



Comparison of different chamber techniques for measuring soil CO₂ efflux

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Abstract

Twenty chambers for measurement of soil CO₂ efflux were compared against known CO₂ fluxes ranging from 0.32 to 10.01 μmol CO₂ m⁻² s⁻¹ and generated by a specially developed calibration tank. Chambers were tested on fine and coarse homogeneous quartz sand with particle sizes of 0.05–0.2 and 0.6 mm, respectively. The effect of soil moisture on chamber measurements was tested by wetting the fine quartz sand to about 25% volumetric water content. Non-steady-state through-flow chambers either underestimated or overestimated fluxes from –21 to +33% depending on the type of chamber and the method of mixing air within the chamber's headspace. However, when results of all systems tested were averaged, fluxes were within 4% of references. Non-steady-state non-through-flow chambers underestimated or overestimated fluxes from –35 to +6%.

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On average, the underestimation was about 13–14% on fine sand and 4% on coarse sand. When the length of the measurement period was increased, the underestimation increased due to the rising concentration within the chamber headspace, which reduced the diffusion gradient within the soil. Steady-state through-flow chambers worked almost equally well in all sand types used in this study. They overestimated the fluxes on average by 2–4%. Overall, the reliability of the chambers was not related to the measurement principle per se. Even the same chambers, with different collar designs, showed highly variable results. The mixing of air within the chamber can be a major source of error. Excessive turbulence inside the chamber can cause mass flow of CO₂ from the soil into the chamber. The chamber headspace concentration also affects the flux by altering the concentration gradient between the soil and the chamber.

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1. Introduction

The two most important processes affecting carbon balance of a terrestrial ecosystem are photosynthesis of above-ground vegetation and soil respiration. The relationship between production and decomposition determines whether a system is a sink or a source of atmospheric CO₂. In old forests, these two fluxes are of similar magnitude (Valentini et al., 2000). Uncertainties involved in measuring the fluxes can cause significant errors in flux estimations, making the estimations of ecosystem carbon balance less reliable.

Soil CO₂ efflux can be measured with several different chamber techniques. We use the classification of Livingston and Hutchinson (1995) to characterize the different chamber types in this paper. The three major chamber techniques used widely for measuring soil gas fluxes are non-steady-state non-through-flow chamber (also known as closed static chamber), non-steady-state through-flow chamber (closed dynamic chamber) and steady-state through-flow chamber (open dynamic chamber). In non-steady-state chambers, of both the through-flow and non-through-flow types, the CO₂ efflux is determined from the rate of concentration increase in an isolated chamber, that has been placed on the soil surface for a known period of time (Jensen et al., 1996; Rochette et al., 1992; Singh and Gupta, 1977). In steady-state chambers, CO₂ efflux is calculated from the difference between CO₂ concentration at the inlet and the outlet of the chamber.

The chambers always affect the object being measured, with each chamber type having its own limitations (Davidson et al., 2002). When a non-steady-state chamber is placed on the soil and the concentration in the chamber headspace starts to change, rising

concentration within the chamber may influence the CO₂ efflux from the soil by altering the natural soil concentration gradient (Davidson et al., 2002; Livingston and Hutchinson, 1995; Nay et al., 1994). Pressure anomalies caused by placing the chamber on the soil surface may also disturb the CO₂ concentration gradient in the soil.

With steady-state chambers, pressure differences between the inside and outside of the chamber can generate mass flow of CO₂ from the soil into the chamber. Pressure differences as low as 1 Pa have been shown to cause errors in CO₂ efflux measurements (De Jong et al., 1979; Fang and Moncrieff, 1996, 1998; Kanemasu et al., 1974; Kutsch, 1996; Lund et al., 1999).

No single method has been established as a standard because methods have seldom been compared with known CO₂ effluxes, i.e. calibrated in an absolute manner. Past comparisons have, however, indicated relative differences between chamber types (Janssens et al., 2000; Norman et al., 1997; Raich et al., 1990) or demonstrated chamber-specific limitations (Fang and Moncrieff, 1998; Gao and Yates, 1998; Nay et al., 1994). Non-steady-state chambers have been shown to give systematically lower fluxes than steady-state chambers, the underestimation ranging from 10% (Rayment and Jarvis, 1997; Rayment, 2000) to 40–50% (Norman et al., 1997; Pumpanen et al., 2003). Chambers based on absorption of CO₂ with alkali materials tend to overestimate low fluxes and underestimate high fluxes (Nay et al., 1994). Differences have also been found between non-steady-state chambers (Janssens et al., 2000).

However, comparison against known CO₂ effluxes is the only way to standardize systematic errors of the different systems used for measuring soil respiration.

Recently, Widén and Lindroth (2003) developed a calibration system for soil CO₂ efflux chambers, in which a known CO₂ efflux was generated through a layer of quartz sand from a box filled with a known CO₂ concentration. The aim of this paper was to determine calibration coefficients for the most common chamber types by testing them against known CO₂ effluxes generated with a principle similar to that of Widén and Lindroth (2003). These coefficients enable more accurate comparison of a wide range of soil CO₂ efflux values measured with various chamber types in different ecosystems.

2. Materials and methods

2.1. Calibration tank

The calibrations were carried out at Hyytiälä Forestry Field Station (61°51'N latitude, 24°17'E longitude), 152 m above sea level. We constructed a calibration tank modified from that described by Widén and Lindroth (2003). Our system consisted of a cylindrical stainless steel tank (diameter 1130 mm, height 1000 mm), a CO₂ analyser, a differential pressure transducer and a data logger (Fig. 1). The tank had a 20 mm thick lid made of high-density polyethylene

and perforated with holes 7 mm in diameter, located at intervals of approximately 12 mm. Before the calibration, we placed a 150 mm layer of quartz sand on top of the lid. The sand was supported on the lid by polypropylene gauze, which enabled the air to move freely between the sand and the tank. We used quartz sand particles of two different sizes for the chamber tests, coarse sand with a particle diameter of 0.6 mm and fine sand with a particle diameter of 0.05–0.2 mm. The coarse and fine sand had an air-filled porosity about 47 and 53%, respectively. We also tested chambers on fine sand wetted to a volumetric water content of approximately 25% by mixing four parts sand and one part deionized water in a separate container. The air-filled porosity of the wet fine sand was 33%. The porosity of sand was determined gravimetrically from core samples taken from the sand after each measurement session. Total porosity was calculated as the water content at saturation.

The testing of individual chambers was done in 5-day sessions carried out between 7 July and 5 October 2002. An equal amount of sand was packed in the same way before each measurement session to ensure equal porosity. If collars were used in the chambers being tested, they were installed on the sand before the measurement session and left there until measurements were finished.

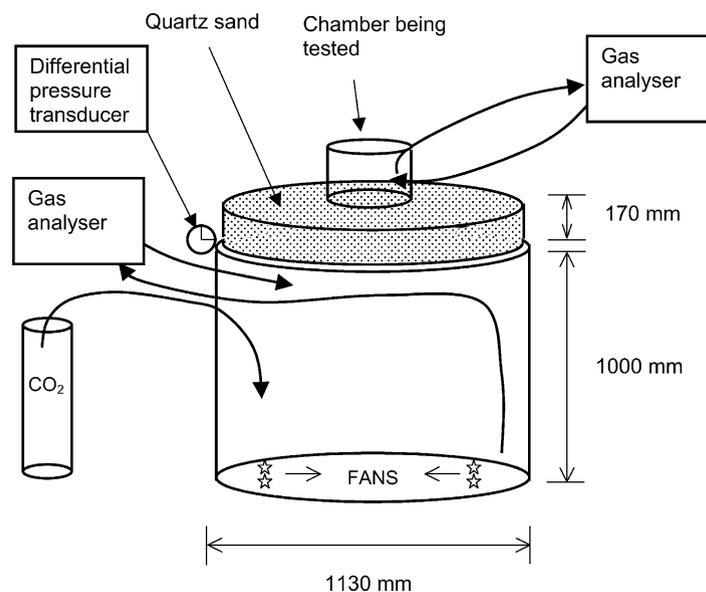


Fig. 1. Schematic representation of the calibration system.

