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CO_2 flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression

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Abstract

Closed (non-steady state) chambers are widely used for quantifying carbon dioxide (CO_2) 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 CO_2 fluxes by altering the concentration gradients between the soil, the vegetation and the overlying air. Thus, the driving factors of CO_2 fluxes are not constant during the closed chamber experiment, and no linear increase or decrease of CO_2 concentration over time within the chamber headspace can be expected. Nevertheless, linear regression has been applied for calculating CO_2 fluxes in many recent, partly influential, studies. This approach was 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 CO_2 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 CO_2 flux measurements (total number: 1764) conducted at three peatland sites in Finland and a tundra site in Siberia. The flux measurements were performed using transparent chambers on vegetated surfaces and opaque chambers on bare peat surfaces. Thorough analyses of residuals demonstrated that linear regression was frequently not appropriate for the determination of CO_2 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 $c(t)$ evolution in the chamber headspace and estimation of the initial CO_2 fluxes at closure time for the majority of experiments. CO_2 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 and even lower for longer closure times. The degree of underestimation increased with increasing CO_2 flux strength and is dependent on soil and vegetation conditions which can disturb not only the quantitative but also the qualitative evaluation

of CO_2 flux dynamics. The underestimation effect by linear regression was observed to be different for CO_2 uptake and release situations which can lead to stronger bias in the daily, seasonal and annual CO_2 balances than in the individual fluxes. To avoid serious bias of CO_2 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 (CO_2) 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 approaches are used to determine CO_2 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 CO_2 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 CO_2 exchange (NEE) 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.) temperature changes of the soil and the atmosphere beneath the chamber (Wagner and Reicosky, 1992; Drösler, 2005), (2.) 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), (3.) suppression of the natural pressure fluctuations (Hutchinson and Mosier, 1981; Conen and Smith, 1998; Hutchinson and Livingston, 2001), (4.) inaccurate determination of the headspace volume (Conen and Smith, 2000; Rayment, 2000), (5.) leakage directly at the chamber components or via the soil pore space, and (6.) the concentration build-up or reduction in the chamber headspace which inherently disturb the normal fluxes. This study deals exclusively with the latter problem, which can lead to serious bias of CO_2 fluxes if not accounted for, even if all other potential errors were kept at minimum.

The closed chamber methodology estimates the CO_2 fluxes by analysing the rates of CO_2 accumulation or depletion in the chamber headspace over time. However, every change of the CO_2 concentration from the normal ambient conditions feeds back on the CO_2 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 CO_2 flux, not the mean rate of the CO_2 concentration change over the chamber closure period but the rate of initial concentration change at the start of the closure period t ($t=t_0=0$) should be used, when the alteration of the headspace air is minimal (Livingston and Hutchinson, 1995). This problem has been discussed at length in the history of using closed chambers for the investigation of trace gas fluxes. However, most published work using non-linear regression has focussed on determining the efflux of trace gases including CO_2 from bare soils based on models derived from diffusion theory (Matthias et al., 1978; Hutchinson and Mosier, 1981; Healy et al., 1996; Hutchinson et al., 2000; Pedersen, 2000; Pedersen et al., 2001; Hutchinson and Livingston, 2001; Welles et al., 2001; Nakano et al., 2004; Livingston et al., 2005, 2006). On the other hand, only few researchers have applied nonlinear models to determine CO_2 exchange fluxes on vegetated surfaces (Dugas et al., 1997; Wagner et al., 1997; Steduto et al., 2002). Most of the recent studies on the CO_2 balance of vegetated surfaces and many studies on the CO_2 efflux from bare soil have applied linear regression for estimating the CO_2 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 CO_2 fluxes using closed chambers above vegetated surfaces with short closure times or if it is necessary to apply a nonlinear model. We adopt the exponential model of Matthias et al. (1978) for trace gas efflux from bare soils, which is based on diffusion theory, and expand it for sites with low-stature vegetation. For this purpose, the effect of changing CO_2 concentrations on photosynthesis had to be added to the model. The developed nonlinear exponential model is tested against the linear model and a quadratic model proposed by Wagner et al. (1997) with four datasets of CO_2 flux measurements (total number=1764) conducted at three boreal peatlands and one tundra site by four separate working groups.

2 Development of the nonlinear exponential model

Presuming that the chamber experiment itself alters the measurand, namely the CO_2 flux, a nonlinear evolution of the CO_2 concentration in the chamber headspace must be expected. In the following, a theoretical model is developed which shall reflect this nonlinear CO_2 concentration evolution as affected by the main relevant processes which contribute to the net CO_2 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 CO_2 concentration change over time in the chamber headspace is the net effect of several individual processes with partly opposing directions (Fig. 1). CO_2 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 CO_2 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 CO_2 efflux from the soil (F_{Soil}) to the overlying air takes place. Inside the headspace, plants photosynthesise and respire, meaning CO_2 removal (F_{P}) from or CO_2 supply (F_{R}) to the headspace air, respectively. The sum of all CO_2 fluxes into or out of the headspace represents the net CO_2 flux (F_{net}) which can be estimated by the change of the CO_2 concentration over time *dc/dt* (t) during chamber closure. The sign convention of this study is that fluxes are defined positive when adding CO_2 to the chamber headspace and negative when removing CO_2 from the chamber headspace.

The net CO_2 flux $F_{net}(t)$, which in effect drives the CO_2 concentration change in the chamber headspace over time *dc/dt* (t), can be written as:

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

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. $F_{Soil}(t)$ is the CO_2 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 CO_2 flux associated with the gross photosynthesis of the plants, $F_R(t)$ is the CO_2 flux associated with the dark respiration of the aboveground biomass, and $F_{Leak}(t)$ is the CO_2 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 CO_2 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:

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

The CO_2 efflux from the soil to the headspace air $F_{Soil}(t)$ is considered to be mainly driven by molecular diffusion between the CO_2-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:

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

where D is the soil CO_2 diffusivity, c_d is the CO_2 concentration at some unknown depth d below the surface where the CO_2 concentration is constant and not influenced by the chamber deployment. $c(t)$ is the CO_2 concentration of the headspace air which is assumed equal to the CO_2 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 CO_2 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 CO_2.

