

## **Chapter 7**

# **Comparison of closed static and dynamic chamber methods for the measurement of soil CO<sub>2</sub> efflux**

## **7.1 Introduction**

Although the study of soil CO<sub>2</sub> efflux dates back more than 100 years (c.f. Schwartzkopf, 1978), it is still very difficult to measure it accurately because of its great temporal and spatial variability and dependence on many environmental and substrate nutrients characteristics (Norman *et al.*, 1997; Lund *et al.*, 1999).

Two of the most widely used techniques for the measurement of soil CO<sub>2</sub> efflux are those known as the closed dynamic chamber (Desjardins, 1985; Rochette *et al.*, 1991; Kim *et al.*, 1992; Norman *et al.*, 1997) and closed static chamber (Grahammer *et al.*, 1991; Smith *et al.*, 1995) techniques. Their difference lies in the presence or absence of air circulation. In dynamic closed chamber systems, air is circulated from the chamber to an IRGA and returned to the chamber, while the operation of closed static chambers consists of sealing a certain volume of atmosphere above the soil surface for a period of time (typically 20 to 60 minutes) to allow the gas to accumulate to a concentration that can be determined by gas chromatographic or infrared analysis (Conen and Smith, 1998). Static chambers have been used for more than 70 years (Lundegardh, 1927)-although not in conjunction with gas chromatography or IRGA methods, but with acid trapping of CO<sub>2</sub> and chemical analysis- while the use of dynamic closed chambers is more recent.

The dynamic closed chamber method often requires the placement of collars in the soil and the area covered is usually very small: from 0.005 m<sup>2</sup> (Janssens *et al.*, 2000)

to 0.019 m<sup>2</sup> (Rochette *et al.*, 1992) and this can have large “edge effects”. The method can also be subject to error from disturbance effects (see below). Because the collars must be located between impermeable areas such as rocks or larger roots near the surface, flux estimates can be larger than those determined with large chambers that cover both permeable and impermeable areas, even if both are equally precise (Norman *et al.*, 1997). The area that a static chamber can cover can vary; reported sizes range from 0.008 m<sup>2</sup> (Ambus *et al.*, 1993) to 0.49 m<sup>2</sup> (Ambus and Christensen, 1995). Chambers with larger areas exhibit less variability between replicates than smaller ones (Ambus *et al.*, 1993).

There are a number of so-called “chamber effects”, that have an impact on the flux measurement. One example is the soil disturbance from the insertion of the chamber into the soil and release of CO<sub>2</sub> from the compacted soil pores (Matthias *et al.*, 1980; Hutchinson and Livingston, 1993); this can be overcome by leaving the chambers in place for some time before measurement takes place (Hutchinson and Livingston, 1993). Also, closure of the chamber for the accumulation of gas produces alterations in soil temperature and moisture in the chamber, which consequently will cause changes in the CO<sub>2</sub> efflux (Rochette *et al.*, 1992; Hutchinson and Livingston, 1993; Welles *et al.*, 2001). This can be more pronounced in the closed static chamber method, since the closure time can be up to the order of an hour, whereas the effect is very small when the dynamic chamber method is used because of the quick sampling (2 minutes for the EGM-3 with SRC-1, PP-Systems).

With the closure of the chamber the concentration of CO<sub>2</sub> in the chamber headspace increases and also storage of CO<sub>2</sub> in the soil continues, resulting in a decreasing concentration gradient with depth. This effect, together with radial diffusion of gas to the outside of the chamber, will result in a lower CO<sub>2</sub> efflux being measured (Freijer and Bouten, 1991; Healy *et al.*, 1996). Again, the quick measurement with a dynamic closed chamber minimises the artifacts caused by altering the CO<sub>2</sub> concentration gradient within the soil profile and between the soil atmosphere interface and the

chamber headspace (Davidson *et al.*, 2002) and by the lateral escape of the gas. Errors associated with the radial diffusion of gas, when the closed static chamber method is used, can be minimised with simple precautions, such as minimising duration of the measurement, increasing the chamber height and radius and inserting the chamber walls down to the depth of gas production (Matthias *et al.*, 1978; Healy *et al.*, 1996; Conen and Smith, 2000). However, deep insertion of the chamber into the soil can result in low estimates, particularly in forest environments, (Anderson *et al.*, 1983), because the chamber severs and isolates surface roots and prevents horizontal root growth into the chamber, thus altering CO<sub>2</sub> production in the soil (Raich and Nadelhoffer, 1989).

The use of closed static chambers can also inhibit pressure fluctuations associated with the turbulence in air movement over the soil surface (Hutchinson and Livingston, 1993), but this problem does not occur with the use of dynamic closed chamber systems. Hutchinson and Mosier (1981) proposed that a properly vented closed chamber prevents perturbation in mean air pressure. However, Conen and Smith (1998), after testing vented and non-vented chambers in field experiments, recommended the use of non-vented chambers for the measurement of trace gases.

In the closed static chamber, the concentration of gas in the chamber starts to increase as soon as the chamber is closed. The exchange rate of a trace gas across the soil-atmosphere boundary is largely a function of its diffusion coefficient and the concentration gradient between sites of production (or consumption) and the soil surface (Hutchinson and Livingston, 1993). A linear increase in chamber headspace concentration with time has been accepted as a desirable feature for field measurements, with the assumption that the rate of change is constant for short periods of time (Anthony *et al.*, 1995). The linear regression approach offers many advantages, including that it deals with measurement variability and tests the model's goodness of fit to the observed concentration data (Livingston and Hutchinson, 1995). However, when concentration changes exhibit non-linear behaviour, the use

of a linear model may seriously underestimate the flux, particularly in highly porous soils and other situations where the change in chamber headspace concentration is not constant with time (Anthony *et al.*, 1995). Healy *et al.* (1996) indicated that even when the concentration is linearly increasing it should not be regarded as the sole indicator for measurement accuracy, as this notion is not necessarily supported by gas diffusion theory. They compared different models (linear, quadratic and cubic) to estimate flux from chamber concentration increases and they concluded that the linear model systematically underestimated true flux density. Matthias *et al.* (1978) used a two-dimensional model on the N<sub>2</sub>O accumulation inside a closed static chamber and concluded that the closure of the chamber caused lateral gas movement, decreasing the flux from the soil in the chamber by up to 55%.

The closed static chamber method has sometimes been criticised for underestimating the soil CO<sub>2</sub> efflux at low flux rates and severely underestimating it at high flux rates, compared to the closed dynamic chamber method which has been shown to be more accurate for a wide range of flux rates (Healy *et al.*, 1996; Jensen *et al.*, 1996; Janssens *et al.*, 2000). However, Rochette *et al.* (1997) found little differences in fluxes measured by either the closed dynamic or the static chamber method. Also, the closed static chamber method is currently the most common method for the measurement of other trace gases such as nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) and has other advantages such as low cost of construction and easy installation and removal (IAEA, 1992), and its application under a wide range of conditions (Smith *et al.*, 1995) make it a popular method.

In this study two methods were used for the measurement of soil CO<sub>2</sub> efflux, a dynamic closed chamber system (DC, EGM-3, PP-Systems) and the closed static chamber method (SC). Because the DC method gave generally higher fluxes than the SC method, a further investigation was made on possible reasons for this discrepancy.

## 7.2 Materials and Methods

A detailed description of the dynamic closed chamber system (DC, EGM-3, SCR-1, PP-Systems, Hitchin, UK) and closed static chamber method (SC), can be found in Chapter 3. Another system also used was the GasCard II plus (Edinburgh Instruments, Ltd) equipped with an IRGA. The GasCard II was used as an alternative method for the measurement of CO<sub>2</sub> in the closed static chambers and for the replacement of the syringes for some of the experiments that took place. For its use, lids with two sampling ports had to be employed. The ports were connected with plastic tubes to the GasCard II. One of the tube carried the gas to the IRGA and the other tube acted as a return path, carrying the gas from the IRGA back into the chamber.

As was previously mentioned, a discrepancy was noted in the fluxes measured by the two systems. A series of measurements took place in order to find possible explanations for this discrepancy.

### 7.2.1 Comparison of soil CO<sub>2</sub> flux measured with the closed dynamic chamber and the closed static chamber methods

The flux of soil CO<sub>2</sub> measured in the field with the DC was compared with the one obtained with the SC method and their ratio was calculated. The average value of each plot for each method and each sampling date was used.

### **7.2.2 Comparison of soil CO<sub>2</sub> fluxes measured with the GasCard II and by gas chromatographic analysis**

In some of the field measurements some of the chambers were sampled with both syringes and the GasCard II. At the end of the closure time and immediately after an air sample had been taken with a syringe, the GasCard II was connected with the sampling ports and a measurement was taken after 22 seconds. Ambient air concentrations were measured from samples taken with syringes as well as from readings with the GasCard II.