Temperature inside and outside the calibration tank was monitored by T-type thermocouples connected to a data logger (Envic DP-158, Envic Oy, Turku, Finland), and the pressure difference between the two locations was determined using a differential pressure transducer (Omega PX653, Omega Engineering Inc., Stamford, CT) with a 0.25 Pa accuracy. To maintain a homogeneous CO₂ concentration within the tank, air in the tank was continuously mixed by fans installed at the bottom of the tank. Sample air from the calibration tank was taken through a perforated nylon tube 4 mm in diameter installed vertically inside the tank to ensure collection of representative air for the entire air space. Air was drawn at a flow rate of 350 ml min⁻¹ into an infrared gas analyser (EGM-4, PP-systems, Hitchin, UK) recording the concentration at 1 min intervals. Analysed air was returned to the opposite side of the calibration tank.

CO₂ effluxes ranging from 0.32 to 10.01 μmol CO₂ m⁻² s⁻¹ were generated by raising the CO₂ concentration to the desired level from a gas cylinder containing 97.5% CO₂. To ensure that the air pressure within the tank did not increase, excess air was allowed to escape from the tank by opening the tube connecting the calibration tank to the differential pressure transducer. According to the differential pressure transducer, the air pressure within the calibration tank during the flux measurements was mostly within ±0.3 Pa of the ambient pressure. No significant pressure fluctuation was observed between tank and ambient air since the tests were carried out in a large hall of about 2000 m³ in volume, which was protected from the wind. The only exceptions to this were chambers NSNF-1 (University of Joensuu) and NSF-10 (University of Helsinki), where testing was carried out in a forest in a large tent protecting the system from the wind. The test site was located at SMEAR II (Station for Measuring Forest Ecosystem–Atmosphere Relations) in Southern Finland (61°51'N latitude, 24°17'E longitude), 181 m above sea level and 300 m from the hall where other chambers were tested. The different chamber types are described (and definitions for abbreviations are provided) in Section 2.2.

After setting the CO₂ concentration, the gas inlet was closed and the pressure tube was connected to the differential pressure sensor. The system was allowed to stabilise for 1 h before the measurements with soil chambers were started. We tested the time required

for the CO₂ flux to stabilise by measuring the fluxes on top of the sand continuously after increasing the CO₂ concentration inside the tank. The flux generally stabilised within 45 min, and therefore, 60 min was conservatively chosen as the stabilisation period needed for dry sand. For wet sand, we increased the stabilisation period to 90 min. The calibration tank was a non-steady-state system where the concentration inside the tank gradually decreased, and consequently, the flux also decreased over time due to the decreasing concentration gradient between chamber and outside air. However, the large volume of the tank increased the stability of the system, i.e. the concentration and the fluxes changed slowly. This improved the accuracy of the calibration because the flux remained quite stable during each flux measurement. Also due to the large volume, the system was less sensitive to perturbations caused by possible pressure fluctuations when the chambers being tested were placed on the sand.

It took 45–120 min to test the chambers on one flux level depending on the number of chambers and the time required for each chamber measurement. Different flux levels were created sequentially so that we started with the lowest flux and after each measurement injected more CO₂ into the calibration tank to generate a new flux. The fluxes from the tank were computed at 1 min intervals and compared with those measured by individual chambers at the same time from the sand surface. When the chamber had been tested with seven different flux levels, the sand was changed to another of different particle size and the procedure was repeated. With wet fine sand, chamber tests were carried out at six flux levels. Fluxes were measured from three collars at each flux level with chambers of diameters less than 300 mm. With chambers larger than this, two flux measurements were carried out on one collar. When more than one chamber was tested simultaneously for a certain flux level, the measurements were performed such that a 10 min recovery period was left between measurements with different chambers to avoid possible interference of the chambers on each other.

Determination of flux out of the calibration tank began by fitting an exponential equation to concentration versus time as follows:

$$C_f(t_i) = C_0 \exp(-\alpha t_i) \quad (1)$$

where $C_f(t_i)$ is the fitted CO₂ concentration inside the tank at time t_i , C_0 the measured concentration in the tank at the beginning of the testing period, t the time and α is a parameter. The fitting was done by using the least squares method over each 45–120 min testing period to eliminate the noise of the analyser used for determining the CO₂ concentration inside the calibration tank. The number of data points was sufficiently large to ensure a reliable fitting; R^2 values were usually larger than 0.995. The flux from the tank was calculated at 1 min intervals using a time discrete function modified by Widén and Lindroth (2003):

$$F = \frac{V(C_f(t_1) - C_f(t_2)) + V_s((C_f(t_1) + C_{amb}(t_1))/2 - (C_f(t_2) + C_{amb}(t_2))/2)}{(t_2 - t_1)A} \quad (2)$$

where $C_{amb}(t_i)$ is the ambient CO₂ concentration at time t_i , V the volume of the tank (1 m³), V_s the volume of air-filled porosity in the sand (0.038 and 0.061 m³ for dry and wet fine sands, respectively) and A is the surface area of the sand layer (0.77 m²). The change in C pool in V_s was taken into account by assuming the concentration in the sand to be an average of C_f and C_{amb} .

The fluctuation in C_{amb} was fast and irregular due to the respiration of persons conducting test measurements in the vicinity of the tank. C_{amb} generally fluctuated between 360 and 440 ppm. However, because the diffusion rate of CO₂ through a thick sand layer is slow, a rapid fluctuation in C_{amb} would have only a minor effect on the diffusion process overall. C_{amb} was therefore assumed to be constant. By assuming this, the flux calculation is based solely on the change in CO₂ concentration within the tank and is represented by:

$$F = \frac{V(C_f(t_1) - C_f(t_2)) + V_s((C_f(t_1) - C_f(t_2))/2)}{(t_2 - t_1)A} \quad (3)$$

The tank volume term dominates the flux generated.

The chambers may affect CO₂ efflux from the soil, especially in situations where the headspace CO₂ concentration is well above the ambient. This may decrease the concentration gradient at the soil surface, resulting in a slowed diffusion of CO₂ in the sand. The highest increase in headspace CO₂ concentrations of the chambers tested during the campaign was from the initial concentration of 400 ppm to 1750 ppm, with this chamber also having the longest measurement time

of 30 min. However, in most cases, headspace concentrations increased by not more than 50 ppm during the measurement and measurement times were much shorter. We evaluated the magnitude of the effect of the increasing concentration on the efflux by estimating the change in the diffusion rate with Fick's first law of diffusion. With the highest effluxes tested, a decrease of 50 ppm, or 0.5% in the sand CO₂ concentration gradient, resulted in a decrease of 0.5% in the efflux. Similarly a decrease of 1350 ppm (14% in the gradient) decreased the efflux by 14%. Thus, the

effects of the chambers on the reference fluxes were small.

2.2. Tested soil respiration chambers

2.2.1. Non-steady-state through-flow chambers (NSF)

2.2.1.1. NSF-1a (Li-Cor LI-6400-09), Weizmann Institute of Science, José M. Grünzweig. This system consisted of a Li-Cor LI-6400 portable photosynthesis system connected to a Li-Cor LI-6400-09 soil respiration chamber (Li-Cor Inc., Lincoln, NE) equipped with a pressure relief vent. The chamber (diameter 95 mm, volume 991 cm³) was placed on a PVC collar (diameter 103 mm, height 50 mm) installed to a sand depth of 40 mm. Air was circulated from the chamber to the infrared gas analyser (IRGA) and back by a mixing fan. Before each cycle of flux measurement, air in the chamber headspace was scrubbed down 3–40 ppm below the ambient CO₂ concentration (depending on the flux), and then allowed to rise as a consequence of CO₂ efflux from the tank. This procedure was repeated four more times for each flux and collar, and each flux was measured on three collars (total of 15 measurement cycles per flux). A measurement cycle usually lasted 1–2 min but was 2–5 min for the lowest rates. The flux was calculated by regressing flux versus CO₂ concentration in the chamber, and computing the flux corresponding to the ambient CO₂ concentration determined prior to the onset of each measurement.

