OZONE DEPOSITION AT A FOREST SITE IN NE BAVARIA

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Abstract. The dry deposition of ozone to a coniferous forest in northeastern Bavaria (southern Germany) was quantified during 1999 with both the eddy correlation method and a big leaf model. The model included parameterizations of the atmospheric transfer resistances from direct measurements, stomatal resistance from a plant ecological model, and an estimation of the cuticle resistance as function of leaf wetness. Early in the season, the measured and the modelled deposition fluxes were in good agreement, although the modelled fluxes tended to underestimate the measured ones. This underestimation was more pronounced in the late summer, when high nocturnal fluxes were frequently measured. The model parameterization of the cuticle and the stomatal resistances did not allow for such high fluxes. In these cases, the 24 hour average of the measured fluxes were up to 4.5 times higher than the modelled ones. The reasons for these large discrepancies remain unknown. However, assigning the unaccounted part of the deposition to a nonþstomatal surface deposition pathway, a new parameterization of the respective resistance yielded an average value of 300 s m^{-1}. It exhibited a decreasing trend through the vegetation period.

Keywords: deposition velocity, eddy correlation, inferential model, leaf wetness, ozone deposition, stomatal conductivity

1. Aims and Scope

In this contribution, we study the deposition flux of ozone to a Norway Spruce forest in NE Bavaria in order to evaluate the correlation between atmospheric ozone concentrations and deposition fluxes, to identify key parameters controlling the deposition, determine the relative importances of various deposition pathways (adsorption to surfaces versus uptake through stomata), and in order to contribute to a phytotoxicological evaluation of high atmospheric ozone concentrations. We use a combination of direct measurements of O_3 deposition fluxes and a simple inferential model.

2. Experimental

2.1. Site description and instrumentation

The experimental forest ‘Waldstein’ is located at 50°09′N, 11°52′E, and 765 m

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above sea leval (a.s.l.) in the low mountain range of the Fichtelgebirge in northeastern Bavaria, Germany. It represents a rural, remote region of Central Europe, with Norway Spruce (*Picea abies* (L.) Karst) dominating the species composition. The 'Weidenbrunnen' site is a 30 m experimental tower within a 45 yr old stand with a canopy height of 19 m. About 300 m to the West is the 'Pflanzgarten' (765 m a.s.l.), a 100 m × 200 m clearing, where routine measurements of air chemistry and meteorology have been conducted since 1994 (Klemm and Lange, 1999). A detailed footprint analysis at the 'Weidenbrunnen' site showed that the source area (90% of the biosphere/atmosphere fluxes) is about 15 ha in cases of a highly unstable stratification of the boundary layer, 40 ha for the unstable cases, 100 ha for neutral stratification, and 750 ha for a stable boundary layer, respectively (Foken *et al.*, 1999; Mangold, 1999). Independent of wind direction and stability, the source area is in most cases is covered with spruce forest of 60–120 yr stand age, except in the highly stable cases in which an influence from the agricultural area to the west may not be excluded. It has further been shown that the complex terrain causes no disturbance in the vertical turbulent wind field, except for some rare cases of a highly stable boundary layer.

We measured the three wind components and the sonic temperature T_{sonic} with a Solent-R2 (Gill, U.K.) sonic anemometer (at 32 m above ground), operating at 20.8 Hz. As a fast response ozone sensor we used a GFAS ozone sonde OS-G-2 in an identical setup as described by Güsten and Heinrich (1996). The leaf wetness was measured continuously by a technique described by Burkhardt and Eiden (1994) and Klemm *et al.* (1999) at 13 m above ground.

2.2. Quantification of O_3 deposition flux with direct measurement

We calculated the deposition flux of ozone with the eddy correlation method (e.g., Foken *et al.*, 1995; Güsten and Heinrich, 1996). A wavelet and power spectra analysis (Lange, 2000, pers. comm.) showed that all frequencies contributing to the fluxes are covered, and that there is no indication for the presence of white noise. We computed the fluxes over 30 min averaging periods. Time lags between the O_3 and vertical wind signals were negligible.

