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Measurement and modelling ozone fluxes over a cut and fertilized grassland

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Abstract

During the GRAMINAE intensive field campaign between 20 May and 15 June 2000, ozone flux was measured and modelled above grassland in northern Germany, Braunschweig. Results of flux measurement and model calculations are presented in this study. Effects of agricultural activities (cut and fertilization) on ozone fluxes have also been analysed. A detailed deposition model for ozone is used to parameterise and to calculate the deposition velocity and flux of the ozone. Model calculations also provide an evaluation of the ratio of stomatal and non-stomatal fluxes. Measured and modelled flux and deposition velocity values have been compared for each period (before cut of grass, after cut, and after fertilization).

Results show that agricultural activities hardly have any influence on total O_3 fluxes, although both cutting and fertilization have complex impacts on different deposition pathways. Reduced vegetation decreased the stomatal exchange, while at the same time for this short canopy, the role of both soil emission of NO (promoting ozone loss close to the surface) and deposition of ozone to soil surface have increased. These effects demonstrate the importance of canopy structure and non-stomatal pathways on O_3 fluxes.

1 Introduction

Tropospheric ozone (O_3) has important effects on human health (Weschler, 2006) and plant functioning (Emberson, 2003). The background O_3 concentration has increased by a factor of two in the last century and will continue to rise according to model predictions (Vingarzan, 2004). Although great progress have been made in the last decades on understanding the O_3 cycling in the troposphere (Crutzen et al., 1999), there are still gaps in our understanding of the deposition process (Ashmore et al., 2007), especially the within-canopy chemical interactions of O_3 with NO (Duyzer et al., 1997) and biogenic volatile organic compounds (VOCs) or hydroxyl and nitrate radicals (Fuentes et al., 2007). Although these latter chemical reactions often represent a small fraction of the O_3 flux they can substantially modify the NO and VOCs fluxes. Ozone deposition has been measured above a number of ecosystems, including grasslands (Padro et al., 1998). Within-canopy gradients of ozone show a strong depletion of ozone to grasslands, especially at low friction velocities (Jäggi et al., 2006). One of the major questions regarding environmental role of O_3 is its impact on plants, which requires to evaluate the fraction of O_3 absorbed through the stomata, which is not straightforward for grassland due to the range of species present and their location within the canopy (Bassin et al., 2007). Hence, it is important to measure O_3 fluxes above grasslands to help characterise the O_3 impacts on the plant community and improving our understanding of the non-stomatal O_3 fluxes (Zhang et al., 2006).

In the framework of the GRAMINAE (GRassland AMmonia INteractions Across Europe) EU-IV programme, dry deposition of O_3 was measured by the eddy-covariance method. A deposition model for ozone is parameterised and tested against measured O_3 fluxes, to provide an evaluation of the ratio of stomatal and non-stomatal fluxes.

The campaign was performed in a way which allowed the determination of the effect of agricultural activities on the respective fluxes: grass cutting and fertilization were carried out at the measuring site. Thus, three different periods were covered in the campaign, namely: 1) pre cutting 2) post cutting, pre fertilizing, 3) post fertilizing. At the beginning of period 3, ammonium nitrate fertilizer (150 kg N ha^{-1}) was applied.

Because the number of stomata is strongly reduced as a consequence of the cut, the comparison of O_3 fluxes and deposition velocities between pre and post cut periods gives a good tool to study the effect of the decrease of the active vegetation surface on the dry deposition processes. Similarly the fertilization of the grass can cause some alteration of the physiological state of plant, and this also affects the aperture of stomata and the fluxes.

2 Measurements

Measurements of O_3 concentrations and fluxes were performed during the Braunschweig GRAMINAE campaign from 21 May to 15 June 2000 over an intensively managed grassland at the experimental fields of the Federal Agricultural Research Centre (FAL) (52° 18′ N, 10° 26′ E, 79 m a.s.l.). The field was cut on the 29 May, the grass was lifted on the 31 May and the grassland was fertilized on the 5 June 2000. For details of the overall experimental setup see Sutton et al., 2008. Details of the meteorological measurements can be found in Nemitz et al., 2009a.