### **7.2.3 Investigation of linearity in CO<sub>2</sub> accumulation in the closed static chamber**

The linearity of CO<sub>2</sub> accumulation in the closed static chamber was investigated both by taking syringe samples and by making GasCard II IRGA readings taken every 15 or 20 minutes, for a total period of 120 minutes. Linearity was checked in one or two chambers at the following sites: the 40-yr stand on 23 April 2002 (chambers 8 and 9) and on 17 September (chambers 1 and 2), in the CF on 16 May 2002 (chamber 4) and in the 30-yr old stand on 24 September 2002 (Chambers 1 and 2).

### **7.2.4 Test 1**

Two collars very close to each other (10 cm) were placed in the garden of the university on homogenous soil and left for a day. Three sets of measurements took place on 2 December 2002. One collar was used for the DC method and the other as a SC with the GasCard II IRGA. The GasCard IRGA was used instead of sampling with syringes, as it was easier and faster to use. First, the emissions within both

collars were measured with the PP-Systems IRGA and then with the GasCard II. Then measurements with both IRGAs took place at the same time. The measurement with the GasCard II lasted for two minutes in order to resemble the measurement time by the PP-Systems. After the end of measurements, a time gap of about 3 minutes was left and then the IRGAs were put again on the collars, but this time the other way around.

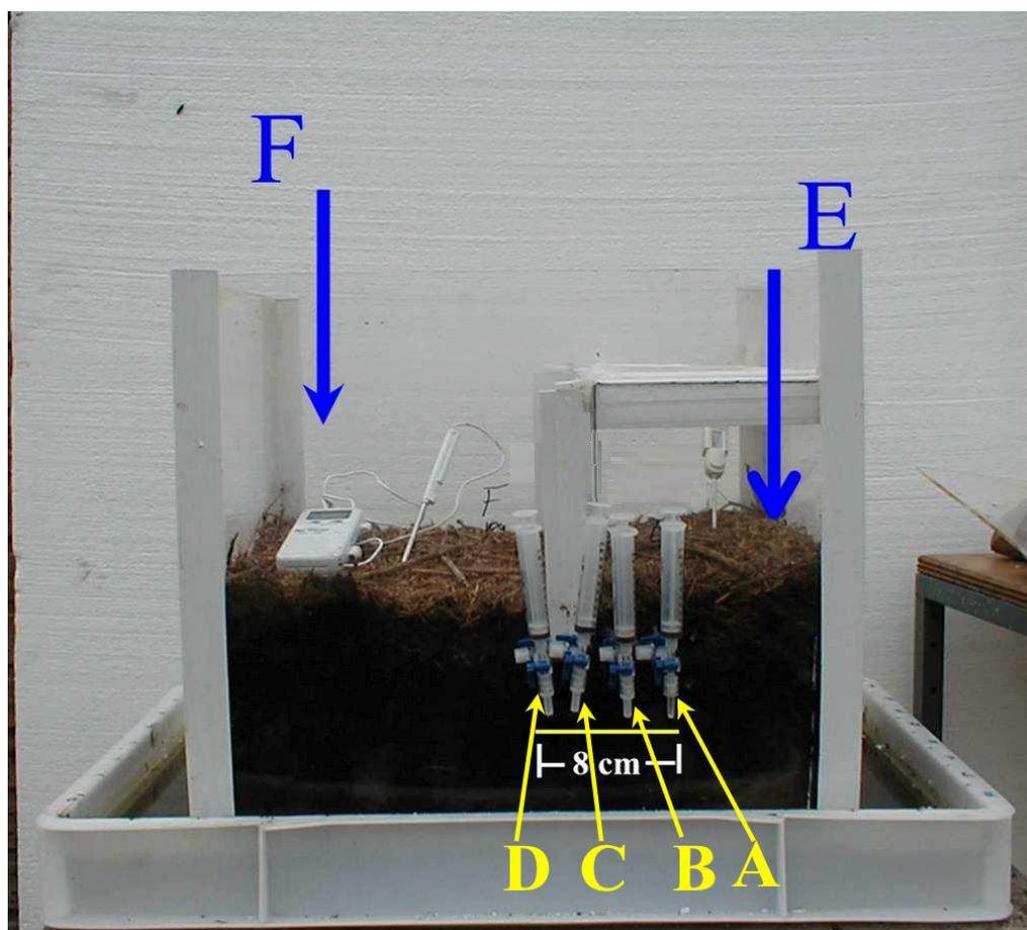
### 7.2.5 Test 2

CO<sub>2</sub> evolution from the soil in a chamber was simulated by injecting CO<sub>2</sub> into a closed glass jar of 3000 ml volume. For each measurement, air containing 2000 μmol mol<sup>-1</sup> of CO<sub>2</sub> was flushed into the jar with a flow rate of 0.50 ml s<sup>-1</sup>, while a small fan inside ensured uniform mixing of the air. CO<sub>2</sub> concentrations in the jar were then monitored with the PP-System and the GasCard II every 30 seconds, on two occasions, while additionally on two occasions air samples were taken with syringes and analysed by gas chromatography.

### 7.2.6 Soil monolith

The potential for lateral losses of CO<sub>2</sub> to occur under the chamber walls was also investigated. An intact soil monolith (20 cm width, 50 cm length, 30 cm depth) was extracted from the 40-yr stand using plexiglass frames and a spade and was transferred to the university greenhouse. A plexiglass sheet was inserted into the monolith to 5 cm depth in order to mimic the wall of a chamber in the field and to partition the surface into a “chamber” area and an “external” area. The chamber area so created could be closed with a horizontal lid. The chamber had a side of 20 cm width, and was assumed to represent the half section of a chamber in the field, with diffusion being tested on one side only (Figure 1). Four air permeable, hydrophobic,

polypropylene tubes (Accurel®) tubes (5.5 mm internal diameter, 20 cm length) were inserted through the outer wall of the monolith to penetrate to 5 cm depth in the soil. With the chamber wall as a centre, two tubes were inserted at a distance 4.0 and 2.0 cm respectively in the soil underneath the chamber (A and B points) and two were inserted 2.0 and 4.0 cm respectively in the soil outside the chamber (C and D). About 3 cm length from each end of the tubes were covered with araldite, a sealing material for the avoidance of edge effects from the walls of the chamber. Three-way stopcocks were attached to the external ends of the tube sampling ports. The sampling ports were kept closed when samples were not taken. Samples were taken simultaneously from each point together with air samples were taken inside the chamber and in the air above the soil outside the chamber (points E and F) for 30 minutes before the chamber was closed with a lid. After the placement of the lid on the chamber, samples were taken at intervals of 10 to 20 minutes, over a total measurement period of 120 minutes.



**Figure 1:** The soil monolith, divided into a “chamber” area (right-hand side) and an external area (left-hand side). A-D: gas sampling probes in soil, terminating in sampling syringes. E, F: air space above soil, within and outside the chamber, respectively.

The monolith was placed in a plastic tray and the tray was filled with water up to 10 cm height in order to create an impermeable lower boundary. Water was added at intervals (every two to four days) by spraying the top of the monolith, and then measurements were taken one to two days after the last water application.

Soil temperature was recorded with two digital thermometers (Fisher Scientific), at a depth of 5 cm, inside and outside the chamber. At the end of the measurements, soil

water content was measured with a Theta probe at 5 positions both inside and outside the chamber, and the average was calculated.

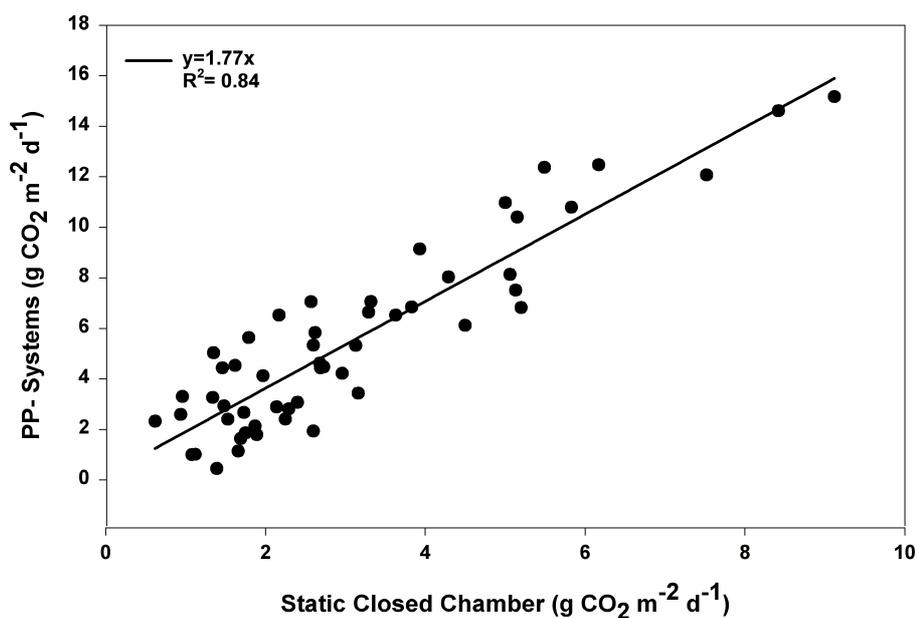
It was assumed that transport of CO<sub>2</sub> from the point of production to the soil surface occurs by gaseous diffusion only. Pressure fluctuations near the surface that may produce some transport of gas by mass flow are small and therefore were ignored.

