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Deposition of nitrogen oxides and ozone to Danish forest sites

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Abstract

Preliminary results of eddy correlation measurements of fluxes of NO_2, and O_3 made over a coniferous and a deciduous forest site in Denmark are presented.

The total resistance to deposition are calculated and subdivided into aerodynamic, viscous sub-layer and surface resistance for investigation of the influence of meteorological factors. The viscous sub-layer resistance is derived by a new theory, taking the bluff roughness elements of the forest and the dimension of the needles/leaves as well as the LAI into account. The fluxes of nitrogen dioxide and ozone are related to the fluxes of water vapour and carbon dioxide.

The results from the coniferous forest site (Norway spruce) show a diurnal variation in the deposition velocities and surface resistances during the growth period, which is consistent with a stomatal uptake of the gases. However, a substantial deposition is also found at night and in winter indicating a significant role of atmospheric chemistry and surface reactions.

The experiment at the deciduous forest site (beech) shows the difference in deposition to the site before and after bud burst, thus describing the influence of the stomatal activity of the leaves on the uptake of gases in the forest ecosystem.

1. INTRODUCTION

The dry deposition of pollutants to forest ecosystems plays an important role in the cycling of as well nutrients (*e.g.* nitrogen) as harmful substances (*e.g.* ozone). Estimation of the flux and examination of the governing processes are important in order to model the deposition and in order to evaluate critical loads.

This paper presents preliminary results of two recent field experiments in Danish forests (one in a coniferous forest and one in a deciduous forest before and after bud burst). The measurements of concentrations and fluxes were used to calculate deposition velocities and subsequently by means of measured meteorological parameters to split the total resistance to deposition in aerodynamic, viscous sub-layer and surface resistances. The role of stomatal uptake was evaluated.

2. MATERIALS AND METHODS

2.1 Experimental sites and instrumentation

The instrumentation for the eddy correlation measurements consisted of a 3D Gill Sonic Anemometer (wind fluctuations), a GFAS OS-G-2 Ozone Sonde, a Scintrex LOZ-3 O_3 analyzer (chemiluminescence with Eosin Y) , a Scintrex LMA-3 NO_2 analyzer (chemiluminescence with luminol) and an Advanet E009A infrared CO_2 and H_2O fluctuation meter. A large number of meteorological measurements were made simultaneously, the most important being wind speed (cup anemometers in different heights), wind direction (wind vane), temperature in different heights, and water vapour flux (Ophir Infrared Hygrometer IR-2000).

Flux measurements were made in Ulborg (a forest in a remote rural area of western Jutland) during the period 7-17 June, 1994. The site is described in Andersen *et al.* [1]. The measurements were carried out from a 36 m tall mast placed in a Norway spruce (*Picea abies*) plantation with trees of a height of approximately 12 m and a good fetch in most directions except from a small sector towards SW. The flux measurements were made at 21 m.

The flux measurements in the deciduous forest were made in Corselitze Forest on the island of Falster in southeast Denmark during April and May 1994. The measurements were made from a 57 m tall mast in a stand of 24 m tall beech (*Fagus sylvatica*) trees. The instruments for eddy correlation measurements were placed at 41 m. There was a good (500 m) fetch in the sector from ENE to SSE. There were no local sources of pollution in this direction since the forest is bordering the Baltic Sea. The incoming air-masses thus carry pollutants from distant sources in Poland and eastern Germany.

2.2 Calculations

Fluxes were measured by the eddy correlation method and calculated from the equation:

$$F_c = \overline{w' \cdot C'} \qquad (1)$$

where F_c is the flux of the compound in question, w the vertical wind velocity and $C(z)$ the concentration of the compound at the measurement height (z). The prime indicates instantaneous deviation from the mean and the over-bar indicates the time average (0.5 h). The measured fluxes were corrected for errors due to changes in atmospheric density caused by heat and water vapour flux [2].

Deposition velocities (V_d) were calculated from the equation:

$$V_d(z) \equiv \frac{-F_c}{\overline{C}(z)} \qquad (2)$$

Resistances were calculated according to the model:

$$\frac{1}{V_d} = r_t = r_a + r_b + r_c \qquad (3)$$

where r_t is the total resistance, r_a the aerodynamic resistance, r_b the viscous sub-layer resistance and r_c the surface or canopy resistance. r_a and r_b can be calculated from meteorological observations; r_c is then calculated from equation 3 as the residual resistance.