Data with electronic spikes, unsatisfactory or too large drift of the ozone sensors sensitivity, and $u_* < 0.1$ m s^{-1} were excluded. According to Foken and Wichura (1996), we used the stationarity test for the scalars O_3, sonic temperature T_{sonic}, vertical wind component, and the horizontal wind. The integral turbulence characteristics test for the vertical wind and sonic temperature was applied following the parameterization as described in Foken *et al.* (1997). This analysis assured that there were no disturbances by additional mechanical turbulence, originating, e.g., from the equipment, or the complex terrain.

The boundary layer stability is characterized by the parameter z/L, where z is the aerodynamic height (= 19.33 m), and L (Stull, 1988) is the Obukhov length, calculated by using the sonic temperature. Following arguments given by Foken and Wichura (1996), a rotation of the coordinate system was not performed.

2.3. Quantification of O_3 deposition flux with a big leaf model

We applied a big leaf model to quantify the ozone deposition with one hour time resolution throughout the entire year according to the equation:

$$F_{O_3} = -v_{d,O_3} \cdot \xi_{O_3} \tag{1}$$

We kept the model approach at a simple level in order to minimize the use of non-quantifiable parameters. In our parameterization, there exist four resistances (in units s m^{-1}) against the deposition of ozone to the vegetation: First, the aerodynamic resistance of the turbulent part of the atmosphere, R_a; secondly, the quasi laminar resistance of the molecular surface layer, R_b; finally, there are two parallel resistances, one for the deposition to the cuticle, R_{cut}, and the resistance against flow through the plant stomata, R_{stom}. With these resistances, the deposition velocity of ozone, v_{d,O_3}, can be quantified as:

$$v_{d,O_3} = \left(R_a + R_b + \left(\frac{1}{R_{cut}} + \frac{1}{R_{stom}} \right)^{-1} \right)^{-1} \tag{2}$$

Following Hicks *et al*. (1987), we parameterized R_a from the wind vector data of the sonic anemometer after computing the friction velocity, the horizontal wind velocity, and the standard deviations of the crosswind velocity and the wind direction, respectively. With knowledge of R_a, R_b can be computed by using the Schmidt and Prandtl numbers and the von Kármán constant (Hicks *et al*., 1987). We parameterized the stomatal resistance by using the STANDFLUX model (Falge *et al*., 2000), which predicts the gas exchange between plants and the atmosphere by using a detailed physiological parameterization, and by using meteorological data as a driver. One of the outputs of STANDFLUX is a stomatal conductance g, in units m s^{-1}, which is the transfer velocity of a gas (i.e., H_2O) through the stomata as function of time. After correction for individual molecular diffusivities, we use the inverse of this transfer velocity as a very elaborated estimate of R_{stom} for O_3.

A particularly difficult parameterization is that of the cuticular surface resistance, R_{cut}. Plant cuticular waxes can absorb O_3 and react with it. Although the water solubility of O_3 is not large, there is evidence that R_{cut} decreases with increasing leaf wetness (Pleijel *et al*., 1995). In most parameterizations, high leaf wetness cuts the resistance against O_3 deposition by a factor of about two (Wesely, 1989; Grantz *et al*., 1995). Wesely (1989) suggests a R_{cut} of 2000 s m^{-1} for coniferous forests in summer, Erisman *et al*. (1994) suggest 1000 s m^{-1}. Based on these data, we parameterized R_{cut} between 1000 and 2000 s m^{-1} as a function of the measured leaf wetness, the latter being valid for dry leaves.

3. Results and Discussion

3.1. Comparison of Measured with Modelled Fluxes

The deposition flux was modelled for the entire year 1999. The flux measurement, applying the eddy correlation method, was realized for the period 10 May through 27 October, 1999. According to the criteria given in Section 2.2, the dataset was reduced to about one third of the whole 8544 half-hourly intervals. This is the basis for our further analysis.

