

CO₂ flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression

L. Kutzbach¹, J. Schneider¹, T. Sachs², M. Giebels³, H. Nykänen⁴, N. J. Shurpali⁴, P. J. Martikainen⁴, J. Alm⁵, and M. Wilming¹

¹Institute for Botany and Landscape Ecology, Ernst Moritz Arndt University Greifswald, Grimmer Straße 88, 17487 Greifswald, Germany

²Foundation Alfred Wegener Institute for Polar and Marine Research, Research Unit Potsdam, Telegrafenberg A43, 14473 Potsdam, Germany

³Institute of Geoecology, Technical University Braunschweig, Langer Kamp 19c, 38106 Braunschweig, Germany

⁴Department of Environmental Science, Biogeochemistry Research Group, University of Kuopio, P.O. Box 1627, 70211 Kuopio, Finland

⁵Finnish Forest Research Institute, Joensuu Research Unit, P.O. Box 68, 80101 Joensuu, Finland

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Abstract. Closed (non-steady state) chambers are widely used for quantifying carbon dioxide (CO₂) fluxes between soils or low-stature canopies and the atmosphere. It is well recognised that covering a soil or vegetation by a closed chamber inherently disturbs the natural CO₂ fluxes by altering the concentration gradients between the soil, the vegetation and the overlying air. Thus, the driving factors of CO₂ fluxes are not constant during the closed chamber experiment, and no linear increase or decrease of CO₂ concentration over time within the chamber headspace can be expected. Nevertheless, linear regression has been applied for calculating CO₂ fluxes in many recent, partly influential, studies. This approach has been justified by keeping the closure time short and assuming the concentration change over time to be in the linear range. Here, we test if the application of linear regression is really appropriate for estimating CO₂ fluxes using closed chambers over short closure times and if the application of nonlinear regression is necessary. We developed a nonlinear exponential regression model from diffusion and photosynthesis theory. This exponential model was tested with four different datasets of CO₂ flux measurements (total number: 1764) conducted at three peatlands sites in Finland and a tundra site in Siberia. Thorough analyses of residuals demonstrated that linear regression was frequently not appropriate for the determination of CO₂ fluxes by closed-chamber methods, even if closure times were kept short. The developed exponential model was well suited for nonlinear regression of the concentration over time $c(t)$ evo-

lution in the chamber headspace and estimation of the initial CO₂ fluxes at closure time for the majority of experiments. However, a rather large percentage of the exponential regression functions showed curvatures not consistent with the theoretical model which is considered to be caused by violations of the underlying model assumptions. Especially the effects of turbulence and pressure disturbances by the chamber deployment are suspected to have caused unexplainable curvatures. CO₂ flux estimates by linear regression can be as low as 40% of the flux estimates of exponential regression for closure times of only two minutes. The degree of underestimation increased with increasing CO₂ flux strength and was dependent on soil and vegetation conditions which can disturb not only the quantitative but also the qualitative evaluation of CO₂ flux dynamics. The underestimation effect by linear regression was observed to be different for CO₂ uptake and release situations which can lead to stronger bias in the daily, seasonal and annual CO₂ balances than in the individual fluxes. To avoid serious bias of CO₂ flux estimates based on closed chamber experiments, we suggest further tests using published datasets and recommend the use of nonlinear regression models for future closed chamber studies.

1 Introduction

Accurate measurements of carbon dioxide (CO₂) fluxes between soils, vegetation and the atmosphere are a prerequisite for the quantification and understanding of the carbon source or sink strengths of ecosystems and, ultimately, for the development of a global carbon balance. A number of different

Correspondence to: L. Kutzbach
(kutzbach@uni-greifswald.de)

approaches are used to determine CO₂ exchange fluxes between ecosystems and the atmosphere, each with its own advantages and limitations. These approaches include micrometeorological methods such as eddy covariance or gradient techniques which are employed on towers or aircrafts, diffusion modelling for bodies of water, and measurements using open (steady state) or closed (non-steady state) chambers (e.g. Matson and Harriss, 1995; Norman et al., 1997).

The closed chamber method is the most widely used approach to measure the CO₂ efflux from bare soil surfaces (e.g. Jensen et al., 1996; Xu and Qi, 2001; Pumpanen et al., 2003, 2004; Reth et al., 2005; Wang et al., 2006). Also, it is often applied to quantify the net CO₂ exchange between the atmosphere and low-stature canopies typical for tundra (Vourlites et al., 1993; Christensen et al., 1998; Oechel et al., 1993, 1998, 2000; Zamolodchikov and Karelin, 2001), peatlands (Alm et al., 1997, 2007; Tuittila et al., 1999; Bubier et al., 2002; Nykänen et al., 2003; Burrows et al., 2004; Drösler, 2005; Laine et al., 2006), forest understorey vegetation (Goulden and Crill, 1997; Heijmans et al., 2004) and agricultural crop stands (Dugas et al., 1997; Wagner et al., 1997; Maljanen et al., 2001; Steduto et al., 2002). Advantageously, the closed-chamber method is relatively low in cost and power consumption, simple to operate and can therefore be used in remote, logistically difficult areas. On the other hand, it is prone to a variety of potential errors (Livingston and Hutchinson, 1995; Welles et al., 2001; Davidson et al., 2002) which the investigator has to consider and to minimise by careful experiment planning and chamber design. Sources of errors are (1) inaccurate determination of the headspace volume (Livingston and Hutchinson, 1995), (2) leakage directly at the chamber components or via the underlying soil pore space (Hutchinson and Livingston, 2001; Livingston et al., 2006), (3) temperature changes of the soil and the atmosphere beneath the chamber (Wagner and Reicosky, 1992; Drösler, 2005), (4) artificial water vapour accumulation which depletes the CO₂ concentration and might influence the stomata regulation of plants (Welles et al., 2001), (5) disturbance of pressure gradients across the soil-atmosphere interface by soil compression or insufficient pressure relief during chamber setting (Hutchinson and Livingston, 2001; Livingston et al., 2006), (6) suppression of the natural pressure fluctuations (Hutchinson and Mosier, 1981; Conen and Smith, 1998; Hutchinson and Livingston, 2001), (7) alteration or even elimination of advection and turbulence and thus modification of the diffusion resistance of the soil- or plant-atmosphere boundary layer (Hanson et al., 1993; Le Dantec et al., 1999; Hutchinson et al., 2000; Denmead and Reicosky, 2003; Reicosky, 2003), and (8) the concentration build-up or reduction within the chamber headspace that inherently disturbs the underlying concentration gradients that were in effect prior to chamber deployment (e.g. Matthias et al., 1978; Hutchinson et al., 2000; Livingston et al., 2006). This study focuses on the latter problem, which can lead to serious bias of CO₂ fluxes if not accounted for, even if all

other potential errors were kept at minimum.

The closed chamber methodology estimates the CO₂ fluxes by analysing the rates of CO₂ accumulation or depletion in the chamber headspace over time. However, every change of the CO₂ concentration from the normal ambient conditions feeds back on the CO₂ fluxes by altering the concentration gradients between the soil or the plant tissues and the surrounding air. In other words, the measurement method itself alters the measurand. Thus, for assessing the pre-deployment CO₂ flux, the rate of initial concentration change at the moment of deployment ($t=t_0=0$) should be used when the alteration of the concentration gradients in soils and plant tissues is minimal, rather than the mean rate of the CO₂ concentration change over the chamber closure period (Livingston and Hutchinson, 1995).

The nonlinear nature of the gas concentration evolution over time in closed chambers has been recognised and discussed early and at length in the history of chamber-based gas flux measurements. However, most studies concerning this issue were conducted for the gas exchange of bare soil surfaces. Matthias et al. (1978) showed for numerical simulations of closed chamber experiments with closure times of 20 min that N₂O emissions could be underestimated by as much as 55% by linear regression. Quadratic regression still underestimated the real fluxes by up to 25%. An exponential function developed from simplified diffusion theory was best suited for the flux estimate with underestimation of the fluxes of maximal 11%. In the following years, further theoretical and numerical studies came to the same conclusion that the use of linear regression can lead to serious underestimation of gas fluxes between soils and atmosphere (Hutchinson and Mosier, 1981; Healy et al., 1996; Hutchinson et al., 2000; Pedersen, 2000; Pedersen et al., 2001; Welles et al., 2001; Hutchinson and Livingston, 2001). The serious underestimation bias of the linear regression method as predicted by the theoretical and numerical studies was confirmed by Nakano et al. (2004) by measurements of CO₂ release and CH₄ consumption from soils under actual field conditions. Recently, Livingston et al. (2005, 2006) introduced the so-called non-steady-state diffusive flux estimator (NDFE) function which is derived from time dependent diffusion theory and can be fitted by nonlinear regression to gas concentration over time data from closed chamber experiments. They demonstrated for numerical model simulations that only the NDFE model was able to accurately determine the predeployment gas fluxes whereas quadratic and also exponential regression still underestimated them. However, the NDFE model is restricted to gas sources in bare soils whereas vegetation and gas sinks are not considered. Only few researchers have applied nonlinear models to determine CO₂ exchange fluxes on vegetated surfaces (Dugas et al., 1997; Wagner et al., 1997; Steduto et al., 2002). The mentioned scientists used the quadratic model proposed by Wagner et al. (1997) which accounts for nonlinear disturbances by the chamber deployment but is not based on the underlying physiology

and diffusion physics. Wagner et al. (1997) demonstrated for the CO₂ exchange of different agricultural crop stands that 60% to 100% of all chamber experiments were significantly nonlinear. Even with a short closure time of 60 s, fluxes derived from quadratic regression were 10% to 40% greater than those calculated with linear regression.

Despite the growing evidence against the use of a linear model for the determination of gas fluxes using closed chambers, most of the recent studies on the CO₂ balance of vegetated surfaces and many studies on the CO₂ efflux from bare soil have applied linear regression for estimating CO₂ fluxes (e.g. Vourlites et al., 1993; Oechel et al., 1993, 1998, 2000; Jensen et al., 1996; Alm et al., 1997, 2007; Goulden and Crill, 1997; Christensen et al., 1998; Tuittila et al., 1999; Maljanen et al., 2001; Xu and Qi, 2001; Bubier et al., 2002; Nykänen et al., 2003; Pumpanen et al., 2003; Burrows et al., 2004; Heijmans et al., 2004; Drösler, 2005; Reth et al., 2005; Laine et al., 2006; Wang et al., 2006). Usually, the authors justify the use of linear regression by keeping the closure time short and assuming the concentration change over time to be still in the linear range.

Here, we investigate if the application of linear regression is really appropriate for estimating CO₂ fluxes from bare or vegetated soils using closed chambers with short closure times or if it is necessary to apply a nonlinear model. The performance of the linear model can be evaluated by comparing its results with the results of nonlinear models developed from biophysical theory. For bare and approximately homogenous soils, we consider nonlinear regression of the NDFE function of Livingston et al. (2005, 2006) as the most advanced approach. However, the extension of this physically-based model of non-steady state diffusion through homogenous soils to the situation of vegetated and substantially heterogeneous soils does not appear feasible to us. Therefore, we develop a conceptual, explicitly simplified biophysical model to include both soils and vegetation processes. The main purpose of this model is to evaluate which type of nonlinear function can be expected to adequately describe the evolution of CO₂ concentrations within closed chambers deployed on vegetated and bare soils. We adopt the exponential model of Matthias et al. (1978) for trace gas efflux from bare soils, which is based on simplified diffusion theory, and expand it for sites with low-stature vegetation. For this purpose, the effect of changing CO₂ concentrations on photosynthesis has to be added to the model.