The aerodynamic resistance (r_a) was calculated by the expression analogous to equation 2:

$$r_a = \frac{\overline{u}}{u_*^2} \tag{4}$$

where $\overline{u}$ is the mean wind speed (m s^{-1}) and u_* the friction velocity, calculated as $-\overline{u'w'}^{\frac{1}{2}}$.

For forests we have developed the following parameterization of r_b [3]

$$r_b = c \cdot \frac{\nu^{\frac{1}{6}}}{D^{\frac{1}{2}}} \cdot \left[\frac{\ell \cdot u_*}{(LAI_e)^2}\right]^{\frac{1}{3}} \cdot u_*^{-1} \tag{5}$$

where ν is the kinematic viscosity of air (=15 · 10^{-6} m^2 s^{-1}), D the diffusion coefficient of gas (for O_3 and NO_2 = 14 · 10^{-6} m^2 s^{-1}), ℓ the leaf dimension , LAI_e is a modified leaf area index (LAI) representing the effective surface area and c is a correction factor, determined empirically from the temperature profile and aerodynamic roughness. The parameter c is set to 3 for both spruce forest and deciduous forest. The leaf dimension (ℓ) is set to 0.005 m for the spruce forest and 0.01 m for the deciduous forest.

What the exact meaning of LAI_e is, depends on the actual chemical compound under consideration. Thus for CO_2 it is strictly the green leaves that counts (ignoring respiration from the forest floor) and in this case $LAI_e \equiv LAI$. For a deciduous forest LAI is zero after fall and until the leaves come out again, and hence r_b is infinitely large (see equation 5).

For O_3 on the other hand, the flux also goes to other parts of the canopy (especially to small branches and twigs due to the r_b dependence on ℓ) and to the forest floor. For this compound the minimum LAI_e (on a bare smooth surface) will be 1. In a deciduous forest without leaves it will have a larger value, perhaps 5. When the leaves come out it will increase with about 5, which is the LAI efficient for CO_2.

The surface resistance to water vapour was calculated according to equations 2 and 3 after subtraction of the saturated water vapour concentration at the surface temperature. The canopy stomatal resistance was calculated by conversion of the resistance to water vapour to resistance to carbon dioxide according to the relation:

$$\frac{r_{H_2O}}{r_{CO_2}} = \frac{D_c}{D_v} \tag{6}$$

where D_c is the molecular diffusivity of CO_2 and D_v, the molecular diffusivity of water vapour.

3. RESULTS AND DISCUSSION

3.1 Coniferous forest

The diurnal variation of the concentration, flux and deposition velocity of O_3 in the period 7-17 June, 1994 is shown in figure 1. The concentrations show a diurnal pattern with a minimum in the early morning and a maximum in the late afternoon. The difference between the minimum and maximum is about 15 ppb, indicating that the air is only moderately polluted. The dominating wind-direction during the experiment was NW; this wind brings relatively clean air from the North Sea.

The fluxes of ozone ranged from about -0.25 $\mu g\ m^{-2}\ s^{-1}$ to -0.6 $\mu g\ m^{-2}\ s^{-1}$ with a maximum around noon. The deposition velocities ranged from 3.5 mm s^{-1} to 7 mm s^{-1} with a sharp rise at dawn and a maximum already in the morning. This pattern indicates that stomatal processes are important for the deposition of O_3. However, the rather high deposition velocities during the night indicate that other processes for removal of O_3 also play a significant role.