2.2.1.2. NSF-1b (Li-Cor LI-6400-09), Max-Planck-Institute, Waldemar Ziegler. This system was similar to that of NSF-1a.

2.2.1.3. *NSF-2 (EGM-3 connected to a SRC-1 soil respiration chamber), Geir Østreg.* The system consisted of an IRGA (EGM-3, PP-systems, Hitchin, UK) and a soil chamber (SRC-1, PP-systems, Hitchin, UK) equipped with a fan. During the measurement the chamber (height 150 mm, diameter 100 mm) was attached to a 50 mm high collar, which was inserted to a soil depth of 40 mm. Air was circulated between the analyser and the chamber at flow rate of 0.11 min^{-1} . The CO_2 concentration was measured every 8 s and the flux was calculated from the concentration increase over time. Each flux measurement lasted 3 min or until a good quadratic fit was obtained.

2.2.1.4. *NSF-3 (EGM-3 connected to a SRC-1 soil respiration chamber), Ivan Janssens and Jorge Curiel Yuste.* This system was similar to that of NSF-2 except for the flow rate, which was set at 0.31 min^{-1} . In addition, the lower part of the chamber was widened with a PVC rim attached to the base of the chamber. The collars were 200 mm in diameter and 200 mm tall and were inserted to a soil depth of 150 mm. The lower part of the collars was perforated with holes 5 mm in diameter at 50 mm intervals.

2.2.1.5. *NSF-4 (PP-systems EGM-1 connected to a SRC-1 soil respiration chamber), Sini Niinistö.* This system was similar to that of NSF-2 except for the flow rate, which was set at 0.31 min^{-1} , and the earlier version of the CO_2 analyser. No collars were used with NSF-4.

2.2.1.6. *NSF-5 (EGM-4 connected to a SRC-1 soil respiration chamber), Annalea Lohila.* This system was similar to that of NSF-2 except for the flow rate, which was set to 0.31 min^{-1} , and the upgraded version of the CO_2 analyser including the water correction. Moreover, the chamber SRC-1 was modified with a metal mesh in the lower part of the chamber to decrease the pressure effects on the soil surface caused by the fan (Upgrade of SRC-1 in 1999).

2.2.1.7. *NSF-6 (University of Bayreuth), Sascha Reth.* The system has been described in detail by Velthof and Oenema (1995) and Velthof et al. (2000). This system consisted of cylindrical steel chambers (height 60 mm,

diameter 197 mm) with plexiglass lids, which were attached during the measurement. No fan was used. The air was sucked for approximately 30 s through a magnetic modulating valve into the Photoacoustic Multi-gas Monitor (INNOVA 1312, AirTech Instruments A/S, Ballerup, Denmark). The concentrations of CO_2 and water were determined from the air stream, after which the air was pumped back into the chamber through the magnetic modulating valve. The control between chambers was regulated by magnetic valves. CO_2 efflux was determined from the slope of the concentration increase within the chamber using four concentrations measured at 238 s intervals.

2.2.1.8. *NSF-7 (Finnish Meteorological Institute), Annalea Lohila.* This system consisted of a plexiglass chamber (600 mm \times 600 mm wide and 800 mm high) that was attached to a collar installed to a sand depth of 150 mm. The chamber was connected to Li-Cor LI-6262 CO_2 analyser, which collected data at rate of 1 Hz. Air mixing in the chamber was ensured with three fans mounted to a corner of the chamber at different heights. Air was circulated between the analyser and the chamber at a flow rate of 11 min^{-1} during the sampling period of 120 s. The measurement period varied between 35 and 230 s depending on the flux rate. The flux was calculated as a linear fit between two values. The first value was calculated as an average of 10 data points (points 40–50 after start of measurement), and the second value as an average of data points 110–120.

2.2.1.9. *NSF-8 (Woods Hole Research Center), Kathleen Savage.* The system has been described in detail by Savage and Davidson (2003). This system consisted of a Li-Cor LI-6252 IRGA mounted on a backpack frame. Polyvinylchloride (PVC) rings (height 100 mm, diameter 250 mm) were placed into the sand to a depth of approximately 50 mm. The chamber top, which fits tightly over the collars, creates a closed chamber, and headspace air was pumped to the IRGA at a rate of 0.51 min^{-1} over a sampling period of 5 min. Pressure differences between the chamber headspace and ambient air have previously been tested and found to be below 0.1 Pa (Infiltech micromanometer). The linear portion of the increase in chamber headspace concentration was used to calculate the soil respiration rates within the chamber.

2.2.1.10. *NSF-9 (Max-Planck-Institute), Peter Anthoni.* This system was based on a non-steady-state chamber design (Goulden and Crill, 1997; Irvine and Law, 2002). The chambers were rectangular (500 mm × 500 mm wide and 100 mm high) and constructed of aluminium sheets. A chamber collar made of 25 mm aluminium U-angles was installed approximately 20 mm into the sand. Water in the collar troughs was used to provide a gas-tight seal. Total volume of the chamber plus the frame and sample tubing was ca. 0.0263 m³. The inner area of the chamber collar was 0.224 m². Flow rate through the chamber and gas analyser was controlled by a MKS mass flow controller (MKS Instruments Inc., Andover, MA) at 41 min⁻¹. CO₂ concentration was monitored by a Li-Cor LI-6262 gas analyser. A CR10X Campbell Scientific data logger (Campbell Scientific Ltd., Leicestershire, UK) recorded 10 s averages of measured CO₂ concentrations. Efflux rates were calculated from the linear change in CO₂ concentration over the 5 min measurement periods.

2.2.1.11. *NSF-10 (University of Helsinki), Jukka Pumpanen.* This system, a hybrid between steady-state through-flow and non-steady-state through-flow chambers, has been described in detail by Hari et al. (1999) and Pumpanen et al. (2001). Compensation air of known CO₂ concentration was introduced into a cylindrical chamber (diameter and height 200 mm) at a flow rate of 31 min⁻¹ and an equal amount of air was pumped from the chamber to the CO₂ analyser. The compensation air was taken from above the tree canopy and pumped through a 0.05 m³ steel container to eliminate possible fluctuations in CO₂ concentrations. The flow rates of the compensation air and the sample air were regulated by two separate pumps and mass flow controllers. Air in the chamber was continuously mixed by a small fan installed in the middle of the chamber.

The chamber was closed for 70 s measurement periods. The CO₂ concentration within the chamber headspace was measured continuously with IRGA (URAS 4, Mannesmann, Hartmann and Braun, Frankfurt am Main, Germany), and the readings were saved every 5 s. The same analyser was used for measuring the compensation air CO₂ concentration immediately before and after each measurement period. Flux measurements were done in transient mode, i.e. the ef-

flux was determined using the concentration increase inside the chamber. The calculation of CO₂ efflux was based on the mass-balance equation for CO₂:

$$Q = \frac{\Delta(V_c C_i)}{\Delta t} - q_1 C_0 + q_2 C_i \quad (4)$$

where V_c is the volume of the chamber, Q the soil CO₂ efflux, q_1 the flow of the compensation air, q_2 the air flow to the analyser, C_0 the CO₂ concentration in the compensation air and C_i the CO₂ concentration in the chamber.

2.2.1.12. *NSF-11 (University of Helsinki), Kari Minkkinen.* In this system, the EGM-4 IRGA was connected to a modified SRC-1 chamber (PP-systems, Hitchin, UK). The chamber consisted of a metal cylinder (diameter 315 mm, height 149 mm) with the tubing and fan of a standard SRC-1 chamber. An aluminium collar was inserted into the sand before the measurements, and the chamber was inserted onto the collar. No water was used as a seal. Measurement time was 81 s (except 182 s for the lowest flux on wet fine sand to get enough points for regression). Fluxes were calculated automatically by the EGM program, using the linear option (linear regression). Temperature correction was applied using the air temperature outside the chamber. All fluxes were also calculated manually (from the saved CO₂ concentration data) and found to be close to the saved flux values.

