

Ozone flux measurements over a Scots pine forest using eddy covariance method: performance evaluation and comparison with flux-profile method

Petri Keronen¹⁾, Anni Reissell¹⁾²⁾³⁾, Üllar Rannik¹⁾, Toivo Pohja⁴⁾,
Erkki Siivola¹⁾, Veijo Hiltunen¹⁾, Pertti Hari⁴⁾, Markku Kulmala¹⁾ and
Timo Vesala¹⁾

¹⁾ *University of Helsinki, Department of Physical Sciences, P.O. Box 64, FIN-00014 University of Helsinki, Finland*

²⁾ *University of Helsinki, Department of Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland*

³⁾ *Finnish Meteorological Institute, Air Quality Research, Sahaajankatu 22 E, FIN-00880 Helsinki, Finland*

⁴⁾ *University of Helsinki, Department of Forest Ecology, P.O. Box 27, FIN-00014 University of Helsinki, Finland*

Keronen, P., Reissell, A., Rannik, Ü., Pohja, T., Siivola, E., Hiltunen, V., Hari, P., Kulmala, M. & Vesala, T. 2003: Ozone flux measurements over a Scots pine forest using eddy covariance method: performance evaluation and comparison with flux-profile method. *Boreal Env. Res.* 8: 425–443. ISSN 1239-6095

Ozone fluxes were measured over a forest in southern Finland between August 2001 and July 2002 using the eddy covariance method. Systematic errors due to the imperfect frequency response of the instrumentation and random errors due to the stochastic nature of turbulence were estimated. Flux underestimation correction factors for unstable stratification were 1.03–1.19. Random errors of the flux estimates were most frequently about 20% of the flux value. Fluxes were highest during the summer, declining to near zero during the winter. In summer, fluxes were higher during daytime than at night coinciding with higher turbulence and higher rate of stomatal uptake. Maximum summertime deposition velocities were 6–7 mm s⁻¹. During winter, the diurnal pattern in ozone flux was weak and the deposition velocity was 0.5–1.5 mm s⁻¹. Comparison between eddy covariance and profile flux measurement results generally showed good agreement during daytime.

Introduction

In order to understand the transfer of ozone (O_3) between the atmosphere and vegetation, atmospheric chemistry, meteorology, transport and vegetation uptake mechanisms need to be considered. That is, several processes affect the ambient air mixing ratios of ozone, as well as fluxes and deposition velocities. Ambient air mixing ratios depend on transport, local formation and destruction in photochemical and other reactions, and on the volume and mixing conditions of the boundary layer. Uptake by vegetation through stomata is considered to be a large sink for surface ozone, and therefore the factors affecting the opening and closing of stomata (light, temperature, humidity, wetness, water availability) have often been examined (e.g. Meyers *et al.* 1998, Wesely and Hicks 2000). However, recent studies provide evidence that non-stomatal routes for O_3 deposition may account for a considerable portion of the total uptake by a forest ecosystem (e.g. Zeller and Nikolov 2000, Lamaud *et al.* 2002).

Several techniques have been used to measure fluxes of chemical species between the atmosphere and the surface (Wesely *et al.* 1989, Dabberdt *et al.* 1993, Zeller 1993, Rinne *et al.* 2001, Altimir *et al.* 2002, Guenther 2002). Aerodynamic (or micro-meteorological) methods rely on measuring the vertical concentration profile (profile method), the concentration difference between up- and downward directed air-drafts (eddy accumulation and relaxed eddy accumulation methods) or the concurrent turbulent fluctuations of vertical wind speed and concentration (eddy covariance and disjunct eddy covariance methods). In the profile and accumulation methods flux-profile and flux-concentration difference relationships are needed to calculate the fluxes. In the eddy covariance (EC) methods the flux is obtained directly from the covariance between the wind speed and concentration data. Non-aerodynamic methods determine the change of concentration in an enclosure or measure the mass deposited on or evaporated from a natural or a surrogate surface.

Aerodynamic methods require relatively large uniform flux source areas, stationary atmospheric conditions and flat topography. On the other

hand, these methods are more representative in a larger scale than non-aerodynamic methods, since they can be used to quantify the average vertical flux over several hundred square meters extending both upwind and crosswind from the measurement point.

The profile technique requires accurate measurements of concentration differences. With the eddy accumulation, relaxed eddy accumulation and disjunct eddy covariance techniques relatively slow sensors can be used (Wesely *et al.* 1989, Rinne *et al.* 2001). The eddy covariance technique requires measurements of very rapid turbulent fluctuations and therefore the used sensors and analysers should have a short response time combined with a high selectivity. The eddy covariance technique is considered as a reliable measurement method for turbulent exchanges of momentum and heat in the atmosphere. It is also suitable for flux measurements in the vicinity of uneven terrain, such as hills, and in slightly non-stationary situations (McMillen 1988), and it is the only method suitable for flux measurements inside forest canopies (Arya 2001).

Ozone flux measurements over Scots pine (*Pinus sylvestris* L.) forests are scarce (Rondon *et al.* 1993, Aurela *et al.* 1996, Tuovinen *et al.* 2001) but fluxes over other coniferous trees encountered in the northern boreal region, such as the Norway spruce (*Picea abies*), have been reported (Pilegaard *et al.* 1995, Mikkelsen *et al.* 2000). Duyzer *et al.* (1995) reported ozone flux measurements above Douglas fir. Suni *et al.* (2003) compared ozone flux results with fluxes for CO_2 , latent heat, and particles. Possible sources of errors in micrometeorological techniques have been reported (Businger 1986, Wesely *et al.* 1989, Kaimal and Finnigan 1994, Lenschow *et al.* 1994, Foken and Wichura 1996), but few publications have actually presented an error analysis (Businger 1986, Rannik 1998a, Finkelstein and Sims 2001) or compared the different flux measurements methods (Zeller 1993, Guenther *et al.* 1996, Mikkelsen *et al.* 2000).

In this paper, we present ozone flux results obtained by eddy covariance method. This study covers the measurement period from August 2001 to July 2002. To our knowledge, no winter-time ozone flux or deposition velocity data over Scots pine forests have previously been reported.

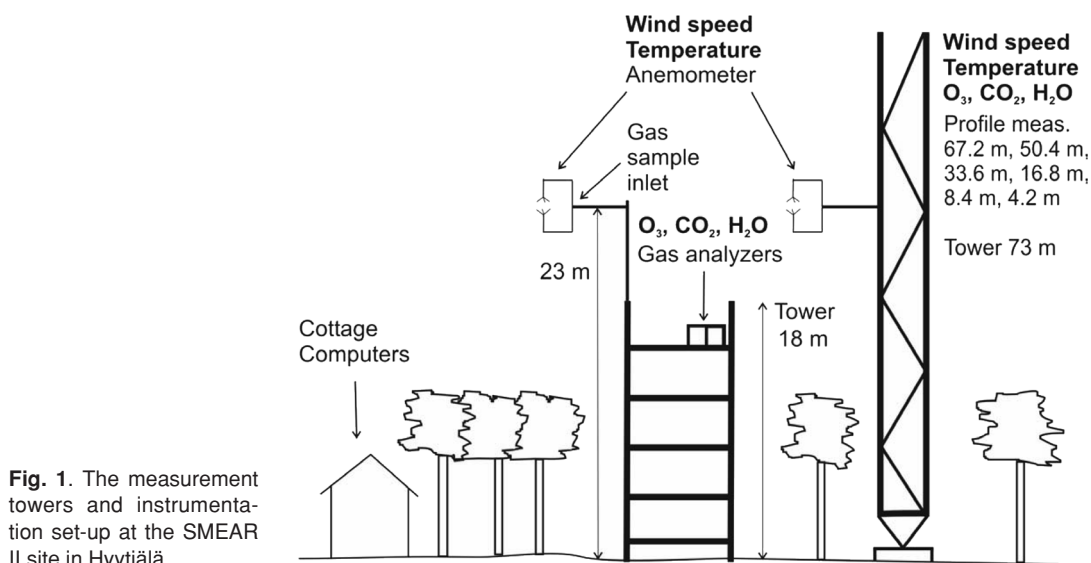


Fig. 1. The measurement towers and instrumentation set-up at the SMEAR II site in Hyttiälä.

We describe the eddy covariance measurement system, estimate the magnitude of systematic and random errors, and compare the eddy covariance flux results with results from profile flux measurements. The diurnal and seasonal variations of ozone flux and deposition velocity are discussed. The ozone concentration profiles are also discussed in relation to turbulence.

