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Vertical advection and nocturnal deposition of ozone over a boreal pine forest

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Abstract

Night-time ozone deposition for a Scots pine forest in Southern Finland was studied at the SMEAR II measurement station by evaluating the turbulent eddy covariance (EC), storage change and vertical advection fluxes. Similarly to night-time carbon dioxide flux, the eddy-covariance flux of ozone was decreasing with turbulence intensity (friction velocity), and storage change of the compound did not compensate the reduction (well-known night-time measurement problem). Accounting for vertical advection resulted in invariance of ozone deposition rate on turbulence intensity. This was also demonstrated for carbon dioxide, verified by independent measurements of NEE by chamber systems. The result highlights the importance of advection when considering the exchange measurements of any scalar. Analysis of aerodynamic and laminar boundary layer resistances by the model approach indicated that the surface resistance and/or chemical sink strength was limiting ozone deposition. The possible aerial ozone sink by known fast chemical reactions with sesquiterpenes and NO explain only a minor fraction of ozone sink. Thus the deposition is controlled either by stomatal uptake or surface reactions or both of them, the mechanisms not affected by turbulence intensity. Therefore invariance of deposition flux on turbulence intensity is expected also from resistance and chemical sink analysis.

1 Introduction

Ozone deposition into forest canopies and sink mechanisms at night are not well understood. In several studies it is assumed that stomatal deposition of ozone at night is negligible and surface reactions are responsible for ozone removal from air (Mikkelsen et al., 2004). Other studies emphasize the role of gas-phase chemical reactions on ozone deposition (Goldstein et al., 2004; Holzinger et al., 2006). Ozone deposition has been studied by different methods, by canopy level micrometeorological as well as by shoot level measurements. The findings so far indicate that ozone deposition is

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affected by humidity conditions of surfaces (Lamaud et al., 2002; Altimir et al., 2006).

The ozone deposition studies by micrometeorological methods at night-time conditions are further complicated by prevailing low-turbulence, stable conditions. The night-time observations of carbon dioxide exchange, for example, are frequently questioned under such conditions and empirical relationships are used for gap-filling of those periods (e.g., Gu et al., 2005). The reason for flux underestimation at night is that turbulent exchange is limited under low turbulence conditions and advective transport becomes important. Most frequently the role of the vertical advection term is evaluated in total ecosystem exchange expression under the assumption that horizontal advection can be ignored (e.g., Paw U et al., 2000; Mammarella et al., 2007). A few studies have made effort in evaluation of the horizontal advection term, but because of spatial variability the uncertainty of this term is found to be in the same order as total ecosystem exchange (Aubinet et al., 2005). These studies, however, are focused only on carbon dioxide and not on any other compound.

The current paper studies ozone deposition primarily at night. Different terms in the scalar conservation equation are evaluated for dependence on turbulence intensity, focusing on the role of vertical advection. The vertical advection term has been used to explain night-time carbon dioxide observations, but no earlier studies on ozone exist to our knowledge.

2 Materials and methods

2.1 Site and measurement station

The SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations) field measurement station is located in Hyytiälä, Southern Finland (61° 51′ N, 24° 17′ E, 181 m a.s.l.). The station is located in the area covered mainly by pine-dominated forests, with the homogeneous Scots pine stand, established in 1962, around the tower for about 200 m to all directions, extending to the North about 1 km. The dominant

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height of the stand near the measurement tower is about 14 m, and the total (all-sided) needle area is about 6 m^2 m^{-2}. About 700 m to the Southwest from the measurement tower there is an oblong lake (about 200 m wide) perpendicular to the S-W direction. The measurement station is described in detail in Vesala et al. (1998) and Hari and Kulmala (2005).

2.2 Eddy covariance measurements

Ozone fluxes were measured by the eddy covariance (EC) technique. The system included a Solent ultrasonic anemometer (Solent Research 1012R2 and HS1199, Gill Instruments Ltd, Lymington, Hampshire, England) and a fast response chemiluminescence gas analyzer for ozone concentration (LOZ-3 Ozone analyzer, Unisearch Associates Inc., Concord, Ontario, Canada). The response time of the analyzer is 0.5 s according to the manufacturer. Further details of the ozone flux measurement system and its performance can be found in Keronen et al. (2003).