We present results from two periods of 48 hr duration in July and September in Figures 1 and 2, respectively. These days were selected because their datasets are almost complete with high quality data, and because they are typical examples of the different diurnal patterns that we observed. During 3 and 4 July (Figure 1), the similarities between the measured and modelled ozone vertical fluxes were striking although the measured fluxes (30 min averages) exhibited a larger scatter. Both flux time series showed a pronounced diurnal behavior with larger fluxes during the daylight hours and reduced fluxes during the nights. In the model, it is the stomatal resistance R_{stom} that controls the flux. Maximum stomatal resistance during the night hours (approximately 9000 s m^{-1}) indicate that the stomata were closed and the stomatal flux was at its minimum. During the days, the stomata opened and the plants took up ozone.

At the same time, the modelled cuticular resistance was relatively large. The measured flux exhibited a pronounced diurnal behavior with low values during the nocturnal stable conditions and higher deposition fluxes during the days with well developed turbulence. In the night between 2 and 3 July, u_* was low and the data quality for T_{sonic} was poor (with measured convective conditions around midnight). In the morning of 4 July, instationarity caused gaps in the time series.

For the entire period presented in Figure 1, the measured flux was higher than the modelled flux by a factor of 1.4, which is in our view a good agreement between model and measurement.

The data presented in Figure 2 reveal a different behavior. The modelled fluxes exhibited again a pronounced diurnal pattern with low fluxes during the nights and higher fluxes of up to about 6 nmol m^{-2} s^{-1} during the days, when the stomata were open. The measured fluxes, however, exhibited no clear diurnal behavior in this example. The high nocturnal fluxes are striking. Similar patterns were observed several times during the entire measurement campaign, but most cases of high nocturnal fluxes occurred later in the vegetation period.

In the model, however, the high resistances R_{stom} and R_{cut} do not allow for high fluxes. For the period presented in Figure 2, the measured to modelled flux ratio is 4.5. In this case, the agreement between measurement and model is certainly not satisfying, not only because of the large differences in absolute numbers, but also because of the lack of agreement of the diurnal pattern.

