

# 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 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, 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.



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## 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 height of the stand near the measurement tower is about 14 m, and the total (all-sided) needle area is about 6 m<sup>2</sup> m<sup>-2</sup>. 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 HS1199, Gill Instruments Ltd, Lymington, Hampshire, England) and a fast response chemiluminescence gas analyzer for ozone (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, its performance and applied corrections to obtain the turbulent flux of ozone molar mixing ratio 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<sub>3</sub> molar mixing ratio 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 was similar to that used for measuring CO<sub>2</sub>-profiles (Rannik et al., 2004). Ozone molar mixing ratio with respect to moist air was measured with an ultraviolet light absorption gas analyzer (TEI 49C Ozone analyzer, Thermo Fisher Scientific, Inc., Waltham, MA, USA), with the sample flow rate of 21 min<sup>-1</sup> through the analyzer. Simultaneous water vapour mixing ratios were used to obtain the mixing ratio with respect to dry air.

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

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

where  $z_r$  refers to observation level (23.3 m) and  $c$  denotes molar mixing ratio of scalar with respect to dry air and the overbar denotes averaging over the turbulent record (30 min). This integral was numerically evaluated using the trapezoidal rule. A linear interpolation between 33.6 and 16.8 m was assumed to estimate the mixing ratio at  $z_r$ . The 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 scalar conservation expression is defined as

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

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

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

where  $\bar{u}$  and  $\bar{v}$  are defined in a non-rotated co-ordinate system.

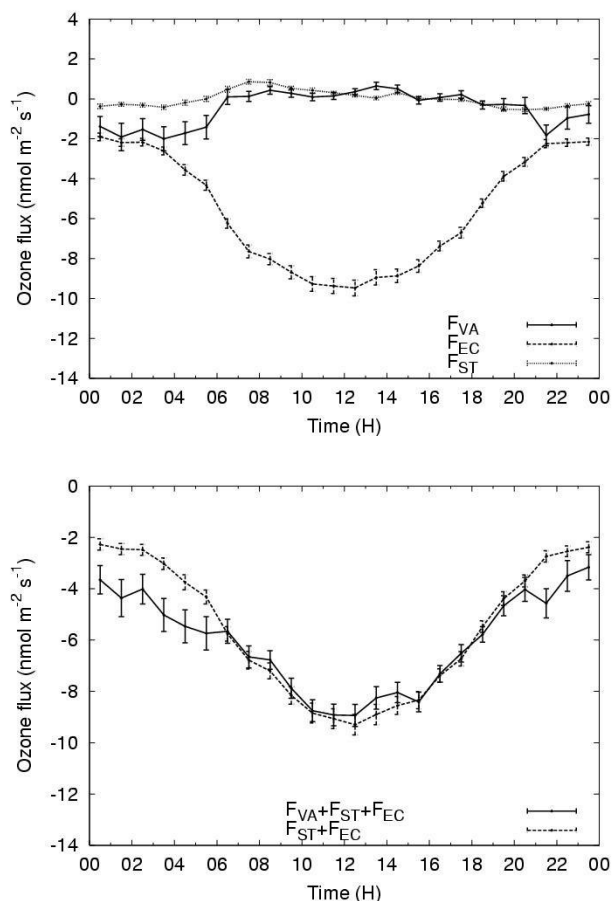
The planar fit flow planes were determined on monthly basis via minimising root-mean-square deviation using the following criteria: regression was made for wind direction sectors (20 degrees) for cases with wind velocities less than 5 m s<sup>-1</sup>.

## 3 Results and discussion

The sum of the different flux terms equals the total source/sink strength below the observation level

$$F_{EC} + F_{ST} + F_{VA} + F_{HA} = S_s + S_a, \quad (4)$$

separated here for canopy and soil surface ( $S_s$ ) and airborne chemical ( $S_a$ ) terms, where  $F_{EC}$  is the eddy covariance and  $F_{HA}$  the horizontal advection terms of molar mixing ratio. The total of source/sink terms 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 the EC measurement level). The surface deposition of ozone  $S_s$  consists