The developed nonlinear exponential model is tested against the linear model and the quadratic model proposed by Wagner et al. (1997) with four datasets of CO₂ flux measurements (total number = 1764) conducted by four separate working groups at two vegetated boreal peatlands, one vegetated tundra, and one non-vegetated boreal peat excavation site. Furthermore, the exponential model was tested against the NDFE model of Livingston et al. (2005, 2006) using the dataset from the non-vegetated peat excavation site.

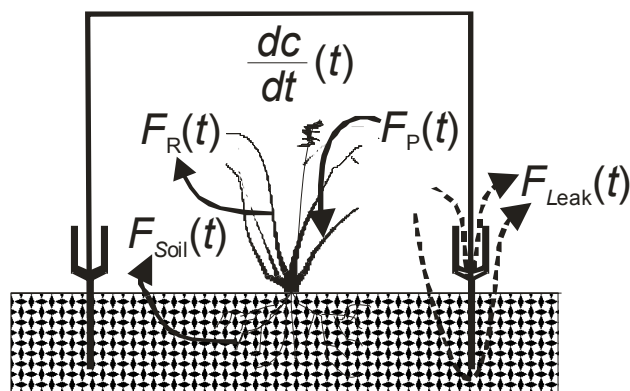


Fig. 1. Schematic of the CO₂ fluxes in the chamber headspace which make up to the net CO₂ flux F_{net} (details in the text, Eq. (1)). $F_{\text{Soil}}(t)$ is the diffusive efflux from the soil, $F_P(t)$ is photosynthesis, $F_R(t)$ is aboveground plant respiration, $F_{\text{Leak}}(t)$ is leak flux. $dc/dt(t)$ is the CO₂ concentration change over time t in the chamber headspace.

The major questions of the test experiment were:

1. How well do the empirical linear and quadratic functions (f_{lin} and f_{qua}) as well as the theory-based exponential and NDFE functions (f_{exp} , f_{NDFE}) describe the chamber CO₂ concentration evolution data from real measurements?
2. Are the linear and quadratic model functions (f_{lin} and f_{qua}) sufficient approximations of the exponential model for the specific experiment set-ups, particularly for short chamber closure times?
3. Is the NDFE function (f_{NDFE}) better fitted to the chamber CO₂ data from the non-vegetated peat excavation site than the exponential function (f_{exp})?
4. Do the initial slopes $f'(t)$ of the different functions (f_{lin} , f_{qua} , f_{exp} , f_{NDFE}), which are directly proportional to the calculated initial CO₂ net fluxes $F_{\text{net}}(t_0)$, deviate significantly from each other?

2 Development of the nonlinear exponential model

Presuming that the chamber experiment itself alters the measurand, namely the CO₂ flux, a nonlinear evolution of the CO₂ concentration in the chamber headspace must be expected. In the following, a conceptual model based on simplified biophysical theory is developed which shall reflect this nonlinear CO₂ concentration evolution as affected by the main relevant processes which contribute to the net CO₂ flux into or from the chamber headspace. The considered processes are (1) diffusion from the soil, (2) photosynthesis of the plants, (3) respiration of the plants and (4) diffusion from the headspace to the surrounding atmosphere by leaks at the chamber or through the soil (Fig. 1).

The model presented here is based on the assumption that all other potential errors of the closed chamber approach which are not connected to the inherent concentration changes in the closed chamber headspace are negligible thanks to careful experiment planning. This means that during chamber deployment, soil and headspace air temperature, photosynthetically active radiation, air pressure and headspace turbulence are assumed to be constant and approximately equal to ambient conditions.

When covering a vegetated soil surface with a closed chamber, the CO₂ concentration change over time in the chamber headspace is the net effect of several individual processes with partly opposing directions (Fig. 1). CO₂ is added to or removed from the headspace by different processes at different interface surfaces. The headspace is isolated from the surrounding atmosphere by the chamber walls. Here, relevant CO₂ flux is only possible through leaks (F_{Leak}) which should be avoided but often cannot be ruled out completely. Of course, the headspace is open to the soil surface where CO₂ efflux from the soil (F_{Soil}) to the overlying air takes place. Inside the headspace, plants photosynthesise and respire, meaning CO₂ removal (F_P) from or CO₂ supply (F_R) to the headspace air, respectively. The sum of all CO₂ fluxes into or out of the headspace represents the net CO₂ flux (F_{net}) which can be estimated by the change of the CO₂ concentration over time $dc/dt(t)$ during chamber closure. The sign convention of this study is that fluxes are defined positive when adding CO₂ to the chamber headspace and negative when removing CO₂ from the chamber headspace.

The net CO₂ flux $F_{\text{net}}(t)$, which in effect drives the CO₂ concentration change in the chamber headspace over time $dc/dt(t)$, can be written as:

$$F_{\text{net}}(t) = \frac{dc}{dt}(t) \frac{pV}{RTA} = F_{\text{Soil}}(t) + F_P(t) + F_R(t) + F_{\text{Leak}}(t) \quad (1)$$

where p is air pressure, R is the ideal gas constant, and T is the temperature (in Kelvin). V and A are the volume and the basal area of the chamber, respectively. $F_{\text{Soil}}(t)$ is the CO₂ efflux from the soil which originates from the respiration of soil microbes, soil animals and belowground biomass of plants, i.e. roots and rhizomes, $F_P(t)$ is the CO₂ flux associated with the gross photosynthesis of the plants, $F_R(t)$ is the CO₂ flux associated with the dark respiration of the aboveground biomass, and $F_{\text{Leak}}(t)$ is the CO₂ flux related to leakage directly at the chamber components or via the soil pore space. These individual process-associated fluxes have to be considered as not constant but more or less variable over time during the chamber deployment. This is due to the direct dependency of some of the individual fluxes on the CO₂ concentration in the headspace which is changing over time.

By reorganising Eq. (1), the concentration change in the chamber headspace over time $dc/dt(t)$, can be written as:

$$\frac{dc}{dt}(t) = [F_{\text{Soil}}(t) + F_P(t) + F_R(t) + F_{\text{Leak}}(t)] \frac{RTA}{pV} \quad (2)$$

The CO₂ efflux from the soil to the headspace air $F_{\text{Soil}}(t)$ is considered to be mainly driven by molecular diffusion between the CO₂-enriched soil pore space and the headspace air and can be modelled following Matthias et al. (1978), Hutchinson and Mosier (1981) and Pedersen (2000) as:

$$F_{\text{Soil}}(t) = D \frac{[c_d - c(t)]}{d} \frac{pV}{RTA} \quad (3)$$

where D is the soil CO₂ diffusivity, c_d is the CO₂ concentration at some unknown depth d below the surface where the CO₂ concentration is constant and not influenced by the chamber deployment. $c(t)$ is the CO₂ concentration of the headspace air which is assumed equal to the CO₂ concentration at the soil surface, which has to be ensured by adequate mixing of the headspace air.

While the nonlinear models of F_{Soil} over the chamber closure time by the above-mentioned authors are well-accepted and frequently applied, the effect of the CO₂ concentration changes in the chamber headspace on the photosynthesis of enclosed vegetation has not been given much attention. However, this effect can be expected to be substantial considering the underlying enzyme kinetics of photosynthesis whose main substrate is CO₂.

As photosynthesis is limited either by the electron transport rate at the chloroplast, which is dependent on irradiation, or the activity of Rubisco, which is mainly dependent on the intercellular CO₂ concentration (Farquhar et al., 1980), F_P can be either strongly dependent on or nearly independent of changes of the headspace CO₂ concentration $c(t)$ depending on the irradiation level. The complex dependence of photosynthetic activity on irradiation and CO₂ concentration which is reflected in full detail by the model of Farquhar et al. (1980) must and can be strongly simplified for our approach. Under non-irradiation-limited conditions, the photosynthesis of C3 plants and mosses is considered to correlate approximately linearly with the ambient CO₂ concentration at CO₂ concentrations between 300 ppm and 400 ppm. This has been shown by several previous studies (Morison and Gifford, 1983; Grulke et al., 1990; Stitt, 1991; Sage, 1994; Luo et al., 1996; Luo and Mooney, 1996; Williams and Flanagan, 1998; Griffin and Luo, 1999). Consequently, $F_P(t)$ can be modelled for periods with non-irradiation-limited photosynthesis of a canopy consisting of C3 plants and/or mosses, which is typical for tundra and peatlands, as:

$$F_P(t) = k_p c(t) \frac{pV}{RTA} \quad (4)$$

where k_p is the constant of proportionality of the approximately linear relationship between CO₂ concentration and photosynthesis-associated flux.

On the other hand, $F_P(t)$ is not a function of $c(t)$ but invariant with changing $c(t)$ if photosynthesis is limited by the irradiation – consequently also during dark conditions – or if the canopy consists mainly of C4 plants. Thus, if the other environmental controls such as irradiation, temperature or air moisture can be assumed constant, $F_P(t)$ can be defined as:

$$F_P(t) = F_P(t_0) \quad (5)$$

where t_0 is $t=0$.

As the effect of ambient CO₂ concentration changes on dark respiration has been shown to be very low or none (Grulke et al., 1990; Drake et al., 1999; Amthor, 2000; Tjoelker et al., 2001; Smart, 2004; Bunce, 2005), CO₂ flux associated with the dark respiration of aboveground biomass $F_R(t)$ is considered invariant with changing $c(t)$ in a considered CO₂ concentration range of 200 ppm to 500 ppm. Thus, if the other environmental controls such as temperature or air moisture can be assumed constant, $F_R(t)$ can be defined as:

$$F_R(t) = F_R(t_0) \quad (6)$$

As leakage often cannot be ruled out completely, CO₂ flux associated with potential leakages $F_{Leak}(t)$ should be integrated into the model. $F_{Leak}(t)$ is considered to be driven by diffusive transport and can therefore be modelled similarly to $F_{Soil}(t)$:

$$F_{Leak}(t) = \left\{ D_{Chamber} \frac{[c_a - c(t)]}{d_{Chamber}} + D_{Soil} \frac{[c_a - c(t)]}{d_{Soil}} \right\} \frac{pV}{RTA} = K_{Leak} [c_a - c(t)] \frac{pV}{RTA} \quad (7)$$

where $D_{chamber}$ is the mean diffusivity of leaks directly at the chamber components, $d_{chamber}$ is the distance between headspace and the surrounding air, D_{Soil} is the mean diffusivity of leaks by air-filled soil pore space, and d_{Soil} is the distance between the headspace and the surrounding air via the air-filled soil pore space. K_{Leak} is a constant which combines $D_{chamber}$, $d_{chamber}$, D_{Soil} , and d_{Soil} and indicates leakage strength. c_a is the CO₂ concentration in the air outside of the chamber which is considered well-mixed and therefore constant during chamber deployment.