The measurements were performed at about 23-m height, roughly 10 m above the forest canopy. The turbulent fluxes were calculated as 30-min average co-variances between the scalars (or horizontal wind speed) and vertical wind speed according to commonly accepted procedures (Aubinet et al., 2000). The high-frequency flux attenuation has been earlier studied for the measurement setup used in current study (Keronen et al., 2003; Rannik et al., 2004), which enabled to recover flux attenuation by using empirical transfer functions and co-spectral transfer characteristics.

2.3 Estimation of storage change

The profiles of O_3 concentration were obtained via six sample lines equal in length from levels of 4.2 m, 8.4 m, 16.8 m, 33.6 m, 50.4 m and 67.2 m in the measurement tower. The set-up for measuring profiles is similar to that used for measuring CO_2-profiles (Rannik et al., 2004). Ozone concentration was measured with an ultraviolet light absorption gas analyzer (TEI 49C Ozone analyzer, Thermo Fisher Scientific, Inc.,

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Waltham, MA, USA), with the sample flow rate of 2 l min^{-1} through the analyzer .

The flux storage term was estimated from 4 levels (up to 33.6 m) according to

$$F_{ST} = \int_0^{z_r} \frac{\partial \overline{c}}{\partial t} dz, \quad (1)$$

where z_r refers to observation level (23.3 m) and c denotes concentration. This integral was numerically evaluated using the trapezoidal rule. A linear interpolation between 33.6 and 16.8 m was assumed to estimate the concentration values at z_r. The concentration values at z=0 was estimated by a linear extrapolation of the 4.2- and 8.4-m measurements to the surface.

2.4 Estimation of vertical advection term

The vertical advection term of the mass balance expression is defined as

$$F_{VA} = \int_0^{z_r} \overline{w} \frac{\partial \overline{c}}{\partial z} dz. \quad (2)$$

It requires estimation of average vertical wind speed as a function of height, but frequently an assumption of linear decrease with height is made (e.g., Lee, 1998) and then only the average vertical wind speed at the measurement level is needed. The evaluation of the vertical advection term is most sensitive to the average vertical wind speed. In current study, the Planar Fit Method (Wilczak et al., 2001) was applied according to relationship

$$\overline{w} = b_0 + b_1 \overline{u} + b_2 \overline{v}, \quad (3)$$

where the overbar denotes averaging over the turbulent record (30 min) and $\overline{u}$ and $\overline{v}$ are defined in a non-rotated co-ordinate system.

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The planar fit flow planes were determined on monthly basis via minimising root-mean-square deviation using the following criteria: regression was made for wind direction sectors (20 degrees) for cases with wind velocities less than 5 m s^{-1}.

3 Results and discussion

The sum of the different flux terms

$$F = F_{EC} + F_{ST} + F_{VA} + F_{HA} \quad (4)$$

forms the total flux, where F_{EC} is the eddy covariance and F_{HA} the horizontal advection terms. In terms of scalar conservation equation the total flux equals to exchange rate by the sources and sinks of a scalar inside the control volume (over a unit surface area bounded from top by EC measurement level). The horizontal advection term was neglected in the current study since no measurements for the determination of this term were available. However, significance of the horizontal advection term was evaluated for carbon dioxide as a residual by using complementary chamber measurements. Thus it is assumed that F_{HA}=0.

Ozone flux and concentration measurements for a 2 months period, from 10 June 2004 to 30 July 2004, were analysed.

3.1 Ozone fluxes

Depending on averaging time and observation conditions, the flux estimates contain the random error component approximately 10 to 20%. In case of low wind speed or non-stationarity of concentration and/or wind records, the random errors can be occasionally much larger (Rannik et al., 2004). This is particularly true for conditions characterised by low friction velocity. Therefore, averaging is necessary to observe evidences of systematic behaviour in measurements. Figure 1a presents EC, storage and vertical advection flux components averaged diurnally for one hour time interval.

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The EC flux catches most of the exchange during the day and the storage term remains relatively small throughout the day. The advection term, being negligible at day, becomes important after midnight. Figure 1b presents the sum of EC and storage flux as well as the sum of all three components as possible estimates for total ozone flux. The difference between the two curves is close to zero at day and between 1 to 2 nmol m^{-2} s^{-1} at night.