2.2.1.13. *NSF-12 (University of Helsinki), Pasi Koları.* This system was based on the same chamber as in NSF-3, except for the determination of CO₂ concentration within the chamber headspace. CO₂ concentration was monitored by IRGA (EGM-3, PP-systems, Hitchin, UK) and recorded at 1 min intervals. During the measurement the chamber was attached for 5 min to a 50 mm tall collar (inner diameter 204 mm) installed to a soil depth of 30–40 mm. Air was circulated between the chamber and the analyser at a flow rate of 0.31 min⁻¹. CO₂ flux was determined from the linear regression of time versus CO₂ concentration for 1–5 min after the installation of the chamber onto the collar. To reduce the effect of the initial disturbance on CO₂ flux, the first reading was taken 1 min after the chamber was placed on the collar.

2.2.2. Non-steady-state non-through-flow chambers (NSNF)

2.2.2.1. NSNF-1 (University of Joensuu), Tuula Larmola. The chamber system consisted of a static chamber made of 2 mm polycarbonate (600 mm × 600 mm wide and 320 mm high or with an extension 720 mm high). The chamber is thermoregulated (within ±1 °C of outside air temperature), vented (Alm et al., 1997) and operated with 1–2 fans depending on the size of the chamber. For measurements, the chamber was placed on a 600 mm × 600 mm collar, which had a water-filled groove for gas-tight sealing. The collar was inserted into the sand to a depth of 140 mm. CO₂ concentration in the chamber headspace was monitored with a portable IRGA (ADC, LCA-2, Analytical Development Company Ltd., Hoddesdon, UK) equipped with a pump (suction from headspace 150–200 ml min⁻¹). To avoid underpressure in the chamber headspace, the air drawn by the analyser was compensated with outside air through a tube (diameter 8 mm, length 3 m to minimise the effect of wind).

CO₂ concentration was recorded every 30 s after closing the chamber for 150–270 s. The rate was calculated from the linear change ($R^2 > 0.90$) in CO₂ concentration during the measurement period. A linear regression equation was fitted for the first 5–6 data points, except for close-to-zero fluxes, where up to nine data points were used.

2.2.2.2. NSNF-2 (Agrifood Research Finland). The chamber made of aluminium (600 mm × 600 mm wide and 200 mm high) was attached for 30 min to a collar with a water seal that was installed to a soil depth of 150 mm. Air samples were drawn from the chamber into syringes 1, 5, 10 and 30 min after installation of the chamber. Simultaneously to sample being extracted with the needle, compensation air was drawn into the chamber through a pressure equilibrium tube (length 1 m, inside diameter 2 mm). Air samples were analysed with a gas chromatograph (Hewlett Packard 6890) including a Porapak Q (1.8 m) pre-column and a Hayesep Q 80/100 (3 m) analytical column. Carbon dioxide was reduced to methane in a methanizer and analysed as methane by a flame ionization (FID) detector. A linear regression of

concentration versus time was used for calculating the fluxes.

2.2.2.3. NSNF-3 (University of Helsinki), Jukka Pumpanen. The chamber (diameter 200 mm, height 300 mm) made of polycarbonate was attached to a 50 mm tall collar installed to a soil depth of 20 mm. A small fan (diameter 20 mm) mixed the air within the chamber headspace. Gas samples (volume 50 cm³, which was 0.9% of the chamber headspace) were taken manually into polyethylene syringes (BD Plastipak 60, BOC Ohmeda, Helsingborg, Sweden) equipped with a three-way valve (BD Connecta™ Stopcock, Becton Dickinson, NJ, USA). Sampling was done 0, 2, 6, and 10 min after the chamber attachment. CO₂ concentration of the air samples was determined within 6 h with an IRGA (URAS 3G, Hartmann and Braun, Frankfurt am Main, Germany). CO₂ efflux was calculated from linear fit of CO₂ concentration versus time over the 10 min measurement period.

2.2.2.4. NSNF-4 (University of Helsinki), Mari Pihlatie. The stainless steel chamber (290 mm × 400 mm wide and 150 mm high) was attached to a collar inserted to a soil depth of 50 mm. The chamber was made air-tight with a rubber sealing between the chamber and the collar, and the air inside the chamber was mixed continuously by a small fan. Gas samples were taken from the chamber with 20 ml syringes (BD Plastipak, BOC Ohmeda, Helsingborg, Sweden) equipped with a three-way valve (BD Connecta™ Stopcock, Becton Dickinson, NJ, USA) through a septum 1, 2, 6 and 10 min after installation of the chamber. Before sampling, each syringe was flushed two times with the air inside the chamber, and on the third flushing, the gas sample was taken. Gas samples were analysed for CO₂ with an IRGA (EGM-3, PP-systems, Hitchin, UK) immediately after sampling. Fluxes were calculated from the increase in CO₂ concentration inside the chamber during the enclosure period (between the sampling at 2 and 6 min).

2.2.3. Steady-state through-flow chambers (SSFL)

2.2.3.1. SSFL-1 (University of Bayreuth), Jens-Arne Subke. The basic design adopted for this soil chamber was that of Rayment and Jarvis (1997); a detailed

description is given by Subke (2002). This system consisted of a steel collar (diameter 200 mm, height 80 mm) and a Perspex lid, fitted onto the collar. Air was drawn at a flow rate of 11 min^{-1} from a lateral channel in the chamber lid, which was connected to the chamber space through perforations ($\text{Ø}1 \text{ mm}$). Replacement air entered the chamber passively through an inlet tube (PVC) in the centre of the lid. During operation the static pressure inside the chamber was around 10 mPa below ambient atmospheric pressure. The inlet tube was covered by a glass dome, which prevents Ventouri-type suction to occur from wind passing horizontally across the inlet during field operations and provides a volume that buffers short-term changes in ambient CO_2 concentration. Reference air for the differential gas analyser was drawn from near the opening of the inlet. Both sampling and reference air were dried chemically during passage from the chamber, and the sampling air stream passed an electronic flow meter before entering the gas analyser (BINOS 100, Fisher-Rosemount, previously Leybold Heraeus, Hanau, Germany), which operated in absolute and differential modes simultaneously.

2.2.3.2. *SSFL-2 (University of Kiel), Werner Kutsch.* This system has been described in detail by Kutsch (1996) and Kutsch et al. (2001). The system contained parallel chambers, each with its own measuring and reference gas units, consisting of a pump (WISA, Wuppertal, Germany), a mechanical flow controller (Krohne, Düsseldorf, Germany) and a magnetic valve (Herion, Fellbach, Germany). Behind the magnetic valve, the air stream was passed through an electronic flow meter (Tylan General, USA) and a gas cooling unit (Walz, Effeltrich, Germany) to an IRGA (Fisher-Rosemount, Hanau, Germany). Ambient air was continuously sucked through the chamber at a flow rate of 11 min^{-1} . The diameter of the inlet was 30 mm, which was sufficiently large to avoid underpressure larger than 0.1 Pa in the system (pressure sensor type 233, MKS Baratron, München, Germany). The channels were measured at 3 min intervals. Air was passed in parallel through a reference tube to the gas analyser set to measure in the differential mode. The chambers were about 2.8 dm^3 in volume and covered an area of $160 \text{ mm} \times 125 \text{ mm}$. During the measurement they were attached to aluminium frames fixed in the sand.

3. Results

3.1. Performance of the calibration system

The CO_2 fluxes generated with the calibration system were repeatable; when fluxes generated on different weeks under the same temperature conditions were compared, they deviated from each other by only 6–7% (Fig. 2). Fluxes were also spatially homogeneous. The standard error between the three collars used ranged from 0.06 at low fluxes ($0.35 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$) to 0.173 at high fluxes ($10 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$), as measured by chamber NSF-1a.