Experimental

Site description and infrastructure

The SMEAR II measurement site (Station for Measuring Forest Ecosystem–Atmosphere Relations) at the Hyttiälä Forestry Field Station of the University of Helsinki is located in southern Finland, 220 km northwest from Helsinki. The measurement station ($61^{\circ}51'N$, $24^{\circ}17'E$, 181 m above sea level) was established in July 1995 and the continuous measurements started in January 1996. The forest stand surrounding the SMEAR II station was established in 1962 by sowing and the most homogeneous area is predominantly Scots pine with other species accounting for only 1% of the stand. The homogeneous area extends approximately 200 m in all directions and the mean height of the dominant trees in the stand is 14 m. A more detailed description of the site is given in Rannik *et al.*

(2002). The site has been evaluated to be suitable for micrometeorological flux measurements in unstable or near-neutral conditions (Rannik 1998b). The site is located in a background area, but a nearby source of pollution is the Forestry station building complex approximately 600 m to the southwest of the site. About 10 km to the southeast, two possible sources of regional pollution are a saw mill and local power plant in the village of Korkeakoski. About 60 km west to southwest from the station is Tampere, a city of about 200 000 inhabitants.

Eddy covariance measurements of momentum (τ), sensible heat (H), carbon dioxide (CO_2), latent heat (LE) and ozone fluxes were carried out at 23-m height, approximately 10 m above the top of the canopy, by means of a low tower (height 18 m) equipped with an extension rod (Fig. 1). Measurements of solar radiation were carried out also in this low tower. O_3 profile measurements were performed at six heights (67.2, 50.4, 33.6, 16.8, 8.4 and 4.2 m) in a high tower (height 73 m). The horizontal separation between the low tower and the high tower is about 25 m. Eddy covariance measurements of momentum, sensible heat, CO_2 , latent heat and aerosol particle fluxes were carried out also in the high tower (at the height 23 m). More information on the infrastructure of the station is given in Vesala *et al.* (1998) and Kulmala *et al.* (2001).

Eddy covariance method

Turbulent flux may be considered as a superposition of eddies of different sizes (frequencies). Generally the vertical mass flux of a substance (F_c) is given as the time average of the product of the con-current vertical wind velocity (w) and concentration of the substance (c) (e.g. Arya 2001). The instantaneous values of w and c can be decomposed into a mean and a fluctuating component (so called Reynolds decomposition). The flux of the substance is thus

$$F_c = \overline{w \cdot c} = \overline{(\bar{w} + w') \cdot (\bar{c} + c')} = \bar{w} \cdot \bar{c} + \overline{w' \cdot c'} \quad (1)$$

The over-bars denote the time average and the primes the fluctuating part. The time averages of the fluctuating components (w' and c') are zero.

With eddy covariance method the flux (Eq. 1) at the measurement height is obtained as a direct result. The frequently used formulation for dry deposition assumes that the deposition flux is directly proportional to the local concentration at the measurement height

$$F = -v_d c \quad (2)$$

where F is the flux, c is the concentration at the measurement height and v_d is a proportionality constant known as deposition velocity (e.g. Seinfeld and Pandis 1998). By convention a flux downwards has a negative sign, giving a positive deposition velocity (Eq. 2) for a depositing substance. The deposition velocity gives an indication of the combined magnitude of all the physical, chemical and physiological processes causing the fluxes regardless of the concentration.

There are several requirements that should be met when applying the eddy covariance method (McMillen 1988, Kaimal and Finnigan 1994, Foken and Wichura 1996). A common assumption is that the mean vertical wind speed is zero. If the area around the measurement point is flat, this assumption holds sufficiently well even though the wind speed is strictly not zero. The deviation from zero is however very small. The eddy covariance method can, however, be applied also in a sloping terrain, because it allows mathematically to force the vertical wind

speed to zero by coordinate rotations, that is by rotating the mean wind vector to local streamlines. The time series should also be stationary during the measurement period, but eddy covariance method can also be applied in slightly non-stationary conditions (McMillen 1988). Furthermore, for the measured flux to represent the surface flux around the measurement site, a horizontal homogeneity is required within the flux measurement source area. The eddy covariance method requires fast measurements of wind speed and concentration. Ideally, the frequency response of the sensors and analyzers should be at least 10 Hz (Wesely *et al.* 1989, Kaimal and Finnigan 1994). Measurement resolution for wind speed and temperature should be at least $\pm 0.05 \text{ m s}^{-1}$ and 0.05°C , respectively (Kaimal and Finnigan 1994), and the measurement resolution of the concentration should give a signal-to-noise ratio of at least 30 (Wesely *et al.* 1989). When using a tower to reach the layer above a canopy, the sensors should be at least three lateral dimensions above the top of the tower and supported by a thinner mast or rod (Kaimal and Finnigan 1994).

Measurements

Wind speed and air temperature

An acoustic anemometer (Solent Research HS1199 ultrasonic anemometer, Gill Ltd., Lymington, Hampshire, England) has been installed at a height of 23 m by means of an 18-m-high tower (dimensions $2 \times 3 \text{ m}$) and 6-m-long rectangular (dimensions $50 \times 50 \text{ mm}$) extension rod. Above 16 m the tower is relatively unobstructed with a ratio of obstructed-to-unobstructed area of the order of 10%. The anemometer is of a horizontal design, with transducers placed at the end of a 1.25-m-long rod (diameter 25.4 mm). In practice the measuring volume (about 0.0013 m^3) is at a distance of about 1 m from the extension rod. Another acoustic anemometer (Solent Research 1012R2, Gill Ltd., Lymington, Hampshire, England) is located in the higher tower also at a height of 23 m.

The measurement rate of the anemometer is 100 Hz. For EC measurements the anemometer

has been set to calculate an average of ten samples before converting the signals to actual wind speed and speed of sound results. Therefore the effective measurement rate is 10 Hz. The anemometer's internal software evaluates all three wind components and also the velocity of sound. It applies a calibration to take into account the effects of transducers and head framework. A crosswind (the wind normal to the measurement axis) correction is also applied.

The wind speed and speed of sound resolutions given by the manufacturer are both 0.01 m s^{-1} . Using the calculated sonic temperature and the speed of sound resolution, the calculated resolution for the air temperature is 0.02°C .

Ozone

The O_3 and $\text{CO}_2/\text{H}_2\text{O}$ analyzers have a common main sample line (length 12 m, diameter $10 \times 8 \text{ mm}$, Teflon® PTFE). The sample intake has been installed along the anemometer's supporting rod at a distance of about 0.25 m from the centre point of the measuring volume. The inlet protecting the sample intake against rain has an opening ($5 \times 15 \text{ mm}$) directed downwards. As a protection against insects and due to the risk of contaminating the main sample line with particulate matter, a coarse filter (FW series SS-316 pleated mesh element, mesh size range $5\text{--}10 \mu\text{m}$, Nupro Company, Willoughby, USA) has been placed at the intake between the inlet and the sample line. To avoid the condensation of water vapor on the tube surfaces, the sample line is slightly heated (ca. 3.5 W m^{-1}). Similarly the inlet and the filter are heated to minimize the risk of ice/frost formation. Instrument boxes housing the gas analyzers and other instrumentation are installed at a height of about 15 m. The O_3 analyzer is connected to the main sample line at about 10 m from the sample intake with Teflon® FEP tubing (length 0.5 m, diameter $3.18 \times 1.59 \text{ mm}$). The analyzer line contains a filter to protect it from particulate contamination. The filter in the O_3 analyzer sampling line is a membrane filter (Mitex PTFE Membrane, diameter 47 mm, pore size $5.0 \mu\text{m}$, Millipore Corporation, Bedford, MA, USA).

Fast measurements of ozone concentration were performed with a chemiluminescence gas analyzer (LOZ-3 Ozone analyzer, Unisearch Associates Inc., Concord, Ontario, Canada). The nominal sampling rate of the analyzer is 10 Hz. Inside the analyzer the sample air flows across a fabric wick saturated with a reagent solution containing Eosin-Y in ethylene glycol. The reaction at the air/liquid interface between ozone and Eosin-Y produces light (chemiluminescence) in proportion to the concentration. Because the reaction coefficient is temperature dependent, the wick area of the reaction vessel is thermostatically controlled to 35°C and the analyzer's internal software also compensates for the effect by taking into account the measured sample cell temperature. The analyzer also compensates for changes in sample pressure by taking into account the measured sample pressure. The sample air inlet to the reaction chamber has a capillary to create a slight vacuum ($\sim 100 \text{ hPa}$). This vacuum then causes the reagent solution to flow from its reservoir to the wick. The solution is re-circulated by removing it from the exhaust air flow in a separation chamber, which in turn is periodically emptied to the feed reservoir. According to the manufacturer, water vapour, hydrocarbons and nitrogen oxides do not result in observable interferences in concentrations.

The ozone fluxes were corrected for air density fluctuations due to the simultaneous water vapour transfer (Webb *et al.* 1980), because the analyzer does not automatically correct the ozone reading for water vapour concentration. In practice a term given by Eq. 3 was added to each half hour O_3 flux value.

$$M_a(c/\rho_a)E \quad (3)$$

Here M_a is the molecular weight of air (g mol^{-1}), c is the concentration of ozone (mol m^{-3}), ρ_a is the density of air (g m^{-3}) and E is the water vapour flux ($\text{mol m}^{-2} \text{ s}^{-1}$).

