrator. The system was configured with a Hayesep Q 2 m 1/8" × 2 mm SS column and a hot wire detector. Helium was used as a carrier gas. The analysis procedure corresponds to Tacket (1968) and Magnusson (1989). During the experiment CO<sub>2</sub> was absorbed by the caustic solution. For all static methods this solution was placed at the bottom of the jar in a small vessel (cross section area = 50 cm<sup>2</sup>). For the dynamic versions air in the jar was circulated through a caustic solution in a washing-bottle connected to the jar. The determination procedures of fixed CO<sub>2</sub> were in accordance with the methods referred to in Table 1.

#### Numerical experiments

Three boundary conditions that simulate the impact of the measuring device on the CO<sub>2</sub> dynamics have previously been described. These boundary conditions were imposed on 4 soil systems, featuring initially steady-state concentration profiles. The simulations were performed with a time interval that was in accordance with the measuring period. The correction procedure for the closed chamber method in accordance with Hutchinson and Mosier (1981) was also

used to calculate fluxes from the increasing concentration simulated under the cover (Equation 2).

The first soil profile (Table 2) concerns a hypothetical homogeneous rather dry profile. The second soil profile (Table 2) is similar to the first case, but with a lower air-filled pore space. Soil profiles three and four (Table 2) have a soil layer succession comparable to the soil profiles used by Bouten et al. (1984). The third profile concerns a dry situation with high CO<sub>2</sub> production levels (in summer), whereas the fourth profile concerns a wet situation with low production levels (in early spring).

#### Field measurements

In order to verify the results of the simulation exercises field measurements with the dynamic CO<sub>2</sub> absorption method and the closed chamber method were performed in a study area near Winterswijk in the eastern part of the Netherlands. The site concerns a lowland catchment covered with a temperate mixed forest. In this area nutrient cycling has been investigated. (Duysings et al., 1991). Additional information on environmental variables, such as temperature has been obtained from this monitoring programme. Carbon dioxide effluxes were measured with the dynamic CO<sub>2</sub> absorption method and

Table 2. Characteristics of the soil profiles used in the simulation runs

Layer	Depth (m)	$\epsilon_g$ (m <sup>3</sup> m <sup>-3</sup> )	$D_s$ (m <sup>2</sup> d <sup>-1</sup> )	$\alpha$ (kg m <sup>-3</sup> d <sup>-1</sup> )	$\epsilon_g$ (m <sup>3</sup> m <sup>-3</sup> )	$D_s$ (m <sup>2</sup> d <sup>-1</sup> )	$\alpha$ (kg m <sup>-3</sup> d <sup>-1</sup> )
		<b>Profile 1</b>			<b>Profile 2</b>		
1	0.00–0.60	0.30	0.269	0.020	0.10	0.090	0.020
2	0.60–2.00	0.00	0.000	0.000	0.00	0.000	0.000
		<b>Profile 3</b>			<b>Profile 4</b>		
1	0.00–0.05	0.26	0.233	0.032	0.11	0.099	0.025
2	0.05–0.10	0.30	0.269	0.031	0.07	0.063	0.024
3	0.10–0.15	0.30	0.269	0.030	0.06	0.054	0.023
4	0.15–0.20	0.31	0.278	0.028	0.06	0.054	0.020
5	0.20–0.30	0.28	0.251	0.025	0.05	0.045	0.012
6	0.30–0.40	0.24	0.215	0.020	0.04	0.034	0.002
7	0.40–0.50	0.16	0.144	0.014	0.02	0.018	0.001
8	0.50–0.70	0.09	0.081	0.007	0.00	0.000	0.000
9	0.70–0.90	0.07	0.063	0.004	0.00	0.000	0.000
10	0.90–1.10	0.06	0.054	0.002	0.00	0.000	0.000
11	1.10–1.40	0.05	0.045	0.001	0.00	0.000	0.000
12	1.40–1.70	0.02	0.018	0.001	0.00	0.000	0.000
13	1.70–2.00	0.00	0.000	0.000	0.00	0.000	0.000

the closed-chamber method during one year. All measurements were performed in duplicate with intervals of one to two weeks.