3.2. Non-steady-state through-flow chambers

On average, non-steady-state chambers gave fluxes similar to the reference on coarse sand and underestimated fluxes by 1% on wet fine sand. On dry fine sand, the NSF chambers overestimated fluxes by 4% (Table 1). However, the individual chambers yielded contradictory results. Li-Cor LI-6400-09 (NSF-1a) showed fluxes close to those of the reference flux both on coarse sand and on dry fine sand but overestimated fluxes by about 5% on wet fine sand (Fig. 3a, Table 1)

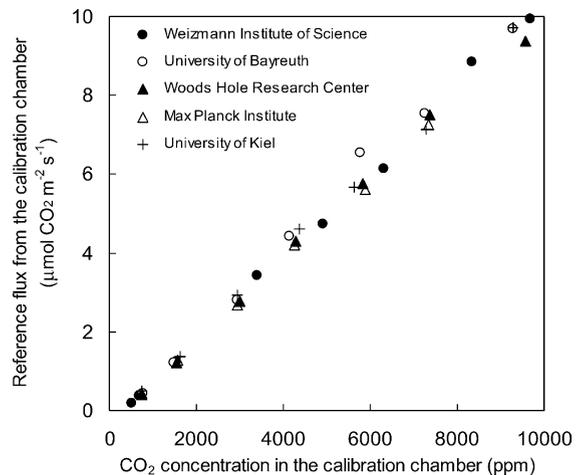


Fig. 2. Reference CO_2 effluxes generated by the calibration system with dry fine sand plotted against measured CO_2 concentrations inside the calibration tank. Different symbols represent the average CO_2 effluxes measured at seven concentration and flux levels during five separate calibration weeks under similar temperature conditions by groups from the named establishments.

Table 1
Correction factors for different chambers

Chamber type	Coarse sand	95% confidence interval	Dry fine sand	95% confidence interval	Wet fine sand	95% confidence interval
NSF-1a (Li-Cor LI-6400-09)	1.01	0.99–1.03	1.01	0.98–1.04	1.05	1.01–1.09
NSF-1b (Li-Cor LI-6400-09)	1.13	1.07–1.18	1.09	0.98–1.19	1.09	1.04–1.14
NSF-2 (EGM-3 + SRC-1)	1.21	1.17–1.26	1.27	1.15–1.39	1.05	0.97–1.13
NSF-3 (EGM-3 + SRC-1 widened collar)	0.86	0.82–0.89	1.00	0.94–1.05	–	–
NSF-4 (EGM-1 + SRC-1 no collar)	1.03	1.01–1.06	1.19	1.14–1.24	0.94	0.86–1.03
NSF-5 (EGM-4 + SRC-1 mesh)	1.16	1.12–1.19	1.19	1.11–1.27	1.33	1.20–1.47
NSF-6 (University of Bayreuth)	0.96	0.91–1.02	0.89	0.86–0.92	0.96	0.87–1.06
NSF-7 (Finnish Meteorological Institute)	1.03	1.01–1.05	1.07	0.99–1.15	1.00	0.92–1.08
NSF-8 (Woods Hole Research Center)	0.83	0.79–0.86	0.91	0.86–0.96	0.83	0.80–0.85
NSF-9 (Max-Planck-Institute)	0.81	0.79–0.83	0.80	0.79–0.82	0.79	0.77–0.80
NSF-10 (University of Helsinki)	1.01	0.96–1.05	1.19	1.14–1.23	1.04	0.96–1.13
NSF-11 (University of Helsinki)	1.00	0.96–1.03	0.85	0.81–0.87	0.87	0.84–0.89
NSF-12 (University of Helsinki)	–	–	1.13	1.08–1.18	0.93	0.87–0.99
NSF-Average	1.00		1.04		0.99	
NSNF-1 (University of Joensuu)	0.98	0.95–1.01	0.94	0.89–0.98	0.85	0.81–0.88
NSNF-1 (University of Joensuu with extension)	0.95	0.86–1.05	0.98	0.92–1.03	0.85	0.75–0.94
NSNF-2 (Agrifood Research Finland, 10 min)	0.96	0.91–1.01	0.96	0.76–1.15	0.95	0.84–1.06
NSNF-2 (Agrifood Research Finland, 30 min)	0.85	0.79–0.90	0.85	0.71–0.98	0.90	0.80–1.00
NSNF-3 (University of Helsinki)	1.06	0.96–1.17	0.82	0.63–1.01	0.85	0.78–0.93
NSNF-4 (University of Helsinki)	–	–	0.65	0.56–0.74	0.84	0.81–0.87
NSNF-Average	0.96		0.86		0.87	
SSFL-1 (University of Bayreuth)	1.03	1.01–1.05	0.96	0.92–1.01	1.09	1.02–1.15
SSFL-2 (University of Kiel)	1.05	0.99–1.11	1.08	1.01–1.15	0.95	0.80–1.09
SSFL-Average	1.04		1.02		1.02	

Each chamber can be scaled to the reference flux obtained from the calibration tank by dividing the measured flux by the correction factor for a specific soil type. NSF: non-steady-state through-flow chamber; NSNF: non-steady-state non-through-flow chamber; SSFL: steady-state through-flow chamber.

when fluxes were greater than $3.8 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$. The overestimation was larger, up to 13%, with another Li-Cor LI-6400-09 (NSF-1b) similar to NSF-1a (Fig. 3b).

The PP-systems chamber (NSF-2–NSF-5) showed over- and underestimation depending on whether or not a collar was used (Fig. 3c–f). When collars were used with an unmodified SRC-1 chamber (NSF-2 and NSF-5), the fluxes were overestimated by as much as 33%. The chambers equipped with mesh (NSF-5) showed similar fluxes to those without mesh (NSF-2) on coarse sand and on dry fine sand but overestimated fluxes by 33% on wet fine sand. Chamber system NSF-3, with a widened lower part, underestimated fluxes by 14% on coarse sand, whereas on dry fine sand, measured fluxes were identical to reference fluxes. NSF-3 was not tested on wet fine sand. When no collar was used (NSF-4), fluxes were overestimated

by 3% on coarse sand and by 19% on dry fine sand. On wet fine sand, fluxes were underestimated by 6%.

The chamber systems of the University of Bayreuth (NSF-6), Woods Hole Research Center (NSF-8) and Max-Planck-Institute (NSF-9) underestimated fluxes on all sand types. NSF-8 underestimated fluxes by up to 17% on coarse sand and on wet fine sand and by up to 9% on dry fine sand, whereas NSF-6 underestimated fluxes by only 4% on coarse sand and on wet fine sand. On dry fine sand, the underestimation was larger, 11%. NSF-9 underestimated fluxes by about 20% on all soil types. NSF-7 showed fluxes within 3% of the reference flux with coarse sand and wet fine sand. With dry fine sand, the overestimation was 7%.

The hybrid system between non-steady-state through-flow and steady-state through-flow chambers (NSF-10) overestimated fluxes by up to 4% on coarse sand and on wet fine sand, but on dry fine sand, the