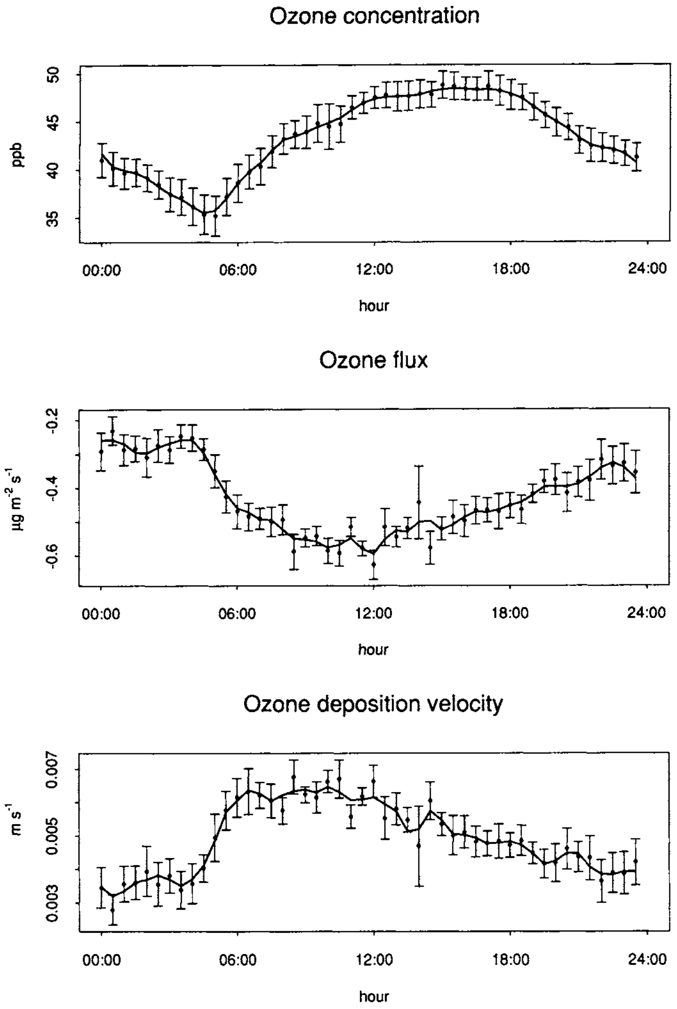
The results of the calculation of resistances are shown in figure 2 and table 1, where data from earlier experiments in the spruce forest [4] are included for comparison. The resistances show a diurnal pattern with the lowest values during daytime. The surface resistance is highly dominating during daytime and the influence of meteorology low. During nighttime the surface resistance to O_3 was substantially lower than the canopy stomatal resistance, which again shows that stomatal uptake is not the only sink for O_3. Table 1 shows that low surface resistances to O_3 also can be found during winter time, when the activity of the trees is low.

	Norway spruce						Beech			
	June 94		July 92		February 93		April 94		May 94	
	day	night	day	night	day	night	day	night	day	night
r_a	8	31	6	68	16	27	17	69	7	11
r_b	9	14	9	20	16	17	14	21	7	8
$r_c(O_3)$	151	288	368	800	208	179	330	692	269	602
$r_c(NO_2)$	347	1023	-	-	1153	428	-	-	-	-

Table 1: Average day (06:00 - 18:00) and night (18:00 - 06:00) values of resistances (s m^{-1}) from Ulborg (Norway spruce) and Corselitze (beech).

3.2 Deciduous forest

Two periods are selected for presentation from the data collected in Corselitze forest. The first period (April 22-25) represents the forest without leaves on the beech trees, and the second period (May 11-14) represents a time when the leaves were fully unfolded. Results for the fluxes of O_3, NO_2 and CO_2 are given in figure



Ozone concentration

Ozone flux

Ozone deposition velocity

Figure 1: Ozone concentration, flux and deposition velocity over a Norway spruce stand at Ulborg Plantation 7-17 June, 1994. The plots show means ± standard error and a smoothed line.