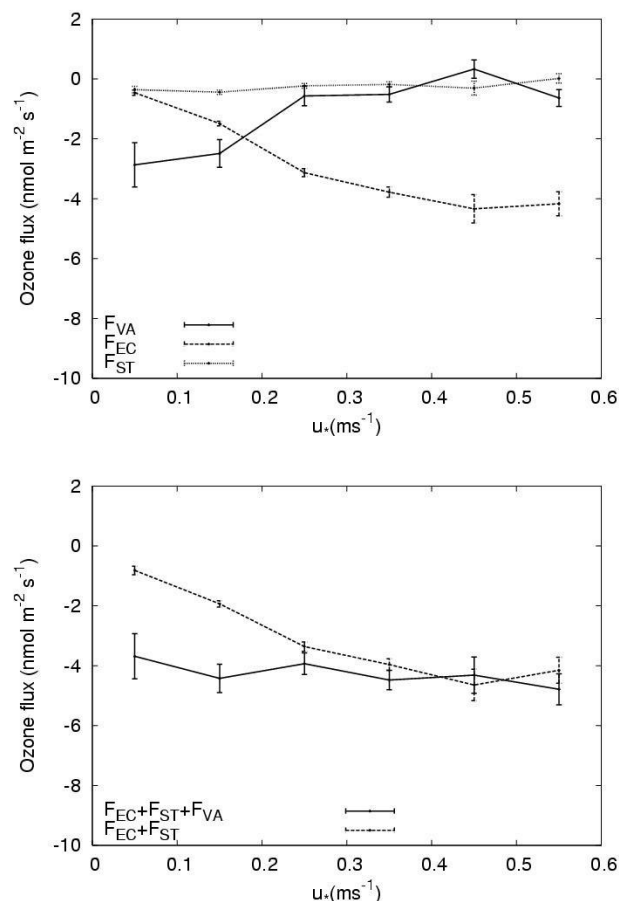
**Fig. 1.** Diurnal average of different ozone flux terms separately (a) and as sums (b).  $F_{EC}$  denotes the eddy covariance,  $F_{ST}$  the storage and  $F_{VA}$  the vertical advection terms. Period from 10 June 2004 to 30 July 2004 was used. Error bars denote standard errors for hourly time intervals.

in turn of stomatal and surface depositions, which involves surface chemical reactions. The contributions of these two surface deposition mechanisms are not separated here and the sink term  $S_a$  will include only chemical reactions in air. 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 measurements for a 2 months period, from 10 June 2004 to 30 July 2004, were analysed.

### 3.1 Ozone fluxes

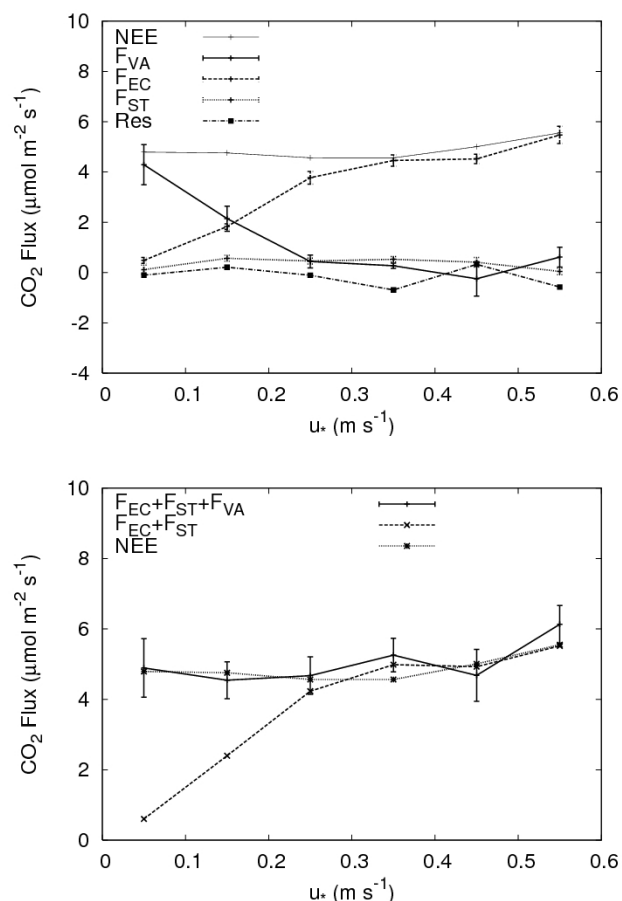
Depending on averaging time and observation conditions, the flux estimates contain the random error component approximately 10 to 20%. In case of low wind speed or non-stationarity of scalar mixing ratio and/or wind records, the



**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<sup>-1</sup> bins for friction velocity.

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. 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<sup>-2</sup> s<sup>-1</sup> 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



**Fig. 3.** Friction velocity dependence of different night-time CO<sub>2</sub> 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<sup>-1</sup> 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.

important parameters and is frequently used as a criterion for reliability of night-time CO<sub>2</sub> flux measurements (Aubinet et al., 2000; Loeschner 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 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<sub>2</sub> and ozone are not identical during night time conditions: CO<sub>2</sub> 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 molar mixing ratio 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  $-4 \text{ nmol m}^{-2} \text{ s}^{-1}$ . With the average observed ozone mixing ratios this corresponds to local dry deposition velocity about  $4 \text{ mm s}^{-1}$ . 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.