For situations with non-irradiation-limited photosynthesis, the concentration change in the chamber headspace over time $dc/dt(t)$ can be derived by inserting the Eqs. (3), (4), (6) and (7) into Eq. (2):

$$\frac{dc}{dt}(t) = D \frac{[c_d - c(t)]}{d} + k_P c(t) + F_R(t_0) \frac{RTA}{pV} + K_{Leak} [c_a - c(t)] \quad (8)$$

which can be reorganised to

$$\frac{dc}{dt}(t) = \left[\frac{D}{d} c_d + F_R(t_0) \frac{RTA}{pV} + K_{Leak} c_a \right] + \left[-\frac{D}{d} + k_P - K_{Leak} \right] c(t) \quad (9)$$

This differential equation expresses mathematically the previously emphasised fact that the measurement method itself alters the measurand. The measurand $dc/dt(t)$ is altered by the change of the headspace concentration $c(t)$ which is forced by the chamber deployment to determine $dc/dt(t)$. The differential equation Eq. (9) is solved by computing its indefinite integral:

$$c(t) = - \frac{\left[\frac{D}{d} c_d + F_R(t_0) \frac{RTA}{pV} + K_{Leak} c_a \right]}{\left[-\frac{D}{d} + k_P - K_{Leak} \right]} + \exp \left[\left(-\frac{D}{d} + k_P - K_{Leak} \right) t \right] B \quad (10)$$

where B is the integral constant.

For situations with irradiation-limited photosynthesis, the concentration change in the chamber headspace over time $dc/dt(t)$ can be derived by inserting the Eqs. (3), (5), (6) and (7) into Eq. (2):

$$\frac{dc}{dt}(t) = D \frac{[c_d - c(t)]}{d} + [F_P(t_0) + F_R(t_0)] \frac{RTA}{pV} + K_{Leak} [c_a - c(t)] \quad (11)$$

which can be reorganised to :

$$\frac{dc}{dt}(t) = \left\{ \frac{D}{d} c_d + F [F_P(t_0) + F_R(t_0)] \frac{RTA}{pV} + K_{Leak} c_a \right\} + \left(-\frac{D}{d} - K_{Leak} \right) c(t) \quad (12)$$

This differential equation is solved by computing its indefinite integral:

$$c(t) = - \frac{\left[\frac{D}{d} c_d + [F_P(t_0) + F_R(t_0)] \frac{RTA}{pV} + K_{Leak} c_a \right]}{\left(-\frac{D}{d} - K_{Leak} \right)} + \exp \left[\left(-\frac{D}{d} - K_{Leak} \right) t \right] B \quad (13)$$

where B is the integral constant.

For both situations, with non-irradiation-limited photosynthesis and with irradiation-limited photosynthesis, the evolution of $c(t)$ over time as given by Eq. (10) and Eq. (13), respectively, can be described and fitted by an exponential function $f_{exp}(t)$ of the form:

$$c(t) = f_{exp}(t) + \varepsilon(t) = p_1 + p_2 \exp(p_3 t) + \varepsilon(t) \quad (14)$$

where $\varepsilon(t)$ is the residual error at a specific measurement time t . The parameters p_1 and p_3 have different meanings for each situation. For the situation with non-irradiation-limited photosynthesis, p_1 is given by

$$p_1 = - \frac{\left[\frac{D}{d} c_d + F_R(t_0) \frac{RTA}{pV} + K_{Leak} c_a \right]}{\left(-\frac{D}{d} + k_P - K_{Leak} \right)} \quad (15)$$

and p_3 is given by

$$p_3 = \left(-\frac{D}{d} + k_P - K_{\text{Leak}} \right) \quad (16)$$

For the situation with irradiation-limited photosynthesis, p_1 is given by

$$p_1 = -\frac{\left\{ \frac{D}{d} c_d + [F_P(t_0) + F_R(t_0)] \frac{RTA}{pV} + K_{\text{Leak}} c_a \right\}}{\left(-\frac{D}{d} - K_{\text{Leak}} \right)} \quad (17)$$

and p_3 is given by

$$p_3 = \left(-\frac{D}{d} - K_{\text{Leak}} \right) \quad (18)$$

For both situations, p_2 is equal to the integral constant B of the solution of the respective differential equation:

$$p_2 = B \quad (19)$$

As shown clearly by Eqs. (15) to (19), the parameters of the exponential model p_1 , p_2 , and p_3 cannot directly be interpreted physiologically or physically since they represent a mathematical combination of several physiological and physical parameters of the investigated soil-vegetation system and the applied closed chamber technique. However, the given derivation demonstrates that an exponential or near-exponential form of the regression model should be applicable for describing the evolution of $c(t)$ over time in the chamber headspace. The initial slope of the exponential regression curve $f'_{\text{exp}}(t_0) = (p_2 p_3)$ can be used to estimate the CO₂ flux rate at the beginning of the chamber deployment $F_{\text{net}}(t_0)$, which is considered to be the best estimator of the net CO₂ exchange flux under undisturbed conditions:

$$F_{\text{net}}(t_0) = \frac{dc}{dt}(t_0) \frac{pV}{RTA} = f'_{\text{exp}}(t_0) \frac{pV}{RTA} = p_2 p_3 \frac{pV}{RTA} \quad (20)$$

Regarding the results of Matthias et al. (1978) and Livingston et al. (2006), nonlinear regression of the exponential function to the $c(t)$ data is still likely to underestimate the predeployment fluxes. However, we consider the application of exponential regression as the most accurate approach which is practicable at all when measuring CO₂ fluxes from complex vegetation-soil systems.

3 Least squares regression of model functions

The evolution of the CO₂ concentration in the chamber headspace $c(t)$ over time was analysed by fitting the following model functions to the experimental data: (1) the exponential model function $f_{\text{exp}}(t)$ developed in Chapter 2, (2) a quadratic model function $f_{\text{qua}}(t)$ as proposed previously by Wagner et al. (1997), (3) the linear model function $f_{\text{lin}}(t)$, which was used in many other studies and (4) the NDFE function proposed by Livingston et al. (2006) only for the

non-vegetated peat excavation site Linnansuo. The quadratic model function has the form:

$$c(t) = f_{\text{qua}}(t) + \varepsilon(t) = a + b t + c t^2 + \varepsilon(t) \quad (21)$$

where a , b and c are the fit parameters of the second-order polynomial. The linear model function has the form:

$$c(t) = f_{\text{lin}}(t) + \varepsilon(t) = a + b t + \varepsilon(t) \quad (22)$$

The NDFE function has the form:

$$c(t) = f_{\text{NDFE}}(t) + \varepsilon(t) = c_0 + f_0 \tau \left(\frac{A}{V} \right) \left[\frac{2}{\sqrt{\pi}} \sqrt{t/\tau} + \exp(t/\tau) \operatorname{erfc}(\sqrt{t/\tau}) - 1 \right] + \varepsilon(t) \quad (23)$$

where c_0 and f_0 represent initial chamber headspace CO₂ concentration and initial CO₂ flux at $t_0=0$, the time constant τ is an indicator of how fast the concentration gradient of the gas in the soil responds to changes in chamber CO₂ concentration (Livingston et al., 2005, 2006).

The parameters of the best-fitted functions were estimated by least-squares regression, i.e. by minimizing the sum of the squared residuals between the observed data and their fitted values. Both, the nonlinear and the linear regressions were conducted with an iterative Gauss-Newton algorithm with Levenberg-Marquardt modifications for global convergence (function *nlinfit* of the Statistics Toolbox of MATLAB[®] Version 7.1.0.246 (R14)).

The parameters of the exponential and quadratic regression functions (Eqs. 20, 21) can only be interpreted by the theoretical model if the curves are convex, i.e. if the absolute value of the slope of the $c(t)$ curve is decreasing with time. However, the parameter estimations of the exponential and quadratic regressions were not restricted to such curvatures only, thus allowing for the detection of clearly nonlinear $c(t)$ curves with curvatures not explainable by the theoretical model. Curves with such “unexplainable” curvatures were separated after the fitting procedure. The parameters of the NDFE model were restricted to positive values as was done also by Livingston et al. (2006).

4 Statistical evaluation and comparison of different models

The first step to test the theory-based models f_{exp} and f_{NDFE} with respect to their ability to describe the $c(t)$ evolution within the chambers was to check if the curvatures of the quadratic f_{qua} and exponential f_{exp} regression functions were consistent with the theoretical considerations (see Sect. 3). Curves with the absolute values of the slopes increasing with time are neither explainable by the exponential model developed in this study nor by the NDFE model of Livingston et al. (2006). They were considered to be caused by violations of the basic assumptions of the developed theoretical models, which means that one of the

factors soil temperature, headspace air temperature, photosynthetically active radiation, the pressure gradient across the soil-atmosphere interface or the headspace turbulence were apparently neither constant nor approximately equal to ambient conditions. Then, the different regression functions f_{lin} , f_{qua} , f_{exp} , f_{NDFE} were evaluated by thorough analyses of residuals. These analyses included the *Durbin-Watson* test for autocorrelation and the *D'Agostino-Pearson* test for normality of the residuals (Durbin and Watson, 1950; D'Agostino, 1971). Furthermore, the goodness of fit of the different regression functions was compared using the adjusted nonlinear coefficient of determination R_{adj}^2 (Rawlings et al., 1998), the *Akaike* information criterion AIC_c (with small sample second order bias correction; Burnham and Anderson, 2004) and an F-test of the residual variances of two compared regression functions (Fisher, 1924).

Autocorrelation of the residuals would indicate that the fitted model does not reflect all important processes governing the $c(t)$ evolution over time. Indeed, autocorrelation of the residuals is a very sensitive indicator of a too simple model. With significantly autocorrelated residuals, the least-squares estimators would no longer be the best estimators of the function parameters (violation of the third *Gauss-Markov* assumption). Also the variance (error) estimators of the parameters would be seriously biased (Durbin and Watson, 1950; Rawlings et al., 1998). That means that autocorrelation must be removed (by data reduction) before correct estimations of the errors of the regression parameters and consequently also of the errors of the flux estimates are possible. For the $c(t)$ evolution data from the closed chamber experiments, checking for autocorrelation becomes particularly important since these data represent time series which are often susceptible to residual autocorrelation. The assumption of normality of the residuals has to be valid for tests of significance and construction of confidence intervals for the regression function (Rawlings et al., 1998). For the $c(t)$ data, the *D'Agostino-Pearson* test is a stricter test for normality than the often used Kolmogorov-Smirnov test, which has to be considered outdated (D'Agostino, 1986). A well-fitted model should neither show autocorrelation nor non-normality of the residuals. Thus, in our case, if autocorrelation and/or non-normality of the residuals are found to be more serious for f_{lin} or f_{qua} compared to f_{exp} , this would indicate that the respective function would be less appropriate for modelling the measurement data than f_{exp} .