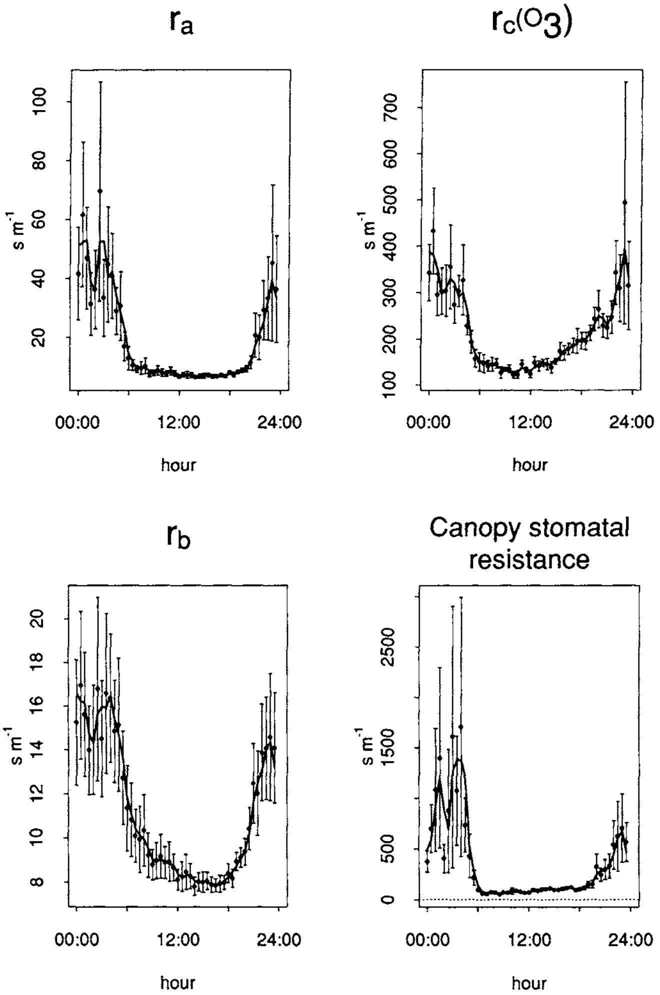


Figure 2: Diurnal variation of aerodynamic resistance (r_a), viscous sub-layer resistance (r_b), surface resistance to O_3 (r_c) and canopy stomatal resistance over a Norway spruce stand at Ulborg Plantation 7-17 June, 1994. The plots show means ± standard error and a smoothed line.

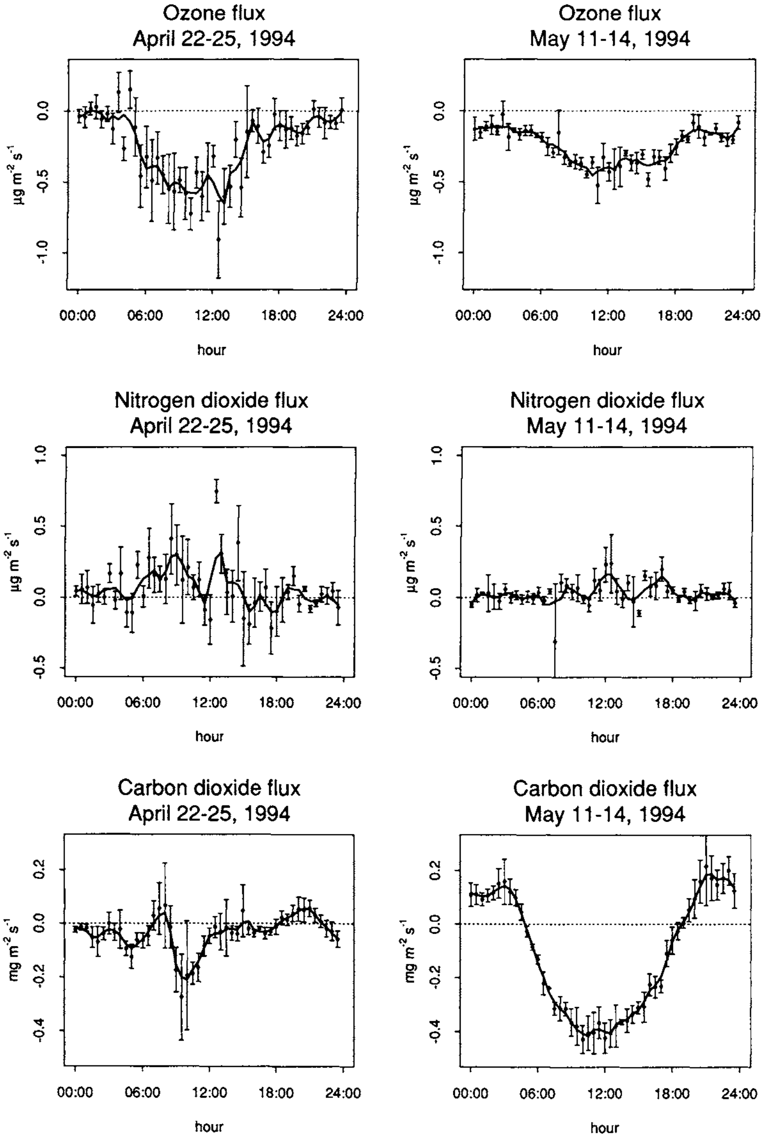


Figure 3: Fluxes of O_3, NO_2 and CO_2 over a beech stand in Corselitze forest before and after bud burst. The plots show means ± standard error and a smoothed line.

3. The mean concentration of O_3 was 48 ppb in the first period and 41 ppb in the second; for NO_2 the values were 10 ppb and 5 ppb, respectively. The concentrations of CO_2 were quite similar in the two periods. These differences should be noted when comparing the fluxes.

The flux of O_3 was almost always downwards, whereas the flux of NO_2 was mostly upwards. Both compounds showed diurnal patterns with the largest fluxes during daytime. There were no significant differences in the deposition velocities between the two periods for these two compounds.

The flux of CO_2 was much larger in the second period and showed a clear diurnal pattern with downward flux during daytime and upward flux during nighttime. In the first period the diurnal pattern was less pronounced although the downward flux peaked in the late morning.