With the purpose of night-time analysis, classification of observation periods of 30-min duration was performed according to friction velocity values. Although friction velocity is not the only significant parameter for characterisation of night-time observation conditions, it is one of the most important parameters and is frequently used as a criterion for reliability of night-time CO_2 flux measurements (Aubinet et al., 2000; Loescher et al., 2006). Figure 2a indicates that the average flux estimates show clearly a dependence on u_*. However, the ozone flux becomes independent of friction velocity when vertical advection term is added (Fig. 2b). Without vertical advection term the flux estimate (i.e. the sum of the EC and storage terms) decreases with lower u_*.

This behaviour is very similar to what has been observed in numerous cases for night-time CO_2 measurements (Staebler and Fitzjarrald, 2004; Marcolla et al., 2005; Vickers and Mahrt, 2006). Here we demonstrate it for the same time period: Fig. 3a shows different terms of the CO_2 flux as a function of friction velocity for night-time conditions. For carbon dioxide also independent estimates of NEE were available as estimated by the chamber-based technique, which included forest floor CO_2 efflux, respiration of woody parts of the trees, and respiration of foliage, each term being measured by corresponding chamber systems (see Mammarella et al., 2007). The independent estimate of NEE allowed evaluation of the difference between NEE and other terms; the estimated remaining term includes everything not accounted by the other terms, including the horizontal advection term. However, on average the residual term is very close to zero. When summed together, the EC, storage and vertical advection terms are very close to NEE and show invariance of u_* (Fig. 3b). The result is similar to night-time ozone fluxes, which behave similarly as a function of turbulence

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intensity and allow to conclude that different flux terms account for the same relative fraction of total flux in case of both scalars.

The current study shows that the vertical advection term can account for significant fraction of total transport also for other compounds and should be carefully considered when interpreting night-time observations. However, CO_2 and ozone are not identical during night time conditions: CO_2 is emitted as part of the respiration process from soil as well as from the canopy, ozone is deposited at night. The processes are different regarding the stomatal control. The emission rate can be virtually independent of stomatal opening due to formation of concentration gradient which drives the flux. When uptake is in question, the same level of stomatal opening might mean virtually infinite stomatal resistance and thus zero flux. Also there is a difference in chemical activity. Many studies suggest that an important or even the main sink of ozone is chemical reactions with biogenic volatile organic compounds, emitted by the forest (Altimir et al., 2006; Goldstein et al., 2004). In context of the current paper, it is useful to consider turbulent transport times and resistances, which are relevant to ozone transport and/or chemical transformation processes and depend on turbulence intensity.

3.2 Resistances and turbulent transport time

Observed night-time ozone dry deposition fluxes were about $-4\,\mathrm{nmol\,m^{-2}\,s^{-1}}$. With the average observed ozone concentrations this corresponds to local dry deposition velocity about $4\,\mathrm{mm\,s^{-1}}$. In the resistance framework, transport route from the measurement level to the needle surface consists of aerodynamic and laminar boundary layer resistances. In a deposition model for aerosol particles by Slinn (1982) these resistances were included by aerodynamic and canopy resistances. Here we repeat the model for Brownian deposition regime. Since for very small particles transport through the laminar boundary layer surrounding the collecting elements is controlled by Brownian diffusion. The same process is responsible for gas molecule transport. The model is relevant for gases if the diffusion coefficient of particles is replaced by the relevant molecular diffusivity.

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The deposition velocity is given by

$$v=\frac{1}{r_a+r_c+r_s}, \tag{5}$$

where r_a, r_c and r_s are aerodynamic, canopy and surface resistances, respectively. The aerodynamic resistance was estimated as

$$r_a=\frac{U_r-U_h}{u_*^2}, \tag{6}$$

where wind speed at measurement height U_r and friction velocity u_* were obtained from measurements and wind speed at canopy height U_h was estimated based on similarity theory (Rannik et al., 2003a).