## 7.3 Results

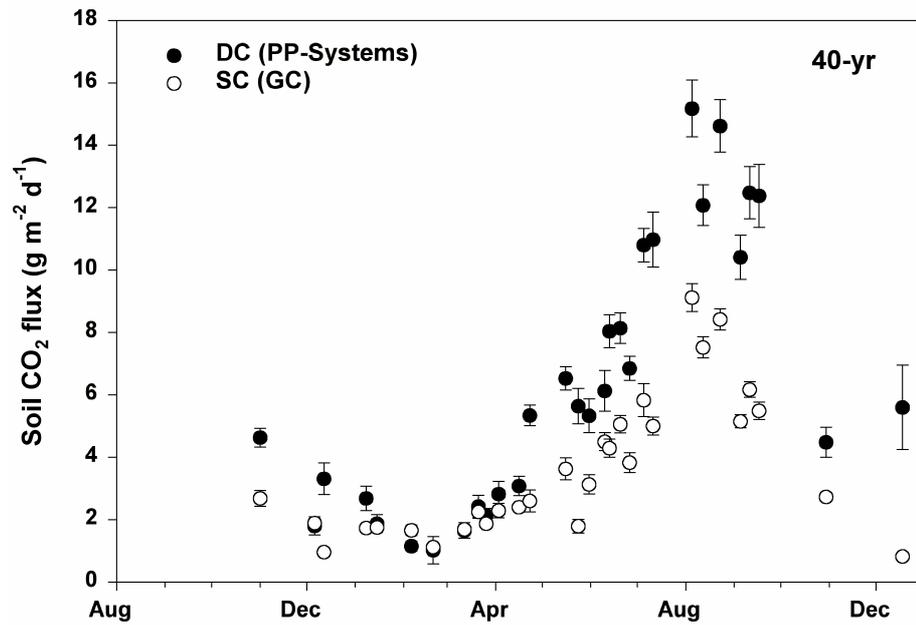
### 7.3.1 Comparison of soil CO<sub>2</sub> flux measured with the closed dynamic chamber and the closed static chamber methods

The CO<sub>2</sub> flux given from the SC method was found to be linearly related to the CO<sub>2</sub> flux given by the DC method ( $R^2 = 0.84$ ,  $P < 0.0001$ , Figure 2). Both methods gave the same trend in soil CO<sub>2</sub> fluxes at all sites (Figures 3, 4). At low soil temperatures the discrepancy of the mean values given by the two methods was small, and the discrepancy increased with increasing temperature (Figure 5). The ratio of the CO<sub>2</sub> flux value given by the DC to the CO<sub>2</sub> flux value given by the SC ranged between 0.3 and 6.8, with the ratio below 1 at five sampling cases during the winter (0.7 on 6 December 2001, 0.3 on 31 December 2001, 0.7 on 15 January 2002 at the CF<sub>before</sub> stand and 0.7 on 6 February 2002 and 0.9 on 20 February 2002 at the 40-yr stand). The SC gave higher values at low temperatures and DC gave much higher values than the SC at higher temperatures. The ratio of the two methods, for all sites, was positively related to  $T_5$  with a power relationship (ratio =  $0.48 * T_5^{0.61}$ ,  $R^2 = 0.40$ ,  $P = 0.0002$ ). The ratio was not related to soil water content. However, in the 40-yr stand only, the ratio was related to soil water content ( $R^2 = 0.46$ ,  $P = 0.004$ ), with the ratio decreasing exponentially with increasing water content. The ratio also increased exponentially with soil temperature at 5 cm ( $R^2 = 0.57$ ,  $P < 0.001$ ). In the CF site the

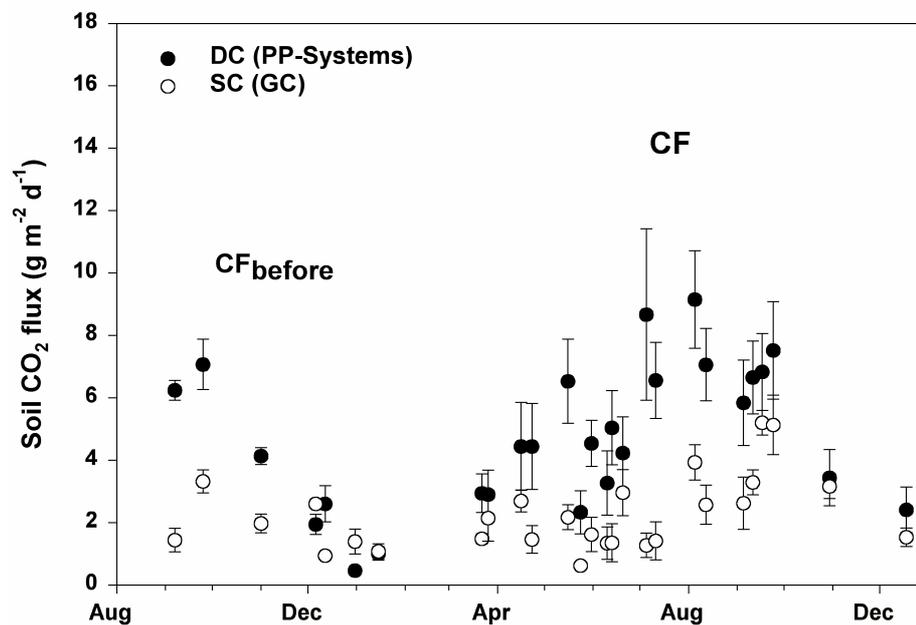
ratio increased exponentially with soil temperature, but the relationship was much weaker ( $R^2=0.15$ ,  $P=0.02$ , for soil temperature at 5 cm depth), while there was no relationship between the ratio and soil water content.



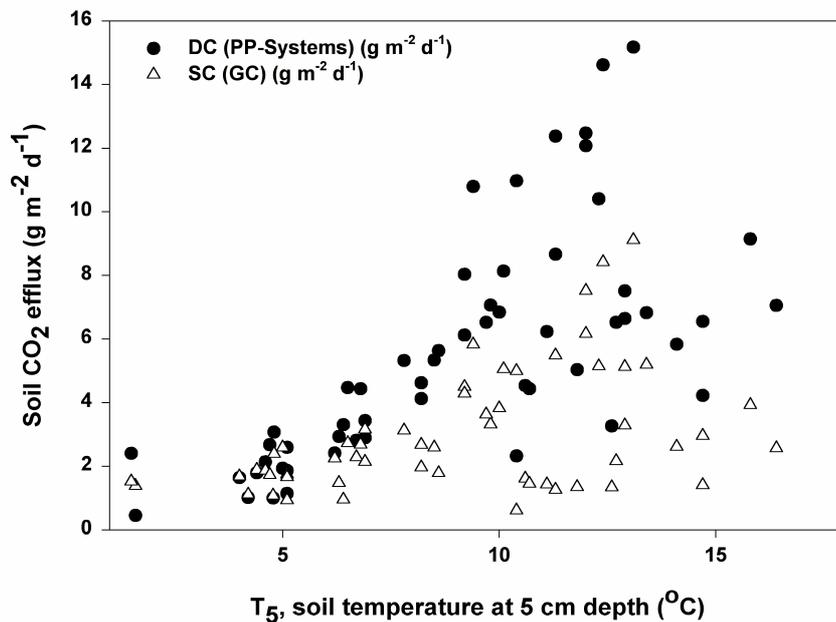
**Figure 2:** Linear relationship between soil respiration (g CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>) measured with the SC and the DC method, in the 40-yr stand and a recently clearfelled site. The regression was forced through the origin.