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 CO_2 concentration (Farquhar et al., 1980), F_P can be either strongly dependent on or nearly independent of changes of the headspace CO_2 concentration $c(t)$ depending on the irradiation level. The complex dependence of photosynthetic activity on irradiation and CO_2 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 CO_2 concentration at CO_2 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:

$$F_P(t) = k_P\, c(t)\, \frac{p\,V}{R\,T\,A} \qquad (4)$$

where k_P is the constant of proportionality of the approximately linear relationship between CO_2 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 as irradiation, temperature or air moisture can be assumed constant, $F_P(t)$ can be defined as:

$$F_P(t) = F_P(t_0) \tag{5}$$

where t_0 is $t=0$.

As the effect of ambient CO_2 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), CO_2 flux associated with the dark respiration of aboveground biomass $F_R(t)$ is considered invariant with changing $c(t)$ in a considered CO_2 concentration range of 200 ppm to 500 ppm. Thus, if the other environmental controls as temperature or air moisture can be assumed constant, $F_R(t)$ can be defined as:

$$F_R(t) = F_R(t_0) \tag{6}$$

As leakage often cannot be ruled out completely, CO_2 flux associated with potential leakages $F_{Leak}(t)$ should be integrated in the model. $F_{Leak}(t)$ is considered to be driven by diffusive transport and can therefore be modelled similarly to $F_{Soil}(t)$:

$$F_{Leak}(t) = \left\{ D_{Chamber} \frac{[c_a - c(t)]}{d_{Chamber}} + D_{Soil} \frac{[c_a - c(t)]}{d_{Soil}} \right\} \frac{p\,V}{R\,T\,A} = K_{Leak} \, [c_a - c(t)] \, \frac{p\,V}{R\,T\,A} \tag{7}$$

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 CO_2 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):

$$\frac{dc}{dt}(t) = D\,\frac{[c_\mathrm{d} - c(t)]}{d} + k_\mathrm{P}\,c(t) + F_\mathrm{R}(t_0)\,\frac{R\,T\,A}{p\,V} + K_\mathrm{Leak}\,[c_\mathrm{a} - c(t)] \tag{8}$$

which can be reorganised to

$$\frac{dc}{dt}(t) = \left[\frac{D}{d}\,c_\mathrm{d} + F_\mathrm{R}(t_0)\frac{R\,T\,A}{p\,V} + K_\mathrm{Leak}\,c_\mathrm{a}\right] + \left[-\frac{D}{d} + k_\mathrm{P} - K_\mathrm{Leak}\right] c\,(t) \tag{9}$$

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:

$$c(t) = -\frac{\left[\frac{D}{d}\,c_\mathrm{d} + F_\mathrm{R}(t_0)\frac{R\,T\,A}{p\,V} + K_\mathrm{Leak}\,c_\mathrm{a}\right]}{\left[-\frac{D}{d} + k_\mathrm{P} - K_\mathrm{Leak}\right]} + \exp\left[\left(-\frac{D}{d} + k_\mathrm{P} - K_\mathrm{Leak}\right) t\right] B \tag{10}$$

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):

$$\frac{dc}{dt}(t) = D\,\frac{[c_\mathrm{d} - c(t)]}{d} + [F_\mathrm{P}(t_0) + F_\mathrm{R}(t_0)]\,\frac{R\,T\,A}{p\,V} + K_\mathrm{Leak}\,[c_\mathrm{a} - c(t)] \tag{11}$$

which can be reorganised to :

$$\frac{dc}{dt}(t) = \left\{\frac{D}{d}\,c_\mathrm{d} + [F_\mathrm{P}(t_0) + F_\mathrm{R}(t_0)]\,\frac{R\,T\,A}{p\,V} + K_\mathrm{Leak}\,c_\mathrm{a}\right\} + \left(-\frac{D}{d} - K_\mathrm{Leak}\right) c\,(t) \tag{12}$$

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This differential equation is solved by computing its indefinite integral:

$$c(t)=-\frac{\left\{\frac{D}{d}c_{\mathrm{d}}+\left[F_{\mathrm{P}}(t_0)+F_{\mathrm{R}}(t_0)\right]\frac{RTA}{pV}+K_{\mathrm{Leak}}c_{\mathrm{a}}\right\}}{\left(-\frac{D}{d}-K_{\mathrm{Leak}}\right)}+\exp\left[\left(-\frac{D}{d}-K_{\mathrm{Leak}}\right)t\right]B \tag{13}$$

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 $f_{\mathrm{exp}}(t)$ of the form:

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

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

$$p_1=-\frac{\left[\frac{D}{d}c_{\mathrm{d}}+F_{\mathrm{R}}(t_0)\frac{RTA}{pV}+K_{\mathrm{Leak}}c_{\mathrm{a}}\right]}{\left(-\frac{D}{d}+k_{\mathrm{P}}-K_{\mathrm{Leak}}\right)} \tag{15}$$

and p_3 is given by

$$p_3=\left(-\frac{D}{d}+k_{\mathrm{P}}-K_{\mathrm{Leak}}\right) \tag{16}$$

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

$$p_1=-\frac{\left\{\frac{D}{d}c_{\mathrm{d}}+\left[F_{\mathrm{P}}(t_0)+F_{\mathrm{R}}(t_0)\right]\frac{RTA}{pV}+K_{\mathrm{Leak}}c_{\mathrm{a}}\right\}}{\left(-\frac{D}{d}-K_{\mathrm{Leak}}\right)} \tag{17}$$

and p_3 is given by

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

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

$$p_2 = B \tag{19}$$

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 mathematical combinations 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 form of the regression model should be appropriate for describing the evolution of $c(t)$ over time in the chamber headspace since it is based on the underlying physiological and physical processes which control the CO_2 fluxes into and out of the chamber. The initial slope of the exponential regression curve $f_{exp}'(t_0)$ can be used to derive the CO_2 flux rate at the beginning of the chamber deployment $F_{net}(t_0)$, which is considered to be the best estimator of the net CO_2 exchange flux under undisturbed conditions:

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

Fitting the exponential model to typical datasets of CO_2 concentration changes in chamber headspaces over short closure times can pose the problem of high dependency of the parameters, which is caused by overparameterisation of the model with respect to the fitted data. The overparameterisation leads to high uncertainty of the estimated parameters p_1, p_2 and p_3. The overparameterisation problem can be significantly reduced by approximating the exponential function by a Taylor power series expansion. The resulting polynomial is much more stable and resistant against overparameterisation. The Taylor power expansion of the exponential function is given by:

$$c(t) = f_{exp}(t) + \varepsilon(t) = p_1 + p_2 \exp(p_3\, t) + \varepsilon(t) = p_1 + p_2 \left(\sum_{k=0}^{\infty} \frac{p_3^k}{k!}\, t^k \right) + \varepsilon(t) \tag{21}$$

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Equation (21) can be rearranged as:

$$c\,(t) = f_{\exp}\,(t) + \varepsilon\,(t) = (p_1 + p_2) + (p_2\; p_3)\;\; t + \left(\sum_{k=2}^{\infty} \frac{p_2\; p_3^k}{k!}\;\; t^k \right) + \varepsilon\,(t) \tag{22}$$

By defining the parameters of the polynomial as

$$a = (p_1 + p_2)\,, \tag{23}$$

$$b = (p_2\; p_3)\,, \tag{24}$$

and

$$c = \frac{p_2\; p_3^2}{2} \tag{25}$$

the power series expansion of the exponential model can be written as:

$$c\,(t) = f_{\exp}\,(t) + \varepsilon\,(t) = a + b\;t + c\;t^2 + \left(\sum_{k=3}^{\infty} \frac{2^{k-1}\; c^{k-1}}{k!\; b^{k-2}}\;\; t^k \right) + \varepsilon\,(t) \tag{26}$$

Expanding the exponential model to a polynomial of 17th order was found to be sufficient to reflect all observed curvatures of the exponential fitting function; higher-order terms were neglected. Advantageously, the fit parameters *a* and *b* of the power series expansion of the exponential model represent the function properties of highest interest for the calculation of the CO_2 fluxes: *a* and *b* represent the y-axis intercept $f_{\exp}(t_0)$ and the initial slope $f'_{\exp}(t_0)$ of the CO_2 concentration curve.

Thus, the CO_2 flux rate at the start of the chamber deployment $F_{net}(t_0)$ can be derived as:

$$F_{net}\,(t_0) = \frac{dc}{dt}\,(t_0)\;\; \frac{p\;V}{R\;T\;A} = f'_{\exp}\,(t_0)\;\; \frac{p\;V}{R\;T\;A} = b\;\; \frac{p\;V}{R\;T\;A} \tag{27}$$

3 Least squares regression of model functions

The evolution of the CO_2 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 $f_{exp}(t)$ (as 17th order Taylor power series expansion) developed in Chapter 2, (2.) a quadratic model function $f_{qua}(t)$ as proposed previously by Wagner et al. (1997) and (3.) the linear model function $f_{lin}(t)$, which was used in many other studies.

The quadratic model function has the form:

$$c(t) = f_{qua}(t) + \varepsilon(t) = a + b\,t + c\,t^2 + \varepsilon(t) \tag{28}$$

The linear model function has the form:

$$c(t) = f_{lin}(t) + \varepsilon(t) = a + b\,t + \varepsilon(t) \tag{29}$$

Comparing Eq. (28) and Eq. (29) with Eq. (26) shows that the quadratic function f_{qua} and the linear function f_{lin} are equal to second order and first order Taylor power series expansions of the exponential model f_{exp}, respectively.

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 b and c of the exponential and quadratic regression functions Eq. (26), Eq. (28) can only be interpreted by the developed theoretical model if they have the opposite sign. However, the parameter estimations of the nonlinear regressions were not restricted to such combinations only, thus allowing for the detection of clearly nonlinear $c(t)$ curves with curvatures not explainable by the theoretical model. Whereas the theoretical model generally expects a decreasing absolute value of the slope of the $c(t)$ curve over time, a part of the actual $c(t)$ curves showed by contrast an increasing absolute value of the slope over time. Curves with such "unexplainable" curvatures were separated after the fitting procedure. They were considered to be caused by violations of the basic assumptions of the developed theoretical model, which means that one of the factors soil temperature, headspace air temperature, photosynthetically active radiation, air pressure or headspace turbulence were apparently neither constant nor approximately equal to ambient conditions.

4 Statistical evaluation and comparison of different models

While an exponential relationship between $c(t)$ and t can be expected from theoretical considerations, the linear and the quadratic model functions can be regarded as first and second order approximations of the exponential model (Chapter 3). Thus, the following major questions had to be addressed:

1. How well does the exponential model function f_{exp} developed from theory describe the $c(t)$ 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. Do the initial slopes $f'(t)$ of the different functions (f_{exp}, f_{lin} and f_{qua}), which are directly proportional to the calculated initial CO_2 net fluxes $F_{net}(t_0)$, deviate significantly from each other?

The first step to answer question 1. was to check the signs of the estimated parameters to ensure their reasonability with regard to the developed theoretical model (see Chapter 3). Then, questions 1. and 2. were evaluated by thorough analyses of the residuals of the different regression functions. 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^2_{adj} (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). Question 3. was then evaluated by plotting the initial slopes $f'(t)$ of the different regression functions against each other as $x-y$ scatter diagrams. The differences between the absolute values of the initial slopes $f'(t)$ 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 automatically adjusted to the degree of observed autocorrelation by a routine included in the applied MATLAB ® regression program.

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, however, has to be considered out-dated (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}.

One measure used in this study for the comparison of the goodness of fit of different regression functions is the adjusted nonlinear coefficient of determination R^2_{adj}, which is a rescaling of the normal nonlinear coefficient of determination R^2 by degrees of freedom (Rawlings et al., 1998). It is defined as:

$$R^2_{adj}=1-\frac{\left(1-R^2\right)\ (n-1)}{n-k} \qquad (30)$$

where n is the number of data points of the respective experiment and k is the number of parameters of the regression function. Unlike R^2, R^2_{adj} increases only if the new term improves the model more than would be expected by chance and is thus better suited for comparing models with different k. A higher R^2_{adj} would indicate a better fitted model.