The question whether the initial slopes $f'(t_0)$ of two different regression functions deviate significantly from each other was then evaluated by plotting them against each other as x - y scatter diagrams. The differences between the absolute values of $f'(t_0)$ of two regression functions were separated by their sign and tested for their significance by one-tailed *Student's* t -tests following Potthoff (1965, cited in Sachs, 1992). The error estimates of the initial slopes were determined after removing autocorrelation by block-averaging the data. The necessary data number for block averages were automati-

cally adjusted to the degree of observed autocorrelation by a routine included in the applied MATLAB[®] regression program. The error estimates of the initial slope of the exponential function were derived by fitting a Taylor power series expansion of 17th order to the data whose curve form and initial slope is practically identical with the original exponential function. Advantageously, the power series expansion is more resistant against overparameterisation than the exponential function and directly estimates the initial slope of the $c(t)$ curve as one of its fit parameters which results in lower error estimates for the initial slopes.

5 Field measurements

5.1 Investigation sites

The closed chamber experiments were conducted at three peatland sites in Finland (Salmisuo, Vaisjeäggi, Linnansuo) and one tundra site in Siberia (Samoylov) by four separate working groups. Salmisuo is a pristine oligotrophic low-sedge-pine fen and is located in eastern Finland (62°46' N, 30°58' E) in the boreal zone. A total of twelve plots were established in different microsite types: four in flarks, four in lawns, and four in hummocks. The hummocks are elevated above the surrounding area and represent the driest conditions. They are covered by *Sphagnum fuscum*, *Pinus sylvestris* and/or *Andromeda polifolia* as well as *Rubus chamaemorus*. The lawns are intermediate microsites with respect to water level. Their vegetation consists mostly of *Eriophorum vaginatum*. The flarks represent the wettest microsites and are covered primarily by *Sphagnum balticum* and *Scheuchzeria palustris*. More information on Salmisuo mire can be found in Alm et al. (1997) and Saarnio et al. (1997).

Vaisjeäggi is a pristine palsa mire in northern Finland (69°49' N, 27°30' E). The climate is subarctic. To consider the different functional surfaces within the mire, four study transects were established. Transects T₁ and T₂ were located on the wet surfaces dominated by *Sphagnum lindbergii* or *Sphagnum lindbergii* and *Sphagnum riparium*. The most common vascular plants were *Eriophorum angustifolium* and *Eriophorum russeolum*, *Vaccinium microcarpum* and *Carex limosa*. Transect T₃ was set at a wet palsa margin and was covered by *Sphagnum riparium*, *E. angustifolium* and *E. russeolum*. Transect T₄ was on the top of the palsa and was occupied by *Vaccinium vitis-idaea*, *Betula nana*, *Empetrum nigrum*, *Rubus chamaemorus*, *Ledum palustre*, *Dicranum polysetum*, *Andromeda polifolia* and lichens like *Cladina rangiferina* and *Cladonia* species. More detailed information is given by Nykänen et al. (2003).

Linnansuo is a cutover peatland complex in eastern Finland (62°30' N, 30°30' E) in the boreal zone. The measurements were done in a drained, actively harvested peat production area. No vegetation was present and the bare peat

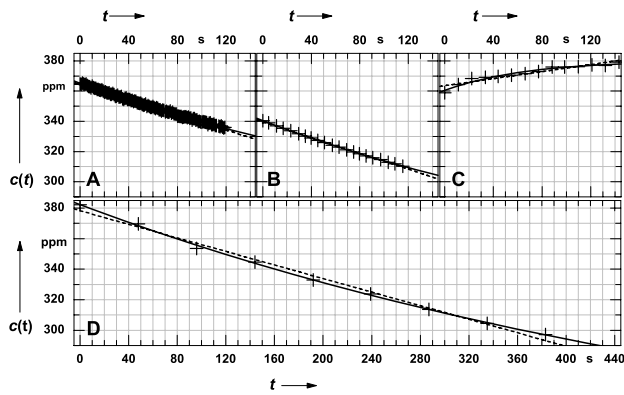


Fig. 2. Examples of the CO₂ concentration $c(t)$ evolution over time t for the different investigation sites. (A) Salmisuo, 11 August 2005, (B) Vaisjeaggi, 17 August 1998, (C) Linnansuo, 12 November 2004, (D) Samoylov, 26 July 2006. The dashed lines indicate linear regression functions f_{lin} , the solid lines indicate exponential regression functions f_{exp} . The absolute values of the initial slopes of the exponential functions $f'_{exp}(t_0)$ are around 0.3 ppm s^{-1} for all examples. An overview of the different set-up characteristics is given in Table 1.

was laid open. No microsites were differentiated. More detailed information will be given by Shurpali et al. (2008).

Samoylov is an island in the southern central Lena River Delta in Northern Siberia ($72^{\circ}22' \text{ N}$, $126^{\circ}30' \text{ E}$). The climate is true-arctic and continental. Samoylov Island is characterised by wet polygonal tundra. In the depressed polygon centres, drainage is strongly impeded due to the underlying permafrost, and water-saturated soils or small ponds are common. In contrast, the elevated polygon rims are characterised by a moderately moist water regime. The vegetation in the swampy polygon centres and at the edges of ponds is dominated by hydrophytic sedges (*Carex aquatilis*, *Carex chodorrhiza*, *Carex rariflora*) and mosses (e.g. *Limprichtia revolvens*, *Meesia longiseta*, *Aulacomnium turgidum*). At the polygon rims, various mesophytic dwarf shrubs (e.g. *Dryas octopetala*, *Salix glauca*), forbs (e.g. *Astragalus frigidus*) and mosses (e.g. *Hylocomium splendens*, *Timmia austriaca*) gain a higher dominance. More detailed information is given in Pfeiffer et al. (1999), Kutzbach et al. (2004) and Kutzbach (2006). A total of 15 plots were established in five different microsite types: three at a polygon rim and three at each of four polygon centres which differed by their moisture and vegetation conditions. More details on the Samoylov site will be given by a manuscript in preparation by T. Sachs et al. (2007).

5.2 Experimental methods

The closed chamber experiments were conducted from July to September 2005 at Salmisuo, from June to August 1998 at Vaisjeaggi, from June to November 2004 at Linnansuo and

from July to September 2006 on Samoylov Island to determine the net ecosystem exchange of CO₂. An overview of the set-up characteristics for the four investigation sites is given in Table 1. For illustration of the differences between the datasets, examples of the $c(t)$ evolution over time for all investigation sites are given in Fig. 2. Permanent and robust boardwalks supported by poles driven in the soils vertically as well as permanently installed collars were established at Salmisuo, Vaisjeaggi and Samoylov. At Linnansuo, neither boardwalks nor permanent collars could be installed due to ongoing peat excavation activities. All chamber experiments were performed manually. Transparent chambers were used at the vegetated sites Salmisuo, Vaisjeaggi and Samoylov while opaque chamber were used at the bare peat site Linnansuo. Experiments were conducted during day and night time at Salmisuo and Samoylov whereas they were conducted only during daytime at Vaisjeaggi and Linnansuo. The chamber headspace air was automatically cooled and mixed by a fan at Salmisuo and Vaisjeaggi. For Samoylov chambers, headspace air was mixed by air cycling through dispersive tubes by a membrane pump but not cooled. For Linnansuo chambers, neither an air mixing device nor a cooling system was provided. Initial pressure shocks during the chamber setting were minimised by additional openings on top of the chambers.

Closure times were rather short at Salmisuo (120 s), Vaisjeaggi (120–160 s) and Linnansuo (150 s), and much longer at Samoylov (480–600 s). Also, the concentration measurement intervals differed considerably in length: 1 s at Salmisuo, 5 s at Vaisjeaggi, 10 s at Linnansuo and 45 s at Samoylov. To avoid initial large noise in the $c(t)$ data which would disturb the regressions seriously, we discarded data points at the start of the chamber deployment and delayed the start point of the experiment $t_0=0$. The discarding interval was 10 s at Salmisuo, 30 s at Linnansuo and 45 s at Samoylov. No data discarding was done for the Vaisjeaggi data. The chamber experiments were filtered to exclude data which appeared strongly disturbed. For Linnansuo data, a visual inspection of $c(t)$ curves was done, and curves that looked strongly disturbed were discarded right away (6.1% of the experiments). All datasets were filtered after regression analysis using the standard deviation of the residuals of the exponential regression function as indicator of experiment noise. Thresholds of residual standard deviation, which indicated unacceptable noise levels, were 1.6 ppm for Salmisuo, 1.2 ppm for Vaisjeaggi, 2.2 ppm for Linnansuo and 1.7 ppm for Samoylov. It should be noted that data screening and flux calculations of the already published data from Vaisjeaggi and Linnansuo was performed using different approaches than in this study (Nykänen et al, 2003; Shurpali et al., 2008).

Table 1. Overview of set-up characteristics for the different investigation sites Salmisuo, Vaisjeäggi, Linnansuo and Samoylov.

	Salmisuo	Vaisjeäggi	Linnansuo	Samoylov
chamber type	manual, transparent	manual, transparent	manual, opaque	manual, transparent
time schedule	24-hour runs	only daytime	only daytime	partly day, partly night
chamber basal area	0.36 m ²	0.36 m ²	0.075 m ²	0.25 m ²
chamber height	32 cm	25 cm	30 cm... 32 cm	5 cm... 15 cm
robust boardwalks	yes	yes	no	yes
permanent collars	yes	yes	no	yes
insertion depth of collar or chamber walls in soil	15 cm... 20 cm	15 cm... 30 cm	5 cm	10 cm... 15 cm
cooling system	yes	yes	no	no
air mixing	fan	fan	no	air cycling by pump
pressure relief provision	only during chamber setting	vent tube open over closure period	relief valve in function over closure period	only during chamber setting
CO ₂ analyser	LI-840, LI-COR	LI-6200, LI-COR	LI-6200, LI-COR	Gas monitor 1412, Innova Airtech Instruments
closure time	120 s	120 s... 160 s	150 s	480 s... 600 s
interval length	1 s	5 s	10 s	45 s
data discarding interval at experiment start	10 s	no	30 s	45 s
instrument noise RMSE	±0.5 ppm	±0.1 ppm	±0.3 ppm	±0.8 ppm
threshold of residual standard deviation used for coarse error filtering	1.6 ppm	1.2 ppm	2.2 ppm	1.7 ppm

Table 2. Goodness-of-fit statistics of linear (lin) and exponential (exp) regression curves for example datasets as shown in Fig. 3. Goodness of fit can be compared by the adjusted coefficient of determination R_{adj}^2 , the Akaike information criterion AIC_c (with small sample second order bias correction) and an F-test checking if the residual variance of the exponential regressions is smaller than that of the linear regression (P is significance level).