2.1 Ozone fluxes

Ozone fluxes were calculated using the eddy-covariance method by means of a Gill-1012R research ultrasonic anemometer and a NOAA fast response ozone sensor (NOAA, 1996), positioned at 2 m above ground. This sensor is based on the chemiluminescent reaction of a silica gel chromatography disk impregnated with coumarin (Speuser et al., 1989). One drawback of this analyser is that the reactivity of the fluorescent dye is gradually exhausted, requiring periodic replacement and continuous recalibration to evaluate the ozone flux (F_{O_3}). The plates were hence changed every five to six days, and the sensor output (U in mV) was "calibrated" by linear regression over 3 to 48 h periods against a reference ozone monitor located at 1 km away giving 30 min averaged concentrations (χ_{O_3} in ppb):

$$\chi_{O_3} = a[U] + b[\text{ppb}], \tag{1}$$

The regressions ranged between 0.80 and 0.96. Although the fast response ozone sensor requires a calibration to evaluate F_{O_3}, it gives a direct estimation of $V_{d\,O_3}$=F_{O_3}/χ_{O_3}.

The Gill-1012R sonic anemometer was used to provide raw data sets of 3-D-wind speed, and to collect the signal of O_3 sensor to a PC at a frequency of 20.695 Hz.

The air inlet tube of the fast response ozone sensor was 2 m long, causing a time lag, which was estimated as the maximum covariance between the vertical wind speed

w and O_3 concentration. The optimum time lag was found to be 1.59 s, based on the period 9 June 8:30–14:30.

The turbulent flux of ozone (F_{O_3}) in [μg m^{-2} s^{-1}] was calculated for each 15 min time period as follows:

$$F_{O_3} = \frac{M_{O_3} p}{R_*(t_a + 273.15)} \overline{w' \chi'_{O_3}}, \tag{2}$$

where w' and χ'_{O_3} are the vertical wind and ozone concentration fluctuation, respectively, M_{O_3} is the molar mass of ozone (48 g mol^{-1}), p is the atmospheric pressure (in Pa), R_* is the universal gas constant (8.314 J mol^{-1} K^{-1}), and t_a is the air temperature (in °C). Vertical wind speed and ozone concentration were detrended using a 400 s window (McMillen, 1988; Weidinger et al., 1999), and a 2-dimensional co-ordinate rotation was performed on the wind speed to set the averaged vertical and cross-wind direction component of the wind speed to zero (Kaimal and Finnigan, 1994).

The relatively long time lag of the NOAA fast response sensor as compared to other sensors (Güsten et al., 1996) with a 0.1 s time lag, allowed temperature of the sampled air to equilibrate with the sensor temperature. Therefore the WPL correction arising from the water vapour flux was only applied (Webb et al., 1980). Moreover, the sensor separation correction of Moore (1986) was neglected as the inlet tube was located very close to the Gill path. Finally, the sensible heat flux H was corrected following Kaimal and Gaynor (1991).

The fluxes were filtered to remove periods of poor fetch. A further filtering was applied to the flux data (and all derived data) to remove periods when the footprints of the flux (calculated according to Horst, 2001) fell below 67% contribution from the field.

3 Ozone deposition modelling

Ozone deposition velocity v_d and flux F_{O_3} were compared with a model for ozone deposition (Lagzi et al., 2004, 2006; Mészáros et al., 2006). The total ozone flux (F_t) is

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calculated as a product of the deposition velocity of ozone (v_d) and the ozone concentration (C_r) at a reference height:

$$F_t = v_d C_r. \tag{3}$$

The deposition velocity is defined as the inverse of the sum of the atmospheric and surface resistances, which retard the ozone flux:

$$v_d = (R_a + R_b + R_c)^{-1}, \tag{4}$$

where R_a, R_b and R_c are the aerodynamic resistance, the quasi-laminar boundary layer resistance, and the canopy resistance, respectively.

The aerodynamic resistance is calculated using the Monin–Obukhov similarity theory taking into account atmospheric stability. The procedure is described in detail in Ács and Szász (2002). The boundary layer resistance is calculated by an empirical relationship after Hicks et al. (1987). The canopy resistance R_c is parameterized by the following equation:

$$R_c = \frac{1}{(R_{st} + R_{mes})^{-1} + (R_{cut})^{-1} + (R_s)^{-1}}, \tag{5}$$

where R_{st}, R_{mes}, R_{cut} and R_s are the stomatal, mesophyll, cuticular and other surface resistances, respectively.