Another measure for the goodness of fit for model comparison is the Akaike information criterion AIC which is based on the concepts of entropy and information theory (Akaike, 1974; Burnham and Anderson, 2004). The AIC with small sample second order bias correction AIC_c is computed as:

$$AIC_c=n\ \ln\left(\frac{\sum \varepsilon_i^{\ 2}}{n}\right)+2\ k+\frac{2\ k\ \ (k+1)}{n-k-1} \qquad (31)$$

where ε_i are the residuals of the fitted model. The AIC_c trades off precision of fit against the number of parameters used to obtain that fit (Rawlings et al., 1998). Comparing several models, the model with the lowest AIC_c has to be considered best.

The F-test was used for checking if the residual variance of one specific regression function was significantly lower than the residual variance of another compared regression function. For example, the F-test statistic was computed for the comparison of the residual variances of f_{exp} and f_{lin} as:

$$F = \frac{\sum \left(\varepsilon_{\mathrm{i-lin}}\right)^2}{\sum \left(\varepsilon_{\mathrm{i-exp}}\right)^2} \tag{32}$$

where $\varepsilon_{\mathrm{i-lin}}$ denotes the residuals of the linear regression, and $\varepsilon_{\mathrm{i-exp}}$ denotes the residuals of the exponential regression. If F was greater than the critical F-value from the F-distribution table for significance level α=0.1 with n-k_{lin} and n-k_{exp} degrees of freedom (Fisher, 1924), the exponential model was considered to be significantly better fitted to the data than the linear model. k_{lin} and k_{exp} denote the numbers of parameters of the linear and exponential models, respectively (k_{lin}=2, k_{exp}=3).

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

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Sphagnum balticum and *Scheuchzeria palustris*. More detailed information 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 T_1 and T_2 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 T_3 was set at a wet palsa margin and was covered by *Sphagnum riparium*, *E. angustifolium* and *E. russeolum.* The transect T_4 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 in 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 was laid open. No microsites were differentiated. More information will be available in an article which is currently under review (N. Shurpali, personal communication).

Samoylov is an island in the southern central Lena River Delta in Northern Siberia (72°22′ N, 126°30′ 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 chordorrhiza*, *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 (2005). A total of 15 plots were established in 5 different microsite types: 3 at a polygon rim and 3 at each of 4 polygon centres which differed by their moisture conditions.

5.2 Experimental methods

The closed chamber experiments were conducted from July to September 2005 at Salmisuo, from June to August 1998 at Vaisjeäggi, from June to November 2004 at Linnansuo and from July to September 2006 on Samoylov to determine the net ecosystem exchange of CO_2 (NEE). Transparent chambers were employed at the vegetated sites Salmisuo, Vaisjeäggi and Samoylov. At the bare peat site Linnansuo, opaque chambers were used. Experiments were conducted during day and night time at Salmisuo and Samoylov whereas they were conducted only during daytime at Vaisjeäggi and Linnansuo. Furthermore, the set-up specifics of the closed chamber experiments differed between the four investigation sites with regard to cooling and ventilation, the type of the CO_2 analyser, chamber closure time, interval length of CO_2 concentration measurements and instrument precision. 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. Further details on the cooled and ventilated chamber systems used at Salmisuo and Vaisjeäggi are given in Alm et al. (1997).

6 Results

6.1 Residual analyses

A summary of the residual analyses for all chamber experiments from the four investigation sites is given in Table 2. The residual analyses were conducted for all regression functions without parameter restrictions. Thus, also regression curves with curvatures

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not explainable by the developed theoretical model were 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 part (20% to 40%) of the significantly nonlinear regression curves showed curvatures which were not conforming with 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 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 could be excluded for 68% of the exponential regressions, 67% of the quadratic regressions and for only 44% of the linear regressions ($d > d_U$). For the Vaisjeäggi and Linnansuo datasets, autocorrelation was generally a bigger problem: For the Vaisjeäggi dataset, significant positive autocorrelation could be excluded for 30% of the exponential regressions, 30% of the quadratic regressions and for only 10% of the linear regressions ($d > d_U$). For the Linnasuo dataset, significant positive autocorrelation could be excluded for 49% of the exponential regressions, 48% of the quadratic regressions and for only 27% of the linear regressions ($d > d_U$). 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 could be excluded for 75% of the exponential and quadratic regressions and for 67% of the linear regressions ($d > d_U$).

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 were 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^2_{adj}, AIC_c and the F-test of the residual variances showed rather differing results between the different indicators and datasets (Table 2). 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^2_{adj} 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^2_{adj} 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^2_{adj}: 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 Vaisjeäggi 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 Vaisjeäggi 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,

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rather many of these regressions showed curvatures not conforming 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 significantly smaller than the residual variance of the quadratic regression only in less than 1% of the experiments of all datasets (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 $f'_{lin}(t_0)$ and $f'_{exp}(t_0)$ by $x-y$ scatter diagrams is shown for the four investigation sites in Fig. 3. The initial slopes of the regression functions are directly proportional to the CO_2 flux at the beginning of chamber closure $F_{net}(t_0)$ which is considered to be the best estimate of the undisturbed flux before chamber closure Eq. (27). Considering the exponential model as more correct, deviating values of $f'_{lin}(t_0)$ and $f'_{exp}(t_0)$ would represent a bias of the CO_2 flux estimate by the linear regression approach. As illustrated in Fig. 3, $f'_{lin}(t_0)$ and $f'_{exp}(t_0)$ partly deviated considerably from each other, in particular for great absolute values of the initial slopes. Mostly, the absolute values of $f'_{lin}(t_0)$ were smaller than the absolute values of $f'_{exp}(t_0)$, which means an underestimation bias of the linear regression approach both for CO_2 uptake and CO_2 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 CO_2 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 (Figs. 3c,d). For high absolute values of the initial slopes in these datasets, $f'_{\mathrm{lin}}(t_0)$ could be as low as 50% or even 20% of the values of $f'_{\mathrm{exp}}(t_0)$. On the other hand, the weakest effects were found for the Vaisjeäggi dataset (Fig. 3b). Also for highest absolute values of the initial slopes in this dataset, $f'_{\mathrm{lin}}(t_0)$ was not below 60% of the value of $f'_{\mathrm{exp}}(t_0)$. The Salmisuo dataset was intermediate in this regard (Fig. 3a). For high absolute values of the initial slope in these datasets, $f'_{\mathrm{lin}}(t_0)$ was often between 40% and 80% of the value of $f'_{\mathrm{exp}}(t_0)$. Salmisuo is the only dataset with nearly equally distributed numbers of experiments for CO_2 uptake and CO_2 release situations. For this dataset, it could be observed that the underestimation effect of the linear regression was on average stronger for CO_2 uptake situations than for CO_2 release situations.