ID	site, date, time	R_{adj}^2		AIC_c		F-test
		lin	exp	lin	exp	Var(exp) < Var(lin)
A	Salmisuo, 13/09/2005, 13:10	0.994	0.998	-56	-180	$P < 0.0001$
B	Salmisuo, 18/8/2005, 10:40	0.994	0.996	-137	-177	$P < 0.05$
C	Salmisuo, 9/9/2005, 2:50	0.979	0.992	-54	-175	$P < 0.0001$
D	Salmisuo, 9/9/2005, 3:30	0.971	0.980	-136	-179	$P < 0.05$
E	Vaisjeäggi, 27/8/1998, 14:40	0.992	0.999	-83	-123	$P < 0.0001$
F	Vaisjeäggi, 22/6/1998, 15:00	0.998	0.9998	-85	-143	$P < 0.0001$

6 Results

6.1 Residual analyses

Examples of the observed $c(t)$ data and fits of the linear and exponential model are given in Fig. 3. The respective goodness-of-fit statistics are given in Table 2. Many of the measured $c(t)$ curves were clearly nonlinear even if chamber closure times were only 120 s (e.g. Fig. 3a–f). However, a rather large fraction of the nonlinear curves showed curvatures which were not consistent with the theoretical model

developed in Chapter 2 (e.g. Fig. 3b, d, f). A summary of the residual analyses for all chamber experiments from the four investigation sites is given in Table 3. The residual analyses were conducted for all regression functions without parameter restrictions. Thus, regression curves with curvatures not consistent with the theoretical model were also included. In general, the residual analyses showed that the exponential model was frequently significantly better suited than the linear model to describe the measured $c(t)$ evolution in the chamber headspace. However, a substantial fraction (20% to 40%) of the fitted curves showed curvatures which did

Table 3. Summary of residual analyses for the linear (lin), quadratic (qua) and exponential (exp) regression models applied to the datasets Salmisuo, Vaisjeäggi, Linnansuo and Samoylov. Autocorrelation of the residuals was examined with the *Durbin-Watson* test. If $d > d_U$, there is statistical evidence that the residuals are not positively autocorrelated ($P < 0.05$). If $d > d_L$, neither positive autocorrelation nor non-autocorrelation could be proved ($P < 0.05$). The *D'Agostino-Pearson* test was applied for checking normality of the residuals. If $P_N > 0.05$, no deviation from normal distribution could be detected. Goodness of fit of the linear (lin) and nonlinear (nlin) regression curves was compared by the adjusted coefficient of determination R_{adj}^2 , the Akaike information criterion AIC_c (with small sample second order bias correction) and an F-test checking if the residual variance of the nonlinear regressions is smaller than that of the linear regression ($P < 0.1$). The percentages of the experiments of a respective dataset which match the test conditions are given in the columns (n_e : total number of experiments in the respective dataset). Residual analyses were conducted for regression functions without parameter restrictions. For the exponential regression, percentages for regressions restricted to parameter combinations explainable by the theoretical model are given in parentheses.

		autocorrelation		normality	goodness-of-fit comparisons		
test		<i>Durbin-Watson</i>		<i>D'Agost.-Pearson</i>	adjusted R^2	Akaike Inf. Criterion.	F-test
test condition		$d > d_U$	$d > d_L$	$P_N > 0.05$	R_{adj}^2 (nlin) > R_{adj}^2 (lin)	AIC_c (nlin) < AIC_c (lin)	Var(nlin) < Var(lin)
		percentage of n_e (%)					
Salmisuo	lin	44	46	84	–	–	–
1 s intervals	qua	67	73	86	84	77	37
($n_e=542$)	exp	68	72	87	83 (63)	77 (58)	37 (30)
Vaisjeäggi	lin	10	12	87	–	–	–
5 s intervals	qua	30	47	93	90	86	60
($n_e=389$)	exp	30	48	92	89 (55)	86 (58)	60 (42)
Linnansuo	lin	27	44	90	–	–	–
10 s intervals	qua	48	88	93	79	66	33
($n_e=368$)	exp	49	88	92	78 (49)	64 (41)	36 (23)
Samoylov	lin	67	92	98	–	–	–
45 s intervals	qua	75	100	97	70	35	15
($n_e=465$)	exp	75	100	98	68 (43)	37 (26)	19 (15)

not conform to the theoretical model. The quadratic and the exponential model performed very similarly with respect to their residual statistics. The extent to which the nonlinear models were better suited than the linear model was different for the four datasets depending on the specifics of the respective experiment set-ups, i.e. measurement intervals, measurement noise, and presumably also by the ecosystem characteristics of the different sites.

Autocorrelation was less often detected by the Durbin-Watson test for the exponential and quadratic models than for the linear model. For the Salmisuo dataset, significant positive autocorrelation ($d > d_U$) could be excluded for 68% of the exponential regressions, 67% of the quadratic regressions and for only 44% of the linear regressions. For the Vaisjeäggi and Linnansuo datasets, autocorrelation was generally a bigger problem: For the Vaisjeäggi dataset, significant positive autocorrelation ($d > d_U$) could be excluded for 30% of the exponential regressions, 30% of the quadratic regressions and for only 10% of the linear regressions. For the Linnansuo dataset, significant positive autocorrelation ($d > d_U$) could be excluded for 49% of the exponential regressions, 48% of the quadratic regressions and for only 27% of the

linear regressions. For the Samoylov dataset, autocorrelation was less of a problem due to a lower number of data points and a higher noise level: Significant positive autocorrelation ($d > d_U$) could be excluded for 75% of the exponential and quadratic regressions and for 67% of the linear regressions.

Evaluated with the *D'Agostino-Pearson* test, normality of the residuals was found to be a minor problem compared to autocorrelation. For the Salmisuo dataset, 84% of the linear regressions, 86% of the quadratic regressions, and 87% of the exponential regressions showed normally distributed residuals. The percentages of regressions with normally distributed residuals are even greater for the other datasets with longer measurement intervals (Vaisjeäggi, Linnansuo, Samoylov). For Salmisuo, removal of autocorrelation by block-averaging also eliminated most of the non-normality problems in the residuals (data not shown).

The different goodness-of-fit indicators for regression model comparison R_{adj}^2 , AIC_c and the F-test of the residual variances showed rather differing results between the different indicators and datasets (Table 3). However, it could be demonstrated that for the majority of experiments of all datasets the exponential and quadratic models were

significantly better fitted than the linear model. For the Salmisuo dataset, R_{adj}^2 was greater for 84% of the quadratic regressions and 83% of the exponential regressions than for the respective linear regressions indicating a better fit. However, only 63% of the exponential regressions showed a greater R_{adj}^2 than the linear regressions while also showing a curvature conforming with the theoretical model. The AIC_c appeared to penalize somewhat stronger the higher number of parameters in the nonlinear models than the R_{adj}^2 : The AIC_c was smaller for only 77% of the quadratic and exponential regressions than for the respective linear regressions indicating a better fit. The F-test of the residual variances indicated that the quadratic and exponential regressions had a significantly ($P < 0.1$) lower residual variance than the respective linear regressions for 37% of the Salmisuo experiments. Thirty percent of the exponential regressions had a significantly lower residual variance than the linear regressions while also showing a curvature conforming with the theoretical model.

Compared to Salmisuo, the Vaisjäggi dataset showed a greater percentage of experiments which were better fitted by the nonlinear regressions than the linear regression. The F-test of the residual variances proved that the quadratic and exponential regressions had a significantly ($P < 0.1$) lower residual variance than the respective linear regressions for 60% of the Vaisjäggi experiments. 42% of the exponential regressions had a significantly lower residual variance than the linear regressions while also showing a curvature conforming with the theoretical model.

The percentage of the Linnansuo experiments which were better fitted by the nonlinear than by the linear model was comparable to that of the Salmisuo dataset. However, rather many of these regressions showed curvatures not consistent with the theoretical model.

The Samoylov data set showed a lower percentage of experiments which were better fitted by the nonlinear than by the linear model compared to the other datasets. The F-test of the residual variances indicated that the quadratic and exponential regressions had a significantly ($P < 0.1$) lower residual variance than the respective linear regressions for only 15% and 19% of the Samoylov experiments, respectively. Only 15% of the exponential regressions had a significantly lower residual variance than the linear regressions while also showing a curvature conforming with the theoretical model.

The F-test of the residual variances revealed that the residual variance of the linear regression was never significantly ($P < 0.1$) lower than the residual variances of the nonlinear regressions in all four datasets (data not shown). Furthermore, the residual variance of the exponential regression was only significantly smaller than the residual variance of the quadratic regression in less than 1% of the experiments of all datasets (data not shown).

An F-test of the residual variances of the exponential and the NDFE function (Livingston et al., 2006) fitted to the Linnansuo data showed that less than 1% of 335 $c(t)$ curves

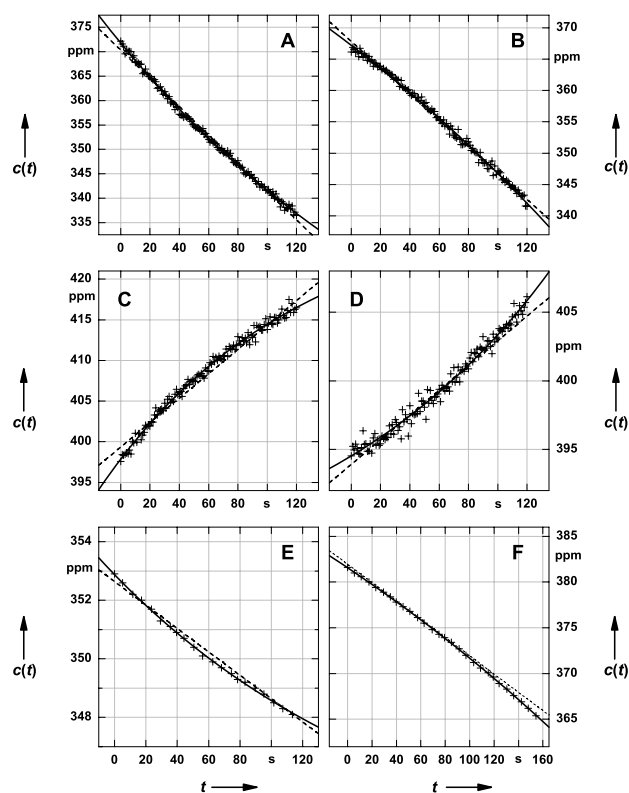


Fig. 3. Examples of the CO₂ concentration $c(t)$ evolution within the chamber and fitted linear and exponential functions. (A) Salmisuo, 13 September 2005 13:10 LT, (B) Salmisuo, 18 August 2005 10:40 LT, (C) Salmisuo, 9 September 2005 03:30 LT, (D) Salmisuo, 9 September 02:50 LT, (E) Vaisjäggi, 27 August 1998 14:40 LT, (F) Vaisjäggi, 22 June 1998 15:00 LT. The dashed lines indicate linear regression functions f_{lin} , the solid lines indicate exponential regression functions f_{exp} . (A), (C) and (E) show exponential regression functions with curvature consistent with the developed theoretical model. (B), (D) and (F) show exponential regression functions with curvature not consistent with the theoretical model. Statistics for the regression functions are given in Table 2.

were significantly ($P < 0.1$) better fitted by the NDFE function compared to the exponential regression function whereas 13% of the $c(t)$ curves were significantly ($P < 0.1$) better fitted by the exponential model (data not shown).