Data collection and processing

Analog signal outputs of the analyzers were connected to the anemometer's data logger, which then sends the combined wind and concentration

data to a computer located in the main measurement building at the station. The data collection, on-line calculation of flux data and turbulence statistics, and storing of calculated flux data and raw signal data is performed with a program described by Rannik (1998a). Disturbances in the time series are removed on-line by the program by comparing instantaneous values with a running mean (300 s) and discarding those values that deviate from the mean more than empirical limit values. The disturbances appear as spikes in the raw data and usually originate from temporary faults in the data transmission. The spikes are not frequent but removing them essentially improves the quality of the on-line calculated flux data (Rannik 1998a). The limits are set for values of concentration, wind speed and sonic temperature. They are chosen so that real, albeit large and sudden, changes in the values that may exist during stable stratification are accepted. In practice non-stationary time series and intermittent turbulence are thus not removed. All the original turbulence raw data is saved. These raw data are post-processed, that is, the flux calculations are performed afterwards using the original saved instrument signals in order to remove incorrect raw data (sensor or other instrumental malfunctions) and to correct for systematic errors, caused by the (non-ideal) measurement system. Also the calibration of the gas analyzers is taken into account during the post-processing by linear interpolation between the calibration checks.

Maintenance, calibration and performance of instrumentation

Anemometer

The anemometer required no maintenance during the summer time. During ice forming conditions at winter the transducer heads became easily inoperative. This is a common problem with anemometers. As the model 1199HS anemometer does not have any transducer heating, there was nothing very efficient that could be done to resume the operation. During November, December and January the anemometer was unfortunately inoperative for several weeks due

to a solid ice cover on the transducers. A couple of times the ice was melted by heating with warm air. But as the weather conditions during the period were characterized by temperatures around 0 °C and rainy days were immediately followed by below-zero temperatures, the melting helped only for short time periods.

Ozone analyzer

The maintenance of the O₃ analyzer required that the amount of the reagent liquid solvent (ethylene glycol) was monitored and adding in after every few months to keep the reservoir bottle full or almost full. Without this preventive operation the re-circulation function seemed to fail, causing the separator to be filled with the liquid which was then drawn into the exhaust line. This malfunction stopped the instrument's operation completely. Also the sample pressure needed to be monitored, because if the pressure difference against the ambient pressure exceeded 200 hPa, the reagent liquid flow rate increased too much so that the re-circulation function failed. Keeping the pressure difference below this limit was also important to prevent the liquid from being drawn into the sample line. This could cause not only the malfunctioning of the O₃ analyzer but also the contamination of the main sample line. The filter at the analyzer inlet was changed every few months during other service/repair work. The filter was not observed to be visibly dirty, and the change of the filter did not show any remarkable and/or long lasting (more than half hour) change in the concentration data and no noticeable change in the flux data.

Regular calibration checks included checking the span coefficient and zero offset. For determining the span correction coefficient for the ozone reading, the ambient O₃ concentration, measured by an ultraviolet photometric analyzer (TEI 49, Thermo Environmental Instruments Inc., Franklin, MA, U.S.A.), was used as the reference. As the LOZ-3 ozone analyzer measured at a height of 23 m and the reference concentration was measured at several heights, but not exactly at 23 m, the geometric mean of the concentrations measured at heights 16.8 and 33.6 m was calculated and used in the calibration check.

The TEI 49 reference analyzer is calibrated regularly against a transfer standard photometer (Dasibi 1008 PC, Dasibi Environmental Corp., Glendale, CA, USA), which in turn is calibrated at the Finnish Meteorological Institute against the Ozone Photometer (S/N 63718-341) traceable to the Standard Reference Photometer (SRP #15, Certificate No 01/2, 12.7.2001, EMPA). For determining the zero offset, the analyzer's internal activated carbon containing scrubber was used to purify the sample air. Since the span stability of the O₃ analyzer was observed to be drifting quite a lot, it was decided that the calibration should be checked weekly. This way the span stability could be kept within the $\pm 10\%$ value. Generally the sensitivity of the analyzer decreases when the reagent liquid ages. According to the manufacturer, one full bottle (100 cm³) should maintain its calibration for at least one month. Because of the rather low ambient O₃ concentrations at the station, this amount seemed to be usable for a longer time. On the other hand the sensitivity increased when the reagent became more concentrated. This change in concentration happened because the solvent ethylene glycol was drawn out of the liquid re-circulation system as small droplets to the exhaust line.

The O₃ analyzer had some malfunctions during the year mainly because of the problems with the liquid flow causing the lack of data between 21 October and 29 November in 2001 and between 27 May and 17 June in 2002. The main reason for the liquid flow problems was clogging of the coarse filter at the intake of the main sample line. During winter clogging was caused by ice build-up and in summer by small insects.

Results and discussion

Measurement error analysis

The accuracy of the measured EC flux estimates is determined by both systematic and random errors. Reasons for the systematic errors include flow distortion by the anemometer, time shift between the wind speed and gas concentration data, imperfect frequency response of the concentration measurement instrumentation, changes

in analyzer's sensitivities, concentration fluctuations caused by air temperature and water vapour concentration fluctuations, and horizontal inhomogeneity (McMillen 1988, Wesely *et al.* 1989, Kaimal and Finnigan 1994, Foken and Wichura 1996, Rannik 1998a). The stochastic nature of turbulence combined with the finite sampling time (Lenschow *et al.* 1994) and un-correlated analyzer noise (Lenschow and Christensen 1985) are the main reasons for the random errors.

Systematic errors

The anemometer affects the air flows that it is used to measure. The anemometer's internal correction software, installed by the manufacturer, takes into account the transducer shadowing and thus no extra correction was performed. The installation of the anemometer 5 m above the top of the tower (at 18 m height) does not quite fulfill the criteria given by Kaimal and Finnigan (1994). However, the wind speed, wind direction, sensible heat flux and momentum flux data obtained with this EC measurement system and the corresponding data obtained with the EC measurement system installed in the high tower agreed well (Pearson correlation coefficients (R^2) 0.92, 0.98, 0.88 and 0.90, respectively). The deviations and variations of the results were small and the systematic differences between the results obtained with the two measurement systems were reasonable, being smaller than the standard errors of the difference between the two systems (A. Kelloniemi, pers. comm.). Because the EC measurement system installed in the high tower was demonstrated to give reliable results (Rannik 1998a), it was concluded that the EC measurement system described in this paper worked equally reliably.

The sloping ground at the measurement site would lead to a non-zero average vertical wind speed without a coordinate rotation to set the wind vector to the local streamlines. The measurement/data collection program performed a three-dimensional coordinate rotation "on-line" according to Kaimal and Finnigan (1994). The time shift between the wind speed and gas concentration time series because of the gas sample line was taken into account to be able to

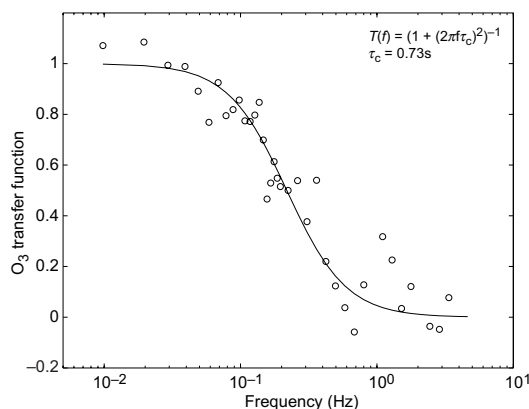


Fig. 2. Transfer function $T(f)$ of the ozone eddy covariance measurement system. τ_c is the first order response time of the system. Circles are the ratios of the co-spectrum of ozone flux relative to the co-spectrum of sensible heat flux and solid line is the fitted curve.

calculate the covariance. This so-called lag-time was determined “on-line” by the measurement/data collection program by maximising the cross correlation between vertical wind velocity and concentration time series.

An imperfect response of the system to the high-frequency fluctuations because of long instrument response times (gas analyzers), attenuation of concentration fluctuations in the sample line, displacement between the sensors and spatial averaging of the wind speed values along the sound pulse measuring paths are a source for underestimating the flux values. These high-frequency losses were corrected afterwards during the post-processing of the raw data by estimating the transfer function of the EC-system (Aubinet *et al.* 2000). The used methods (Horst 1997, Aubinet *et al.* 2000) are presented in the Appendix. For the ozone flux measurement system, the response time was determined to be 0.73 s (Fig. 2), which is larger than the carbon dioxide and water vapour flux response times of 0.30 and 0.25 s, respectively. These whole system response times were reasonable taking into account the (approximate) analyzer response times given by the manufacturers (0.5 and 0.2 s for O_3 and CO_2/H_2O analyzers, respectively).