An overview of the significances of the deviations between $f'_{\mathrm{lin}}(t_0)$ and $f'_{\mathrm{exp}}(t_0)$ is given in Table 3. The percentages of experiments with significant (Student's t-test, $P<0.1$) deviations between $f'_{\mathrm{lin}}(t_0)$ and $f'_{\mathrm{exp}}(t_0)$ are listed separately for situations with underestimation (H1) and overestimation (H2) by the linear regression. The absolute values of $f'_{\mathrm{exp}}(t_0)$ were significantly greater than the absolute values of $f'_{\mathrm{lin}}(t_0)$ (H1 is true at $P<0.1$) for 57% of the Salmisuo experiments, 55% of the Vaisjeäggi experiments, 42% of the Linnasuo 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 $f'_{\mathrm{exp}}(t_0)$ were significantly smaller than the absolute values of $f'_{\mathrm{lin}}(t_0)$ (H2 is true at

$P<0.1$) for 19% of the Salmisuo experiments, 30% of the Vaisjeäggi experiments, 26% of the Linnasuo experiments and 19 % of the Samoylov experiments. These portions of experiments were not conforming 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 $f'_{\mathrm{exp}}(t_0)$ and $f'_{\mathrm{lin}}(t_0)$ 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 Vaisjeäggi 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 Vaisjeäggi datasets. On the other hand, the Vaisjeäggi 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) for the nonlinearity problem became obvious.

A comparison of the initial slopes of the quadratic and the exponential regression functions $f'_{\mathrm{qua}}(t_0)$ and $f'_{\mathrm{exp}}(t_0)$ by $x-y$ scatter diagrams is shown for the four investigation sites in Fig. 4. An overview of the significances of the deviations between $f'_{\mathrm{qua}}(t_0)$ and $f'_{\mathrm{exp}}(t_0)$ is given in Table 4. The initial slopes $f'_{\mathrm{qua}}(t_0)$ and $f'_{\mathrm{exp}}(t_0)$ differ significantly ($P<0.1$) for only 5%...9% of the experiments of the four datasets. However, 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 CO_2 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 Vaisjeäggi dataset. The Salmisuo dataset was intermediate in this regard.

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7 Discussion

This study presents the first theory-based model 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 CO_2 flux estimates. The exponential model was not significantly better fitted than the quadratic model with respect to the residual 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 nonlinear nature of the gas concentration evolution over time in closed chambers has been recognised and discussed early 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; Hutchinson and Mosier, 1981; Healy et al., 1996; Hutchinson et al., 2000; Pedersen, 2000; Pedersen et al., 2001; Hutchinson and Livingston, 2001; Welles et al., 2001; Nakano et al., 2004; Livingston et al., 2005, 2006). Matthias et al. (1978) showed for numerical simulations of closed chamber experiments with closure times of 20 min that N_2O emissions could be underestimated by as much as 10% to 55% by linear regression depending on chamber size and geometry. Quadratic regression still underestimated the real fluxes by 3% to 25%. An exponential function developed from 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; Livingston et al., 2005, 2006). Livingston et al. (2005, 2006) showed that quadratic and also exponential regression still underestimated the real initial flux which could be optimally fitted by the "non-steady state diffusion estimator" function developed by the authors. 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 CO_2 release and CH_4 consumption from soil under actual field conditions.

Only few researchers have applied nonlinear models to determine CO_2 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. A quadratic model can be regarded as a second order approximation of the exponential model which is developed in this study from simplified photosynthesis physiology and diffusion physics. Wagner et al. (1997) demonstrated for the CO_2 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. The results from this study suggest that for situations with high CO_2 uptake or release the quadratic model also underestimates the fluxes compared to the exponential model although seldom significantly. Thus, a second order approximation of the exponential function is not always appropriate to reflect the partly pronounced curvature of the exponential function.

Modelling of the CO_2 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 have 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, these assumptions were not valid for all experiments: Although the observed nonlinearity conformed with the theoretical exponential model for the majority of experiments, also significantly nonlinear $c(t)$ curves were observed whose curvature was not explainable with the theoretical model. These unexplainable curvatures are considered to have been caused by violations of the basic assumptions of the theoretical model. As at least the closed chambers at Salmisuo and Vaisjeäggi 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 nonlinearity difficult to model. Although the possible disturbing effects of altering turbulence conditions by closed chambers were discussed previously by several studies (Hanson et al., 1993; Le Dantec et al., 1999; Hutchinson et al., 2000; Denmead and Reicosky, 2003; Reicosky, 2003), additional investigations are certainly needed concerning this matter.

Even if the curvature of the $c(t)$ curves could not be explained by the theoretical exponential model, the exponential form of the model function allowed for a more accurate determination of the initial slope of the $c(t)$ than the linear model. If the residual analyses show that the observed $c(t)$ curve is nonlinear, then a nonlinear model should be favoured over the linear model even if the curvature is not explained by the theoretical model.

For the evaluation of the validity of models, we recommend to apply thorough 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 proves for 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. 5a). In this context, a better filter criterion would be the standard deviation of the residuals s_{yx} (Fig. 5b).

The measurement interval length, the number of measurement points and the precision of the CO_2 concentration measurements determine whether the nonlinearity can be detected with sufficient statistical significance. It has to be stressed that strong nonlinearity and so serious bias of the flux estimates can be present although it can not be detected due to long measurement intervals, few data points or poor measurement precision.

Considering the results of this study, a list of practical recommendations for closed chamber measurements shall be given in the following:

Nonlinear regression should be favoured over linear regression to fit the data and to estimate the initial slopes of the $c(t)$ curves.

For closure times of two to ten minutes, exponential functions as given in Eq. (14) or in Eq. (26) as Taylor power series expansion are well suited as regression functions to reflect the observed $c(t)$ curves. To avoid overparameterisation, the power series expansion should be favoured for short closure times.

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.

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.