The usage of the closed-chamber method was in accordance with the directives given by Hutchinson and Mosier (1981) and Rolston (1986), whereas for the dynamic CO<sub>2</sub> absorption method an optimised procedure was chosen, based on the results of the laboratory experiments: A chamber of stainless steel (cross section area = 0.07 m<sup>2</sup>; length = 0.3 m) with a vent tube to permit pressure equilibrium with the surroundings is driven 4–6 cm into the soil and is connected to a washing-bottle containing a solution of 0.1 mol L<sup>-1</sup> BaCl<sub>2</sub> and 0.2 mol L<sup>-1</sup> NaOH. The air under the cover is circulated through the solution (Fig. 1). All available CO<sub>2</sub> precipitates as solid BaCO<sub>3</sub> at sufficient pumping capacity (0.15 m<sup>3</sup> h<sup>-1</sup>). In this way the concentration of CO<sub>2</sub> under the cover is kept low. After a period of two hours the bottle is removed from the pumping system and samples of gas under the cover are withdrawn to check the CO<sub>2</sub> concentration. A sample of the solution is then titrated with 0.25 mol L<sup>-1</sup> HCl, using a titro processor. Both [OH<sup>-</sup>] of this solution and the original solution are determined to compute the amount of absorbed CO<sub>2</sub> (Anderson, 1982). Measurements for periods longer than 3 hours should be avoided. The availability of O<sub>2</sub> may then become a limiting factor for CO<sub>2</sub> production in the artificially closed system, due to continuous O<sub>2</sub> consumption.

## Results and discussion

### *Laboratory experiments*

The laboratory experiments give insight into the quality of the different techniques of trapping CO<sub>2</sub> in a caustic solution. The results are given in Table 1. Both the potential to absorb and the potential to detect the absorbed amount of CO<sub>2</sub> can be read from this table. The amount of absorbed CO<sub>2</sub> is derived from the change of concentration in the jar. The mass balance error is defined as the difference between the original amount of injected CO<sub>2</sub> and the sum of the amounts of CO<sub>2</sub> fixed in the caustic solution and

CO<sub>2</sub> remaining in the jars. The values are expressed as a fraction of the total amount of injected CO<sub>2</sub>. A mass balance error that does not equal zero indicates either inadequate measurements or an absorption behavior that is not selective for CO<sub>2</sub>.

The worst results have been obtained with the static CO<sub>2</sub> absorption method. Absorption was impeded during the measuring period, due to slow diffusion processes. The results, obtained with NaOH on a carrier, are slightly better. However, the calculated mass balance error turns out to be negative. This error has probably been caused by the absorption of water from the air during the experiment. Better results have been found when using a pumping system that circulates the air in the jar through the caustic solution. This establishes a good contact between CO<sub>2</sub> and the absorbing medium. The NaOH/BaCl<sub>2</sub> solution has yielded better results than a KOH solution. The reliability of the titration volumes depends on the behaviour of the equilibria between CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>CO<sub>3</sub> in relation to pH. The chemical reaction of NaOH/BaCl<sub>2</sub> with CO<sub>2</sub> yields solid BaCO<sub>3</sub>, while the reaction with KOH yields dissolved K<sub>2</sub>CO<sub>3</sub>. In the latter case CO<sub>2</sub> is released from the solution, when the pH is lowered during the titration, thus propagating an error in the titration volume.

### *Numerical experiments*

The simulated surface effluxes versus time for all soil profiles are given in Fig. 2, while Fig. 3 shows the corresponding CO<sub>2</sub> concentration profiles. The stationary undisturbed situation yields a constant surface efflux, while the other computed surface effluxes, as a result of the simulated measuring device, deviate from this line. The largest deviation is found for the closed-chamber method. Carbon dioxide is trapped under the cover and causes an increase in concentration at the soil surface. Storage of CO<sub>2</sub> not only occurs under the cover but carries on to the soil compartment, resulting in a decreasing concentration gradient (Fig. 3) and a decreasing surface efflux (Fig. 2). Effluxes calculated from the correction equation 2 (Hutchinson and Mosier, 1981) also show a considerable deviation from the stationary efflux under undisturbed