The canopy resistance is expressed by

$$r_c=\frac{U_h}{u_*^2}\frac{1}{\sqrt{\varepsilon}}\left(\frac{1+\sqrt{\varepsilon}\tanh\left(\gamma\sqrt{\varepsilon}\right)}{\sqrt{\varepsilon}+\tanh\left(\gamma\sqrt{\varepsilon}\right)}\right), \tag{7}$$

where γ is a coefficient of exponential decrease of wind speed inside a canopy (1.9 for the pine forest in Hyytiälä, see Rannik et al., 2003b) and ε total collection efficiency by canopy elements, presented as

$$\varepsilon=C_\varepsilon E_B. \tag{8}$$

C_ε is a collection efficiency factor determined empirically for the pine forest in Hyytiälä as C_ε=2.9 (Rannik et al., 2003a). E_B is the collection efficiency for Brownian diffusion, well described by

$$E_B=\frac{c_v}{c_d}Sc^{-2/3}, \tag{9}$$

where $\frac{c_v}{c_d}$ is the ratio of viscous to total drag (taken to be 1/3 according to Slinn, 1982) and

$$Sc=\frac{\eta}{\rho_a D} \tag{10}$$

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the Schmidt number (ρ_a is the density of air) with D being the diffusion coefficient and η the dynamic viscosity. The canopy resistance as presented by Eq. (7) represents the sum of the aerodynamic resistance from the canopy top to the surface elements and the bulk boundary layer resistance. The surface resistance can represent the stomatal resistance and/or the resistance accounting for ozone reactions on the liquid films on the foliage surface. The resistances r_a and r_c are functions of friction velocity. However, if the resistance r_s (or a chemical sink in the canopy air space) dominates no dependence of ozone deposition on friction velocity should be observed.

The median values for resistances r_a and r_c for night-time conditions were 22 and 25 s m^{-1}. In terms of deposition rate these resistances together would allow deposition velocity of about 20 mm s^{-1}. This is much higher than is observed and thus indicates that ozone deposition is actually limited by surface resistance or chemical sink strength. The residual resistance was estimated for each 30 min averaging period and compared to the aerodynamic and laminar boundary layer resistances – on the average the residual resistance was approximately an order of magnitude larger (not shown).

In addition to stomatal uptake the surface reactions and/or reactions in the canopy air space can account for ozone depletion (Altimir et al., 2006). The potential of chemical compounds for ozone depletion in air depends on the available time for reactions and is determined by turbulent transport time. To estimate turbulent transport time from measurement level to canopy elements, Lagrangian trajectory simulations were performed according to Rannik et al. (2003b). The simulations were performed with particle release from canopy with the probability distribution proportional to leaf area density and trajectory calculation was performed until the first crossing of observation level. Table 1 presents turbulent transport time statistics for u_*=1 m s^{-1}. The transport time is inversely proportional to friction velocity and to obtain estimate for other turbulence conditions the values have to be rescaled with u_*. Average transport times for low turbulence (u_*=0.2 m s^{-1}) night-time conditions and stability range from LH^{-1}=+100 to +1 are from about 5 to 10 min. Here the Monin-Obukhov stability length L was scaled with the canopy height H. The simulation results are consistent with the value ~1.5 min,

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estimated as day-time residence time in a canopy by Holzinger et al. (2005).

For a range friction velocities between 0.1 to 0.5 $m\,s^{-1}$, turbulent transport times ranges from about 15 to 3 min. According to several studies chemical reactions inside canopy air space are probable candidates for ozone destruction (e.g., Holzinger et al., 2005). The chemical sinks with life-times of the same magnitude as turbulent transport time could cause the ozone flux dependence on friction velocity. Emissions of such compounds, for example the sesquiterpenes with chemical lifetime between one to two minutes reacting almost exclusively with ozone, have been detected at the site with a clear seasonal pattern (Hakola et al., 2006).

The sesquiterpene emission rates for June 2004 has been estimated to be up to 40 $mg\,m^{-2}\,month^{-1}$ (B. Bonn, personal communication). Under the assumption that all emitted sesquiterpenes react below the observation level the corresponding ozone consumption rate is up to 0.1 $nmol\,m^{-2}\,s^{-1}$. This is far too small amount in comparison to ozone deposition rates. The nitrogen oxide (NO) emission at the site was estimated to be about 6 $ng(N)\,m^{-2}\,hr^{-1}$ by Pilegaard et al. (2006). The corresponding ozone destruction rate would be about 10^{-4} $nmol\,m^{-2}\,s^{-1}$. This is also negligible compared to the observed ozone deposition rate. Thus fast chemical reactions in the air can not be the main ozone sink during night-time conditions implying that other processes are responsible for ozone removal.