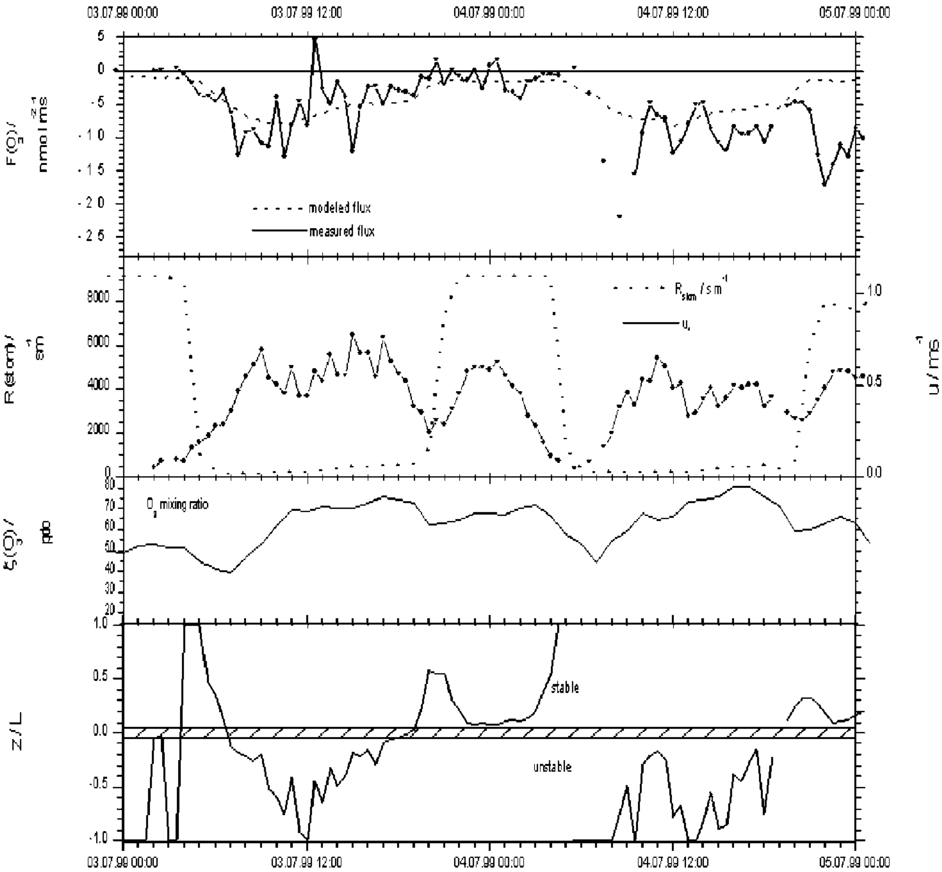

Figure 1. Measured and modelled ozone deposition flux (top panel), friction velocity and stomatal resistance (2nd panel), ozone mixing ratio (3rd panel), and the stability parameter z/L (4th panel) during a 48 hr period on 3 and 4 July, 1999. The hatched area in the 4th panel represents the neutral case according to Foken *et al.* (1997). A plot of the deposition velocity (not shown) looks very similar to the flux pattern (top panel).

In Figure 3, we present daily averages of the measured and modelled fluxes throughout the season, and their respective ratios. The measured fluxes were, in all but one case, larger than the modelled ones. The modelled fluxes decreased with time, which is due to a decline of both the ozone mixing ratios (from 40–60 ppb daily averages from May through July, to about 20 ppb by the end of October), and the modelled deposition velocity (from 0.002 to 0.0012 m s^{-1} within the same time period, mainly due to a reduced daily opening time of the stomata). On the other hand, the measured fluxes showed no clear seasonality. Later in the season, high nocturnal fluxes (as shown in Figure 2) occured more frequently, and thus, contributed more efficiently to the 24 hr flux averages. This led to an increase of the ratios of the measured versus the modelled fluxes (Figure 3).

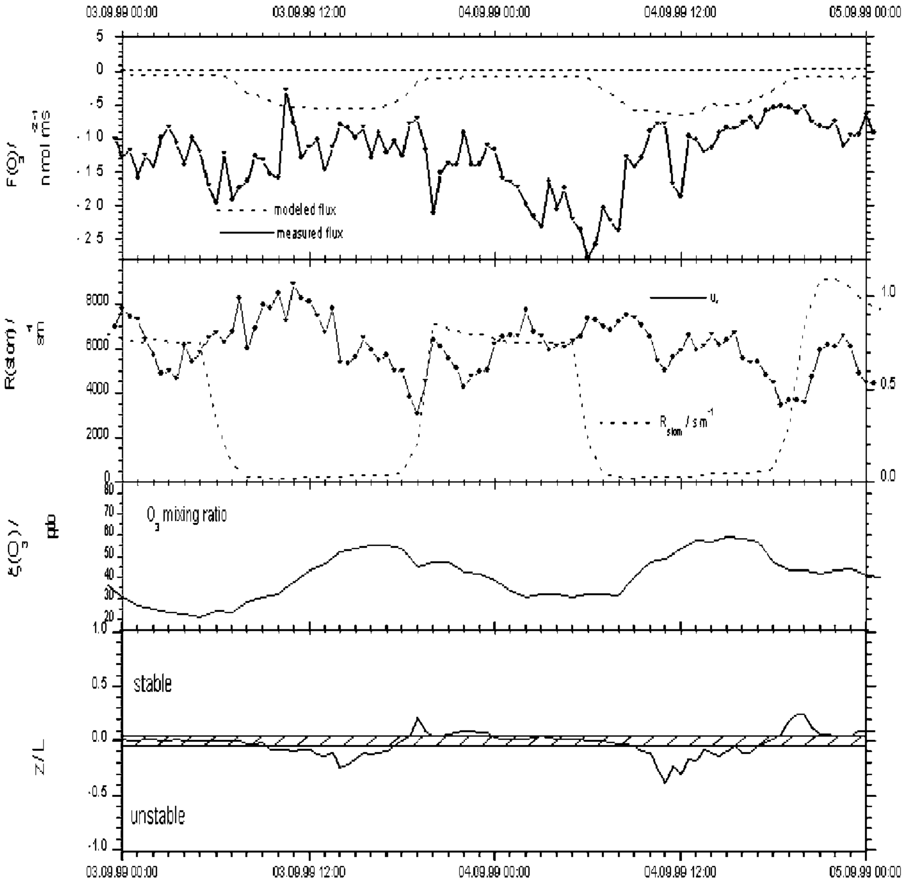

Figure 2. Same as Figure 1 but for 3 and 4 September, 1999.