For unstable stratification, the flux underestimation and normalised frequency were independent on stability (Fig. 3), as has been

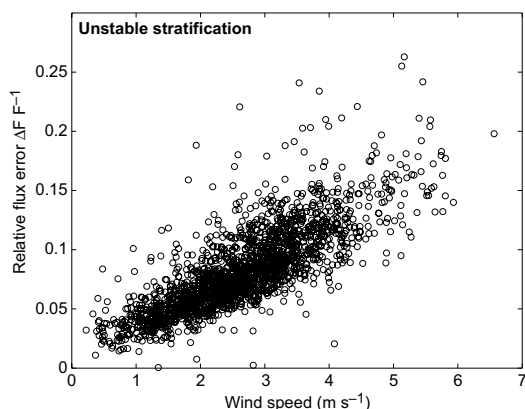


Fig. 3. Relative flux underestimation of the ozone eddy covariance measurement system due to imperfect instrument frequency response under unstable stratification.

usually observed. The normalized frequency was determined to be 0.092 ± 0.029 for the unstable cases (the variation range is 1 standard deviation), and the required correction factor was 1.03–1.19 depending on the wind speed (*see* Fig. 3). This range of corrections was considered to be reasonable when comparing it with values obtained for CO_2 (about 1.05) by Rannik (1998b) and O_3 (about 1.15) by Tuovinen *et al.* (1998). In stable cases the required corrections were larger (1.13–1.22) with also a larger variability. Even many-fold correction factors were obtained, but these high values occurred during situations when the absolute values of the fluxes were near zero. The strong dependence of normalised frequency on stability (*see* Fig. 4) implied a high underestimation of flux estimates under strongly stable situations.

The high-pass filtering of the signals during data acquisition (linear trend removal over 30 min according to Kristensen 1998) is also a source for underestimating the flux values. This low frequency loss was not analysed for the results presented in this paper and so was not taken into account in the results. The estimated magnitude based on previous analyses was about 3% depending, for example, on wind velocity and stability.

Calibration shifts of the gas analyzers were taken into account by linear interpolation between calibration values. The estimated errors for the

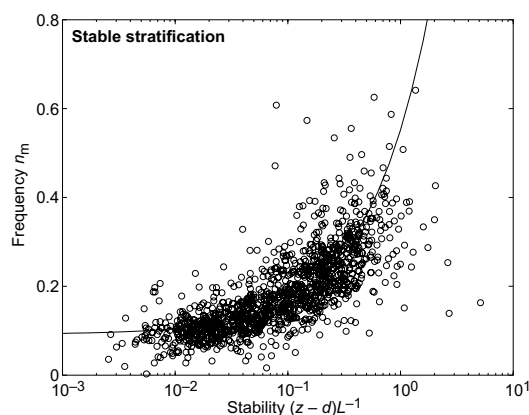


Fig. 4. Normalized frequency response corresponding to the maximum of the co-spectrum under stable stratification (Obukhov stability length $L > 0$).

corresponding flux values after the correction were 5% for O_3 , 5% for H_2O and 1% for CO_2 .

Air density fluctuations, related to simultaneous heat and water vapour transfer, are a source for apparent fluxes of gaseous compounds (Webb *et al.* 1980). No correction for density fluctuations due to heat flux was needed in our measurement system because temperature fluctuations were expected to be dampened in the sample line (Rannik *et al.* 1997). The ozone fluxes were, however, corrected for density fluctuations arising from simultaneous water vapour transfer. In most cases, this correction was less than 3% of the flux values.

Different source and/or sink areas at different wind direction sectors and during different atmospheric stability conditions were not taken into account. The storage or release of gas below the eddy measurement level was also not taken into account.

During the winter time, freezing conditions affected the measurements by causing the build-up of ice/frost on the anemometer transducer heads. This either completely stopped the operation of the anemometer or at least induced large measurement errors making the data unusable. These phenomena were the reason for (in practice) a complete lack of data during November and December. During January they most probably also caused bias in the wind speed data as the situations with low wind speed were also most affected by the ice/frost build-up.

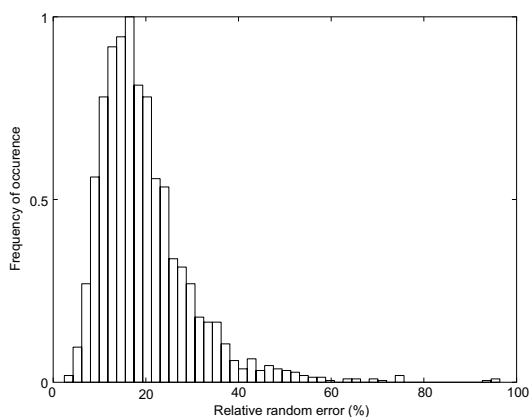


Fig. 5. Distribution of the random error of the half hour average ozone fluxes. The scale is obtained by normalising the data with the mode value. The data is from the period May–July 2003.

Random errors

Turbulent fluxes averaged over a limited time period have random errors because of the stochastic nature of turbulence (Lenschow *et al.* 1994). The random uncertainty of each 30-minute-average flux was obtained as presented in the Appendix. The random errors of ozone fluxes were most frequently around 20% of the flux value (Fig. 5).

Analyzer noise also contributed to the random error. Its magnitude was estimated to be less than $0.1 \text{ nmol m}^{-2} \text{ s}^{-1}$ according to Lenschow and Christensen (1985) and thus the instrumental noise was low as compared with other random errors.

Ozone concentration profiles

Comparison between fluxes obtained with the EC and profile methods

Ozone fluxes were also determined by the profile technique by applying the atmospheric surface layer similarity theory for concentration profiles (measured at 16.8, 33.6, 50.4 and 67.2 m heights). The concentration profiles could be measured with the measurement system and therefore the results could be used to estimate the fluxes with the flux-profile method (Fig. 6).

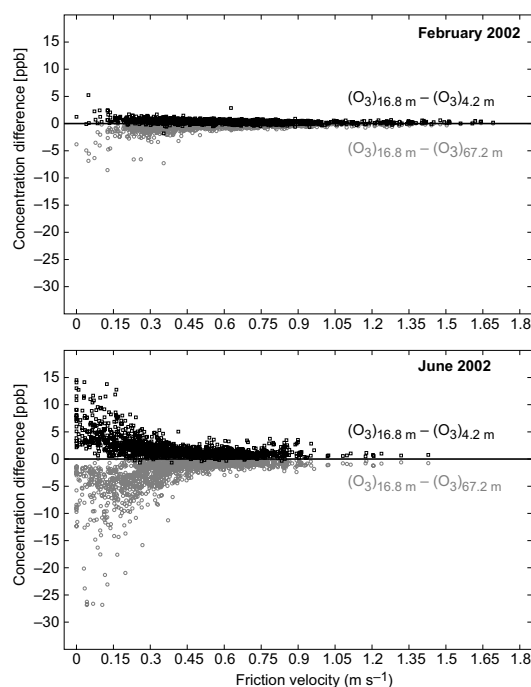


Fig. 6. Differences in half-hour-average ozone concentrations between the 16.8 and 67.2-m measurement heights and between the 16.8 and 4.2-m heights as a function of turbulence (expressed as friction velocity) in February 2002 and June 2002.

Similar to Rannik (1998b), the fluxes and error estimates were obtained by applying a linear regression technique to the observed and similarity profiles: the flux concentration values were obtained by using the measured profiles and by using the Obukhov stability length obtained from EC measurements. Flux was then calculated as given by Kaimal and Finnigan (1994). In general, a reasonably good correspondence between EC and profile fluxes was observed (Fig. 7). Random errors in the flux estimates caused scatter in both EC and profile flux data (Fig. 8). However, for profile fluxes the random errors were larger.

In order to compare the diurnal variation in ozone fluxes obtained by the two methods, average diurnal curves based on the measured half-hour flux values were calculated (Fig. 9). The variation range, presented by vertical bars, includes differences between days as well as random errors of flux estimates. The average values obtained by the two techniques were quite

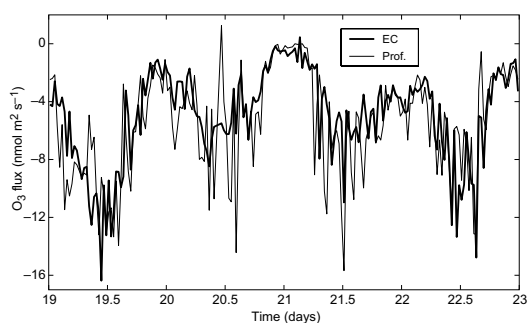


Fig. 7. Simultaneous half hour average ozone fluxes measured by eddy covariance and profile method, 19–22 June 2002.

similar after about 08:00. During night-time and early morning the two techniques gave fluxes with significantly different patterns: the ozone fluxes obtained from the profile technique indicated larger deposition. Generally the flux-profile method is thought to be quite uncertain around sunrise and sunset hours, and this could be the reason for the large discrepancy. However, we believe that this discrepancy originated from the influence of ozone chemistry on the vertical flux, which the applied profile technique ignored. For example Vilà-Gerau de Arellano and Duynkerke (1995) reported that in the case of a reactive compound, the vertical flux becomes a function of height because of chemical production/depletion of the compound and so a modification of the flux-profile similarity relationship is needed. The influence of chemistry was probably important during early morning hours when the chemistry time scale became comparable to the time scale of turbulent transport. The chemistry could be accelerated in the morning because of the accumulation of chemical compounds participating ozone chemistry in near-surface layer during the night.