The slope of the $c(t)$ evolution curve is changing most pronouncedly at the start of the chamber closure time. Consequently, the interval length of discarding data at the beginning to avoid disturbances is critical and should not be too long.

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 can be proved.

When adopting the nonlinear approach, closure times can be longer, headspaces can have smaller volumes, and leaks through the chamber or the soil are less critical compared to the linear regression approach, for which all experiment conditions must be optimised with regard to the best possible approximate linearity (short closure times, large headspace volumes, no leaks).

Changing light, temperature and humidity conditions during chamber closure are less critical when applying nonlinear regression compared to the use of linear regression as long as these changes are continuous and can be accounted for by relatively simple nonlinear functions. However, wind speed and turbulence in the chamber should be as similar as possible to the ambient conditions since abrupt turbulence changes can obstruct the assumption that the initial slope of the $c(t)$ is the best estimator of the undisturbed CO_2 flux before chamber closure (Hutchinson et al., 2000).

One scientific question for which the possible bias of closed chamber CO_2 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 CO_2 fluxes. Thus, the underestimation of the CO_2 fluxes by the linear regression method not only disturbs the quantitative but also the qualitative evaluation since differences between sites with strong and weak CO_2 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 of strongly differing CO_2 fluxes between sites although in fact only the response to the chamber disturbance on diffusion and physiology of plants 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 CO_2 uptake and CO_2 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 CO_2 source or sink. This high potential for serious bias of the CO_2 balances is exemplified by Fig. 6 for a diurnal cycle of CO_2 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 CO_2 balance to asymmetric biases of CO_2 uptake and CO_2 release is of major importance as closed chamber CO_2 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 CO_2 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 developed exponential model is well suited for nonlinear regression of the $c(t)$ evolution in the chamber headspace and estimation of the initial CO_2 fluxes at closure time for the majority of experiments.

However, the curvature of the nonlinear $c(t)$ curves is for a substantial percentage of the experiments not explainable with the presented theoretical model. This is considered to be caused by violations of the basic assumptions of the theoretical model. In particular, the change of turbulence conditions 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 CO_2 flux estimates for situations with strong CO_2 uptake or release.

Inappropriate application of linear regression can lead to serious underestimation of CO_2 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 CO_2 flux strength and is dependent on soil and vegetation conditions which can disturb not only quantitative but also qualitative evaluation of CO_2 flux dynamics.

The underestimation effect by linear regression was observed to be different for CO_2 uptake and CO_2 release situations which can lead to stronger bias in the daily, seasonal and annual CO_2 balances than in the individual fluxes.

To avoid serious bias of CO_2 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 will be made available online.

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

	Salmisuo	Vaisjeäggi	Linnansuo	Samoylov
chamber type	transparent	transparent	opaque	transparent
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
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
ventilation	fan	fan	no	air cycling by pump
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
instrument noise RMSE	±0.5ppm	±0.1ppm	±0.3ppm	±0.8ppm
time schedule	24-h runs	only daytime	only daytime	partly day, partly night

Table 2. 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^2_{adj}, 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 was 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		Durbin-Watson		D'Agost.-Pearson	adjusted R^2	Akaike Inf. Criterion.	F-test
test condition		$d>d_U$	$d>d_L$	$P_N>0.05$	R^2_{adj}(nlin)>R^2_{adj}(lin)	AIC_c(nlin)<AIC_c(lin)	Var(nlin)< Var(lin)
		percentage of n_e (%)					
Salmisuo 1 s	lin	44	46	84	–	–	–
intervals	qua	67	73	86	84	77	37
(n_e= 542)	exp	68	72	87	83 (63)	77 (58)	37 (29)
Vaisjeäggi 5 s	lin	10	12	87	–	–	–
intervals	qua	30	47	93	90	86	60
(n_e= 389)	exp	30	48	92	89 (55)	86 (58)	60 (42)
Linnansuo 10 s	lin	27	44	90	–	–	–
intervals	qua	48	88	93	79	66	33
(n_e =368)	exp	49	88	92	78 (49)	64 (41)	36 (23)
Samoylov 45 s	lin	67	92	98	–	–	–
intervals	qua	75	100	97	70	35	15
(n_e=465)	exp	75	100	98	68 (43)	37 (25)	19 (15)

Table 3. Significance of deviations between the initial slopes of the exponential regression $f_{exp}'(t_0)$ and the linear regression $f_{lin}'(t_0)$. 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 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).

	Student's t-test of hypotheses (P< 0.1)		
	H1: $\lvert f_{exp}'(t_0)\rvert-\lvert f_{lin}'(t_0)\rvert>0$	H2: $\lvert f_{exp}'(t_0)\rvert-\lvert f_{lin}'(t_0)\rvert<0$	H0: $\lvert f_{exp}'(t_0)\rvert-\lvert f_{lin}'(t_0)\rvert=0$
		percentage of n_e (%)	
Salmisuo (n_e=542)	57.4	18.5	24.2
Vaisjeäggi (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

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Table 4. Significance of deviations between the initial slopes of the exponential regression $f_{exp}'(t_0)$ and the quadratic regression $f_{qua}'(t_0)$. 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).

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

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CO_2 flux determination biased by linear regression

L. Kutzbach et al.

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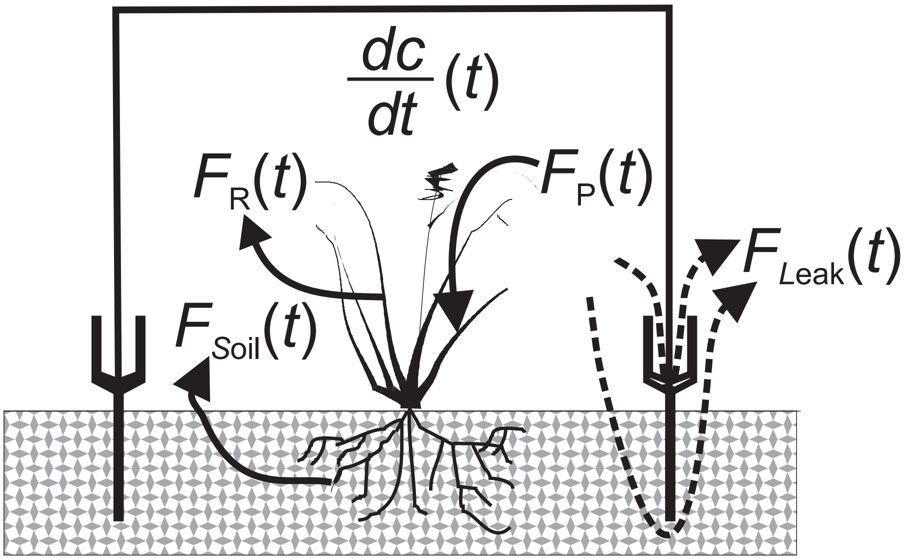