The stomatal resistance can be calculated according to Jarvis (1976). This parameterization requires knowledge of the soil and plant physiological characteristics:

$$R_{st} = \frac{1}{G_{st}(\mathrm{PAR}) f_t(t) f_e(e) f_\theta(\theta) f_{D,i}}, \tag{6}$$

where G_{st}(PAR) is the unstressed canopy stomatal conductance, a function of PAR, the photosynthetically active radiation. In this parameterization, the canopy is divided into sunlit leaves and shades leaves, and G_{st} is calculated with the following form:

$$G_{st}(\mathrm{PAR}) = \frac{\mathrm{LAI}_s}{r_{st}(\mathrm{PAR}_s)} + \frac{\mathrm{LAI}_{sh}}{r_{st}(\mathrm{PAR}_{sh})}, \tag{7}$$

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$$r_{st}(\mathrm{PAR}) = r_{st,\min}(1 + b_{st}/\mathrm{PAR}), \quad (8)$$

where LAI_s and LAI_{sh} are the total sunlit and shaded leaf area indexes, respectively, PAR_s and PAR_{sh} are PAR received by sunlit and shaded leaves, respectively, $r_{st,\min}$ is the minimum stomatal resistance for water vapour and b_{st} is the a plant species-dependent constant. LAI_s, LAI_{sh}, PAR_s and PAR_{sh} terms are parameterized after Zhang et al. (2001), based on leaf area index (LAI). LAI was changing during the experiment (Fig. 1b). The grassland was cut on the 29 May 2000, when LAI decreased significantly (from around 3 $m^2\,m^{-2}$ to 0.14 $m^2\,m^{-2}$). After lifting of cut grass, the vegetation started to grow with a continuous increase of LAI (around 1.5 at the end of the experiment).

The stress functions in the denominator in Eq. (9) range between 0 and 1 and modify the stomatal resistance: $f_t(t)$, $f_e(e)$ and $f_\theta(\theta)$ describe the effect of temperature, the vapour pressure deficit and plant water stress on stomata.

The temperature stress function is described by following equation:

$$f_t = \frac{t - t_{\min}}{t_{\mathrm{opt}} - t_{\min}} \left(\frac{t_{\max} - t}{t_{\max} - t_{\mathrm{opt}}} \right)^{b_t}, \quad (9)$$

where

$$b_t = \frac{t_{\max} - t_{\mathrm{opt}}}{t_{\max} - t_{\min}}. \quad (10)$$

Here $t_{\min}$, t_{opt} and $t_{\max}$ are the minimum, optimal and maximum temperatures for grass (10 °C, 40 °C and 55 °C, respectively). The stress of the vapour pressure deficit can be parameterised by the following form:

$$f_e = 1 - b_e(e_s - e), \quad (11)$$

where b_e is a vegetation dependent constant (b_e=0.02 hPa^{-1}) e and e_s are the water vapour pressure and the saturated water vapour pressure, respectively.

The water stress function $f_\theta(\theta)$ is parameterized using soil water content (θ):

$$f_\theta = \begin{cases} 1 & \text{if } \theta > \theta_f \\ \max\left\{\dfrac{\theta-\theta_w}{\theta_f-\theta_w}, 0.05\right\} & \text{if } \theta_w < \theta \le \theta_f \\ 0.05 & \text{if } \theta \le \theta_w \end{cases} \quad (12)$$

where θ_w=0.02 m^3 m^{-3} and θ_f=0.15 m^{3}m^{-3} are the wilting point and the field capacity soil moisture contents, respectively after Ács (2003). The function $f_{D,i}$ modifies the stomatal resistance for the pollutant gas of interest (for ozone, $f_{D,i}$=0.625 after Wesely, 1989).

The mesophyll resistance for ozone in the model is taken to be zero. Because agricultural activities can cause sudden changes in vegetation properties, R_{cut} and R_s were parameterized as a function of the Leaf Area Index (LAI) and the vegetation height (h_v).

Cuticular resistance for grass was parameterized using the following equation:

$$R_{cut} = \frac{1000}{exp(-c_{\mathrm{LAI}}\mathrm{LAI})}, \quad (13)$$

where c_{LAI}=1 for grass after Nussbaum et al. (2003).