6.2 The effect of different regression models on the flux estimates

A comparison of the initial slopes of the linear and exponential regression functions $f'_{\text{lin}}(t_0)$ and $f'_{\text{exp}}(t_0)$ by x - y scatter diagrams is shown in Fig. 4 for all investigation sites. The initial slopes of the regression functions are directly proportional to the CO₂ flux at the beginning of chamber closure $F_{\text{net}}(t_0)$ which is considered to be the best estimate of the undisturbed flux before chamber closure (Eq. 20). Considering the exponential model as more correct, deviating values

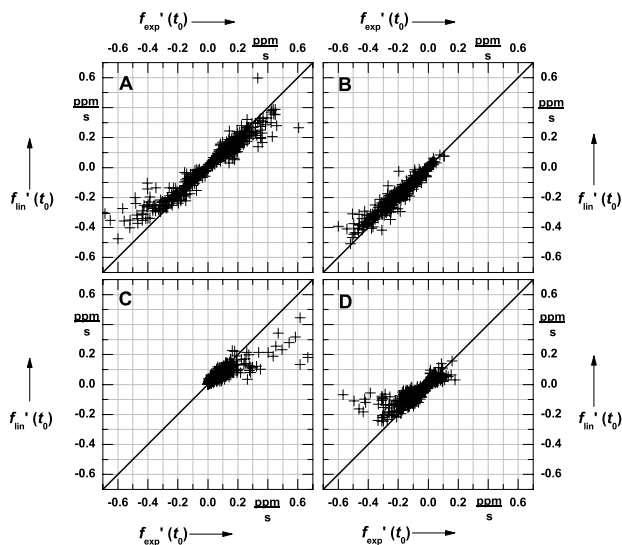


Fig. 4. Comparison of initial slopes of the linear and exponential regression curves for the different investigation sites. (A) Salmisuo, (B) Vaisjeaggi, (C) Linnansuo, (D) Samoylov. On the x-axes, the initial slopes of the exponential regression $f'_{\text{exp}}(t_0)$ are plotted. On the y-axes, the initial slopes of the linear regression curves $f'_{\text{lin}}(t_0)$ are plotted. The $y=x$ relationship is given as solid line. As the initial slopes of the regression curves are directly proportional to the CO₂ flux estimates, a deviation between $f'_{\text{lin}}(t_0)$ and $f'_{\text{exp}}(t_0)$ indicates a bias of the CO₂ flux estimate by the application of the linear model presuming that the undisturbed CO₂ fluxes are better reflected by the exponential model.

of $f'_{\text{lin}}(t_0)$ and $f'_{\text{exp}}(t_0)$ would represent a bias of the CO₂ flux estimate by the linear regression approach. As illustrated in Fig. 4, $f'_{\text{lin}}(t_0)$ and $f'_{\text{exp}}(t_0)$ partly deviated considerably from each other, in particular for great values of the initial slopes. Mostly, the absolute values of $f'_{\text{lin}}(t_0)$ were smaller than the absolute values of $f'_{\text{exp}}(t_0)$, which means an underestimation bias of the linear regression approach both for CO₂ uptake and CO₂ release situations, which is expected by the theoretical exponential model. However, the inverse relationship was also frequently observed, which means an overestimation bias by the linear regression compared to the exponential regression, which indicated apparent violations of the basic assumptions of the theoretical model. The effect of the underestimation of the absolute values of the initial slopes increased with increasing absolute values of the initial slopes and thus with increasing absolute values of CO₂ fluxes. The underestimation bias by linear regression could be observed for all four datasets although to different degrees. The strongest underestimation effects were found for the Linnansuo and Samoylov datasets (Fig. 4c, d). For high absolute values of the initial slopes in these datasets, $f'_{\text{lin}}(t_0)$ could be as low as 50% or even 20% of the values of $f'_{\text{exp}}(t_0)$. On the other hand, the weakest effects were found for the Vaisjeaggi dataset (Fig. 4b). Also for highest absolute val-

ues of the initial slopes in this dataset, $f'_{\text{lin}}(t_0)$ was not below 60% of the value of $f'_{\text{exp}}(t_0)$. The Salmisuo dataset was intermediate in this regard (Fig. 4a). For high absolute values of the initial slope in these datasets, $f'_{\text{lin}}(t_0)$ was often between 40% and 80% of the value of $f'_{\text{exp}}(t_0)$. Salmisuo is the only dataset with nearly equally distributed numbers of experiments for CO₂ uptake and CO₂ release situations. For this dataset, it could be observed that the underestimation effect of the linear regression was on average stronger for CO₂ uptake situations than for CO₂ release situations.

An overview of the significances of the deviations between $f'_{\text{lin}}(t_0)$ and $f'_{\text{exp}}(t_0)$ is given in Table 4. The percentages of experiments with significant (*Student's t-test*, $P < 0.1$) deviations between $f'_{\text{lin}}(t_0)$ and $f'_{\text{exp}}(t_0)$ are listed separately for situations with underestimation (H1) and overestimation (H2) by the linear regression. The absolute values of $f'_{\text{exp}}(t_0)$ were significantly greater than the absolute values of $f'_{\text{lin}}(t_0)$ (H1 is true at $P < 0.1$) for 57% of the Salmisuo experiments, 55% of the Vaisjeaggi experiments, 42% of the Linnansuo experiments and only 29% of the Samoylov experiments. These portions of experiments showed that a nonlinearity of an exponential form as predicted by the theoretical model often produced a significant underestimation effect of the initial slopes by linear regression. On the other hand, the absolute values of $f'_{\text{exp}}(t_0)$ were significantly smaller than the absolute values of $f'_{\text{lin}}(t_0)$ (H2 is true at $P < 0.1$) for 19% of the Salmisuo experiments, 30% of the Vaisjeaggi experiments, 26% of the Linnansuo experiments and 19% of the Samoylov experiments. These portions of experiments were not consistent with the theoretical model because of their curvature but showed that unexplained nonlinearity can occur and can cause a significant overestimation effect of the initial slopes by linear regression. The absolute values of $f'_{\text{exp}}(t_0)$ and $f'_{\text{lin}}(t_0)$ did not deviate significantly from each other (H0 could not be rejected at $P < 0.1$) for 24% of the Salmisuo experiments, 14% of the Vaisjeaggi experiments, 32% of the Linnansuo experiments and 52% of the Samoylov experiments. Thus, although the nonlinearity effects on the flux estimates of the Linnansuo and Samoylov datasets were pronounced, they were significant for a rather small percentage of experiments compared to the Salmisuo and Vaisjeaggi datasets. On the other hand, the Vaisjeaggi dataset had a high percentage of significant effects on the flux estimates but these effects were comparatively moderate. Here, the importance of the closure time, measurement interval length, and instrument precision (Table 1) on the nonlinearity problem became obvious.

A comparison of the initial slopes of the quadratic and the exponential regression functions $f'_{\text{qua}}(t_0)$ and $f'_{\text{exp}}(t_0)$ by x - y scatter diagrams is shown in Fig. 5 for all investigation sites. An overview of the significances of the deviations between $f'_{\text{qua}}(t_0)$ and $f'_{\text{exp}}(t_0)$ is given in Table 5. The initial slopes $f'_{\text{qua}}(t_0)$ and $f'_{\text{exp}}(t_0)$ differ significantly ($P < 0.1$) for only 5%–9% of the experiments of the four datasets. However,

Table 4. Significance of deviations between the slope estimates at $t=0$ as yielded by the exponential $f'_{\text{exp}}(t_0)$ and linear $f'_{\text{lin}}(t_0)$ regression models. The hypothesis H1 states that the absolute value of the initial slope of the exponential regression is greater than the absolute value of the initial slope of the linear regression. The hypothesis H2 states that the absolute value of the initial slope of the exponential regression is smaller than the absolute value of the initial slope of the linear regression. The null hypothesis H0 states that the absolute value of the initial slope of the exponential regression is equal to the absolute value of the initial slope of the linear regression. While H1 is conforming with the developed theoretical model, H2 is not which implies the occurrence of disturbing processes not considered by the model. The hypotheses were tested by one-tailed *Student's* t-tests ($P < 0.1$) following Potthoff (1965, cited in Sachs, 1992). The percentages of the experiments of a respective dataset for which the respective hypotheses could be confirmed are given in the columns (n_e : total number of experiments in the respective dataset).

	<i>Student's</i> t-test of hypotheses ($P < 0.1$)		
	H1: $ f'_{\text{exp}}(t_0) - f'_{\text{lin}}(t_0) > 0$	H2: $ f'_{\text{exp}}(t_0) - f'_{\text{lin}}(t_0) < 0$	H0: $ f'_{\text{exp}}(t_0) - f'_{\text{lin}}(t_0) = 0$
	percentage of n_e (%)		
Salmisuo ($n_e=542$)	57.4	18.5	24.2
Vaisj�aggi ($n_e=389$)	55.3	30.3	14.4
Linnansuo ($n_e=368$)	42.4	25.8	31.8
Samoylov ($n_e=465$)	29.0	19.3	51.6

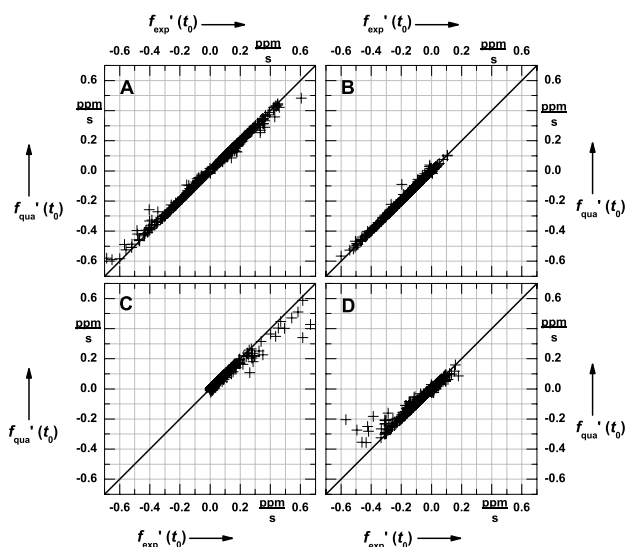


Fig. 5. Comparison of initial slopes of the exponential and quadratic regression curves for the different investigation sites. (A) Salmisuo, (B) Vaisj aggi, (C) Linnansuo, (D) Samoylov. On the x-axes, the initial slopes of the exponential regression $f'_{\text{exp}}(t_0)$ are plotted. On the y-axes, the initial slopes of the quadratic regression curves $f'_{\text{qua}}(t_0)$ are plotted. The $y=x$ relationship is given as solid line. As the initial slopes of the regression curves are directly proportional to the CO₂ flux estimates, a deviation between $f'_{\text{qua}}(t_0)$ and $f'_{\text{exp}}(t_0)$ indicates a bias of the CO₂ flux estimate by the application of the quadratic model presuming that the undisturbed CO₂ fluxes are better reflected by the exponential model.

the quadratic regression functions tended to show lower absolute values of the initial slopes than the exponential regression functions, in particular for situations with strong CO₂ uptake or release. The underestimation of the absolute value of the initial slope of the quadratic regression compared to the exponential regression was strongest for the Linnansuo and Samoylov datasets and lowest for the Vaisj aggi dataset. The Salmisuo dataset was intermediate in this regard.