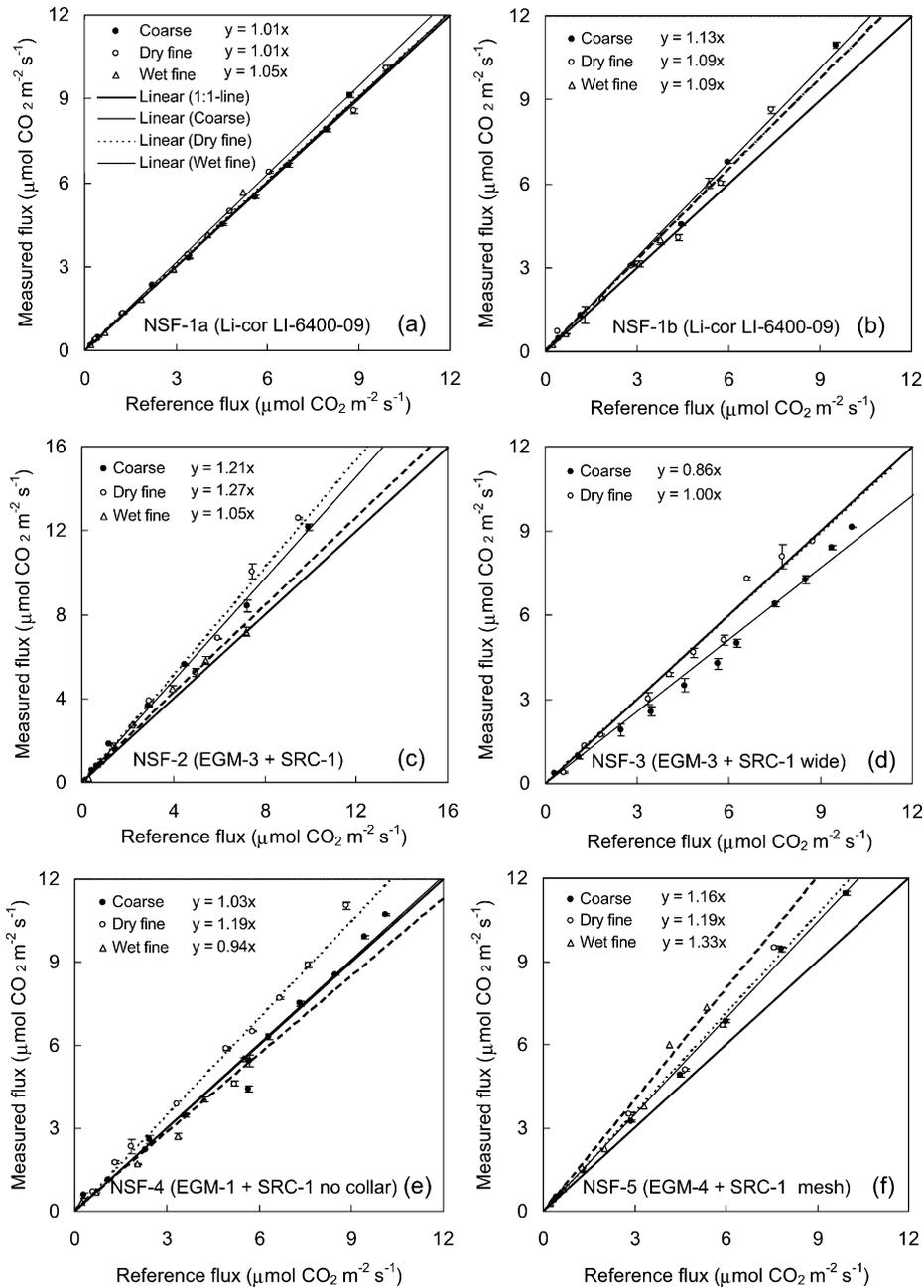


Fig. 3. CO_2 effluxes measured by non-steady-state through-flow systems: (a) NSF-1a (Li-Cor LI-6400-09, Weizmann Institute of Science), (b) NSF-1b (Li-Cor LI-6400-09, Max-Planck-Institute), (c) NSF-2 (PP-systems EGM-3 connected to a SRC-1 soil respiration chamber), (d) NSF-3 (PP-systems EGM-3 connected to a SRC-1 soil respiration chamber with widened collar), (e) NSF-4 (PP-systems EGM-1 connected to a SRC-1 soil respiration chamber without collar), (f) NSF-5 (PP-systems EGM-4 connected to a SRC-1 soil respiration chamber with mesh), (g) NSF-6 (University of Bayreuth), (h) NSF-7 (Finnish Meteorological Institute), (i) NSF-8 (Woods Hole Research Center), (j) NSF-9 (Max-Planck-Institute), (k) NSF-10 (University of Helsinki), (l) NSF-11 (University of Helsinki) and (m) NSF-12 (University of Helsinki) plotted against reference fluxes generated by the calibration tank with coarse, dry fine and wet fine sands.

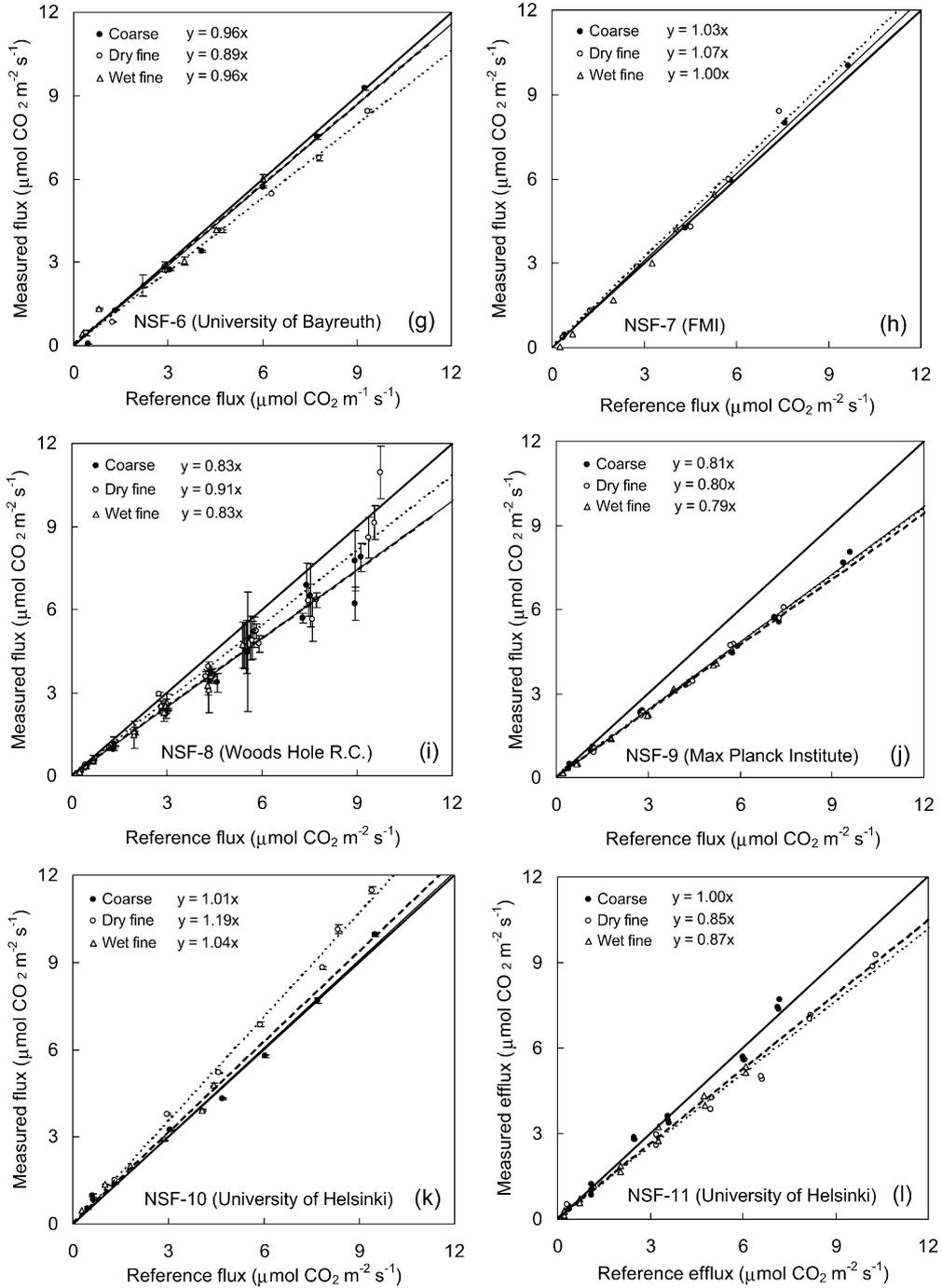


Fig. 3. (Continued)

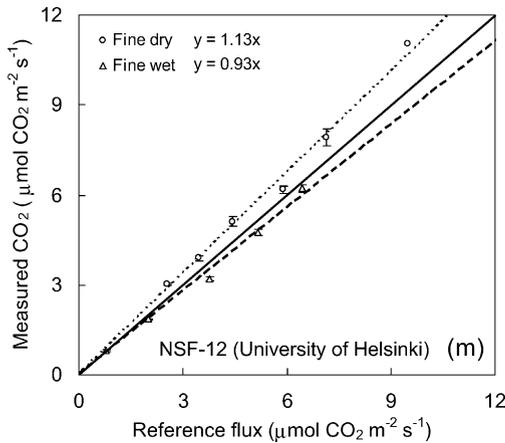


Fig. 3. (Continued).

overestimation increased to 19%. Another modified chamber of PP-systems (NSF-11) underestimated fluxes by 15 and 13% on dry fine and wet fine sands, respectively. However, the fluxes measured on coarse sand were similar to the reference flux. NSF-12 overestimated fluxes by 13% on dry fine sand and underestimated by 7% on wet fine sand. NSF-12 was not tested on coarse sand.