R_s is the sum of soil resistance (R_{soil}) and in canopy resistance (R_{inc}). The soil resistance, R_{soil} was chosen to 700 s m^{-1} before cut and to 600 in other periods. The in canopy resistance is parameterized in general by the formula of Erisman et al. (1994):

$$R_{inc} = \frac{b\,\mathrm{LAI}\,h_v}{u_*}, \quad (14)$$

where b is an empirical constant, b=14 m^{-1}, the values of LAI and h_v are known for the whole modelling period, and u_* is the friction velocity calculated from micrometeorological measurements.

Since we assumed that the flux is constant between the reference height and the top of the canopy, the total flux (Eq. 3) can be rewritten as follows (Cieslik, 2004):

$$F_t = c_c R_c^{-1}, \quad (15)$$

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where c_c is the concentration at the top of canopy. For estimating stomatal ozone flux, the stomatal part of total flux at the canopy top level can be written:

$$F_{st} = c_c R_{st}^{-1}. \quad (16)$$

According to Eqs. (15) and (16), the stomatal flux is calculated separately:

$$F_{st} = F_t R_c R_{st}^{-1}. \quad (17)$$

4 Results and discussions

4.1 Meteorological conditions

Figure 1 shows the evolution of meteorological conditions, soil wetness and canopy structure during the experiment. The weather was variable: showers were frequent and air temperature ranged from less than 10 °C to more than 30 °C, while wind speed varied from 0 to more than 5 m s^{-1}. The soil water content varied from 0.15 m^3 m^{-3} at the beginning of the experiment to 0.07 m^3 m^{-3} at the end of the experiment, despite the frequent rain events, because of the well draining soil. The canopy LAI was larger than 3 m^2 m^{-2} at the beginning of the experiment and decreased to less than 0.5 m^2 m^{-2} after the cut, before the canopy started re-growing.

4.2 Ozone concentration and fluxes

The variation in time of ozone concentrations during the campaign can be seen in Fig. 2a. Ozone concentration levels were significantly higher after the cut, so a comparison of the different periods meets some difficulties. Before the cut (29 May 2000), the daily maximum χ_{O_3} were around 40 ppb, while after the cut they often exceed this level (Fig. 2a). The daily maximum ozone fluxes varied from below 0.2 to more than 0.6 µg m^{-2} s^{-1}. The ozone deposition velocities v_d were similar before and after the cut, but decreased during 6 days following fertilization, a period of very large NH_3 fluxes

(Milford et al., 2008). However this later period also corresponds to lower wind-speeds and therefore lower u_*.

Average diurnal variations of ozone concentrations, fluxes and deposition velocity are illustrated in Fig. 3 for the three periods; before the cut, after the cut and after fertilization. It can be seen that:

- Diurnal variations of χ_{O_3} are more pronounced in periods 2 and 3 (higher maxima, lower minima).

- The daily pattern of ozone fluxes were similar between the three periods, except for larger averaged midday fluxes in the second period.

- The daily pattern of measured deposition velocities were similar during three periods although in Fig. 2 it seems that v_d were smaller after the cut. This is unexpected since the leaf area index was divided by more than 10 before and after the cut, indicating that the non-stomatal flux may increased or that the stomatal flux before the cut was not proportional to the LAI due to shading of the lower canopy leaves.

- The daily pattern of the modelled v_d is different in period 1 with consistently smaller night-time modelled deposition velocity, which is explained by the change in R_{inc} with LAI: R_{inc}~$25/u_*$ before the cut and R_{inc}~$0.14/u_*$ after the cut (in $\mathrm{s\,m^{-1}}$).

- In general the model underestimates the daytime v_d and overestimates the nightime v_d.

The daily pattern of the ratio of stomatal to total ozone fluxes for the three periods (Fig. 4) indicates that the stomatal flux represented 60% of the flux before the cut but only 40% after the cut.

The statistics of the measured and modelled deposition fluxes and velocities are given in Table 1 for the three periods, together with the stomatal flux.

5 Discussions

The measured ozone deposition velocities are in the same order as found in the literature (Wesely and Hicks, 2000). The cutting did not have any effects on v_d (Figs. 2 and 3, Table 1), though a decrease is expected due to a decrease of the stomatal flux, as indicated by the model (Fig. 4). However, the non-stomatal flux has increased at the same time to maintain an average deposition velocity similar to before the cut. This is due to the relationship among R_{inc}LAI and h_v, which is essentially a ~LAI^2 relationship since LAI and h_v can be considered as proportional in a first order approach. This induces an increase of the ground flux with decreasing LAI. However, Zhang et al. (2002) adopts a much different relationships between R_{inc}, LAI and, which gives larger R_{inc} at small LAI.