Diurnal and seasonal variation in O_3 concentrations and concentration profiles

Only the data for three above canopy heights (67.2, 33.6 and 16.8 m) and one below canopy height (4.2 m) are presented (Fig. 10). The height of the EC measurements was 23 m. The measured ozone concentrations as well as con-

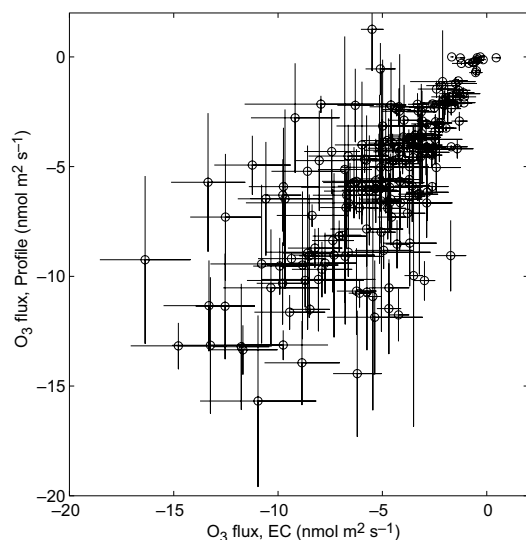


Fig. 8. Comparison between half hour average ozone fluxes measured by eddy covariance and profile method, 19–22 June 2002. The vertical and horizontal bars represent ± 1 standard error calculated by Eq. A6 in the Appendix.

centration profiles showed both diurnal and seasonal behaviour (*see also* Fig. 6).

During summertime there was a distinct and systematic decrease in ozone concentrations during the dark hours of the day. This was particularly obvious for the lowest measurement height (4.2 m) when the friction velocity was low. In January, that is winter time, the diurnal variability in concentrations was not as clear. However, it became discernible already in February.

In October there was a clear concentration profile above the canopy during the dark hours of the day (about 17:00–07:00). The profile started to build up early in the afternoon even before friction velocity started to decrease, and it persisted several hours after the friction velocity started to increase the next morning. Between about 11:00 and 14:00 the profile was almost undetectable except between 4.2 m and heights above the canopy. The concentrations had a clear diurnal cycle.

Throughout February the concentration profile was hardly detectable and there was no diurnal behaviour in the concentrations. Also the friction velocity showed only a weak diurnal pattern.

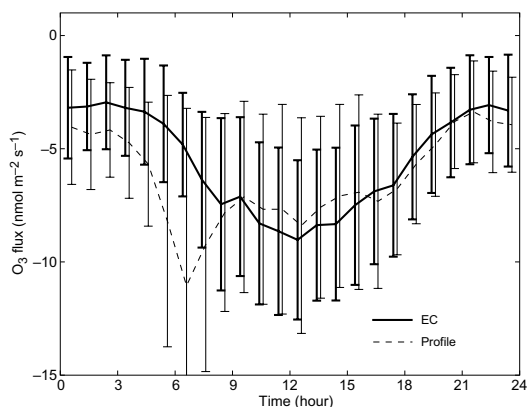


Fig. 9. Diurnal variation of ozone fluxes during June and July 2002 as measured by eddy covariance and profile method. Variation range (standard deviation for an hour, illustrated by vertical bars) includes differences between days as well as random errors of the flux estimates. Data are presented as medians of hourly average values.

In March there was again a detectable concentration profile during the dark hours (about 18:00–06:00). For this month, however, the behaviour was different from that in October: the profile started to build-up and vanished almost simultaneously with the decrease and increase of the friction velocity, respectively. The concentrations showed again a diurnal cycle.

In June there was a very clear concentration profile during the dark hours (about 22:00–02:00), and it was already detectable during the afternoon. The profile started to build up several hours before the friction velocity started to decrease. In the morning the profile persisted several hours after the friction velocity started to increase. Between about 08:00 and 12:00 the profile was almost undetectable. The concentrations had a strong diurnal cycle.

The inverse dependence of concentration profiles on turbulence, evident during the winter time, was consistent with the weakness of the vegetation uptake processes during the winter dormancy. The stronger diurnal variation in ozone concentrations and concentration profiles during summer time in comparison with that in winter time was consistent with the fact that more intense solar radiation and higher air temperature lead to stronger photochemically initiated ozone formation and destruction processes and plant stomatal activity.

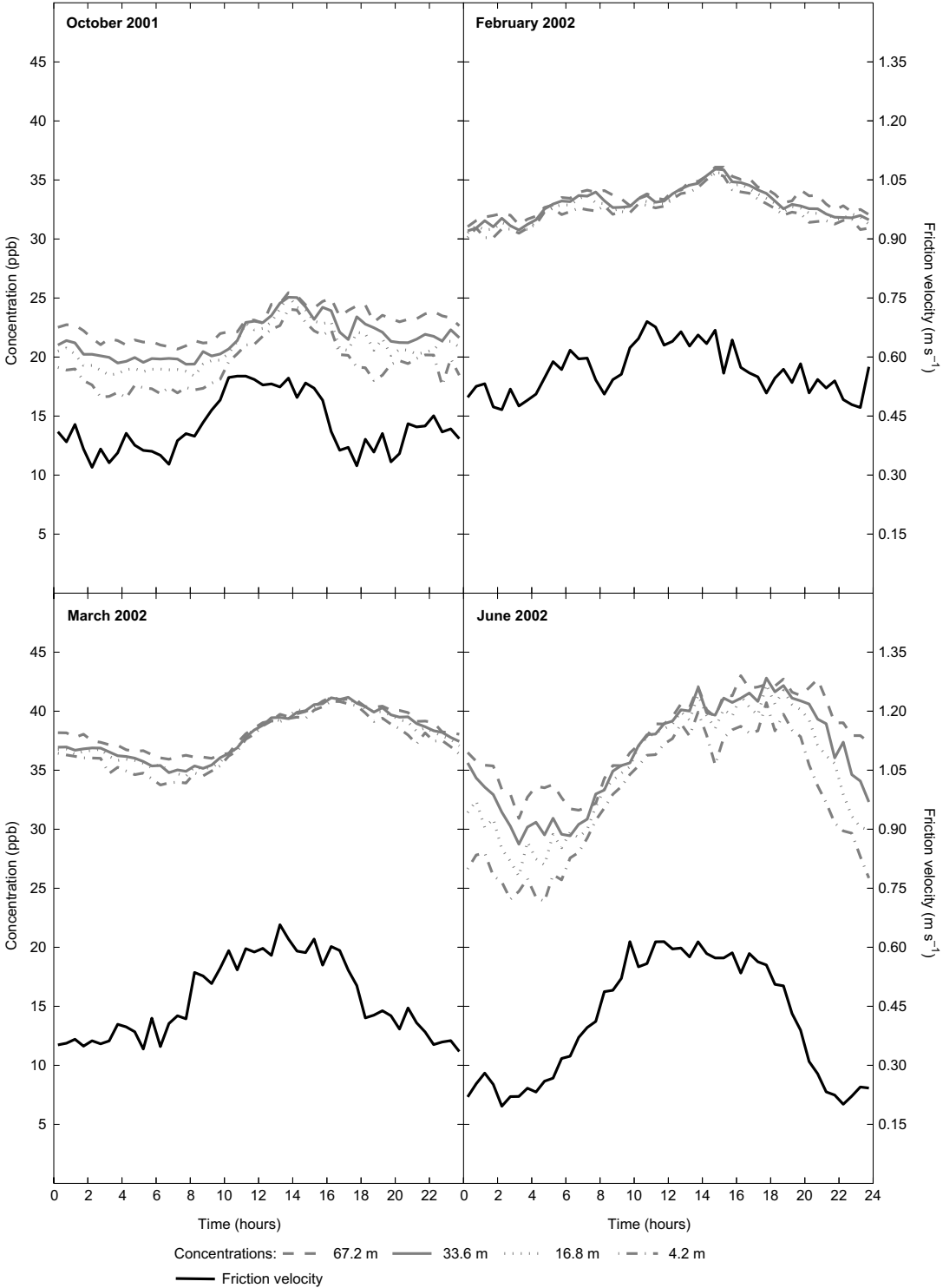


Fig. 10. Diurnal profiles for ozone concentration and friction velocity in October 2001, February 2002, March 2002 and June 2002. Dash, continuous, dot and dash-dot line are for 67.2 m, 33.6 m, 16.8 m and 4.2 m measurement heights, respectively. Data are presented as medians of half-hour average values.