There is no indication for any problems in the parameterization of the atmospheric resistances R_a and R_b. They are often low enough to allow for much higher fluxes. Consequently, we paid further attention to R_{cut} and R_{stom}. In order to identify potential problems in the parameterization of R_{stom}, we conducted a sensitivity analysis within the STANDFLUX model by varying the leaf area index (LAI) between 4.3 and 6.3, accounting for the heterogeneity of the vegetation within the source area, and varying the plant physiology within reasonable limits (E. Falge, pers. comm.). However, all these variations did not affect R_{stom} and, in consequence, the vertical flux of O_3, by more than a few percent in extreme cases. We hypothesize that an additional deposition to surfaces (e.g., cuticles) accounts for the higher ozone fluxes. Therefore, we recalculated the cuticular resistance R_{cut} on the basis of the results as presented so far.

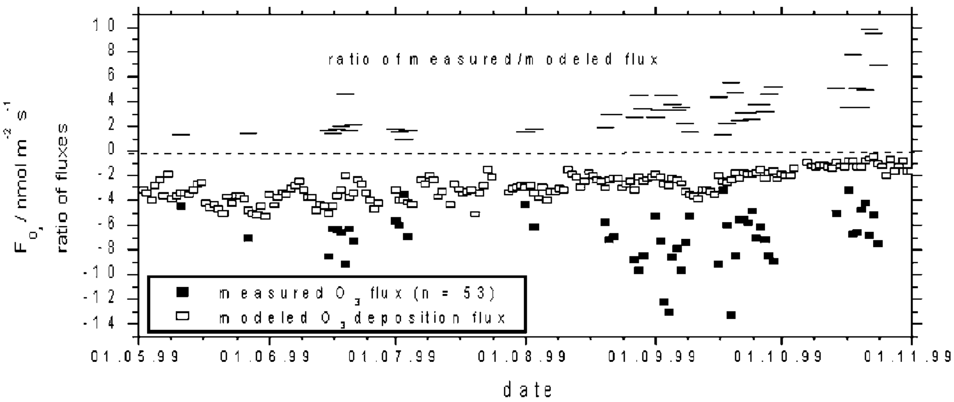

Figure 3. Daily means of measured and modelled ozone deposition fluxes and their respective ratios. For this analysis, days with at least 5 hr of good quality flux data were selected.

3.2. Recalculation of R_{cut}

From the measured fluxes, the O_3 mixing ratio, and the resistances R_a, R_b, and R_{stom} of the big leaf model, a new cuticular resistance can be computed, that would be necessary to allow for the observed fluxes under the given atmospheric conditions. Although we do not know if the cuticles or other plant surfaces or the soil may contribute to the depression of this resistance, we stay with our nomenclature and call the recalculated resistance $R_{cut,c}$:

$$R_{cut,c} = \left(\left(\frac{\xi_{O_3}}{F_{O_3}} - R_a - R_b \right)^{-1} - \frac{1}{R_{stom}} \right)^{-1} \tag{3}$$

We computed 1501 hourly averages of $R_{cut,c}$ for those cases where the data quality was high and, in addition, the measured flux was greater than the modelled flux at least by a factor of 1.2. According to arguments discussed above, this $R_{cut,c}$ should be quantifiable through parameters such as the leaf wetness. However, our analysis showed that there is no correlation whatsoever between leaf wetness and $R_{cut,c}$. The temporal pattern in Figure 4 indicates the presence of a trend of $R_{cut,c}$ with the tendency of lower values later in the season. This trend is highly significant ($p <$ 0.01%) and quantified as –1.4 s m^{-1} d^{-1}, corresponding to a $R_{cut,c}$ of about 440 s m^{-1} for 1 May, and approximately 180 s m^{-1} for 30 October. This recalculated $R_{cut,c}$ is the apparent resistance of all vegetation and/or soil surfaces against the deposition of ozone. For the time periods as presented in Figures 1 and 2, the averages and standard deviations for $R_{cut,c}$ are 493±202 and 190±154 s m^{-1}, respectively.