Nevertheless, the night-time overestimation of the deposition velocities by the model can be explained by too small values of R_{inc} or R_s after the cut. Indeed, all resistance modelling of NH_3 fluxes (Personne et al., 2009), in-canopy turbulence measurements and radon measurements (Nemitz et al., 2009b) suggest that the very bottom of the canopy has a much smaller diffusivity (or a much larger resistance) than predicted by usual resistance analogue model. This is probably due to the large biomass density of the bottom layer of the canopy.

The day-time underestimation of the flux by the model may be as a consequence of larger modelled stomatal resistances.

Fertilization is known to favour NO emissions from soils by nitrification, or denitrification. Nitrification should have occurred following fertilization as indicated by the soil NO_3^- concentrations build up following fertilization (Sutton et al., 2008). The ozone deposition velocity however seemed to slightly decreased immediately following fertilization, instead of increasing as would be expected if an NO flux occurred (as NO would consume O_3). This may be explained by the increased diffusivity and hence decreased time transfer of O_3 within the canopy, following cutting, which will leave less time for the NO–O_3 reaction to occur. This may also be explained by the lower relative

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humidity within the canopy which would decrease the cuticular resistance (Zhang et al., 2002).

6 Conclusions

The results of ozone flux measurements during the joint field campaign do not show a distinctive difference between uncut and cut grassland. There is no significant difference between the dry deposition fluxes in the two periods, disregarding to the small increase in the morning after the cut. After the cut the leaf area index has decreased, at the same time soil water content also decreased, therefore the stomatal resistances increased accordingly and the stomatal ozone fluxes show significant differences among each period. While before cut, the stomatal part of ozone fluxes have reached 70% around noon, until in other period this term was only around 40%. In contrast to this, the dry deposition velocity figures have not changed significantly in each period (0.25, 0.23, 0.21 in daily average, respectively), which is surprising because the effect of one of the most important deposition processes, i.e. the uptake by stomata has been strongly reduced as a consequence of the cut. We deduce that other mechanisms compensate the increase of stomatal resistance. First of all, with decreasing vegetation height and LAI, the ground flux is increasing. After the fertilization an increasing NO emission also affects the ozone deposition. As higher NO flux occurred, a higher O_3 deposition velocity would be expected, however due to the lower canopy and therefore the higher transfer time, there is less time for the NO–O_3 reaction.

In summary, similar ozone flux and deposition velocity were found during the measuring period in spite of different environmental conditions and agricultural activities (cut, fertilization). The lack of the significant changes of ozone flux and deposition velocity after the cut may be attributed to the i) very low vegetation and increased importance of surface sinks, ii) moderately low vegetation combined by potential soil NO emission after the fertilization.

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Table 1. Statistics of (a) measured ozone fluxes, (b) modelled ozone fluxes, (c) modelled stomatal ozone fluxes (d) ozone deposition velocity calculated from measured ozone fluxes and ozone concentration, (e) modelled ozone deposition velocity for three periods: 1. period: 20 May 2000–29 May 2000 (pre cut), 2. period: 29 May 2000–05 June 2000 (post cut, pre fertilization), 3. period: 5 June 2000–15 June 2000 (post fertilization). Daytime was defined as time between 06:00 and 17:00 UTC, and nigh-time is between 20:00 and 04:00 UTC. Negative flux values represent deposition.