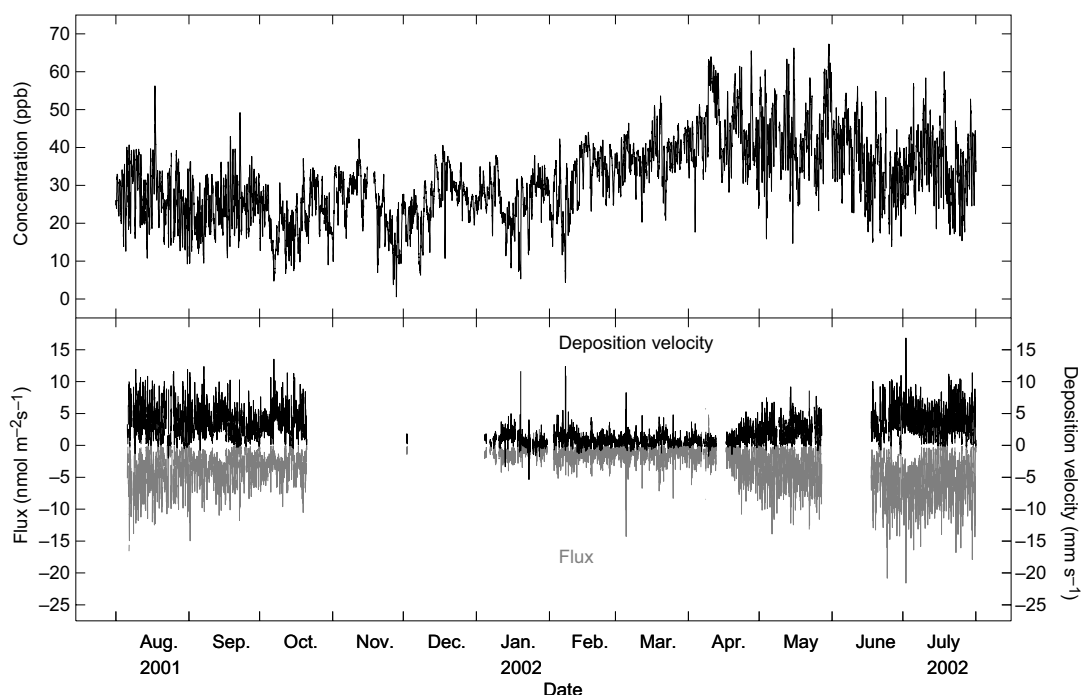


Fig. 11. Ozone concentrations, fluxes and calculated deposition velocities between August 2001 and July 2002. Data are given as half-hour average values.

Ozone fluxes

The EC method gave deposition flux as a direct result. Because the flux depends on the concentration, the deposition velocity was also calculated in order to study the diurnal and seasonal changes. The data for O_3 concentration was taken from the profile measurements (geometric mean of concentrations at heights 16.8 and 33.6 m) because the analyzer used in those measurements had a better absolute accuracy.

Both the flux and deposition velocity were higher during the growing season, declining to values close to zero in winter. The deposition velocity had values of up to about 10 mm s^{-1} from June until the middle of October (Fig. 11). Between January and April the deposition velocity was less than 1 mm s^{-1} but was not observed to have negative values (meaning a flux upwards). The deposition flux had a similar seasonal pattern as the deposition velocity.

During the growing season (approximately April–October) both flux and deposition velocity

were distinctively higher during daytime while in winter the diurnal pattern was either almost or completely missing (Fig. 12).

In October (autumn) a difference between the day and night was evident. The flux had a maximum at midday. The deposition velocity showed a maximum a couple of hours earlier, at about 10:00. The flux and deposition velocity were smaller during the night-time (about 17:00–07:00) than during daytime but did not reach zero values. The daytime deposition velocities were in the range $4\text{--}6 \text{ mm s}^{-1}$, whereas night-time deposition velocities were about 4 mm s^{-1} with the lowest values reaching almost 2 mm s^{-1} . The fluxes ranged from -2 to $-4 \text{ nmol m}^{-2} \text{ s}^{-1}$.

In February (winter) there was no detectable differences between the night-time (about 17:00–08:00) and daytime values. Both the deposition velocity and flux were small, about 1 mm s^{-1} and $-1 \text{ nmol m}^{-2} \text{ s}^{-1}$, respectively.

In March (spring) there were no distinctive daytime peaks in the fluxes or deposition velocities. For the deposition flux, a slight maximum

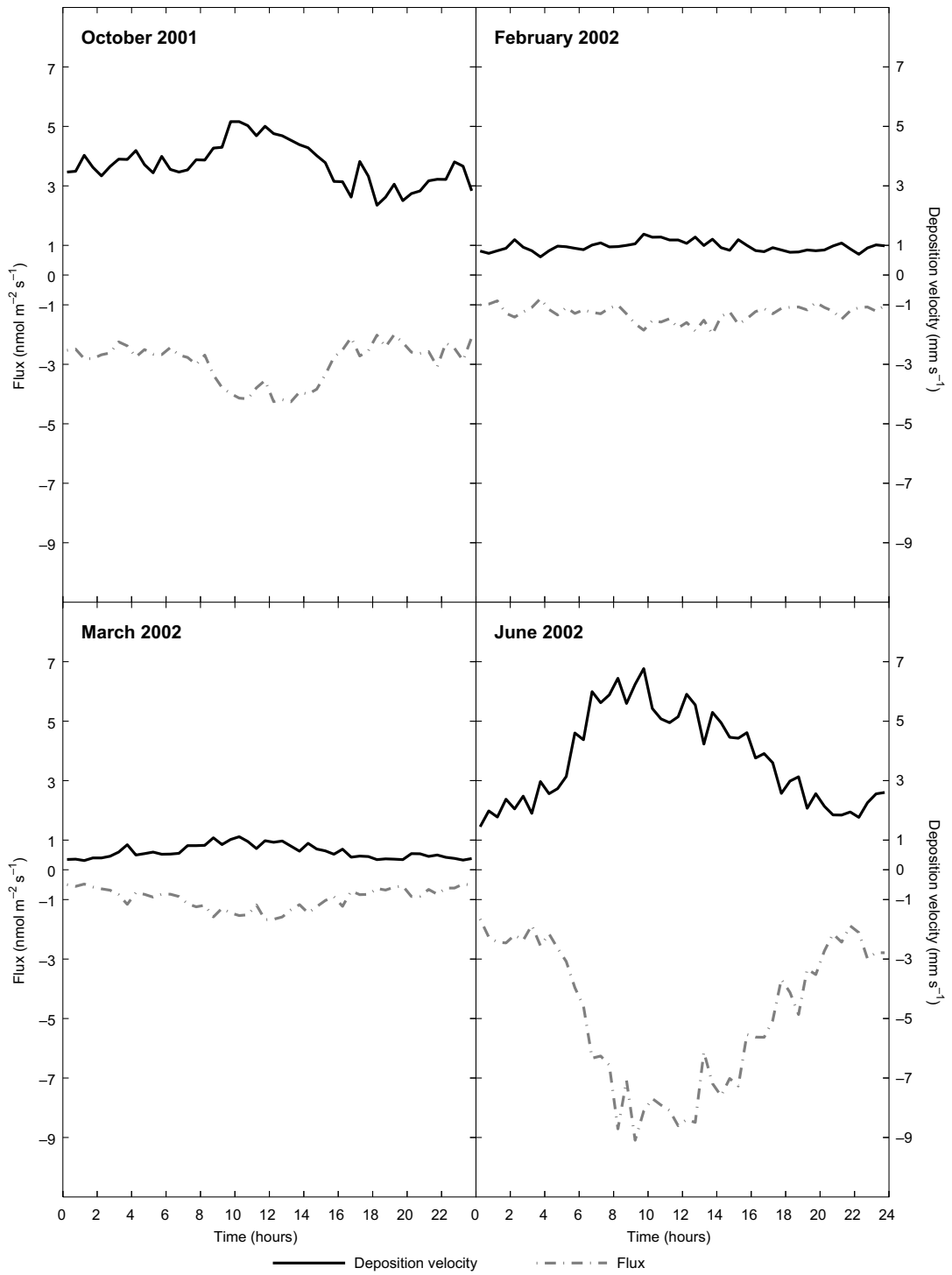


Fig. 12. Diurnal profiles of ozone fluxes and deposition velocities given as medians of half-hour average values in October 2001, February 2002, March 2002 and June 2002.

extended from about 09:00 to 15:00, whereas for the deposition velocity the maximum was not so evident. The daytime deposition velocity was about 1 mm s^{-1} and during the night it decreased to slightly below 0.5 mm s^{-1} . The daytime flux ranged from -1 to $-2 \text{ nmol m}^{-2} \text{ s}^{-1}$. During night time the flux decreased to values below (towards zero) $-0.4 \text{ nmol m}^{-2} \text{ s}^{-1}$.

In June (summer), the diurnal cycle was strong for both flux and deposition velocity. In comparison with that in October, the maximum of the flux was broader extending a couple of hours before and after 12:00. The maximum of the deposition velocity occurred a couple of hours earlier (at about 08:00) than in October. The daytime (about 02:00–22:00) deposition velocity ranged from 2 to 6 mm s^{-1} . During night-time the deposition velocity was about 2 mm s^{-1} with even the lowest values clearly above zero. The daytime flux ranged from -2 to $-9 \text{ nmol m}^{-2} \text{ s}^{-1}$. During night-time the flux was about $-2 \text{ nmol m}^{-2} \text{ s}^{-1}$.