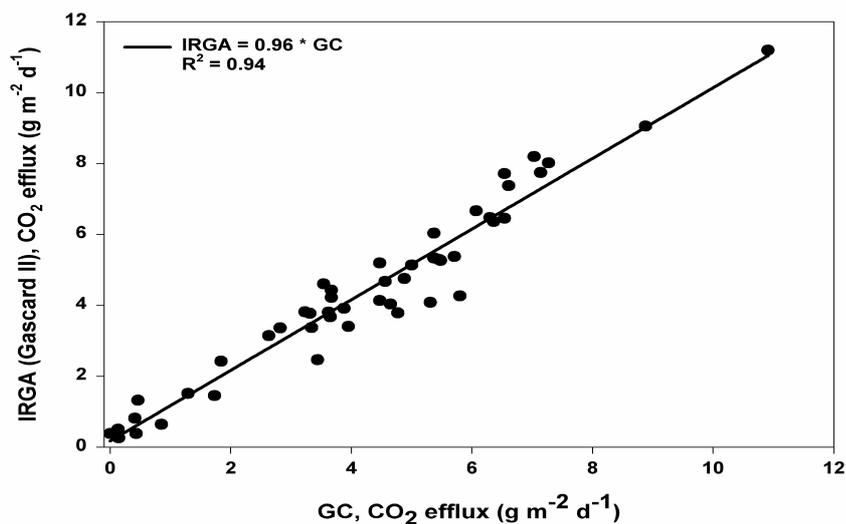
**Figure 3:** Soil CO<sub>2</sub> flux (g m<sup>-2</sup> d<sup>-1</sup>) in the 40-yr stand measured with the DC and SC methods. The vertical bars indicate the standard error of the mean. Each point is the weekly average of 10 collars and 12 chambers.



**Figure 4:** Soil CO<sub>2</sub> flux (g m<sup>-2</sup> d<sup>-1</sup>) in CF<sub>before</sub> and CF measured with the DC and SC methods. The vertical bars indicate the standard error of the mean. Each point is the weekly average of 10 collars and 12 chambers.



**Figure 5:** Soil CO<sub>2</sub> flux as given by the DC and SC methods (for all sites) in various soil temperatures in the field. Each point is the average of 10 collars (DC method) and 12 chambers (SC method). Some values which coincided at the same temperature and had similar discrepancy were omitted, in order to make the graph more clear.



**Figure 6:** Linear relationship between soil CO<sub>2</sub> efflux (g m<sup>-2</sup> d<sup>-1</sup>) measured on different static closed chambers in the 40-yr stand and CF site, with the Gascard II and from air samples analysed in the Gas Chromatograph. The regression was forced through the origin.

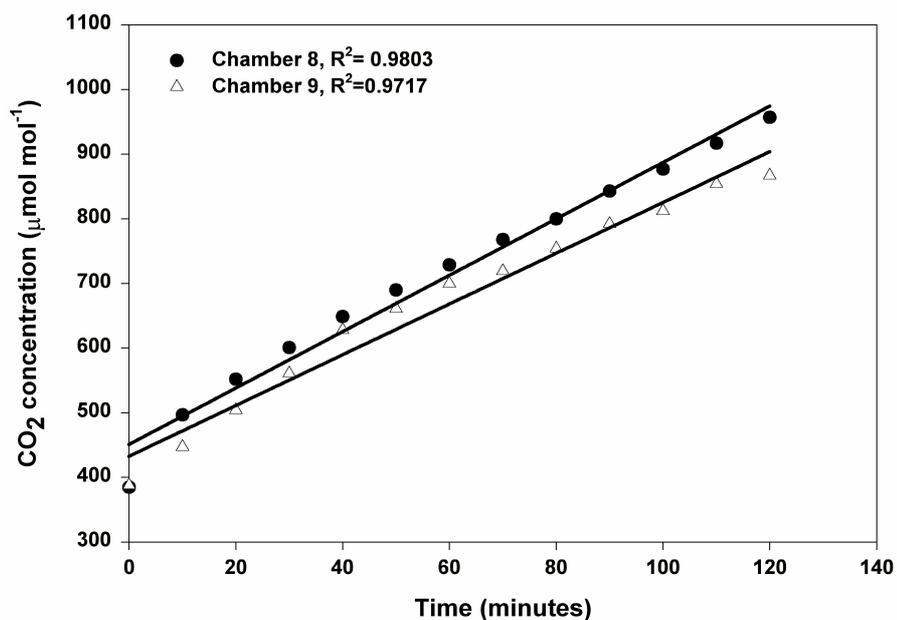
### 7.3.2 Comparison of soil CO<sub>2</sub> fluxes measured with the Gascard II and gas chromatographic analysis

The values of CO<sub>2</sub> efflux measured with the Gascard II IRGA and from air samples taken with syringes and analysed in the gas chromatograph are shown in Figure 6. The two methods were strongly related with a linear relationship (IRGA = 0.96\*GC, R<sup>2</sup>= 0.94).

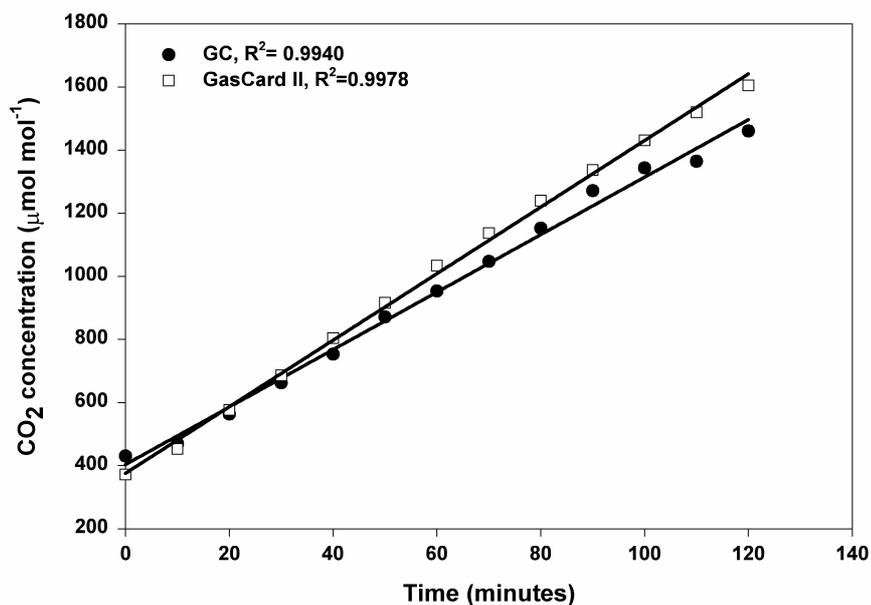
### 7.3.3 Investigation of linearity of CO<sub>2</sub> accumulation in closed static chambers

In the 40-yr stand CO<sub>2</sub> accumulation in the chamber departed from linearity, during the check on the 23 April 2002 despite the very high R<sup>2</sup> (R<sup>2</sup> = 0.9803, P=0.02 and R<sup>2</sup>= 0.9717, P<0.0001 for chambers 8 and 9 respectively, Figure 7). The soil water content next to the chambers was 0.11 and 0.17 cm<sup>3</sup> cm<sup>-3</sup> respectively and average soil temperature at 5 cm depth was 8.1 °C. CO<sub>2</sub> accumulation in the 40-yr stand was checked again on 17 September 2002 in another pair of chambers and accumulation exhibit higher R<sup>2</sup>, however it was still significant different from linear (R<sup>2</sup>= 0.9892, P=0.04 and R<sup>2</sup>=0.9909, P=0.02 for chamber 1 and 2 respectively). The soil water content was 0.35 and 0.37 cm<sup>3</sup> cm<sup>-3</sup> next to chambers 1 and 2, respectively and average soil temperature at 5 cm depth was 11.2 °C. Accumulation of CO<sub>2</sub> in the chamber was very close to linear (R<sup>2</sup> = 0.9940, P=0.28) in one chamber in the CF site (Figure 8). Soil water content was not measured due to failure of the instrument. Average soil temperature at 5 cm depth was 12.7 °C. The CO<sub>2</sub> concentration increase was also measured in two chambers in the 30-yr stand and the results concentration increase in chamber 1 was significant different from linear (R<sup>2</sup>=0.9967, P=0.0002), while the concentration increase in chamber 2 was not significantly different from

linear ( $R^2=0.9932$ ,  $P=0.11$ ). Average soil water content was  $0.32 \text{ cm}^3 \text{ cm}^{-3}$  and average soil temperature at 5 cm depth was  $11 \text{ }^\circ\text{C}$ .