	1. period			2. period			3. period		
	whole day	day-time	night-time	whole day	day-time	night-time	whole day	day-time	night-time
(a) measured O_3 fluxes [$\mu g\, m^{-2}\, s^{-1}$]									
N	158	106	29	153	118	16	168	105	39
Average	−0.13	−0.16	−0.05	−0.17	−0.20	−0.05	−0.11	−0.15	−0.04
Median	−0.11	−0.13	−0.04	−0.16	−0.18	−0.04	−0.10	−0.12	−0.02
Standard dev.	0.09	0.09	0.02	0.10	0.09	0.01	0.08	0.08	0.04
Minimum	−0.02	−0.02	−0.02	−0.00	−0.06	−0.03	−0.00	−0.00	0.01
Maximum	−0.39	−0.39	−0.11	−0.55	−0.55	−0.07	−0.43	−0.43	−0.15
(b) modelled O_3 fluxes [$\mu g\, m^{-2}\, s^{-1}$]									
Average	−0.14	−0.17	−0.05	−0.18	−0.21	−0.09	−0.14	−0.16	−0.07
Median	−0.13	−0.16	−0.05	−0.17	−0.19	−0.09	−0.13	−0.14	−0.07
Standard dev.	0.08	0.07	0.02	0.08	0.07	0.01	0.07	0.07	0.03
Minimum	−0.01	−0.03	−0.03	−0.07	−0.09	−0.07	−0.02	−0.04	−0.02
Maximum	−0.31	−0.31	−0.09	−0.37	−0.37	−0.11	−0.36	−0.36	−0.14
(c) modelled stomatal O_3 fluxes [$\mu g\, m^{-2}\, s^{-1}$]									
Average	−0.08	−0.11	–	−0.06	−0.07	–	−0.04	−0.07	–
Median	−0.07	−0.11	–	−0.04	−0.05	–	−0.02	−0.05	–
Standard dev.	0.07	0.06	–	0.05	0.05	–	0.05	0.05	–
Minimum	0.00	0.01	–	0.00	−0.00	–	0.00	−0.01	–
Maximum	−0.25	−0.25	–	−0.18	−0.18	–	−0.20	−0.20	–
(d) O_3 deposition velocity [$cm\, s^{-1}$]									
Average	0.25	0.29	0.11	0.23	0.26	0.10	0.21	0.26	0.10
Median	0.22	0.27	0.09	0.21	0.23	0.10	0.17	0.21	0.07
Standard dev.	0.13	0.13	0.06	0.12	0.11	0.03	0.14	0.15	0.05
Minimum	0.05	0.12	0.05	0.00	0.07	0.06	0.00	0.00	0.03
Maximum	0.60	0.60	0.34	0.57	0.57	0.14	0.67	0.67	0.21
(e) modelled O_3 deposition velocity [$cm\, s^{-1}$]									
Average	0.25	0.30	0.12	0.25	0.26	0.19	0.24	0.26	0.18
Median	0.24	0.28	0.12	0.24	0.25	0.19	0.23	0.24	0.19
Standard dev.	0.11	0.09	0.01	0.05	0.05	0.01	0.06	0.05	0.02
Minimum	0.07	0.14	0.11	0.17	0.17	0.18	0.13	0.14	0.13
Maximum	0.49	0.49	0.16	0.36	0.36	0.21	0.37	0.37	0.20