Fig. 1. Schematic of the CO_2 fluxes in the chamber headspace which make up to the net CO_2 flux F_{net} (details in the text, Eq. 1). $F_{Soil}(t)$ is the diffusive efflux from the soil, $F_P(t)$ is photosynthesis, $F_R(t)$ is aboveground plant respiration, $F_{Leak}(t)$ is leak flux. $dc/dt\ (t)$ is the CO_2 concentration change over time t in the chamber headspace.

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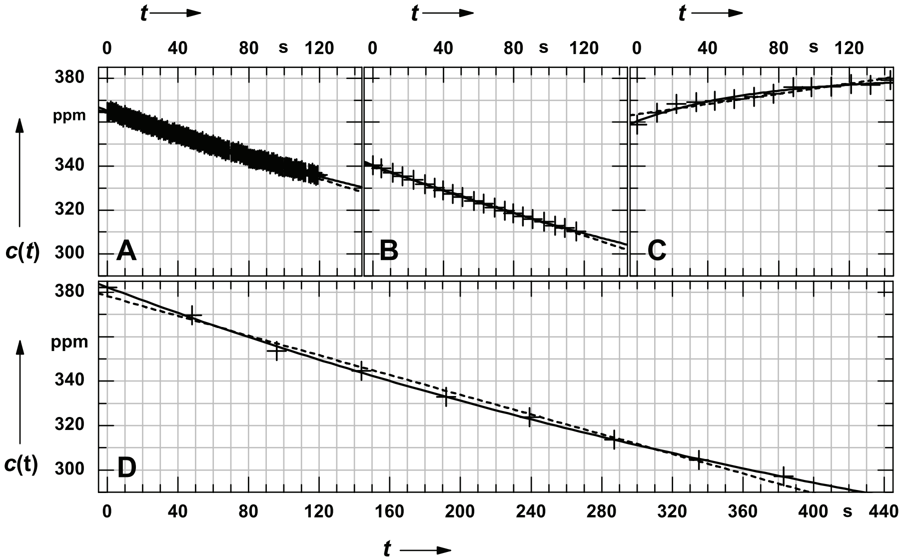

Fig. 2. Examples of the CO_2 concentration $c(t)$ evolution over time t for the different investigation sites. **(A)** Salmisuo, 11 August 2005, **(B)** Vaisjeäggi, 17 August 1998, **(C)** Linnansuo, 12 November 2004, **(D)** Samoylov, 26 July 2006. The dashed lines indicate linear regression functions 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.

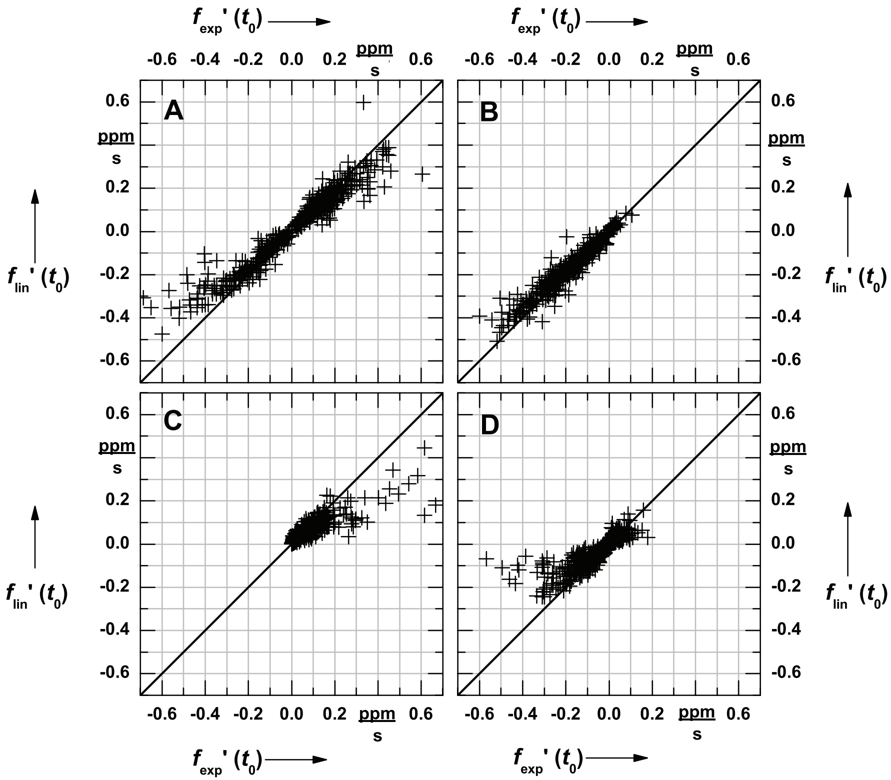

Fig. 3. Comparison of initial slopes of the linear and exponential regression curves for the different investigation sites. **(A)** Salmisuo, **(B)** Vaisjeäggi, **(C)** Linnansuo, **(D)** Samoylov. On the x-axes, the initial slopes of the exponential regression $f_{exp}'(t_0)$ are plotted. On the y-axes, the initial slopes of the linear regression curves $f_{lin}'(t_0)$ are plotted. The $y=x$ relationship is given as solid line. As the initial slopes of the regression curves are directly proportional to the CO_2 flux estimates, a deviation between $f_{lin}'(t_0)$ and $f_{exp}'(t_0)$ indicates a bias of the CO_2 flux estimate by the application of the linear model presuming that the undisturbed CO_2 fluxes are better reflected by the exponential model.