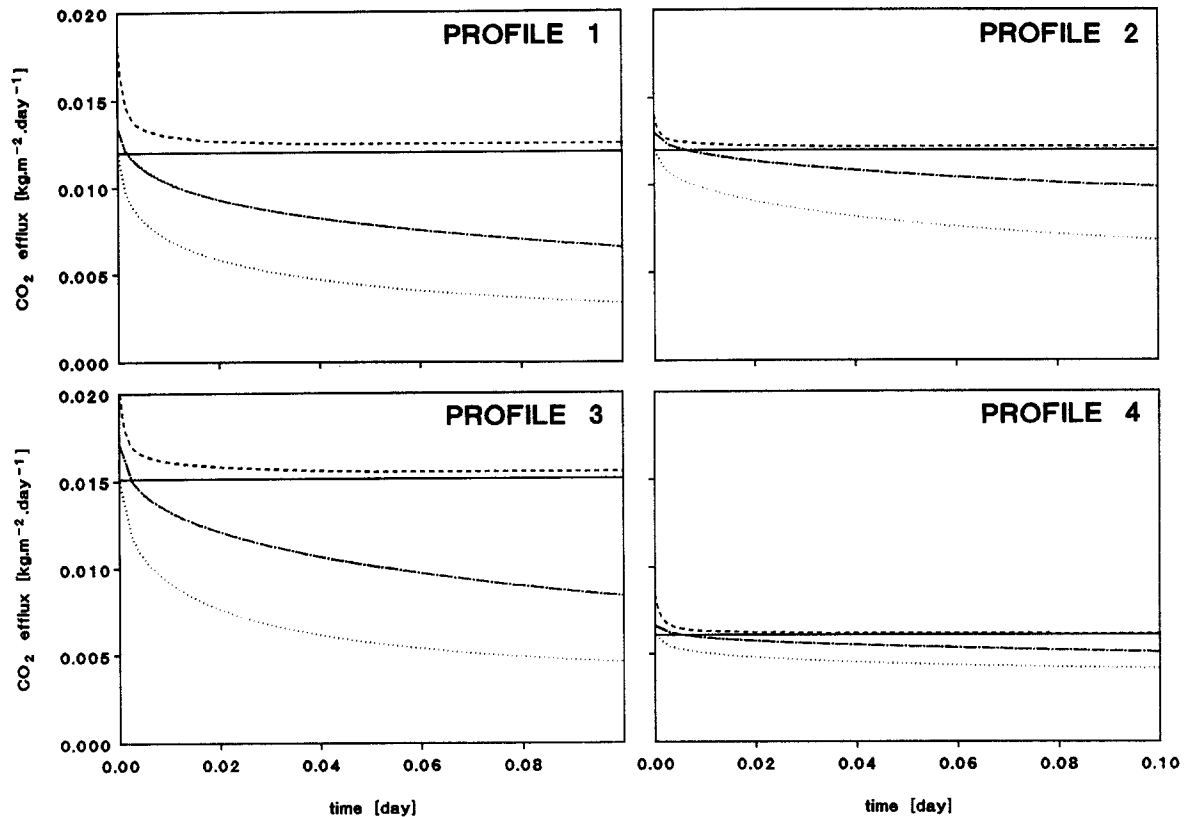


Fig. 2. Simulated  $\text{CO}_2$  effluxes at the soil surface versus time, starting with initially stationary profiles (solid: undisturbed, dotted: closed-chamber method, dashed-dotted: closed chamber with correction for decreasing gradient, dashed: dynamic  $\text{CO}_2$  absorption method). For information on the soil profiles, see Table 2.

conditions. This is due to the fact that the change in  $\text{CO}_2$  storage within the soil is not taken into account. However, from Fig. 3 it can be seen that the storage of  $\text{CO}_2$  increases in all profiles, which is not negligible. The figure also shows the depth to which the concentration changes during a 0.05-day measuring period. This is the depth to which the inverted box should be driven into the soil in order to avoid deflection of the vertical  $\text{CO}_2$  flow.