The mean daytime deposition velocity of O_3 was around 4 mm s^{-1} in both periods and the mean nighttime deposition velocity was 1 mm s^{-1} in April and 2 mm s^{-1} in May. A maximum of around 7 mm s^{-1} was found in both periods.

The surface resistance to O_3 show a diurnal pattern in both periods, although it is more pronounced in the second period (figure 4 and table 1). The daytime minimum lies around 200 s m^{-1}.

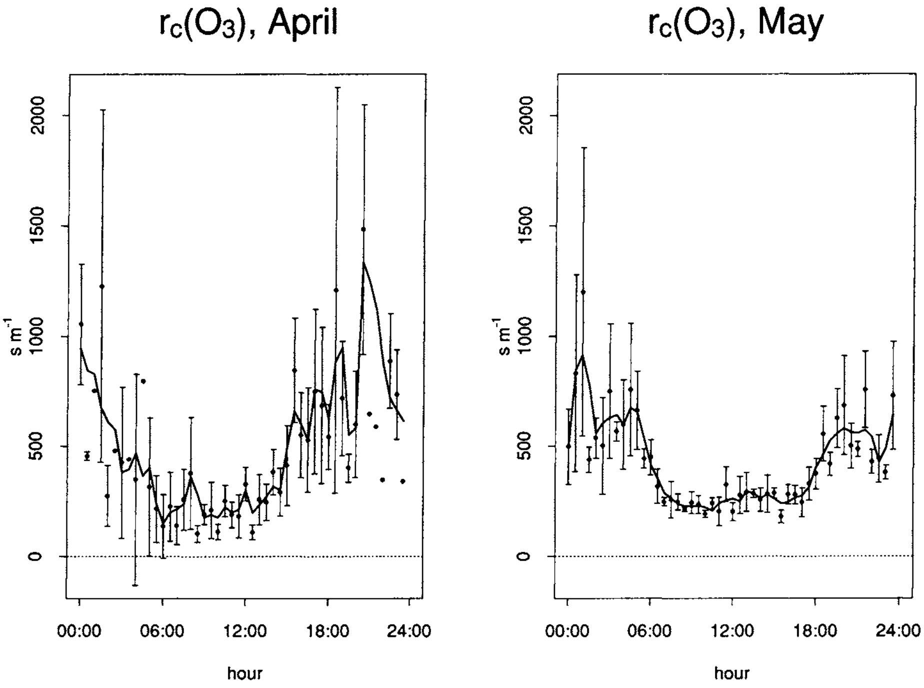
The effect of the beech leaves is seen most clearly in the fluxes of CO_2, whereas the effects on the fluxes of O_3 and NO_2 are much less than expected. The diurnal pattern of the surface resistance to O_3 indicates an influence of stomata, especially in the second period. The reason for the absence of a strong difference in deposition of O_3 before and after bud burst might be that O_3 is taken up by vegetation on the forest floor (mainly *Anemone nemorosa* in the April period) and removed by other means than stomatal uptake, such as destruction on leaf surfaces, deposition to soil ([5]) and reaction with NO.

The upward flux of NO_2 is most likely explained by the reaction of O_3 with NO, emitted as a result of bacterial activity in the forest soil ([6]). The amount of O_3 removed in this way is, however, only a small part of the total O_3 flux. There seems to be a larger NO_2 flux in the first period than in the second. This might be either a result of lower bacterial activity in the second period due to the shadowing effect of the beech leaves, which leads to lower temperatures, or the result of uptake in the canopy.

4. CONCLUSIONS

The fluxes of O_3 over both a spruce forest and a beech forest exhibited a diurnal pattern. When the resistances of the atmospheric boundary layer and the viscous sub-layer were subtracted from the total resistance to deposition, the remaining canopy resistance still showed a diurnal pattern, which indicates that stomatal activity is important for O_3. However, a substantial flux was found during nighttime and other sinks for O_3 like destruction at surfaces, uptake in the soil and reaction with NO must be taken into consideration.

Measurements over a beech forest before and after bud burst showed that the influence of the beech leaves on the O_3 flux was small, probably due to uptake by


$r_c(O_3)$, April

$r_c(O_3)$, May

Figure 4: Surface resistance to O_3, in a beech stand in Corselitze forest before and after bud burst. The plots show means ± standard error and a smoothed line.

the forest floor vegetation and destruction at other surfaces. The upward flux of NO_2 in the beech forest is attributed to emission of bacterial NO from the soil and rapid chemical reaction with O_3.

5. ACKNOWLEDGEMENTS

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