A comparison of the initial slopes of the exponential $f'_{\text{exp}}(t_0)$ and the NDFE function proposed by Livingston et al. (2005, 2006) $f'_{\text{NDFE}}(t_0)$ by x - y scatter and diagrams is shown in Fig. 6 for the non-vegetated peat excavation site Linnansuo. The $f'_{\text{NDFE}}(t_0)$ was generally higher as $f'_{\text{exp}}(t_0)$. The steeper the fluxes and thus the initial slopes the stronger was the deviation between $f'_{\text{exp}}(t_0)$ and $f'_{\text{NDFE}}(t_0)$. The $f'_{\text{NDFE}}(t_0)$ was often 1.5 to 3 times higher than $f'_{\text{exp}}(t_0)$ and in extreme cases up to 10 fold higher.

7 Discussion

This study presents the first derivation of a theory-based model function of gas concentration changes over time $c(t)$ in closed chambers above vegetated land surfaces. Residual analyses demonstrated that the developed exponential model could be significantly better fitted to the data than the linear model even if closure times were kept short, for example two minutes as for the Salmisuo experiments. On the other hand, application of linear regression was often not appropriate and led to underestimation of the absolute values of the initial slope of the $c(t)$ curves and thus of the CO₂ flux estimates. The exponential model was not significantly better fitted than the quadratic model with respect to the residual

Table 5. Significance of deviations between the slope estimates at $t=0$ as yielded by the exponential $f'_{\text{exp}}(t_0)$ and linear $f'_{\text{qua}}(t_0)$ regression models. The hypothesis H1 states that the difference between the initial slopes of the exponential and quadratic regression is significantly different from zero. The null hypothesis H0 states that the difference between the initial slopes of the exponential and quadratic regression are not significantly different from zero. The hypotheses were tested by a two-tailed *Student's* t-test ($P < 0.1$) following Potthoff (1965, cited in Sachs, 1992). The percentages of the experiments of a respective dataset for which the respective hypotheses could be confirmed are given in the columns (n_e : total number of experiments in the respective dataset).

	<i>Student's</i> t-test of hypotheses ($P < 0.1$)	
	H1: $f'_{\text{exp}}(t_0) - f'_{\text{qua}}(t_0) \neq 0$	H0: $f'_{\text{exp}}(t_0) - f'_{\text{qua}}(t_0) = 0$
	percentage of n_e (%)	
Salmisuo ($n_e=542$)	7.2	92.8
Vaisjeaggi ($n_e=389$)	8.7	91.3
Linnansuo ($n_e=368$)	7.6	92.4
Samoylov ($n_e = 465$)	4.7	95.3

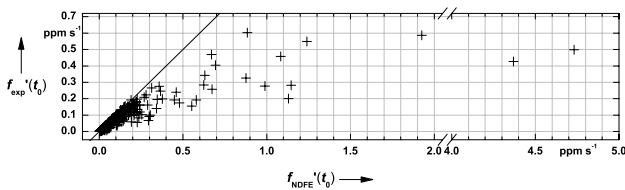


Fig. 6. Comparison of initial slopes of the NDFE (Livingston et al., 2006) and the exponential regression curves for the non-vegetated peat excavation site Linnansuo. On the x-axes, the initial slopes of the NDFE regression function $f'_{\text{NDFE}}(t_0)$ are plotted. On the y-axes, the initial slopes of the exponential regression curves $f'_{\text{exp}}(t_0)$ are plotted. The $y=x$ relationship is given as solid line. The NDFE curves have drastically higher initial slopes than the exponential curves particularly for high fluxes. Notice the break in the x-axis.

analyses. However, the absolute values of initial slopes of the $c(t)$ curves were often systematically lower for the quadratic compared to the exponential regression function. The exponential model could be better fitted to the $c(t)$ curves observed on the non-vegetated peat excavation site Linnansuo than the physically most profound NDFE model function proposed by Livingston et al. (2005, 2006). This can be explained by the probable serious violations of the underlying model assumptions of the NDFE model, in particular by the likely leakage through the peat pore space since no permanent collars were installed at Linnansuo. The great difference between the initial slopes of the NDFE and the exponential model demonstrates the sensibility of CO₂ flux estimation to the choice of the applied model. If applying physically based nonlinear models, violations of model assumptions have to be minimised with great care.

Modelling of the CO₂ concentration changes over time in chamber headspaces is more complicated for vegetated surfaces than for bare soil surfaces since additional processes

such as photosynthesis and plant respiration have to be considered. The complex processes in plants and soils had to be substantially simplified for the development of a model that is simple enough for nonlinear regression of actual, often noisy data. Furthermore, some strong assumptions have to be made as basis for such a model development: Soil and headspace air temperature, photosynthetically active radiation, air pressure and headspace turbulence were assumed to be constant and approximately equal to ambient conditions. Apparently, however, these assumptions were not valid for all experiments. Whereas the majority of fitted $c(t)$ curves were consistent with the proposed theoretical model, a substantial fraction of the experiments were not. These unexplainable curvatures are considered to have been caused by violations of the basic assumptions of the theoretical model. The obvious violation of model assumptions indicates that the experiment design was sub-optimal and that the reason for it must be identified and accounted for. Otherwise, the calculated fluxes would be biased to an unknown extent. As at least the closed chambers at Salmisuo and Vaisjeaggi were temperature-controlled by an effective cooling system, we consider the change in headspace turbulence by the closed chamber, which is not yet covered by the theoretical model, as a likely problematic process which could introduce non-linearity difficult to model. An additional reason for the unexplainable curvature could have been small positive pressure perturbations during chamber placement (Hutchinson and Livingston, 2001). Although the possible disturbing effects of altering turbulence or pressure conditions by closed chambers were discussed previously by several studies (Hanson et al., 1993; Le Dantec et al., 1999; Hutchinson et al., 2000; Livingston and Hutchinson, 2001; Denmead and Reicosky, 2003; Reicosky, 2003; Livingston et al., 2006), additional investigations are certainly needed concerning these issues.

To evaluate the validity of candidate models, we recommend the use of residual analysis including tests for autocorrelation and normality. In particular, autocorrelation has to be excluded for unbiased estimates of the uncertainty of regression parameters. Goodness of fit can be evaluated by the adjusted nonlinear coefficient of determination R^2_{adj} , the Akaike Information Criterion AIC and by an F-test of the residual variances.

We note that the linear coefficient of determination r^2 was frequently misused during the history of closed chamber measurements. The linear r^2 and the nonlinear R^2 are neither appropriate measures of regression model correctness (often used for checking linearity) nor appropriate filter criteria for measurement performance (Granberg et al., 2001; Huber, 2004; Hibbert, 2005). The expressions $(1-r^2)$ and $(1-R^2)$ are measures of the unexplained variance normalized to the total variance. The significance of r^2 and R^2 is strongly dependent on the number of data points n which is often disregarded. In extreme cases, the r^2 values were calculated for only three data points and were considered as evidence of linearity when greater than typically 0.95. However, applying the F-test to check if a R^2 value of 0.95 for three data points is significantly different from zero reveals an error probability P of 0.14, which is higher than the typically used significance levels of 0.05 or 0.1. Furthermore, even an R^2 value significant at the 0.05 level does not prove linearity and cannot exclude serious bias of the flux estimates. A linear regression can show a rather high r^2 value of above 0.99 although significant nonlinearity can be demonstrated by more appropriate statistical methods like the F-test for the residual variances (Huber, 2004; Hibbert, 2005). Only for comparison of two regression functions with the same numbers of data points n and parameters k , r^2 or R^2 can give an indication which function is better suited. Moreover, r^2 as well as R^2 are not usable as filter criteria for measurement performance because they arbitrarily discriminate the lower fluxes: r^2 and R^2 values increase with constant unexplained variance and increasing total variance which is inherently higher for greater fluxes (Fig. 7a). In this context, a better filter criterion would be the standard deviation of the residuals s_{yx} (Fig. 7b).

The measurement interval length, the number of measurement points and the precision of the CO₂ concentration measurements determine whether the nonlinearity can be detected with sufficient statistical significance. It has to be stressed that strong nonlinearity can be present even when it cannot be detected because of long measurement intervals, few data points or low measurement precision.

Considering the results of this study, a list of practical recommendations for closed chamber measurements follows:

- A nonlinear model should be favoured over a linear model to reflect the various biophysical processes in effect and thus to better estimate the predeployment flux.

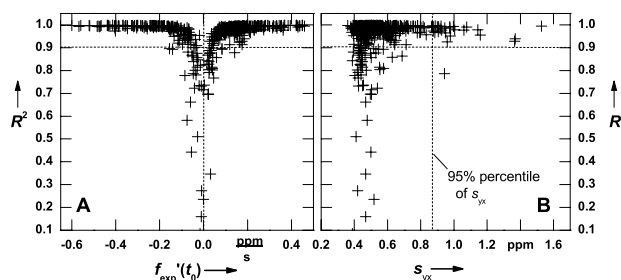


Fig. 7. The relationships of the nonlinear coefficient of determination R^2 with the initial slope $f'_{\text{exp}}(t_0)$ of the regression function and the standard deviation of the residuals s_{yx} exemplified by the dataset Salmisuo 2005. **(A)** The R^2 value is plotted against the initial slope $f'_{\text{exp}}(t_0)$. The use of R^2 as a filter criterion (e.g. $R^2=0.9$) would discriminate strongly the regressions with low slope values $f'_{\text{exp}}(t_0)$. **(B)** The R^2 value is plotted against the standard deviation of residuals s_{yx} which is a better filter criterion for measurement performance. The application of R^2 (e.g. $R^2=0.9$) or s_{yx} (e.g. the 95% percentile of s_{yx} : 0.87 ppm) as filter criteria would identify completely different experiments as disturbed.