The  $\text{CO}_2$  absorption method has a small impact on the  $\text{CO}_2$  dynamics. The efflux evolving under the cover (Fig. 2) is only marginally influenced in the beginning. This results from the unrealistic one-step decrease in  $\text{CO}_2$  concentration at infinitely high pumping capacity. This effect will diminish when a lower pumping capacity is chosen. However, the pumping capacity needs to be high enough to handle the  $\text{CO}_2$  efflux. Carbon dioxide concentration pro-

files (Fig. 3) hardly deviate from the original situation when the  $\text{CO}_2$  absorption method is used.

The comparison of the wet and the dry situations shows that errors are lowest at low air-filled pore volumes. This is due to the fact that a lower air-filled pore volume implies a lower storage capacity.

#### Field measurements

Measurement results for 1987 are given in Fig. 4. This year is characterised by moderate  $\text{CO}_2$  evolution rates and low to medium air-filled pore volumes (Fig. 4d). The course of  $\text{CO}_2$  evolution (Fig. 4a, b) is very distinct, expressing the effect of temperature (Fig. 4c) on the production of  $\text{CO}_2$  (Edwards, 1975; Reinke et al., 1981; Witkamp, 1969). A significant correlation between

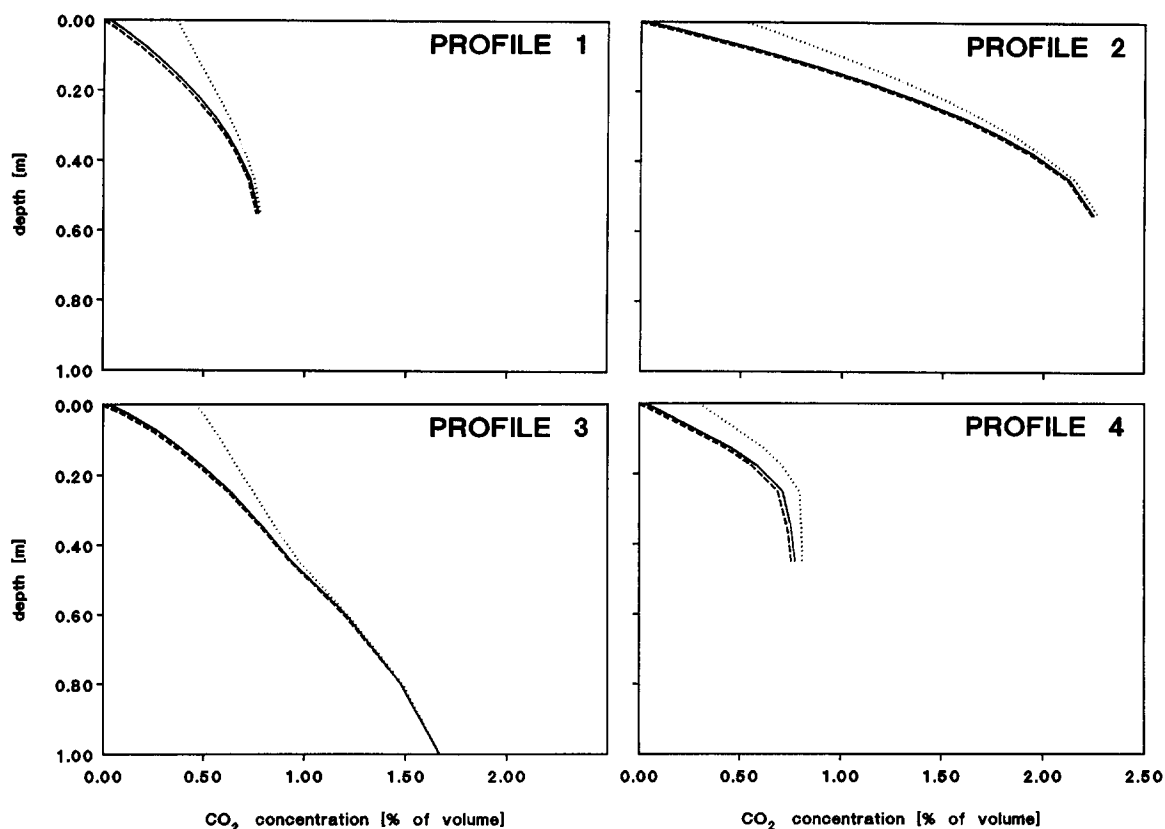


Fig. 3. Simulated CO<sub>2</sub> concentration depth curves after 0.05 day. (solid: undisturbed, dotted: closed-chamber method, dashed: dynamic CO<sub>2</sub> absorption method). For information on the soil profiles, see Table 2.

temperature and efflux has been calculated at the 0.01 confidence level. The measurements also demonstrate the high temporal and spatial variability of soil CO<sub>2</sub> evolution.