The clear difference in the deposition velocity and flux between the summer and wintertime implies that ozone deposition was controlled by plant stomatal activity at the measurement site. However, also surface deposition could be totally different between the winter and in summer. The clear difference in their diurnal behaviour between summer and autumn was consistent with the different physiological activities of the vegetation due to the longer daytime in summer than in late autumn.

Eddy covariance ozone flux measurements performed by Aurela *et al.* (1996) over a Scots pine stand in Eastern Finland in August showed similar diurnal flux and deposition velocity profiles to this study. The daytime deposition velocity during the two-day measurement period was $1\text{--}5 \text{ mm s}^{-1}$ (30-minute averages), compared with the median values of $2\text{--}6 \text{ mm s}^{-1}$ (calculated from 30-minute averages) obtained for June in this study. Night-time values were typically less than 0.5 mm s^{-1} (Aurela *et al.* 1996). Our results indicated higher night-time deposition velocity with values of about 2 mm s^{-1} .

Pilegaard *et al.* (1995) and Mikkelsen *et al.* (2000) reported diurnal behaviours of ozone flux, deposition velocity and concentration above Norway spruce (*Picea abies*) similar to

our results above Scots pine. Pilegaard *et al.* (1995) conducted EC measurements at a Danish forest site that consisted of 12-m high Norway spruce. The diurnal variation of the flux and deposition velocity during ten days in June showed a broad midday peak in the flux and a corresponding peak in the deposition velocity a couple of hours earlier. The deposition velocity ranged from 3.5 mm s^{-1} at night to 7 mm s^{-1} during the day with a sharp rise at dawn and a maximum in the morning. The diurnal mean O_3 flux and deposition velocity measured at a Danish site in September (Mikkelsen *et al.* 2000) showed a maximum at approximately the same time in the morning. Duyzer *et al.* (1995) reported a diurnal behaviour for the canopy resistance of ozone above an 18 to 20-m high Douglas fir stand. The diurnal variation of the resistance to uptake during two days in July showed a broad minimum between about 10:00 and 12:00 with a sharp decrease in the morning and a slower increase during afternoon and evening. The concept “canopy resistance” used by the Duyzer *et al.* group comes from the widely-used resistance model where the deposition processes are interpreted in terms of an electrical resistance analogy, in which the transport to the surface is assumed to be governed by three resistances in series: an aerodynamic resistance for transport through the atmosphere, quasi-laminar layer resistance for transport across the layer adjacent to the vegetation surface and canopy resistance for deposition at the vegetation surface (see e.g. Seinfeld and Pandis 1998, Wesely and Hicks 2000). The inverse of the sum of the resistances is then by definition deposition velocity. During the day in summertime the canopy resistance is the major parameter controlling ozone deposition at a maritime pine forest (Lamaud *et al.* 2002). Assuming that the total resistance was mainly due to the canopy resistance at our measurement site allowed us to compare the diurnal behaviour of the deposition velocity reported in this study and the canopy resistance reported by the Duyzer *et al.* group. The diurnal behaviour of the canopy resistance for ozone reported by the Duyzer *et al.* group was similar to our results for the ozone deposition velocity. A more detailed investigation of O_3 deposition processes is presented in Suni *et al.* (2003).

Conclusions

The EC instrumentation and measurement setup used in this study at the SMEAR II site in Hyytiälä worked well giving results comparable to other studies using both different and similar instrumentation. The systematic errors due to imperfect frequency response of the instrumentation and random errors arising from the stochastic nature of turbulence were estimated and found to be within reasonable limits. The ozone analyzer required regular maintenance and calibration. Several weeks of wintertime data was lost due to ice forming conditions rendering the anemometer inoperative.

Flux results obtained using the EC method agreed well with results from a gradient method, particularly during daytime. At night and towards the morning the flux results were significantly different, being indicative of an influence of ozone chemistry on the concentration profiles and fluxes making the fluxes to be a function of height.

The seasonal variation of ozone concentrations during the time period August 2002–July 2002 (excluding November 2001, December 2001 and part of June 2002) showed a generally higher concentration in spring as compared with those in summer and winter. The ozone flux and deposition velocity started to increase at the end of April and had maximum values during the summertime until the end of August. Maximum deposition velocities in October were comparable to the maximum values during summertime.

Distinct diurnal profiles of ozone concentrations, fluxes, and deposition velocities were observed in summer with highest values during daytime and lowest values at night. The flux and deposition velocity had maxima in the morning and before noon in contrast to the ozone concentrations that had highest values in the afternoon. Very little diurnal variation was seen in winter.

Further studies will include analysis of ozone uptake mechanisms using the measurement data more extensively for separate evaluation of aerodynamic, quasi-laminar layer and canopy resistances. Stomatal resistance will be determined and compared with non-stomatal canopy resistance in order to study the relative importance of these two deposition pathways. Also the observed discrepancy between the results obtained by flux-

profile and EC method will be examined in order to study the significance of chemistry on the ozone concentration profiles and fluxes.

Acknowledgements: We gratefully acknowledge support from the European Commission (NOFRETETE, contract no. EVK2-CT2001-00106), the Academy of Finland (project FIGARE/CORE), and the University of Helsinki Environmental Research Center.

References

- Altimir N., Vesala T., Keronen P., Kulmala M. & Hari P. 2002. Methodology for direct field measurements of ozone flux to foliage with shoot chambers. *Atmos. Environ.* 36: 19–29.
- Arya S.P. 2001. *Introduction to micrometeorology*, 2nd ed. International Geophysics Series, vol. 79, Academic Press, London, Great Britain.
- Aubinet M., Grelle A., Ibrom A., Rannik Ü., Moncrieff J., Foken T., Kowalski A.S., Martin P.H., Berbigier P., Bernhofer Ch., Clement R., Elbers J., Granier A., Grünwald T., Morgenstern K., Pilegaard K., Rebmann C., Snijders W., Valentini R. & Vesala T. 2000. Estimates of the annual net carbon and water exchange of European forests: the EUROFLUX methodology. *Advances in Ecological Research* 30: 113–175.
- Aurela M., Laurila T. & Tuovinen J.-P. 1996. Measurements of O₃, CO₂ and H₂O fluxes over a Scots pine stand in Eastern Finland by the micrometeorological eddy covariance method. *Silva Fennica* 30: 97–108.
- Businger J.A. 1986. Evaluation of the accuracy with which dry deposition can be measured with current micrometeorological techniques. *J. Appl. Meteorol.* 25: 1100–1124.
- Dabberdt W.F., Lenschow D.H., Horst T.W., Zimmerman P.R., Oncley S.P. & Delany A.C. 1993. Atmosphere surface exchange measurements. *Science* 260: 1472–1481.
- Duyzer J., Westrate H. & Walton S. 1995. Exchange of ozone and nitrogen oxides between the atmosphere and coniferous forest. *Water, Air, Soil Pollut.* 85: 2065–2070.
- Finkelstein P.L. & Sims P.M. 2001. Sampling error in eddy correlation flux measurements. *J. Geophys. Res.* 106: 3503–3509.
- Foken T.H. & Wichura B. 1996. Tools for quality assessment of surface-based flux measurements. *Agric. For. Meteorol.* 78: 83–105.
- Guenther A., Baugh W., Davis K., Hampton G., Harley P., Klinger L., Vierling L., Zimmerman P., Allwine E., Dilts S., Lamb B., Westberg H., Baldocchi D., Geron C. & Pierce T. 1996. Isoprene fluxes measured by enclosure, relaxed eddy accumulation, surface layer gradient, mixed layer gradient, and mixed layer mass balance techniques. *J. Geophys. Res.* 101: 18555–18567.
- Guenther A. 2002. Trace gas emission measurements. In: Burden F.R., McKelvie I., Förstner U. & Guenther A. (eds.), *Environmental monitoring handbook*, McGraw-Hill, chapter 24, pp. 1–12.