- We recommend to fit an exponential function as given in Eq. (14) to the observed $c(t)$ curves for experiments on vegetated soils. For experiments on non-vegetated soils, the NDFE model function proposed by Livingston et al. (2005, 2006) should be applied. When applying the NDFE model, however, violations of the underlying assumptions of the NDFE model, i.e. no-leakage, must be strictly avoided.
- When adopting a nonlinear approach, investigators should employ chambers with smaller headspace volumes and longer deployment times as warranted to emphasize the non-linearity of the $c(t)$ response. For vegetated soils, however, the advantages of this approach must be carefully balanced with the risk of unpredictable plant responses due to strongly lowered CO₂ concentrations or artificially high water vapour contents in the chamber headspace.
- Light, temperature and humidity conditions as well as wind speed and turbulence during chamber closure should be as similar as possible to the ambient conditions. Changes of light, temperature and humidity would change plant physiology and thus complicate the form of the $c(t)$ curve whereas artificial changes of pressure, wind and turbulence may additionally impact transport processes and thus even compromise the assumption that the initial slope of the $c(t)$ is the best estimator of the predeployment CO₂ flux (Hutchinson et al., 2000; Hutchinson and Livingston, 2001).
- Generally, leaks should be avoided (Hutchinson and Livingston, 2001; Livingston et al., 2006). If this is not possible, fitting of an exponential function would allow

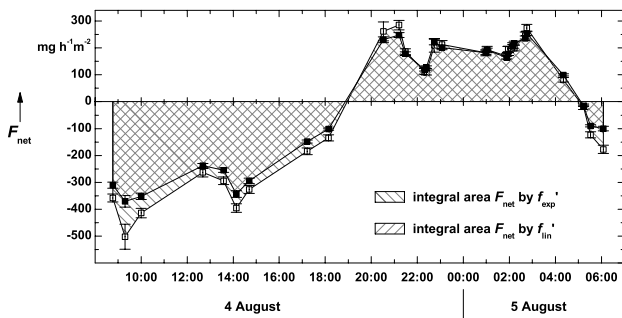


Fig. 8. Example of the effect of the different regression approaches on the estimated CO₂ balance over one diurnal cycle (04/08/2005 08:45 to 05/08/2005 06:05 LT) at the flark sites of Salmisuo. The black squares indicate CO₂ flux estimates F_{net} by the linear model approach, the white squares indicate CO₂ flux estimates F_{net} by the exponential model approach. The error bars indicate the standard errors of the flux estimates. Simple integrations of the two CO₂ flux estimate time series according to the trapezoidal rule yield carbon balances over the 21.33 h of -0.86 g CO_2 and -1.30 g CO_2 for the linear and exponential model approaches, respectively. Thus, the estimate of CO₂ uptake using the exponential model is 150% of the estimate using the linear model!

for better approximation of the initial slopes of the $c(t)$ curves and thus for more realistic estimation of predeployment fluxes compared to linear regression.

- High noise levels at the start of the chamber deployment due to eventual pressure or turbulence disturbances or insufficient purging of residual gases in the analyser lines have to be avoided since this noise would be very critical regarding the results of nonlinear regression. If initial noise is obviously present, the data from the respective time period has to be discarded, and the starting time of the experiment $t_0=0$ should be delayed accordingly. It has to be stressed that this initial data discarding would lead to inherent underestimation of fluxes because the slope of the $c(t)$ evolution curve is expected to be greatest and changing most strongly at the start of the chamber closure time (Hutchinson et al., 2000; Livingston et al., 2006, this study). Still, this underestimation would be less when applying a nonlinear model compared to the use of linear regression. Anyhow, experimental set-ups should be improved to make an initial data discarding unnecessary. The interval of initial data discarding must be as short as possible.
- When using the presented exponential or quadratic regression functions (number of parameters $k=3$), not less than seven data points ($n \geq 7$) should be collected over the closure time to achieve an acceptable value for the degrees of freedom ($n-k \geq 4$). More data points are recommended, particularly if the measurement precision is not optimal.

- The better the measurement precision and the more data points are available for the regression, the better the nonlinearity can be detected and its significance demonstrated.
- Autocorrelation and non-normality of residuals should be checked for and can be reduced by block-averaging to avoid biased estimations of parameters and their errors.

One scientific question for which the possible bias of closed chamber CO₂ flux measurements is important is the comparison of micrometeorological eddy covariance data and chamber data where often a considerable mismatch can be observed. Mostly, this mismatch is attributed to methodological problems of the eddy covariance approach (e.g. Law et al., 1999; Van Gorsel et al., 2007). While the methodological problems of the eddy covariance method are undoubtedly real, it has to be stated that also the flux estimates by closed chambers can be prone to significant biases and should be interpreted using much caution (see also Reicosky, 2003; Livingston et al., 2005, 2006).

The underestimation effect by linear and quadratic regression compared to exponential regression increases with increasing absolute values of the CO₂ fluxes. Thus, the underestimation of the CO₂ fluxes by the linear regression method not only disturbs the quantitative but also the qualitative evaluations since differences between sites with strong and weak CO₂ exchange would be smoothed. Furthermore, the effect should be dependent on ecosystem characteristics such as soil texture, peat density, soil moisture status or vegetation composition (Hutchinson et al., 2000; Nakano et al., 2004). Here, the uneven underestimation bias between sites can lead to the conclusion that CO₂ fluxes differ greatly between sites although, in fact, only the response to the chamber disturbance on of soil gas diffusion and plant physiology differs.

As the underestimation of the absolute values of the initial slope of the $c(t)$ curves by linear regression was observed to be of different magnitude for CO₂ uptake and CO₂ release situations, there is a high potential for serious bias of carbon balances which can, in extreme cases, lead to changing of the sign, which determines an ecosystem as CO₂ source or sink. This high potential for serious bias of the CO₂ balances is exemplified by Fig. 8 for a diurnal cycle of CO₂ exchange fluxes at the flark sites of Salmisuo. The bias on the daily balance can be very large because it is equal to the sum of integrated daytime uptake and integrated night time release. The sum is much smaller than the two summands due to their similar magnitude but opposing signs. If the bias of one summand is stronger than for the other summand, the relative bias of the balance can be much more pronounced than the relative bias of the respective summands. This high sensitivity of the CO₂ balance to asymmetric biases of CO₂ uptake and CO₂ release is of major importance as closed chamber CO₂ flux measurements based on linear regression are used for local, regional and global carbon budgets and for the evaluation

of the carbon source or sink characteristics of ecosystems or even vegetation zones (e.g. Oechel et al., 1993, 1998, 2000).

In this context, we fully agree with Hutchinson et al. (2000) and Livingston et al. (2005, 2006) who emphasised that the bias of flux estimates by using linear regression for closed chamber experiments is systematic, not random. Therefore, “although such errors are relatively small in comparison to the temporal and spatial variability characteristic of trace gas exchange, they bias the summary statistics for each experiment as well as larger scale trace gas flux estimates based on them” (Hutchinson et al., 2000).

8 Conclusions

Thorough analyses of residuals demonstrate that linear regression is frequently not appropriate for the determination of CO₂ fluxes by closed-chamber methods, even if closure times are kept short.

The coefficient of determination R^2 should not be used as proof of linearity. For comparing the performance of models, goodness-of-fit measures such as the adjusted R^2 , the Akaike Information Criterion or an F-test of the residual variances are recommended. Additionally, the residuals should be checked for autocorrelation and normality to allow for unbiased estimations of the parameters and their errors.

The assumptions inherent in the proposed exponential model fit the majority of the observations examined in this investigation, thus suggesting the potential value of biophysical models in future chamber-based emissions studies.

However, the curvature of the nonlinear $c(t)$ curves is for a substantial percentage of the experiments not explainable with the proposed theoretical model. This is considered to be caused by violations of the basic assumptions of the theoretical model. In particular, the effects of turbulence alteration and pressure disturbances across the soil-atmosphere interface by setting a closed chamber on the ecosystem should be investigated in more detail in the future.

In many cases, a quadratic model as proposed by Wagner et al. (1997) can be equally well fitted to the data as the exponential model. However, the estimates of the absolute values of the initial slopes of the $c(t)$ curves tended to be systematically lower for quadratic than the exponential regression. This can have a considerable effect on the CO₂ flux estimates for situations with strong CO₂ uptake or release.

The NDFE model proposed by Livingston et al. (2005, 2006) could not be better fitted to the $c(t)$ observations at the bare peat site Linnansuo than the exponential function. This was probably due to violations of the NDFE model assumptions, in particular the required non-existence of leakage.

Inappropriate application of linear regression can lead to serious underestimation of CO₂ fluxes. Initial slopes of linear regression can be as low as 40 % of the initial slope of exponential regression for closure times of only 2 min.

The degree of underestimation increased with increasing CO₂ flux strength and is dependent on soil and vegetation conditions which can disturb not only quantitative but also qualitative evaluation of CO₂ flux dynamics.

The underestimation effect by linear regression was observed to be different for CO₂ uptake and CO₂ release situations which can lead to stronger bias in the daily, seasonal and annual CO₂ balances than in the individual fluxes.

The fitting of observed closed-chamber data to biophysical models in combination with thorough statistical tests of the different models' validities offers at least two major advantages over the simple use of linear regression: (1) the ability to control the quality of observations, detect major problems of the methodology and thus to improve experimental protocols, and (2) improved accuracy and lower uncertainty in resultant flux estimates.

To avoid serious bias of CO₂ balance estimates on the local, regional or even global scale, we suggest further tests for biases of published flux estimates and recommend the use of nonlinear regression models for future closed-chamber studies.

We developed a MATLAB[®] routine which can perform linear and nonlinear regression including residual analyses for data of a wide range of chamber experiment setups. This routine is available online at <http://biogeo.botanik.uni-greifswald.de/index.php?id=264>.

Appendix A

Symbols and abbreviations

A	basal area of the chamber
a, b, c	parameters of polynomials of different order
AIC_c	Akaike information criterion with small sample second order bias correction
B	integral constant
c_a	CO ₂ concentration in the air outside of the chamber
c_d	CO ₂ concentration at depth d
$c(t)$	CO ₂ concentration of the headspace air at time t
d	unknown depth below the surface where the CO ₂ concentration is constant and not influenced by the chamber deployment
d	Durbin-Watson test statistic
d_L	lower critical value of Durbin-Watson test
d_U	upper critical value of Durbin-Watson test
D	soil CO ₂ diffusivity
d_{chamber}	distance between headspace and the surrounding air
D_{chamber}	mean diffusivity of leaks directly at the chamber components
d_{Soil}	distance between the headspace and the surrounding air via the air-filled soil pore space
D_{Soil}	mean diffusivity of leaks by air-filled soil pore space
$dc/dt(t)$	change of the CO ₂ concentration over time
$\varepsilon(t)$	residual error at time t
ε_i	residuals of the fitted model
$\varepsilon_{i-\text{exp}}$	residuals of the exponential regression
$\varepsilon_{i-\text{lin}}$	residuals of the linear regression
f_{exp}	exponential function
f_{lin}	linear function
f_{qua}	quadratic function
f'_{exp}	initial slope of exponential function
f'_{lin}	initial slope of linear function
f'_{qua}	initial slope of quadratic function
F_{Leak}	CO ₂ flux through leaks
F_{net}	net CO ₂ flux into the chamber
F_P	CO ₂ flux by photosynthesis
F_R	CO ₂ flux by respiration
F_{Soil}	CO ₂ efflux from the soil
k	number of parameters of the regression function
K_{Leak}	constant which combines D_{chamber} , d_{chamber} , D_{Soil} , and d_{soil} and indicates leakage strength
k_p	constant of proportionality between CO ₂ concentration and photosynthesis-associated flux
LT	local time
n	number of data points of the respective experiment
p	air pressure
p_1, p_2, p_3	parameters of exponential model
P	significance level of tests
R	ideal gas constant
r^2	linear coefficient of determination
R^2	nonlinear coefficient of determination
R^2_{adj}	adjusted nonlinear coefficient of determination
$s_{y,x}$	standard deviation of the residuals
t	time
t_0	start time of chamber closure
T	temperature
V	volume of the chamber

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