**Figure 7:** CO<sub>2</sub> concentration ( $\mu\text{mol mol}^{-1}$ ) increase in two static closed chambers in the 40-yr stand. The measurements took place on 23 April 2002, the same time in both chambers. Soil water content next to the chambers was  $0.11$  and  $0.17 \text{ cm}^3 \text{ cm}^{-3}$  and average soil temperature at 5 cm depth  $8.1 \text{ }^\circ\text{C}$ .



**Figure 8:** CO<sub>2</sub> concentration ( $\mu\text{mol mol}^{-1}$ ) increase in a static closed chamber in the CF site, measured with the GasCard II in the field and via samples analysed by gas chromatography (GC). The measurements took place on 16 May 2002. Soil water content was not measured due to failure of the instrument and average soil temperature at 5 cm depth was 12.7 °C.

### 7.3.4 Test 1

The results from the measurements on two collars very close to each other with the DC method and with the GasCard II IRGA are shown in Table 1. When both collars were measured with the PP-System the measured CO<sub>2</sub> flux was 0.86 and 0.84 g m<sup>-2</sup> d<sup>-1</sup> for collars 1 and 2, respectively. When both collars were measured with the GasCard II the measured CO<sub>2</sub> flux was 0.28 and 0.32 g m<sup>-2</sup> d<sup>-1</sup> for collars 1 and 2, respectively. The DC method constantly gave higher soil CO<sub>2</sub> flux values compared to the SC method, with a range of ratios from 2.6 to 4.9.

**Table 2:** Soil CO<sub>2</sub> efflux (g m<sup>-2</sup> d<sup>-1</sup>) measured in two collars very close to each other (10 cm) with two IRGAs, and with one collar acting as a static close chamber and the other as a dynamic chamber. The gap between measurements when systems were switched was 3 minutes.

Measurements	Collar 1		Collar 2	
	<u>PP-System</u>	<u>GasCard II</u>	<u>PP-System</u>	<u>GasCard II</u>
Set 1	0.86	0.28	0.84	0.32
Set 2	1.14	0.18	1.39	0.48
Set 3	1.14	0.23	1.12	0.32

### 7.3.5 Test 2

When CO<sub>2</sub> evolution was simulated in a glass bottle with controlled gas flow, the increase in concentration was very close to linear from all methods (Table 2). Under the same conditions the three methods gave similar differences in CO<sub>2</sub> concentrations, although the range was different for each system. The PP-System gave a higher range of concentrations than the other two methods (Table 2). The PP-System also gave higher concentration differences, which were 1 and 4 μmol mol<sup>-1</sup> higher than the concentration differences obtained from the GC method, and between 1 and 5 μmol mol<sup>-1</sup> higher than the concentration differences given by the GasCard II.

**Table 2:** Simulated CO<sub>2</sub> evolution and its measurement by the three methods (PP-Systems, GasCard II and GC), the coefficient of determination of linearity and the range in the increase of concentration. CO<sub>2</sub> of 2000  $\mu\text{mol mol}^{-1}$  was injected in the glass jar with a constant flow of 0.5 ml s<sup>-1</sup>.

	Method	R <sup>2</sup>	Range of CO <sub>2</sub> concentration ( $\mu\text{mol mol}^{-1}$ )	$\Delta\text{C}$
<b>Test A</b>	PP-Systems	0.9919	389-437	48
	GasCard II	0.9994	348-395	47
<b>Test B</b>	PP-Systems	0.9961	378-426	48
	GasCard II	0.9945	343-385	42
<b>Test C</b>	PP-Systems	0.9945	353-401	48
	GasCard II	0.9991	325-368	43
	GC	0.9970	346-390	44
<b>Test D</b>	PP-Systems	0.9903	435-484	49
	GasCard II	0.9945	406-450	44
	GC	0.9921	418-465	47

### 7.3.6 Soil monolith

The CO<sub>2</sub> concentration in the air inside the chamber increased linearly on all sampling dates but the degree of linearity ranged from an R<sup>2</sup> value of 0.9535 to 0.9979 (all P>0.05). The relationship was closer to linear during days with low temperature, between 0.994 and 0.9979 in the measurements that took place on 30 January, 3 February and 17 February 2003, when soil temperatures during measurement ranged between 4.7 and 6.4 °C, 6.8 and 7.2 and 9.5 °C and 12.6 °C, respectively (for the whole course of measurement, both inside and outside the chamber). In the next three measurements, when soil temperatures had increased, the relationships departed further from linearity with an R<sup>2</sup> of 0.9535 on 4 March, 0.9683 on 1 April and 0.9603 on 26 May 2003, while the respective soil temperatures ranged between 11.1 and 12.7 °C, 20 and 28.2 °C and 19.6 and 23.5 °C, respectively.

During the period of measurements before the closure of the chamber, the air concentration inside and outside the chamber was very similar and lower than the concentration in the soil at 5 cm depth. Soil CO<sub>2</sub> concentrations at the measurement points, during the 30 minutes of measurement before the closure of the chamber, exhibited different patterns on different days, with no specific trend in concentrations; however the concentration differed up to 200  $\mu\text{mol mol}^{-1}$  from point to point.

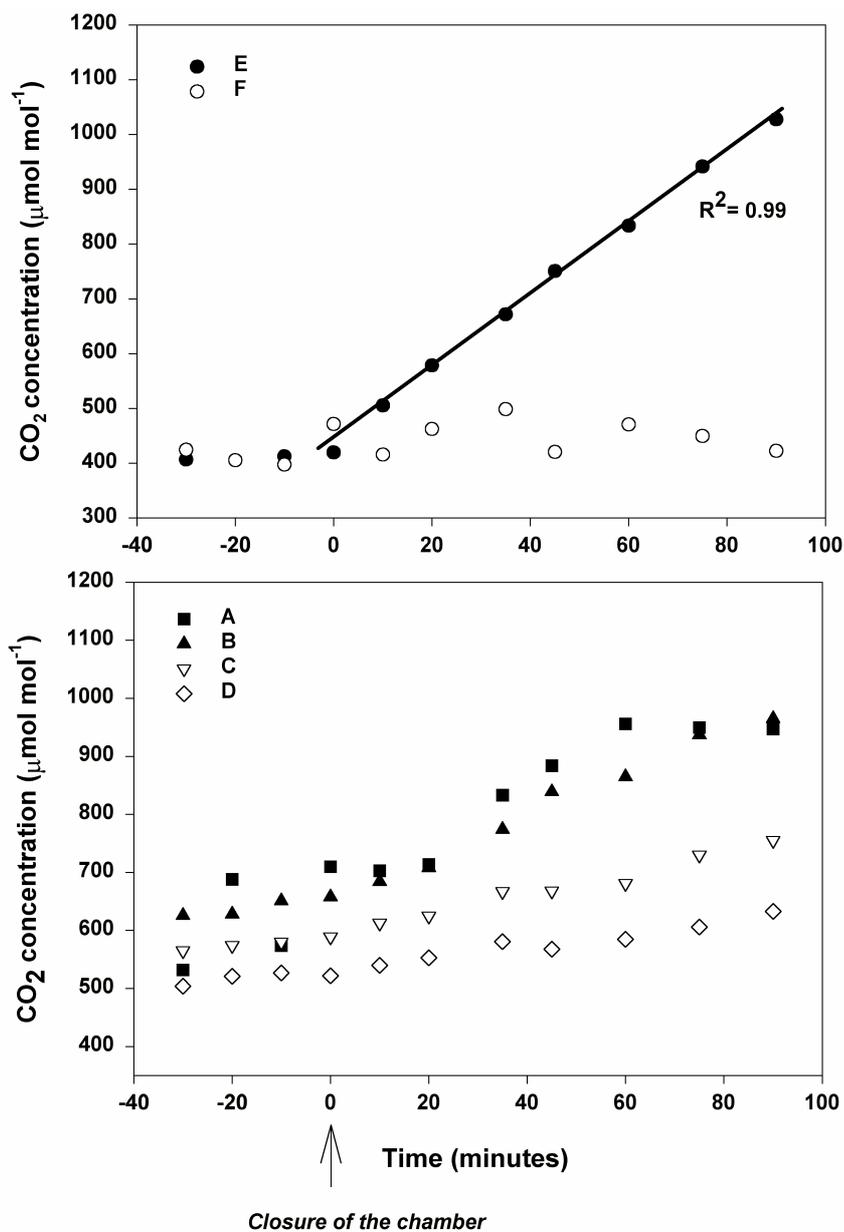
After the placement of the chamber, air CO<sub>2</sub> concentration inside the chamber started increasing linearly, while the air concentration outside the chamber fluctuated around ambient CO<sub>2</sub> concentration. The concentration in the soil started increasing linearly at points A and B (4 and 2 cm inside the chamber wall) as well as at point C (2 cm outside the chamber wall), while concentration in point D (4 cm outside the chamber wall) did not change on three measurement days, although it increased linearly on the other three. The rate of CO<sub>2</sub> increase was always higher in the air inside the chamber than in the soil. In the soil it was always higher at point A (4 cm inside the chamber wall) and then at point B, while the rate of increase at point C was 2 to 4 times lower compared with the rate in point B and rate of increase at point D was even less, 3 to 298 times lower compared to the rate of point B.