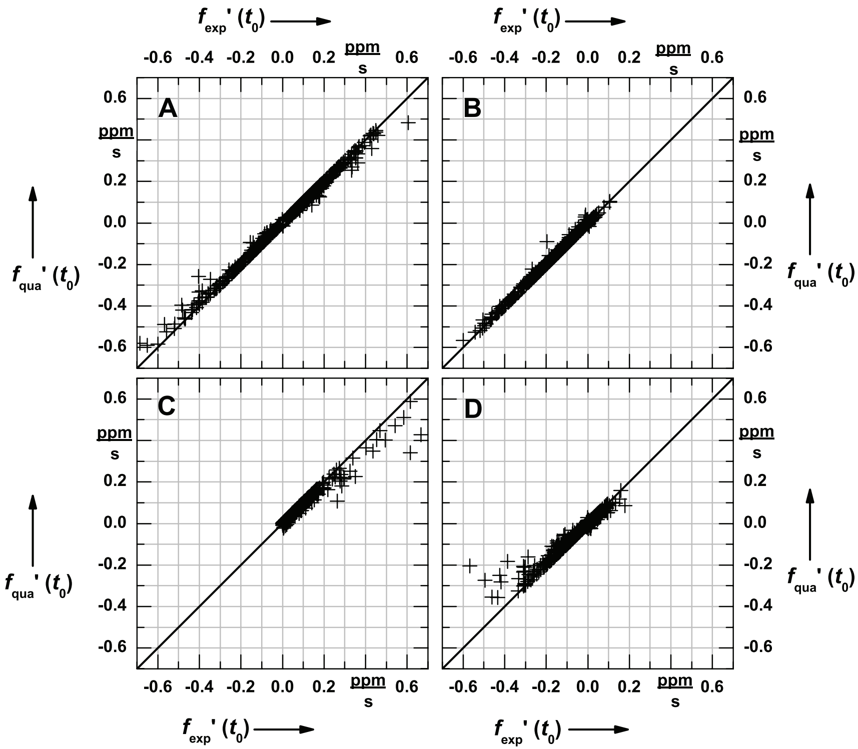

Fig. 4. Comparison of initial slopes of the exponential and quadratic regression curves for the different investigation sites. **(A)** Salmisuo, **(B)** Vaisjeäggi, **(C)** Linnansuo, **(D)** Samoylov. On the x-axes, the initial slopes of the exponential regression $f_{exp}'(t_0)$ are plotted. On the y-axes, the initial slopes of the quadratic regression curves $f_{qua}'(t_0)$ are plotted. The $y=x$ relationship is given as solid line. As the initial slopes of the regression curves are directly proportional to the CO_2 flux estimates, a deviation between $f_{qua}'(t_0)$ and $f_{exp}'(t_0)$ indicates a bias of the CO_2 flux estimate by the application of the quadratic model presuming that the undisturbed CO_2 fluxes are better reflected by the exponential model.

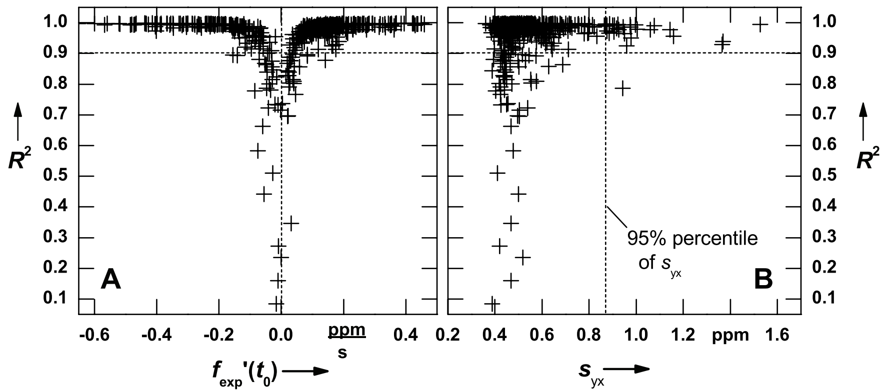

Fig. 5. The relationships of the nonlinear coefficient of determination R^2 with the initial slope $f_{exp}'(t_0)$ of the regression function and the standard deviation of the residuals s_{yx} exemplified by the dataset Salmisuo 2005. **(A)**: The R^2 value is plotted against the initial slope $f_{exp}'(t_0)$. The use of R^2 as a filter criterion (e.g. R^2=0.9) would discriminate strongly the regressions with low slope values $f_{exp}'(t_0)$. **(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.

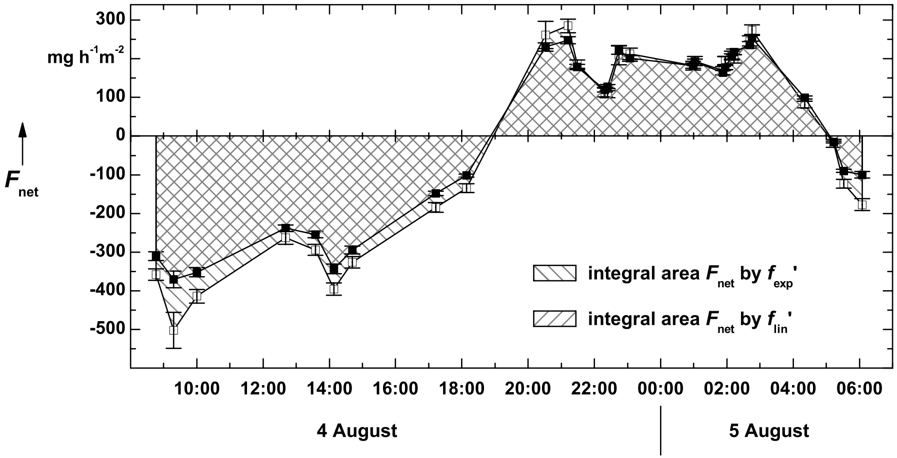

Fig. 6. Example of the effect of the different regression approaches on the estimated CO_2 balance over one diurnal cycle (4 August 2005 08:45 to 5 August 2006 06:05 LT) at the flark sites of Salmisuo. The black squares indicate CO_2 flux estimates F_{net} by the linear model approach, the white squares indicate CO_2 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 CO_2 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 CO_2 uptake using the exponential model is 150% of the estimate using the linear model!