In this paper discrepancies between effluxes measured with the dynamic CO<sub>2</sub> absorption method (Fig. 4a) and the closed chamber method (Fig. 4b) are more relevant. Although the lines show the same trend, it is clear that values are higher for the dynamic CO<sub>2</sub> absorption method. Integration of effluxes over the measured period (day 90 to day 360) gives a rough estimate of the total soil CO<sub>2</sub> evolution. For the dynamic CO<sub>2</sub> absorption method integration yields 2.5 kg m<sup>-2</sup>, whereas for the closed-chamber method a value of 1.5 kg m<sup>-2</sup> is computed. The ratio of these values confirms the trends of ratios as predicted by the simulation model.

## Conclusions

All methods impose a new artificial boundary condition upon the original situation. For the closed-chamber method this results in a rapidly decreasing efflux. The correction method of Hutchinson and Mosier (1981) cannot be applied successfully because it does not correct for increasing storage of CO<sub>2</sub> in the soil profile. Simulation results and field measurements show that this factor is not negligible. When using the dynamic CO<sub>2</sub> absorption method a new CO<sub>2</sub> concentration gradient stabilises and effluxes only slightly differ from the original situation. As CO<sub>2</sub> concentrations hardly change, there is no need to drive the chamber into the soil for more than a few centimetres, thus minimizing the mechanical disturbance. Laboratory experiments show that static absorption is not sufficient to



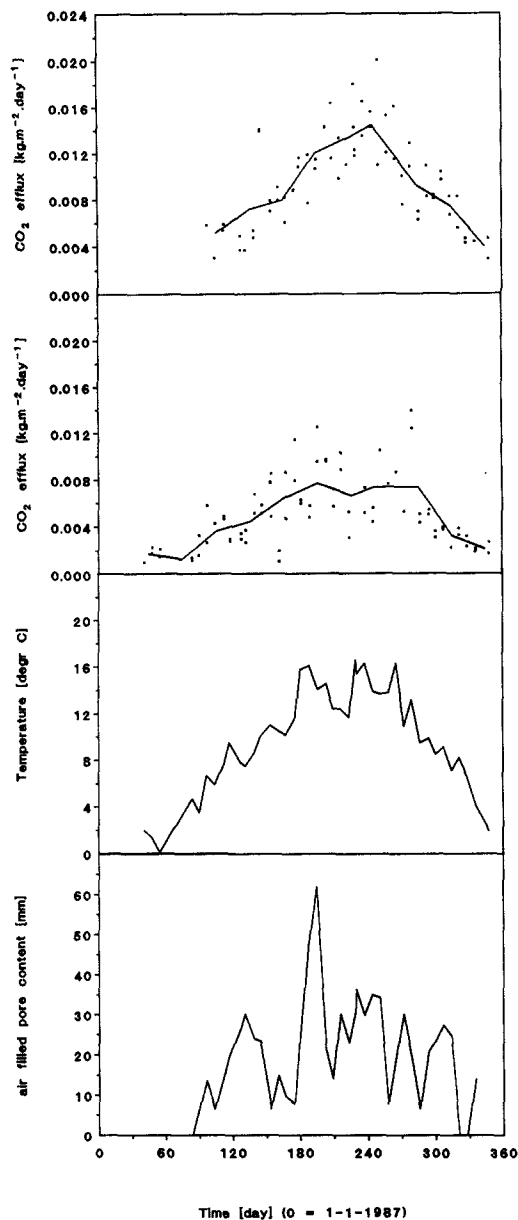


Fig. 4. Field measurements. **a.** Measured CO<sub>2</sub> effluxes at the soil surface versus time, according to the dynamic CO<sub>2</sub> absorption method with air circulation. (points: individual measurements, line: monthly averages). **b.** Measured CO<sub>2</sub> effluxes at the soil surface versus time, according to the closed-chamber method with correction for decreasing gradient (points: individual measurements, line: monthly averages). **c.** Measured temperature at the soil surface versus time. **d.** Vertically integrated air-filled pore volumes of the unsaturated zone of the mineral soil, calculated from laboratory determined water retention curves and daily measurements of pressure heads throughout the soil profile.