Soil water content over the period of measurements ranged between 0.19 and 0.33  $\text{cm}^3 \text{cm}^{-3}$  and it was always higher outside the chamber on all 6 days of measurements, with the differences ranging between 6 and 66%. Soil temperature over the period of measurements ranged from 4.7 to 28.2 °C. On the contrary, soil temperature at 5 cm depth, was always higher inside the chamber. Before the placement of the lid, the temperature inside the chamber was most of the times higher by 0.4 to 1.1 °C, one time it was the same and in one case the temperature outside was higher by 0.2 to 0.3°C. After the placement of the lid the temperature inside was most of the times higher than the soil temperature outside and by the end

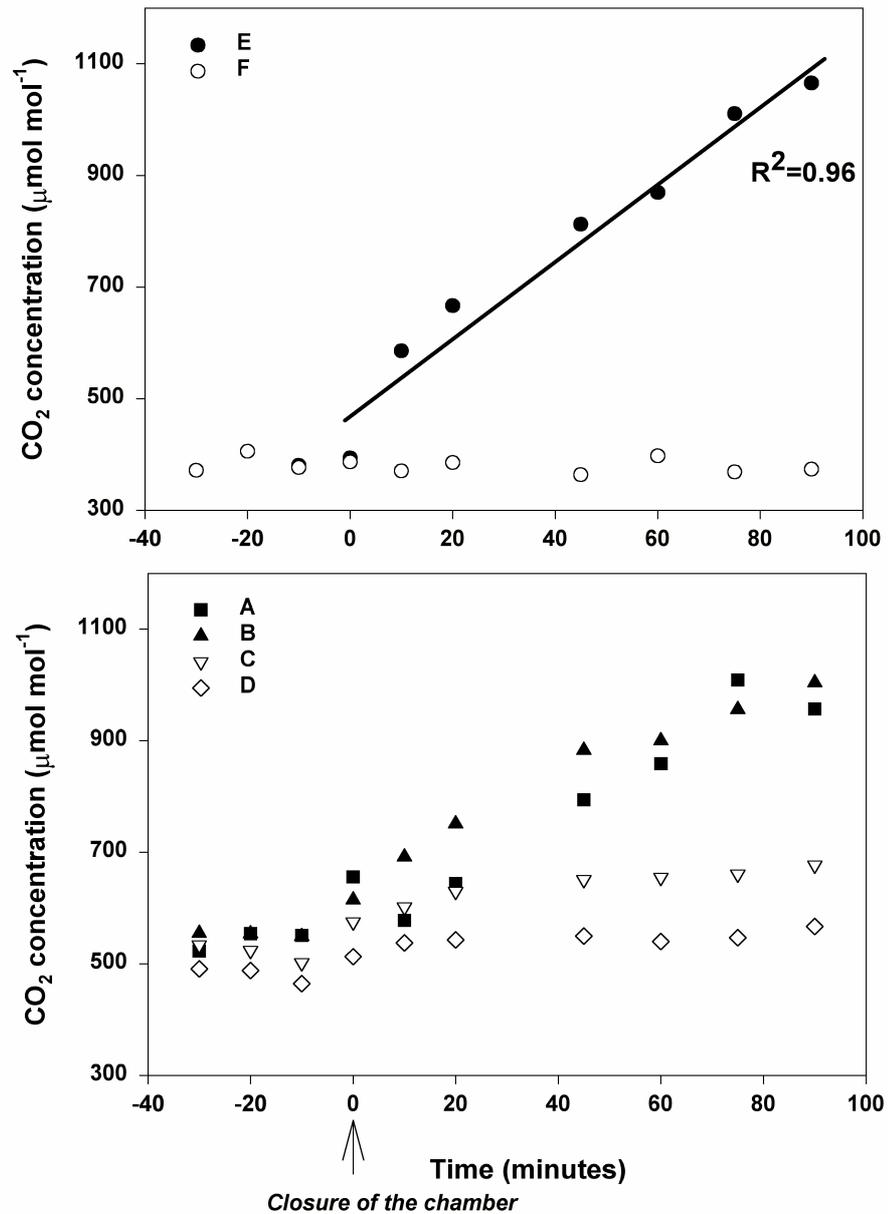
of the measurements it was between 0.3 and 6.9 °C higher than the soil temperature outside the chamber.

Two typical sets of measurements at lower and higher temperatures are shown in Figures 9 and 10. Figure 9 depicts the measurements on the soil monolith on 17 February 2003. For 30 minutes before the closure of the chamber, CO<sub>2</sub> concentrations in the air inside and outside the chamber (points E and F) are very similar and around 400 μmol mol<sup>-1</sup>. With the placement of the lid on the chamber at time 0, CO<sub>2</sub> concentrations inside the chamber (point E) started increasing with a relationship very close to linear ( $R^2=0.9979$ ) while concentration in the air outside the chamber fluctuates around ambient. Soil CO<sub>2</sub> concentration in the soil (points A, B, C and D) were much higher than air, between 504 and 688 μmol mol<sup>-1</sup>. After the closure of the chamber, the concentrations at points A and B (4 and 2 cm inside the chamber wall) started increasing linearly ( $R^2= 0.87$  and  $0.98$  respectively), while concentration at points C and D (2 and 4 cm outside the chamber wall) also increased linearly ( $R^2=0.97$  and  $0.94$  respectively). The rate of increase in the soil inside the chamber was higher than outside the chamber (slope of the equation 3.35 μmol mol<sup>-1</sup> min<sup>-1</sup> and 3.63 μmol mol<sup>-1</sup> min<sup>-1</sup> at points A and B, and 1.77 and 1.09 at points C and D respectively), but lower than the rate of increase inside the chamber (slope 6.68 μmol mol<sup>-1</sup> min<sup>-1</sup>). The soil water content inside the chamber was 0.28 cm<sup>3</sup> cm<sup>-3</sup> and outside the chamber 0.31 cm<sup>3</sup> cm<sup>-3</sup>.

On 26 May 2003 (Figure 10), CO<sub>2</sub> concentration at points E and F was similar, while after the closure of the chamber the concentration inside (E) started increasing while the concentration outside (F) fluctuated around ambient. CO<sub>2</sub> concentration in the soil was higher than the air, between 491 and 555 μmol mol<sup>-1</sup> (points A, B, C, D) and after the closure of the chamber it started increasing linearly both inside and outside the chamber ( $R^2= 0.89, 0.96, 0.88$  and  $0.64$  for points A, B, C, D respectively). The rate of increase in CO<sub>2</sub> concentration in the soil inside the chamber was much higher than the increase



**Figure 9:** Measurements of soil CO<sub>2</sub> concentration in the soil monolith before and after the closure of the chamber on 17 February 2003. CO<sub>2</sub> concentration inside the chamber increased linearly after the closure of the chamber ( $R^2=0.99$ ,  $P=0.06$ ) and soil CO<sub>2</sub> concentration inside and outside the chamber walls increased as well. Soil temperature at 5 cm depth ranged between 9.5 to 12.6 °C.



**Figure 10:** Measurements of soil CO<sub>2</sub> concentration in the soil monolith before and after the closure of the chamber on 26 May 2003. CO<sub>2</sub> concentration inside the chamber increased linearly after the closure of the chamber ( $R^2=0.96$ ,  $P=0.19$ ) and soil CO<sub>2</sub> concentration inside and outside the chamber walls increased as well. Soil temperature at 5 cm depth ranged between 19.6 to 23.1 °C.

outside the chamber (slopes of the equation at points A and B were 4.5 and 4.1  $\mu\text{mol mol}^{-1} \text{min}^{-1}$  respectively, while at C and D they were 0.98 and 0.38  $\mu\text{mol mol}^{-1} \text{min}^{-1}$ , respectively), but less than the rate of increase in the air inside the chamber (slope 6.87  $\mu\text{mol mol}^{-1} \text{min}^{-1}$ ). The water content inside the chamber was 0.19  $\text{cm}^3 \text{cm}^{-3}$  and outside the chamber 0.31  $\text{cm}^3 \text{cm}^{-3}$ .