- Horst T.W. 1997. A simple formula for attenuation of eddy fluxes measured with first-order-response scalar sensors. *Boundary-Layer Meteorol.* 82: 219–233.
- Kaimal J.C. & Finnigan J.J. 1994. *Atmospheric boundary layer flows. Their structure and measurement*. Oxford University Press, New York.
- Kristensen L. 1998. *Time series analysis. Dealing with imperfect data*. Risø National Laboratory, Roskilde, Denmark.
- Kulmala M., Hämeri K., Aalto P.P., Mäkelä J.M., Pirjola L., Nilsson D., Buzorius G., Rannik Ü, Dal Maso M., Seidl W., Hoffman T., Janson R., Hansson H.-C., Viisanen Y., Laaksonen A. & O'Dowd C.D. 2001. Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus* 53B: 324–343.
- Lamaud E., Carrara A., Brunet Y., Lopez A. & Druilhet A. 2002. Ozone fluxes above and within a pine forest canopy in dry and wet conditions. *Atmos. Environ.* 36: 77–88.
- Lenschow D.H. & Christensen L. 1985. Uncorrelated noise in turbulence measurements. *J. Atmos. Oceanic Tech.* 2: 68–81.
- Lenschow D.H., Mann J. & Kristensen L. 1994. How long is long enough when measuring fluxes and other turbulence statistics? *J. Atmos. Oceanic Tech.* 18: 661–673.
- McMillen R. 1988. An eddy correlation technique with extended applicability to non-simple terrain. *Boundary-Layer Meteorol.* 43: 231–245.
- Meyers T.P., Finkelstein P., Clarke J., Ellestad T.G. & Sims P.F. 1998. A multilayer model for inferring dry deposition using standard meteorological measurements. *J. Geophys. Res.* 103: 22645–22661.
- Mikkelsen T.N., Ro-Poulsen H., Pilegaard K., Hovmand M.F., Jensen N.O., Christensen C.S. & Hummelshøj P. 2000. Ozone uptake by evergreen forest canopy: temporal variation and possible mechanisms. *Environ. Pollut.* 109: 423–429.
- Pilegaard K., Jensen N.O. & Hummelshøj P. 1995. Seasonal and diurnal variation in the deposition velocity of ozone over a spruce forest in Denmark. *Water, Air, Soil Pollut.* 85: 2223–2228.
- Rannik Ü., Vesala T. & Keskinen R. 1997. On the dampening of temperature fluctuations in a circular tube relevant to the eddy covariance measurement technique. *J. Geophys. Res.* 102: 12789–12794.
- Rannik Ü. 1998a. *Turbulent atmosphere: Vertical fluxes above a forest and particle growth*. Report Series in Aerosol Science. No 35, Finnish Association for Aerosol Research, Helsinki, Finland.
- Rannik Ü. 1998b. On the surface layer similarity at a complex forest site. *J. Geophys. Res.* 103: 8685–8697.
- Rannik Ü., Altimir N., Raittilä J., Suni T., Gaman A., Hussein T., Hölttä T., Lassila H., Latokartano M., Lauri A., Natsheh A., Petäjä T., Sorjamaa R., Ylä-Mella H., Keronen P., Berninger F., Vesala T., Hari P. & Kulmala M. 2002. Fluxes of carbon dioxide and water vapour over Scots pine forest and clearing. *Agric. For. Meteorol.* 111: 187–202.
- Rinne H.J.I., Guenther A.B., Warneke C., de Gouw A.D. & Luxembourg S.L. 2001. Disjunct eddy covariance technique for trace gas flux measurements. *Geophys. Res. Lett.* 28: 3139–3142.
- Rondon A., Johansson C. & Granat L. 1993. Dry deposition of nitrogen dioxide and ozone to coniferous forests. *J. Geophys. Res.* 98: 5159–5172.
- Seinfeld J.H. & Pandis S.N. 1998. *Atmospheric chemistry and physics. From air pollution to climate change*. John Wiley & Sons, Inc., New York, 1326 pp.
- Suni T., Rinne J., Reissell A., Altimir N., Keronen P., Rannik Ü., Dal Maso M., Kulmala M. & Vesala T. 2003. Long-term measurements of surface fluxes above a Scots pine forest in Hyytiälä, Southern Finland, 1996–2001. *Boreal Env. Res.* 8: 287–301.
- Tuovinen J.P., Aurela M. & Laurila T. 1998. Resistances to ozone deposition to a flark fen in the northern aapa mire zone. *J. Geophys. Res.* 103: 16953–16966.
- Tuovinen J.-P., Simpson D., Mikkelsen T.N., Emberson L.D., Ashmore M.R., Aurela M., Cambridge H.M., Hovmand M.F., Jensen N.O., Laurila T., Pilegaard K. & Ro-Poulsen H. 2001. Comparison of measured and modeled ozone deposition to forests in Northern Europe. *Water, Air, Soil Pollut., Focus* 1: 263–274.
- Vesala T., Haataja J., Aalto P., Altimir N., Buzorius G., Garam E., Hämeri K., Ilvesniemi H., Jokinen V., Keronen P., Lahti T., Markkanen T., Mäkelä J.M., Nikinmaa E., Palmroth S., Palva L., Pohja T., Pumpanen J., Rannik Ü, Siivola E., Ylitalo H., Hari P. & Kulmala, M. 1998. Long-term field measurements of atmosphere-surface interactions in boreal forest combining forest ecology, micrometeorology, aerosol physics and atmospheric chemistry. *Trends in Heat, Mass and Momentum Transfer* 4: 17–35.
- Vilà-Gerau de Arellano J. & Duynkerke P.G. 1995. Atmospheric surface layer similarity theory applied to chemically reactive species. *J. Geophys. Res.* 100: 1397–1408.
- Webb E.K., Pearman G.I. & Leuning R. 1980. Correction of flux measurements for density effects due to heat and water vapour transfer. *Quart. J. Royal Meteorol. Soc.* 106: 85–100.
- Wesely M.L., Lenschow D.H. & Denmead O.T. 1989. Flux measurement techniques. In: Lenschow D.H. & Hicks B.B. (eds.), *Global tropospheric chemistry, chemical fluxes in the global atmosphere. Report of the Workshop on Measurements of Surface Exchange and Flux Divergence of Chemical Species in the Global Atmosphere*, Prepared by National Center for Atmospheric Research, Boulder, Colorado, USA, for the National Science Foundation, the National Aeronautics and Space Administration and the National Oceanic and Atmospheric Administration, pp. 31–46.
- Wesely M.L. & Hicks B.B. 2000. A review of the current status of knowledge on dry deposition. *Atmos. Environ.* 34: 2261–2282.
- Zeller K.F. 1993. *Eddy diffusivities for sensible heat, ozone and momentum from eddy correlation and gradient measurements*. Res. Pap. RM-313. Fort Collins, CO: US Department of Agriculture, Forest Service, Rocky Mountain Forest and Range Experiment Station, 44 pp.
- Zeller K.F. & Nikolov N.T. 2000. Quantifying simultaneous fluxes of ozone, carbon dioxide and water vapor above a subalpine forest ecosystem. *Environ. Pollut.* 107: 1–20.

Appendix

Correction for high-frequency losses

High-frequency losses were corrected during post-processing of the raw data by estimating the transfer function of the EC-system (Aubinet *et al.* 2000) and by estimating the ratio of the observed and not-attenuated flux (Horst 1997). The co-spectral transfer function ($T(f)$) of an EC system for a system behaving as a first order response sensor can be described by

$$T(f) = \frac{1}{1 + (2\pi f \tau_c)^2} \quad (\text{A1})$$

where f is natural frequency and τ_c the (first order) response time of the attenuator (sensor) (Horst 1997). The effective transfer function of the EC system can be determined experimentally by (co-)spectral analysis of measurements. The transfer function can be estimated as a ratio of co-spectral density of scalar flux relative to co-spectrum of sensible heat flux (Aubinet *et al.* 2000). Such a procedure assumes that temperature measurements are not affected by attenuation (true for a sonic anemometer) and includes normalisation with integral over frequencies not affected by attenuation (Aubinet *et al.* 2000).

The observed flux (F_m) can be formally presented as the integral over multiplication of the true co-spectrum (Co , unaffected by frequency attenuation) with the co-spectral transfer function as

$$F_m = \int_0^{\infty} T(f) Co(f) df \quad (\text{A2})$$

In cases of atmospheric turbulence and transfer function a good approximation for the attenuated (observed) flux is (Horst 1997)

$$\frac{F_m}{F_t} = \frac{1}{1 + 2\pi f_m \tau} \quad (\text{A3})$$

where F_t is the true (un-attenuated) flux and f_m is the frequency at which the co-spectrum $f Co(f)$ attains its maximum value. The frequency f_m is determined by average wind speed (U), observation level (z) above displacement height (d) and also by atmospheric stability via dependence on the normalised frequency (n_m)

$$f_m = \frac{n_m U}{z - d} \quad (\text{A4})$$

By applying the transfer function T with a time constant 0.7 s to the co-spectrum of temperature (estimated by Fast Fourier Transform technique), the flux underestimation was determined. In stable cases, the dependence of n_m on the stability was established as

$$n_m = 0.092 \left(1 + 5.0 \left(\frac{z - d}{L} \right)^{0.78} \right) \quad (\text{A5})$$

where L is the Obukhov stability length and $d = 10.5$ m. The measured fluxes were then corrected for frequency attenuation on a 30 min basis using the expression for flux underestimation (Eq. A3).

Random error due to turbulence

Turbulent fluxes averaged over a limited time period have random errors because of the stochastic nature of turbulence (Lenschow *et al.* 1994). The random uncertainty of each 30-minute-average flux

F_m was obtained as

$$\sigma_F = \frac{\sqrt{\sigma_{F_i}}}{\sqrt{N}} \quad (\text{A6})$$

where

$$\sigma_{F_i} = \sqrt{\langle F_i^2 \rangle - \langle F_i \rangle^2} \quad (\text{A7})$$

is the standard deviation of flux estimates calculated for six sub-records ($N = 6$) of five minute duration F_i , $i = 1, \dots, N$. In Eq. A7 $\langle \rangle$ denote averaging over sub-records.