absorb all CO<sub>2</sub> evolving from the soil, due to the lack of contact between CO<sub>2</sub> and the caustic solution. The dynamic approach of CO<sub>2</sub> absorption, which uses a circulation system that pumps air through the caustic solution, appears to yield reliable results. This method is not expensive, and the use of battery-operated air pumps avoids the necessity of electrical mains. The method is therefore suitable for research on the temporal and spatial dynamics of soil CO<sub>2</sub> evolution.

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#### **b** References

- Anderson J P E 1982 Soil Respiration. *In* Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties. Agronomy Monograph no. 9. Ed. A L Page. pp 831-871. Am. Soc. Agron., Madison, WI.
- Bouten W, De Vré F M, Verstraten J M and Duysings J J H M 1984 Carbon dioxide in the soil atmosphere: Simulation model parameter estimation from field measurements. *In* Hydrochemical Balances of Freshwater Systems. IAHS Publication no. 150. Ed. E Eriksson, pp 23-30. IAHS Press, Wallingford, Oxfordshire.
- De Jong E and Schappert H J V 1972 Calculation of soil respiration and activity from CO<sub>2</sub> profiles in the soil. *Soil Science* 113, 328-333.
- Duysings J J H M, Verstraten J M, Bouten W, Tietema A and Oostroom M 1991 Hydrochemical budgets of a forest ecosystem in the Netherlands. *J. Ecol.* *Submitted*.
- Edwards N T 1975 Effects of temperature and moisture on carbon dioxide evolution in a mixed deciduous forest floor. *Soil Sci. Soc. Am. J.* 39, 361-365.
- Edwards N T and Ross-Todd B M 1983 Soil carbon dynamics in a mixed deciduous forest following clear-cutting with and without residue removal. *Soil Sci. Soc. of Am. J.* 47, 1014-1021.
- Garret H E and Cox G S 1973 Carbon dioxide evolution from the floor of an oak-hickory forest. *Soil Sci. Soc. Am. J.* 37, 641-644.
- Hutchinson G L and Mosier A R 1981 Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Sci. Soc. Am. J.* 45, 311-316.
- Jury W A, Letey J and Collins T 1982 Analysis of chamber

- methods used for measuring nitrous oxide production in the field. *Soil Sci. Soc. Am. J.* 46, 250–256.
- Magnusson T 1989 A method for equilibration chamber sampling and gas chromatographic analysis of the soil atmosphere. *Plant and Soil* 120, 39–47.
- Matthias A D, Blackmer A M and Bremner J M 1980 A simple chamber technique for field measurement of emissions of nitrous oxide from soils. *J. Environ. Qual.* 9, 251–256.
- Reinke J J, Adriano D C and McLeod K W 1981 Effects of litter alteration on carbon dioxide evolution from a South Carolina pine forest floor. *Soil Sci. Soc. Am. J.* 45, 620–623.
- Rolston D E 1986 Gas Flux. *In* *Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods*. Agronomy Monograph no. 9. Ed. A Klute. pp 1103–1119. Am. Soc. Agron., Madison, WI.
- Tacket J L 1968 Theory and application of gas chromatography in soil aeration research. *Soil. Sci. Soc. Am. Proc.* 32, 346–350.
- Witkamp M and van der Drift J 1961 Breakdown of forest litter in relation to environmental factors. *Plant and Soil* 15, 295–311.
- Witkamp M 1966a Decomposition of leaf litter in relation to environment, microflora and microbial respiration. *Ecology* 47, 194–201.
- Witkamp M 1966b Rates of carbon dioxide evolution from the forest floor. *Ecology* 47, 492–494.
- Witkamp M 1969 Cycles of temperature and carbon dioxide evolution from litter and soil. *Ecology* 50, 922–924.
- Witkamp M and Frank M L 1969 Evolution of CO<sub>2</sub> from litter, humus and subsoil of a pine stand. *Pedobiologia* 9, 358–365.