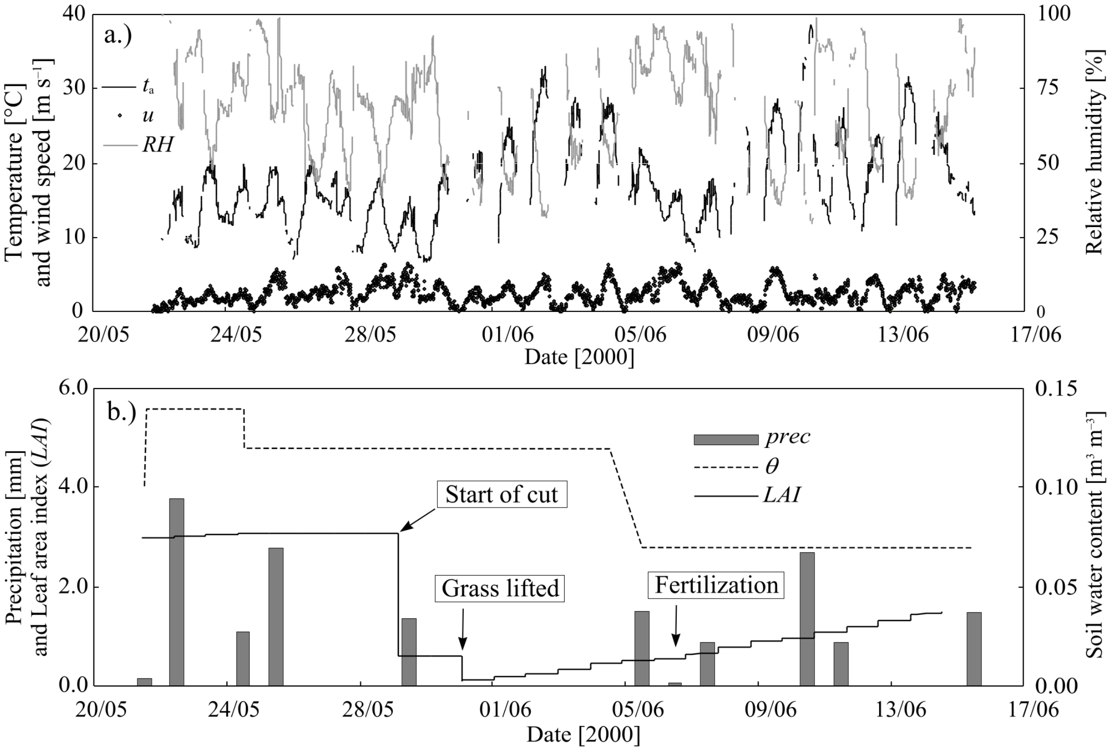

Fig. 1. Meteorological conditions and LAI during the campaign: **(a)** air temperature (t_a), wind speed (u) and relative humidity (RH) measured 2 m above the vegetation, **(b)** daily amount of precipitation (prec), root-zone soil water content (θ) and leaf area index (LAI). The field was cut the 29 May, the grass was lifted the 31 May and the grassland was fertilized the 6 June 2000.

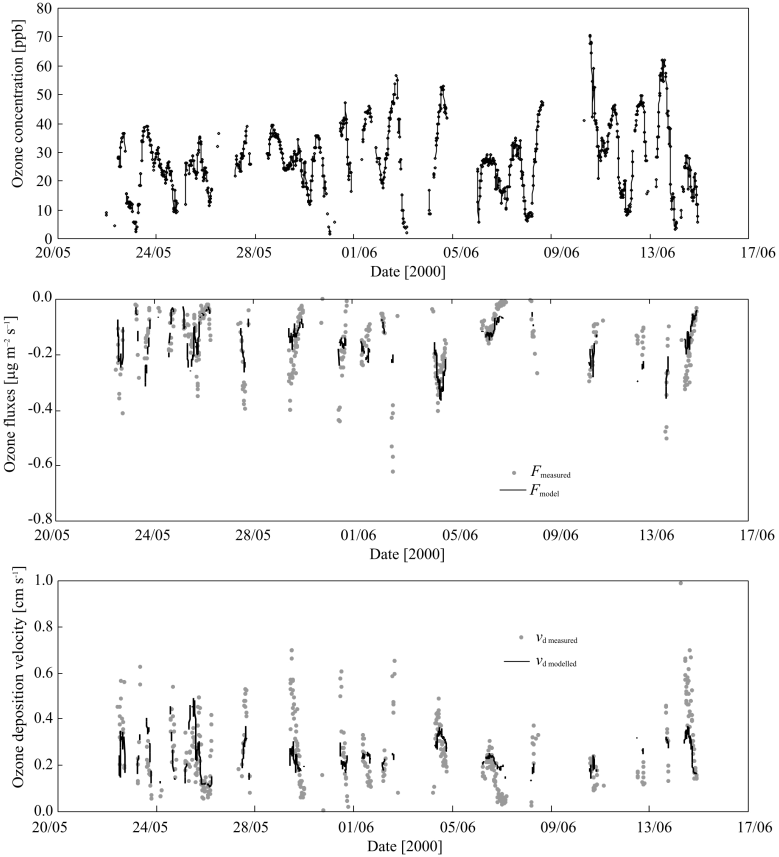

Fig. 2. (a) Ozone concentration during the campaign, measured at Federal Agricultural Research Centre (FAL, Braunschweig) **(b)** measured and modelled ozone fluxes during the campaign and **(c)** measured and modelled ozone deposition velocity during the campaign.