3.3. Non-steady-state non-through-flow chambers

On average, non-steady-state non-through-flow chambers underestimated fluxes by 4% on coarse sand and by 14 and 13% on dry and wet fine sands, respectively (Table 1). The systems of the University of Joensuu (NSNF-1) and the Agrifood Research Finland (NSNF-2) showed fluxes very close to the reference on dry fine sand, but on wet fine sand NSNF-1 underestimated fluxes by 15%. The extension did not affect the results (Fig. 4a and b, Table 1). When the measurement period with NSNF-2 was increased from 10 to 30 min, the fluxes were underestimated by 15% on coarse and dry fine sands and by 10% on wet fine sand. The system of the University of Helsinki (NSNF-3) underestimated fluxes by 18% on dry fine sand and by 15% on wet fine sand. On coarse sand, however, the system showed a small overestimation. The other chamber of the University of Helsinki (NSNF-4) also underestimated fluxes. The underestimation was largest, 35%, on dry fine sand, but on wet fine sand, the underestimation was smaller, 16%.

3.4. Steady-state through-flow chambers

On average, steady-state through-flow chambers overestimated fluxes by 4% on coarse sand and by 2% on dry and wet fine sands. Both systems showed fluxes within 9% of references on all soil types (Fig. 5a and b). SSFL-1 overestimated fluxes by 9% on wet fine sand, in contrast to SSFL-2, which underestimated these fluxes by 5%. The chambers also showed contradictory results on dry fine sand, with SSFL-1 underestimating by 4% and SSFL-2 overestimating by 8%. Fluxes measured on coarse sand with both systems were 3–5% higher than the reference flux.

4. Discussion

4.1. Stability of the calibration system

Fluxes generated with the calibration system were quite repeatable between different weeks under the same temperature conditions. The differences shown between the chamber systems are therefore real, with the error caused by possible bias in the calibration system being small. However, one can argue that the homogeneous quartz sand used in the system does not represent soil in a realistic manner. The soil surface is usually more porous in forests, where porosity in the humus layer can exceed 80%. Thus, air currents move even more easily in forest soil than in quartz sand. Quartz sand does, however, simulate mineral soil well, which is of use for grasslands, agricultural fields and some forests with no extended organic layer (Grünzweig et al., 2003). In addition, the source of CO₂ in forest soils is often at the very surface of the soil, whereas in the calibration system used in this study, the source was at a depth of 150 mm in the chamber headspace. Despite lacking some characteristics of a natural soil, the calibration system enables measurement of known, homogeneous and stable fluxes under controlled conditions protected from the wind and direct solar radiation.

4.2. Non-steady-state chambers

Our results confirmed the findings of previous comparisons of different chamber types. Most of the non-steady-state systems seem to underestimate fluxes

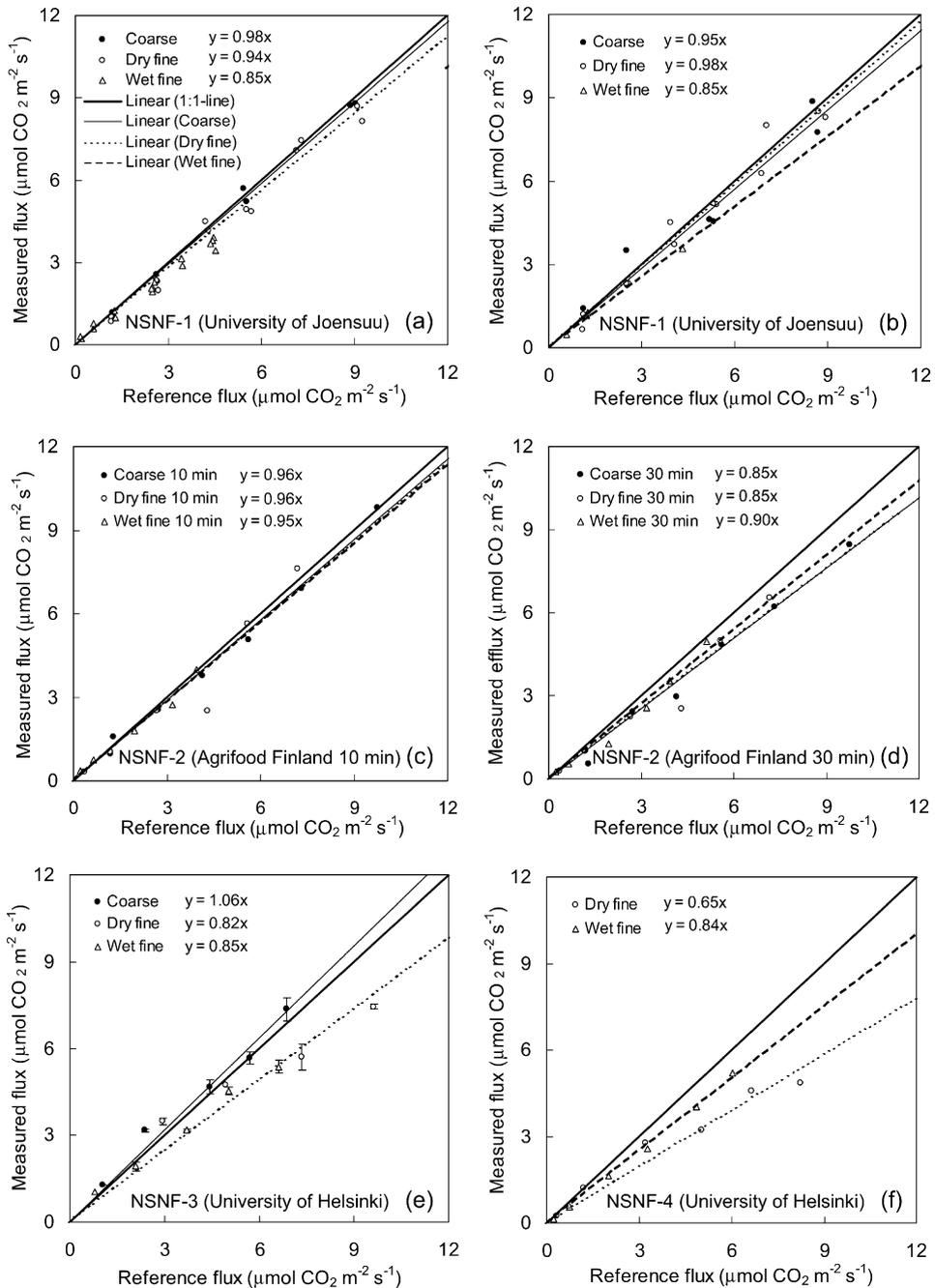


Fig. 4. CO₂ effluxes measured by non-steady-state non-through-flow systems: (a) NSNF-1 (University of Joensuu) without extension, (b) NSNF-1 (University of Joensuu) with extension, (c) NSNF-2 (Agrifood Research Finland) with a 10 min measurement period, (d) NSNF-2 (Agrifood Research Finland) with a 30 min measurement period, (e) NSNF-3 (University of Helsinki) and (f) NSNF-4 (University of Helsinki) plotted against reference fluxes generated by the calibration tank with coarse, dry fine and wet fine sands.