The canopy resistance is expressed by

$$r_c = \frac{U_h}{u_*^2} \frac{1}{\sqrt{\varepsilon}} \left( \frac{1 + \sqrt{\varepsilon} \tanh(\gamma \sqrt{\varepsilon})}{\sqrt{\varepsilon} + \tanh(\gamma \sqrt{\varepsilon})} \right), \quad (5)$$

where  $\gamma$  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  $\varepsilon$  total collection efficiency by canopy elements, presented as

$$\varepsilon = C_\varepsilon E_B. \quad (6)$$

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

$$E_B = \frac{c_v}{c_d} Sc^{-2/3}, \quad (7)$$

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

$$Sc = \frac{\eta}{\rho_a D} \quad (8)$$

the Schmidt number ( $\rho_a$  is the density of air) with  $D$  being the diffusion coefficient and  $\eta$  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<sup>-1</sup>. In terms of deposition rate these resistances together would allow deposition velocity of about 20 mm s<sup>-1</sup>. 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).

The deposition velocity is given by

$$v = \frac{1}{r_a + r_c + r_s}, \quad (9)$$

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

$$r_a = \frac{U_r - U_h}{u_*^2}, \quad (10)$$

**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<sup>-1</sup>. 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    |

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).

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 chemical reaction time scale as well as available time for reactions, which is determined by turbulent transport time. Turbulent transport time denotes here the time that an air parcel spends after being in contact with sources or sinks until travelling to the flux measurement level. To estimate turbulent transport time 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<sup>-1</sup>. The transport time is inversely proportional to friction velocity and to obtain estimate for other turbulence conditions the values have to be rescaled with respective  $u_*$  values. Average transport times for low turbulence ( $u_*=0.2$  m s<sup>-1</sup>) night-time conditions and stability range from  $LH^{-1}=+100$  to +1 are from about 6 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  $\sim 1.5$  min, 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<sup>-1</sup>, the estimated average turbulent transport times can vary from about 20 to 2 min for stabilities  $LH^{-1}=+1$  and +100, respectively. 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 reacting almost exclusively with ozone, have been detected at the site with a clear seasonal pattern (Hakola et al., 2006). The most abundant sesquiterpene observed at site is beta-caryophyllene. The reaction rate of this sesquiterpene with ozone is  $1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Shu and Atkinson, 2004). With typical ozone mixing ratio observed at site around  $30 \text{ nmol mol}^{-1}$  the first-order time-scale for sesquiterpene destruction is around two minutes. To our knowledge there is no other volatile organic compounds with fast enough reaction time-scales to be able to cause significant sink of ozone within comparable time scales to turbulent transport time. For example, the most abundant monoterpene observed at the site alpha-pinene has a reaction rate constant  $8.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 1997), which corresponds to first-order chemical degradation time about 4.3 h.

The sesquiterpene emission rates for June 2004 has been estimated to be up to  $40 \text{ mg m}^{-2} \text{ month}^{-1}$  (Bonn et al., 2008). Under the assumption that all emitted sesquiterpenes react below the observation level the corresponding ozone consumption rate is up to  $0.1 \text{ nmol m}^{-2} \text{ s}^{-1}$ . This is far too small amount in comparison to ozone deposition rates. Another compound reacting with ozone is nitrogen oxide (NO), which has a reaction rate constant with ozone for night-time conditions at  $T=293 \text{ K}$   $1.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Michael et al., 1981). This is equivalent to chemical lifetime in the order of 1 min. The nitrogen oxide (NO) emission at the site was estimated to be about  $6 \text{ ng(N) m}^{-2} \text{ h}^{-1}$  by Pilegaard et al. (2006). The corresponding ozone destruction rate would be about  $10^{-4} \text{ nmol m}^{-2} \text{ s}^{-1}$ . 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 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 20 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 can 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. However, the night-time forest-atmosphere exchange of reactive and non-reactive gases is different due to chemical sink in air below the observation level. The potential of chemical reactions to produce/destroy the compound depends on the time scale of chemical reactions relative to average turbulent transport time between sources/sinks and observation level. Also, carbon dioxide is emitted and ozone deposits into forest canopy at night. Under strongly stable conditions the emission of a substance leads to significant accumulation inside canopy, which results in large storage term but can lead also to large horizontal as well as vertical advection terms (terms being proportional to horizontal and vertical gradients of concentration). On the contrary, ozone is deposited into forest canopy and under limited turbulent transport conditions the ozone depletion leads to lower concentrations inside canopy. However, the horizontal and vertical gradients formed under such conditions can not be as large as for emitted quantity and thus the conservation equation of ozone is probably less affected by advection terms.

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