## 7.4 Discussion

### 7.4.1 Comparison of soil CO<sub>2</sub> flux measured with the closed dynamic chamber and the static closed chamber methods

Both methods that were used to measure soil CO<sub>2</sub> flux gave the same seasonal trend in soil CO<sub>2</sub> fluxes, despite the discrepancy in the values given, especially at higher soil temperatures. The CO<sub>2</sub> flux measured with the DC method was linearly related to the CO<sub>2</sub> flux measured by the SC method ( $R^2=0.84$ ). This strong relationship indicate that the SC method, when it is properly calibrated, can be a useful method to measure soil CO<sub>2</sub> efflux. Janssens *et al.* (2000) found that CO<sub>2</sub> fluxes measured with the closed static chamber with soda lime were lower only by 10% than the CO<sub>2</sub> flux measured with a closed dynamic chamber (CIRAS-1, PP-Systems, Hitchin, UK) and both systems were strongly correlated ( $R^2 = 0.76$ ). Jensen *et al.* (1996) found that fluxes measured with a closed dynamic chamber system (EGM-1, PP Systems, Hitchin, UK) and with a closed static chamber method with an alkali absorbent chamber were exponentially related to each other ( $R^2=0.70$ ). Ewel *et al.* (1987a) found a logarithmic relationship between a closed static chamber method (using soda lime) and a closed dynamic chamber method in a slash plantation in Florida. Rochette *et al.* (1992) found that the soil CO<sub>2</sub> efflux measured with a closed static chamber ( again with an alkali absorbent) was lower than the flux measured with a

closed dynamic chamber method (LI-COR 6250) in a sandy and a organic soil in Canada. They also observed exponential relationships between the two methods. However, the parameters of the exponential relationships were different for each soil type, indicating that diffusion is not the only factor affecting soil CO<sub>2</sub> efflux and that an interaction between CO<sub>2</sub>, temperature and soil properties may exist.

The ratio between the DC and the SC ranged from 0.3 to 6.8, with the SC giving higher CO<sub>2</sub> values at low temperatures and DC giving much higher values at higher temperatures. Since soil CO<sub>2</sub> flux is strongly dependent on soil temperature (see Chapter 3), at low temperatures soil CO<sub>2</sub> efflux is low and it increases exponentially with temperature. Overestimation of CO<sub>2</sub> by the SC method at low rates and underestimation at high rates has been commonly observed. Yim *et al.* (2002) compared a closed static chamber with an alkali-soaked sponge disk with a closed dynamic chamber (LI-COR 6200 and LI-COR 6400). They found that the closed chamber method gave higher results at soil CO<sub>2</sub> rates below 7.2 g m<sup>-2</sup> d<sup>-1</sup>, but lower results at soil CO<sub>2</sub> effluxes above 7.2 g m<sup>-2</sup> d<sup>-1</sup>. Jensen *et al.* (1996) compared a closed dynamic chamber system (EGM-1, PP Systems, Hitchin, UK) with a closed static chamber method with an alkali absorbent, in a wide range of field conditions. They observed that when the closed dynamic chamber gave CO<sub>2</sub> fluxes lower than 8.8 g m<sup>-2</sup> d<sup>-1</sup> the closed static chamber gave higher values by 12% on average. However, when the closed dynamic chamber gave values of more than 8.8 g m<sup>-2</sup> d<sup>-1</sup>, the closed static chamber was giving values 5 times lower. In this study, the SC method gave a value about five times lower when the DC method gave a flux of 6.6 g m<sup>-2</sup> d<sup>-1</sup>. Norman *et al.* (1992) compared the closed static chamber method against a closed dynamic chamber method (LI-COR 6200) and observed that the closed static chamber after 30 minutes of closure time gave fluxes of similar magnitude with the closed dynamic chamber when the soil CO<sub>2</sub> fluxes were low (<7.6 g m<sup>-2</sup> d<sup>-1</sup>), whereas at higher soil CO<sub>2</sub> fluxes it resulted in smaller flux estimates. They also suggested the use of a correction factor to bring the two systems into agreement. Rochette *et al.* (1992) attributed the lower values of soil CO<sub>2</sub> measured with the

static closed chamber method (previous paragraph) to the decreasing absorption over time of CO<sub>2</sub> by the alkali solution (NaOH), due to diffusion and also to the reduced soil temperature (up to 4 °C in 2 cm depth) inside the chamber that might have resulted in lower CO<sub>2</sub> fluxes. Soil temperatures inside the closed static chamber in this study were not measured, but since the closure time of the chamber was much less than the closure time for the measurement with alkali solution that Rochette *et al.* (1992) used, the effect should be much smaller in this study. Rochette *et al.* (1997) found that in seven field studies out of nine in Canada, using the closed static chamber method with an alkali trap, results of CO<sub>2</sub> efflux were very close to the ones measured by a closed dynamic method (LI-COR), while in two of the studies the results with closed static chamber were about 22% lower than those with the dynamic chamber.

#### **7.4.2 Comparison of CO<sub>2</sub> fluxes measured with the GasCard II and by gas chromatographic analysis**

CO<sub>2</sub> fluxes obtained in the field with the portable IRGA GasCard were very well correlated with fluxes obtained from the syringe samples analysed in the gas chromatograph ( $R^2 = 0.94$ ). That could exclude the possibility of underestimation of CO<sub>2</sub> fluxes from the closed static chambers due to syringe leakage from the time the samples were taken in the field till their analysis in the field. However, no published studies could be found in order to compare the GasCard II with another method of measurement of soil CO<sub>2</sub> efflux.

### 7.4.3 Investigation of linearity of CO<sub>2</sub> accumulation in the closed static chamber

Another possible estimation of the lower values of CO<sub>2</sub> given by the SC method compared to the DC method could be the leakage of CO<sub>2</sub> from the chamber. That would result in a divergence of concentration increase from linearity. The increase of soil CO<sub>2</sub> in the two closed static chambers (8 and 9) on 23 April 2002 in the 40-yr departed from linearity ( $R^2 = 0.9803$ ,  $P = 0.02$  and  $R^2 = 0.9717$ ,  $P < 0.001$  for chamber 8 and 9 respectively). When CO<sub>2</sub> concentration increase was checked again on 17 September 2002 in chamber 1 and 2, increases were closer to linear but still significantly different ( $R^2 = 0.9892$ ,  $P = 0.04$  and  $R^2 = 0.9909$ ,  $P = 0.02$ , respectively). Since the beginning of the experiment efforts were made to ensure that leakage of CO<sub>2</sub> from the chamber would be avoided by making a perfect seal of the lid on the chamber. Also, after the chamber was put in the soil the area around it was checked for possible cracks that could lead CO<sub>2</sub> to escape, extra soil was added to make a seal, and the chambers were periodically checked. According to Fick's first law, as the CO<sub>2</sub> concentration within the chamber increases, the diffusion gradient decreases, thus causing a decline in the apparent CO<sub>2</sub> flux. It thus seems that soil CO<sub>2</sub> flux is dependent on the concentration gradient and the air-filled porosity. During the linearity checks on the 17 September 2002 when soil had a higher water content than on 16 May 2002, the CO<sub>2</sub> increase was much closer to linear. Also, at the CF site and in the 30-yr old stand, where had higher water contents, CO<sub>2</sub> increase was very near to linear ( $R^2 = 0.9940$  and  $0.9967$ , respectively). However, Davidson *et al.* (2002) argued that even if the concentration appears to be very linear there may still be an underestimation of the flux. But, since diffusion decreases with increasing water content (Conen and Smith, 2000, Hutchinson *et al.*, 2000) in a wet soil (where soil diffusivity is lower) the diffusion gradient is altered more slowly than the increasing chamber headspace concentration, resulting in a smaller underestimation of the flux (Davidson *et al.*, 2002).

### 7.3.5 Test 1

Another possible reason for the discrepancy of the two measurement methods could be the high spatial variability in the field, that could cause very large differences in the fluxes measured. Therefore, since the chambers covered larger area they could encompass more spatial variability in soil CO<sub>2</sub> efflux than the smaller size collars. So, it was decided to test the two methods with collars of the same size and on homogenous soil so as to avoid variability effects. Thus, two collars were placed very close to each other (10 cm) and in the one the CO<sub>2</sub> efflux was measured with the PP-System and in the other the CO<sub>2</sub> efflux was measured with the GasCard II. The PP-System gave constantly higher values than the GasCard II, and the order was 2.6 to 4.9 times.