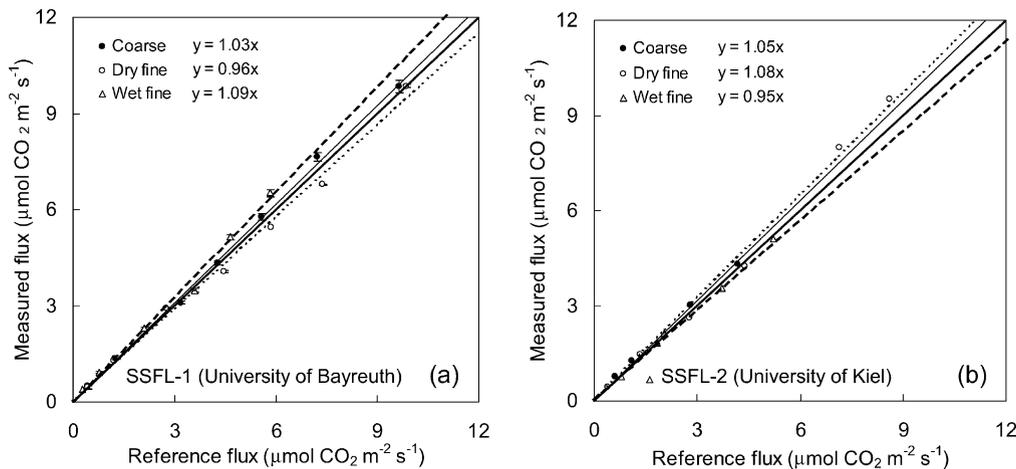


Fig. 5. CO₂ effluxes measured by steady-state through-flow systems: (a) SSFL-1 (University of Bayreuth) and (b) SSFL-2 (University of Kiel) plotted against reference fluxes generated by the calibration tank with coarse, dry fine and wet fine sands.

by about 10%. Non-steady-state non-through-flow chambers (static chambers) based on syringe sampling showed even larger underestimations of up to 35%. These differences are of the same magnitude as those reported by Norman et al. (1997), who compared non-steady-state non-through-flow chambers based on syringe samples with a vented non-steady-state through-flow chamber (Li-Cor LI-6400-09) and with a steady-state through-flow chamber by Rayment and Jarvis (1997). Fluxes measured by non-steady-state non-through-flow chambers were shown to be about 23–31% lower than those of the Li-Cor LI-6400-09 chamber and about 28–36% lower than those of the steady-state through-flow chamber.

The non-steady-state chamber of PP-systems worked best without a collar (NSF-4). However, in forest soils, collars are usually necessary in chambers where the flux measurement is based on concentration increase in the chamber headspace. The chamber cannot be enclosed in the soil without a collar because of the presence of moss and other surface vegetation. While the PP-systems (NSF-2 and NSF-5) overestimated fluxes significantly when a collar was used to seal the chamber to the soil, the widening at the lower part of the chamber in NSF-3 decreased the overestimation somewhat. The same was observed in another modified chamber (NSF-11). The overestimation of fluxes by chambers NSF-2 and NSF-5 may be due to turbulence caused by the fan. The normally

high boundary layer over the forest floor has been observed to be disrupted by excessive turbulence within a closed chamber (Hanson et al., 1993). The boundary layer on the surface may have been affected less when the lower part of the chamber was widened. The effective fan and tightly sealed soil may have caused mass flow of CO₂ from the soil directly under the chamber. Better results without the collars could be explained by leakage through the soil under the edges of the chamber, which would have compensated for the disturbance caused by the fan on the CO₂ flux from the soil beneath the chamber. However, many of the 95% confidence intervals presented in Table 1 in cases where the coefficient is close to 1 are below or over 1. Thus, minor under- and overestimations cannot be considered to be statistically significant. Only in chambers with a larger bias ($\pm 10\%$), can they be considered significant.

Underestimation of the fluxes by non-steady-state chambers is often explained by an altered diffusion gradient which slows the CO₂ diffusion from soil when the chamber is placed on the soil surface (Healy et al., 1996; Livingston and Hutchinson, 1995; Nay et al., 1994). Accordingly, the underestimation should be larger when the measurement period is longer, as observed in NSNF-2 (Fig. 4c and d). Fluxes calculated over a 30 min period were about 15% lower than those of a 10 min period, indicating that the increased CO₂ concentration inside the chamber had decreased the

flux from the soil. In addition, the disturbance after placing the chamber on the soil can also cause unrealistic flux values during the first 1–2 min of the measurement period (Davidson et al., 2002). Thus, the flux values should be taken after the flux has stabilised, 2–3 min after the chamber placement.

The rather good results from the Li-Cor LI-6400-09 chamber (NSF-1a) may be due to the CO₂ concentration inside the chamber being scrubbed down to just below ambient levels and the concentration inside the chamber calculated for ambient CO₂ using a regression line of flux versus chamber CO₂ concentration. Thus, the saturation effect was avoided. However, the resulting flux is sensitive to accurate determination of ambient CO₂, as the whole measurement centres around that CO₂ concentration. Furthermore, in Li-Cor LI-6400-09, the air was mixed by pushing air from the analyser back into the chamber through a perforated manifold circulating around the chamber. Together with a pressure relief vent, this prevented formation of localized pressure gradients, which can cause uncontrolled air flow in the soil. This air flow may be the reason that most NSF chambers overestimated fluxes on dry fine sand, which had the highest porosity. In porous soil, the air flow can transport CO₂ from deeper in the soil where the concentration is higher. On wet fine sand, the air-filled porosity was only about 30–36%, and this probably restricted the air movement effectively. High variation and relatively large underestimation in the fluxes of the Woods Hole chamber (NSF-8) may be related to the collars, which did not stay firmly in place on the loose quartz sand. When the chamber was put onto or removed from the collar, small cracks appeared in the sand, which might have had some effect on the system yielding underestimations relative to reference fluxes.

4.3. Steady-state chambers

Steady-state through-flow chambers generally overestimated rather than underestimated the fluxes from soil, but the overestimation was in most cases very small. No major differences were discovered between the sand types, indicating that the chambers did not generate mass air flow from the soil or disturb the soil CO₂ gradient significantly. However, according to Kutsch et al. (2001), open chambers with side openings are sensitive to pressure differences produced by

the wind. They found significant over- or underpressurization in relation to wind speed and direction. Radial-symmetrical chambers such as that used by Rayment and Jarvis (1997) may overcome this problem. Pressure fluctuations caused by the wind may also affect short-term effluxes in the radial chambers, but in the long run, this disturbance would be less important since the production of CO₂ remains unaffected. The tests in our study were carried out in a wind-free place to ensure standard conditions for all chambers being tested. The results of the tests may well have been different had the measurements been obtained in windy conditions. Moreover, under field conditions, solar radiation also influences the chambers by heating them. If heated suddenly during the measurement, the expansion of gas inside the chamber could result in expansion of air in the chamber affecting the flux measurement.

5. Conclusions

The fluxes generated with the calibration system were stable and appeared to be spatially homogeneous, allowing conversion factors for different chambers to be produced. Reliability of the chamber systems was not related to the measurement principle. Good results can be achieved with both steady-state and non-steady-state chambers. However, even the same chambers with different collar designs showed highly variable results. The general trend seemed to be that non-steady-state non-through-flow chambers systematically underestimated by 4–14%, whereas no significant differences between through-flow chambers were observed.

Special attention should be paid to the mixing of air in the chamber since it can be a major source of error. Excessive turbulence inside the chamber can cause mass flow of CO₂ between the soil and the chamber. However, when using non-steady-state chambers, proper mixing of the air is needed because the CO₂ concentration must be evenly distributed within the chamber headspace to calculate the flux correctly (Eq. (3)). The turbulence can be decreased by extracting the sample air and by pushing air from the analyser back into the chamber through a perforated manifold circulating around the chamber. This ensures a representative sample and adequate mixing of air

with minimal turbulence. Finally, since the headspace concentration inside the chamber affects the flux by altering the concentration gradient between the soil and the chamber, the chamber should be designed to minimise the increase in CO₂ concentration in its headspace.

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