Figure 5 shows that there is virtually no correlation (correlation coefficient r = 0.088) between the measured deposition flux and the O_3 mixing ratio in air.

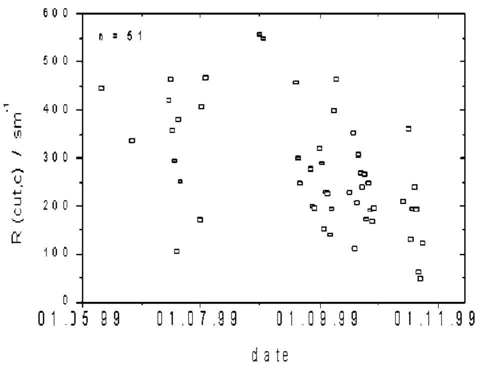

Figure 4. Daily averages of $R_{cut,c}$ as function of time. For this analysis, all days with a flux ratio of at least 1.2 were selected.

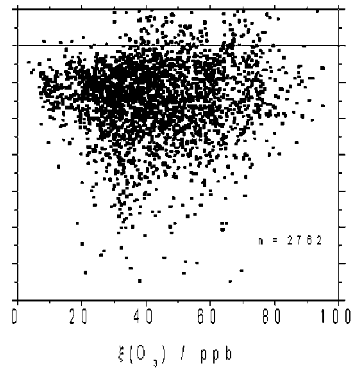

Figure 5. Scatter plots of the measured flux of ozone, versus the ozone mixing ratio.

The deposition is more efficiently driven by the deposition velocity than by the atmospheric ozone mixing ratio (r = 0.762).

4. Conclusions

We presented measured and modelled ozone fluxes to a coniferous forest throughout the summer season 1999. In many cases, there is good agreement between measured and modelled fluxes with synchronous diurnal behavior. In accordance to earlier findings, it is often the canopy resistance (R_{stom} and/or R_{cut}) that limits the dry deposition of ozone (Padro, 1996). We also found that the observed flux was significantly higher than the parameterized stomatal flux (Coe *et al.*, 1995; Granat and Richter, 1995). Particularly during the nights and later in the season, the measured fluxes were larger than those predicted with the big leaf model.

We applied a rigorous quality assurance protocol for these high nocturnal fluxes. They typically occured within a relatively narrow range of stability conditions with fully developed turbulence ($|z/L|$ near neutral, $u_* > 0.5$ m s^{-1}, c.f., Figure 2), and did not correlate with any drainage flow. The NO_x mixing ratios were always below 5 ppb during the time period shown in Figure 2. Although there is a nocturnal stomatal conductivity that will allow some flux during the nights (c.f., Musselman and Minnik, 2000), this could not account for the large observed fluxes. Also, the biogenic emissions of organic compounds and their reaction rates with atmospheric ozone seem not to be large enough to account for the observed downward flux of ozone.

In consequence, it must be deposition to surfaces in the ecosystem, that leads to higher fluxes of ozone than represented in the model. We are not sure if these are the cuticles or other surfaces of the plant/soil system. We estimate this parameter ($R_{cut,c}$) to be 300 s m^{-1} on average throughout the entire season with a temporal trend of –1.4 s m^{-1} d^{-1}. In any case, there seems to be a strong seasonal trend of increasing suceptibility of the surfaces to uptake of ozone.

The absence of a good correlation between the ozone concentration and deposition contradicts the general assumption that a high concentration of ozone in the air leads to a high deposition flux. This finding emphasizes the importance of studying the deposition velocity of ozone.

A further important yet unanswered question is how much of the deposited ozone has a harmful effect on plants. How important is stomatal uptake in comparison to surface uptake? If the former is the more important flux in this respect, then the modelled fluxes may even be a better estimate of the phytotoxicologically relevant deposition flux of ozone. The modelled flux is governed by 70% through stomatal uptake. If, on the other hand, surface uptake has a negative effect on plants, then the deposition flux must be measured in order to arrive at better estimates of the surface resistances under various climatologic and plant ecological conditions. All these questions must be the object of further research.

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