Again, according to Fick' s first law, as the CO<sub>2</sub> concentration within the chamber increases, the diffusion gradient decreases, thus causing a decline in the apparent CO<sub>2</sub> flux but this alteration in the concentration gradient should be minimised by the short time of sampling (Davidson *et al.*, 2002). This could explain the lower values by the SC method in the field, however it cannot explain the much lower values by the GasCard II when the same collar was measured during the same time. The higher fluxes measured by the PP-System could be due to better mixing of the air inside the chamber with a fan. The presence of a fan inside the chamber headspace for the mixing of air can prevent the build-up of a thick soil boundary layer. However, a fan in the chamber can also induce turbulence on the soil surface and increase CO<sub>2</sub> efflux; Hanson *et al.* (1993) found that the rate of soil CO<sub>2</sub> efflux was proportional to the degree of turbulence caused by the fan inside the chamber. It is believed that in this study the pressure effects on soil surface were avoided since the chamber of the DC was fitted with a metal mesh and that greatly decreased the pressure effects at the soil surface, but left the circulation unimpeded. Pressure measurements with a micro-manometer across the chamber base showed very small pressure differentials of  $\pm 0.1$

Pa. So probably the lower fluxes measured by the GasCard II could be due to inadequate mixing of air inside the chamber and slower rates of accumulation in the chamber headspace.

### 7.4.5 Test 2

The next experiment was carried out to check the range of concentrations given by the PP-System, the GasCard II and the GC. The purpose was not to examine the absolute accuracy of the methods, but rather to check the discrepancy in the concentrations they measure at a constant flux. CO<sub>2</sub> of 2000  $\mu\text{mol mol}^{-1}$  concentration was flushed at 0.5 ml s<sup>-1</sup> through a 3000 ml glass jar and four sets of measurements took place, with a measurement taken every 30 seconds (following the PP-Systems pattern of measurement). The chamber with the fan was removed from the PP-System and only concentration values were measured. Although the range of the concentration found with the three methods was different, with the PP-Systems having the higher initial and final concentrations, the concentration differences were similar, although the PP-Systems gave again the higher difference. The GasCard II gave concentration differences slightly lower than the GC, which is in agreement with the relationship between the fluxes from these two methods, where CO<sub>2</sub> fluxes obtained with the GasCard II are 0.94 times the fluxes obtained with the GC.

The absolute accuracy of closed dynamic and closed static chambers on measuring soil CO<sub>2</sub> flux has been investigated by some researchers. Nay *et al.* (1994) attempted to evaluate the absolute accuracy of a closed dynamic chamber system (LI-COR) and a closed static chamber with a soda-lime absorbent using known fluxes from the surface of a simulated soil. They found that the closed static chamber greatly overestimated a zero flux and overestimated by about 25% fluxes up to 5.76 g m<sup>-2</sup> d<sup>-1</sup>, while the closed dynamic chamber consistently underestimated all fluxes above zero by 15%. They attributed the overestimation and underestimation of the closed

static chamber to the use of the soda lime as a CO<sub>2</sub> absorbent, that caused changes in the diffusion of CO<sub>2</sub> from the foam (simulated soil) into the chamber. Widén and Lindroth (2003) used a calibration system where CO<sub>2</sub> was allowed to diffuse through a layer of sand on top of a box of known volume and calculated the exact CO<sub>2</sub> efflux by measuring the decrease in CO<sub>2</sub> concentration inside the box. Then they compared this flux with the fluxes measured with a closed dynamic chamber (LI-COR 6200) and a with dynamic open chamber. For the closed dynamic chamber they found that any errors were proportional to the flux. CO<sub>2</sub> flux was overestimated by 21% when the sand water content was 0.06 cm<sup>3</sup> cm<sup>-3</sup>, compared to the flux when the sand was dry. CO<sub>2</sub> flux was underestimated by 19% in sand with high porosity and low water content (dry), and that may have been due to the increased air volume in the soil that was not accounted for in the total system volume. Conen and Smith (2000) found that although gas concentration inside the chamber was linear or very nearly linear, the flux was still underestimated because a proportion of the gas emitted was stored within the soil profile rather than being emitted at the surface and the proportion of flux missed was directly related ( $R^2 = 0.99$ ) to the ratio of the total air volume within the soil profile underneath the chamber to the chamber's volume. Bekku *et al.* (1997) tested the fluxes given by a closed static chamber and a closed dynamic chamber (LI-COR 6000-09) by using an artificial soil medium inoculated with *Trichoderma* sp., in which the absolute CO<sub>2</sub> flux could be estimated by measuring the weight loss of the medium. They found that the rates of CO<sub>2</sub> measured by the closed static chamber were slightly lower than those measured by the closed dynamic system, but they were not significantly different; the accuracy of the two systems was 94 and 95%, respectively. However, the chambers of both systems covered the whole surface from where CO<sub>2</sub> was emitted and thus any chamber effects were avoided; therefore the conclusion may not be completely reliable. It seems that no system can provide absolute values of CO<sub>2</sub> flux, although the use of a closed dynamic chamber would be more appropriate, and the error in the flux estimation it gives depends on the soil properties and soil water content.

### 7.4.6 Soil Monolith

The CO<sub>2</sub> concentration inside the chamber on the soil monolith increased linearly on all sampling days; however, the degree of linearity ranged from 0.9535 to 0.9979. The discrepancy from linearity in the CO<sub>2</sub> concentration inside the chamber was larger when the soil temperature was higher. After the placement of the lid on the chamber, the concentration started increasing in the chamber air as well as in the soil beneath the chamber. However, concentrations in the soil outside the chamber, at a distance of 2 cm from the chamber wall, started to increase as well, indicating lateral diffusion of CO<sub>2</sub>. Lateral diffusion could also be noticed at a distance of 4 cm outside the chamber wall on most of the measurement days. However, although the rates of increase in CO<sub>2</sub> concentration outside the chamber were lower than the rates of increase of CO<sub>2</sub> in the soil inside the chamber wall, this would result in a lower CO<sub>2</sub> estimation. The discrepancy from linearity with higher temperatures can be directly compared with the ratio between the field measurements taken with the DC and the SC method in the 40-yr stand where the monolith was taken. The ratio increased exponentially with increasing soil temperature ( $R^2 = 0.57$ ), and it decreased exponentially with soil water content ( $R^2=0.46$ ). The range of soil water content in the monolith experiment was not very wide, so as to be able to confirm if the same trend with the soil water content was as in the field observations. In the CF site the ratio was weakly related to soil temperature with an exponential function ( $R^2=0.15$ ). Also, no relationship between the ratio and the soil water content was found, indicating that the high water content of the site acted as a barrier to horizontal diffusion.

The horizontal diffusion of CO<sub>2</sub> outside the chamber has been demonstrated with computer simulations. Healy *et al.* (1996) used a three-dimensional model to simulate gas headspace concentration increase by diffusion. The results showed that increasing chamber concentrations caused CO<sub>2</sub> to move horizontally towards the

outlying atmosphere and the influence of radial diffusion was negligible initially but increased steadily during 30-min simulations. Lateral diffusion increased with increasing air-filled porosity and the effect was retarded as the radius of the chamber increased from 3.75 to 20 cm. Lateral diffusion was also reduced as the chamber insertion depth increased from 0 to the bottom boundary depth, where lateral diffusion was completely suppressed. However, in practice this would be difficult to implement in a forest, as insertion of the chamber deep in the soil would exclude tree roots from the chamber and thus exclude the contribution of autotrophic respiration to the total soil CO<sub>2</sub> efflux. Jury *et al.* (1982) used computer simulations to show that when diffusion is low the gas moves upward in the vertical direction below the chamber, but higher diffusion rates result in part of the gas that was produced in the soil layer beneath the chamber moving below the chamber walls it to the uncovered soil surface. Matthias *et al.* (1981) used a two-dimensional computer simulation of a closed chamber over the soil surface and concluded that CO<sub>2</sub> concentration in the chamber caused lateral gas movement, and that resulted in decreasing the flux into the chamber by up to 55%.

## 7.5 Conclusions

The use of the closed static chamber method can lead to lateral diffusion of soil CO<sub>2</sub> outside the chamber and that results in lower CO<sub>2</sub> flux estimation. The effect is more pronounced at high temperatures, when CO<sub>2</sub> flux is higher, and water content lower.

The closed dynamic chamber method gives more reliable estimates. Also, the short period of sampling (2 minutes) of a closed dynamic chamber method reduce many problems that arise from the use of the closed static chamber method, such as changes of temperature and moisture inside the collar.

The strong relationship between the closed dynamic chamber and the closed static chamber suggests that the latter method, that is the main method for measuring other trace gases such CH<sub>4</sub> and N<sub>2</sub>O, can be also used for the measurement of soil CO<sub>2</sub>, provided that it is calibrated and corrected against an accepted closed dynamic chamber method.