4 Conclusions

The vertical advection term of ozone exchange accounted for a significant fraction of ozone transport under low turbulence conditions at night. By summing EC, storage and vertical advection terms night-time ozone flux became invariant of turbulence intensity (friction velocity) and stability. This finding is opposite to what was observed by Lamaud et al. (2002) and Sun and Massman (1999), who found that conductance and therefore also deposition velocity of ozone was strongly correlated with friction velocity. In the current study the aerodynamic and laminar boundary layer resistances were not

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limiting the ozone deposition rate. The surface uptake can consist of stomatal and non-stomatal parts, the latter being affected by dew formation at the foliage surface (Altimir et al., 2006). Both uptake mechanisms are not dependent on friction velocity.

The evaluation of possible chemical sinks also supported the idea that there is no deposition mechanism which could depend on turbulence. Turbulent transport time between measurement level and effective sink height was estimated to be from a few minutes to about 10 min under stable conditions. This is time long enough to allow for partial chemical depletion of ozone by compounds emitted from forest during vertical transport. However, the ozone consumption by known fast chemical reactions is insufficient to explain observed deposition fluxes. Thus we expect that night-time ozone deposition is not controlled by turbulence and accounting for vertical advection in deposition estimation gives a consistent result.

Carbon dioxide exchange at night is most extensively studied by micrometeorologists. The experience should be transferred also to other trace gas studies. In turn, the estimation of advection terms for other scalars, including the chemically reactive ones, would contribute also to understanding of night-time turbulent transfer of carbon dioxide.

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Table 1. Statistics for Lagrangian transport time (s) from average sink level (approximated by the average leaf area distribution) to measurement level for u_*=1 m s^{-1}. Q denotes quartiles and median statistics. For scaling the stability length L the forest height H=14 m was used.

LH^{-1}	Average time (s)	Q25 (s)	Q50 (s)	Q75 (s)
+100	70.2	25.2	50.4	93.6
+10	81.8	27.5	56.4	108.7
+1	117.9	35.1	78.2	157.9
−10	59.6	21.4	42.7	79.9
−1	33.5	12.7	24.5	45.2

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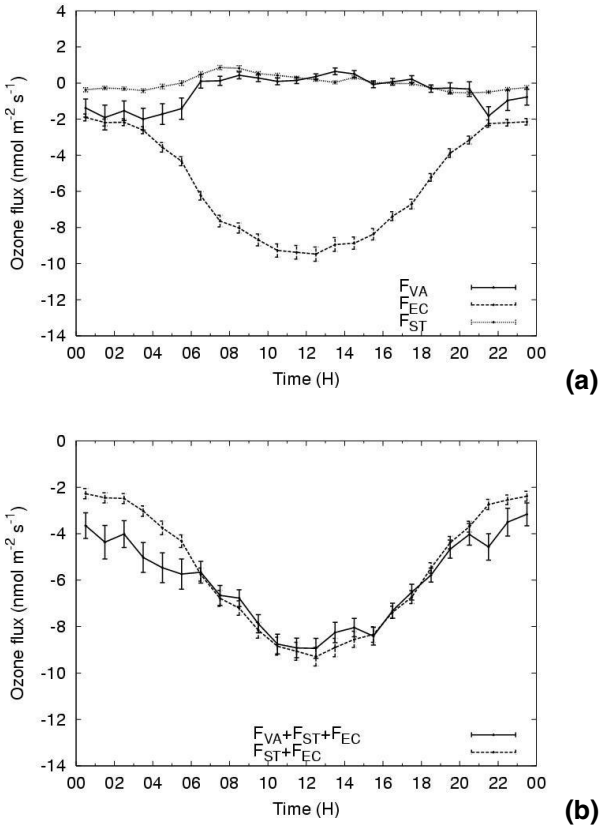

Fig. 1. Diurnal average of different ozone flux terms separately **(a)** and as sums **(b)**. F_{EC} denotes the eddy covariance, F_{ST} the storage and F_{VA} the vertical advection terms. Period from 10 June 2004 to 30 July 2004 was used. Error bars denote standard errors for hourly time intervals.