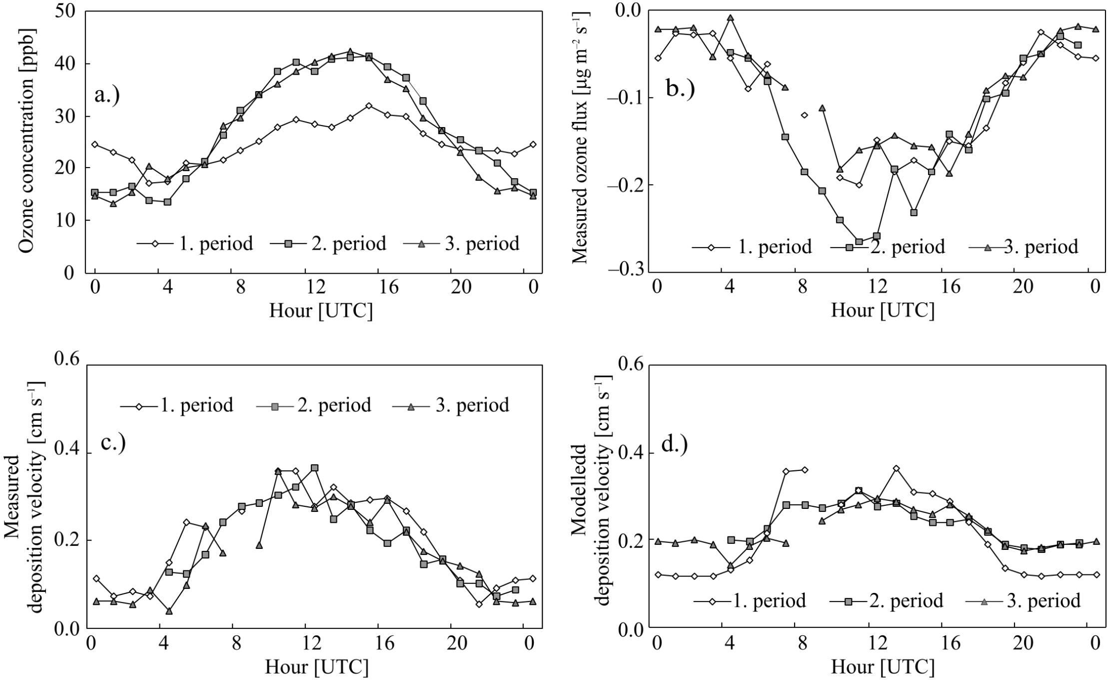

Fig. 3. Average daily courses of **(a)** ozone concentration, **(b)** measured ozone fluxes, **(c)** measured deposition velocities and **(d)** modelled deposition velocities in three periods: 1. period: 20 May 2000–29 May 2000 (pre cut), 2. period: 29 May 2000–5 June 2000 (post cut, pre fertilization), 3. period: 5 June 2000–15 June 2000 (post fertilization).

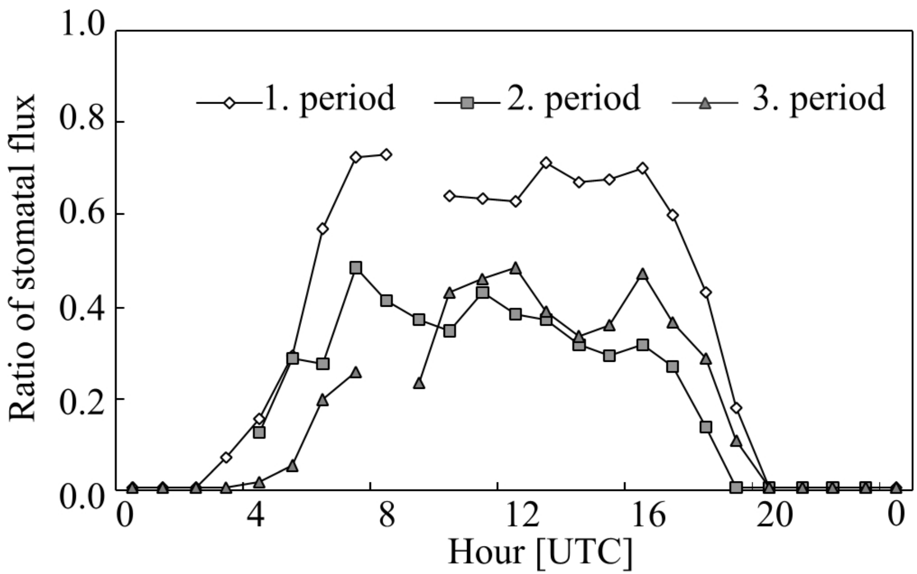

Fig. 4. Average daily courses of ratio of stomatal to total ozone fluxes in three periods: 1. period: 20 May 2000–29 May 2000 (pre cut), 2. period: 29 May 2000–5 June 2000 (post cut, pre fertilization), 3. period: 5 June 2000–15 June 2000 (post fertilization).