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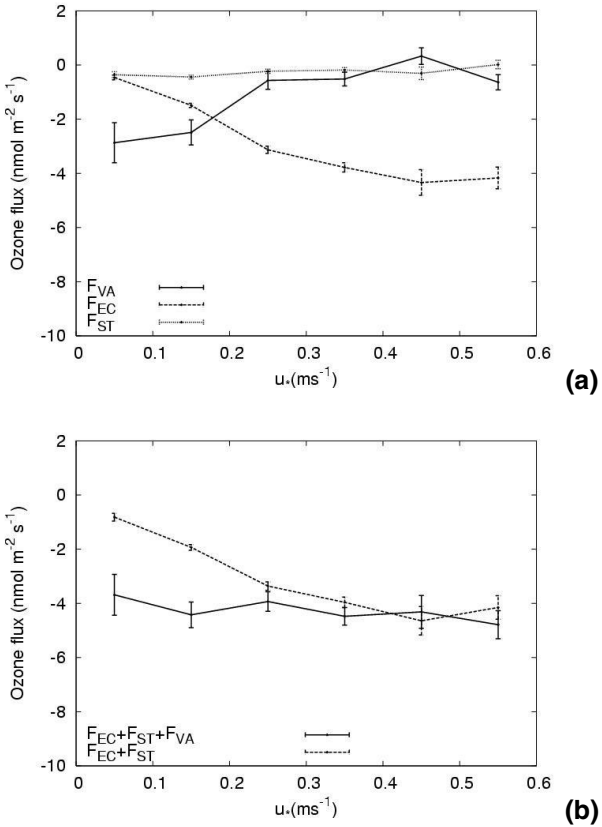

Fig. 2. Friction velocity dependence of different night-time ozone flux terms separately **(a)** and as sums **(b)**. Night-time was defined according to local time/elevation of Sun. Error bars denote standard error values for 0.1 m s^{-1} bins for friction velocity.

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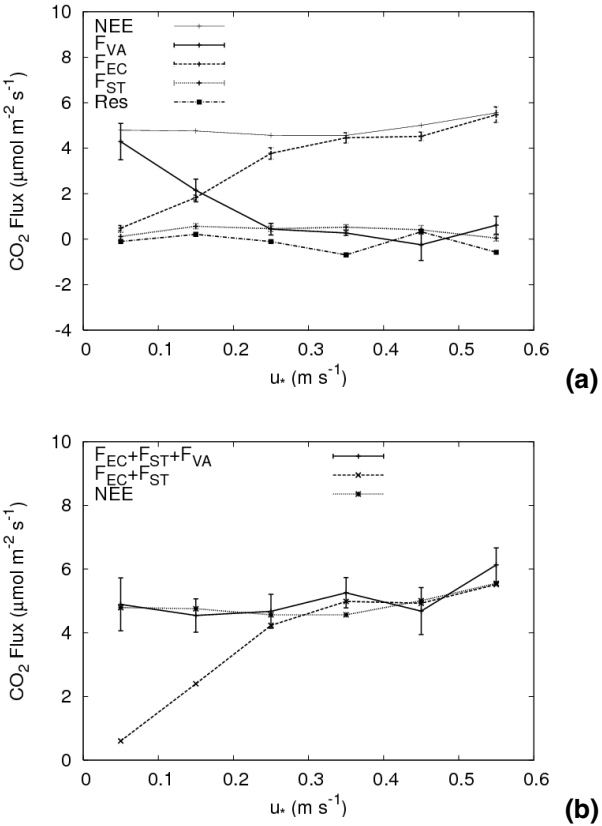

Fig. 3. Friction velocity dependence of different night-time CO_2 flux terms separately **(a)** and as sums **(b)**. Night-time was defined according to local time/elevation of Sun. Error bars denote standard error values for 0.1 m s^{-1} bins for friction velocity. The NEE denotes an independent estimate of respiration flux by chambers (Mammarella et al., 2007). Res denotes residual obtained by subtracting all other terms from NEE.

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