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The use of the gradient method to monitor trace gas fluxes over forest:

Flux-profile functions for ozone and heat

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ABSTRACT

To asses the achievement of environmental policy goals regarding the input of acidifying species by atmospheric deposition a monitoring system needs to be available. Such a monitoring system is now being developed for sulphur dioxide and ammonia in the Speulderbos, a Douglas fir stand in the centre of the Netherlands. The deposition will be monitored by the micro-meteorological gradient method. This indirect method is used because monitors fast enough to be used in the eddy correlation method are not available. The deposition flux is determined from measurements of the concentration of gases at several heights above the forest and a turbulent diffusion coefficient. Over low vegetation this diffusion coefficient can be determined from empirical flux-profile functions given in the literature. Because of the large roughness and the use of towers barely extending above the canopy the situation is more complex over forest. Measurements may take place in the so-called roughness layer where large deviations from classical flux-profile functions may be expected. To calculate the flux of acidifying gases from the concentration gradient observed in the Speulderbos, local flux-profile functions are required.

One of the goals of this study is to assess the relation between fluxes and profiles above forest for trace gases. To this purpose the flux of ozone to Speulderbos was measured continuously by eddy correlation for seven months in 1993. During the same period vertical profiles of air temperature and the concentration of ozone and nitrogen oxides were determined over the forest. In addition several turbulent parameters were recorded.
As part of a collaboration project within the framework of a contract with the European Commission, linked to this project, a large measurement campaign was organised in the Speulderbos in June 1993. During this experiment a comprehensive set of equipment was used to study fluxes and profiles of ozone and nitrogen oxides above and below the canopy. Some of the results of this campaign are also reported here. The measurements carried out during this campaign and an analysis of the results are reported in more detail elsewhere.

From the observed temperature profiles and sensible heatfluxes flux-profile functions could be derived. Due to the scatter in the vertical profiles, flux-profile functions for ozone could not be derived with the same confidence. However, a significant difference with the observed flux-profile functions for heat could not be detected. Fluxes of ozone calculated according to the gradient method using the derived functions for heat showed very good agreement with the fluxes observed by the eddy correlation method.

This result shows, for the first time, that the gradient method can be used for trace gases over forest provided local flux-profile functions are used.
During the intensive campaign the flux of ozone was measured on two individual towers in the Speulderbos. The comparison of the fluxes observed on both towers shows that a fairly homogeneous flux field for ozone exists over the forest. Measurements of the ozone flux at two levels above the forest did not reveal a flux divergence either. These observations endorse the conclusion that the measurements of fluxes of trace gases such as ozone can be carried out with confidence at the Speulderbos. The results of this study form an important scientific basis for flux monitoring in the Speulderbos.
From the measurements a clear relationship between the canopy resistance for ozone on one end and photosynthetic active radiation and water vapour deficit on the other was observed. A comparison was made between the observed uptake rate of ozone and the uptake rate calculated using an inference model. This comparison showed that large errors (over 200 % relative difference) can be made if parameters are derived from (scarce) literature information based on measurements carried out elsewhere. An optimisation procedure was used to derive better parameters. Using these parameters the comparison could be improved leading to an average difference between observed and modelled fluxes less than 80 %.

The observations for nitrogen dioxide indicate fluxes away from the canopy. This is an unexpected result. Nitrogen dioxide is commonly considered to be taken up by the canopy. Detailed measurements carried out during the intensive campaign showed that this emission is probably related to emission of nitric oxide from the forest floor. Calculations with a comprehensive model which simulates exchange processes and chemical reactions in and above the forest endorse these assumptions. It appears that the nitric oxide emitted from the forest floor is converted rapidly by ozone to nitrogen dioxide in the trunk space. Part of this nitrogen dioxide is taken up in the canopy. Under many conditions the part not taken up in the canopy is emitted into the atmosphere. In the framework of the EC project other groups showed that this phenomenon is also observed in some other forests in Europe. It is not clear whether this emission is related to input of nitrogen (for example ammonia) through the atmosphere.
The input of nitrogen through dry deposition of NO_x (the sum of nitric oxide and nitrogen dioxide) is probably low compared to other inputs. There is a need to improve currently used procedures to estimate the deposition input of nitrogen oxide to forest. The emission of nitrogen dioxide from forest canopies may however have a significant impact on photochemical air pollution.

1. INTRODUCTION

To asses the achievement of environmental policy goals regarding the input of acidifying species by atmospheric deposition a monitoring system needs to be available. Such a monitoring system is now being developed for sulphur dioxide and ammonia in the Speulderbos, a Douglas fir stand in the centre of the Netherlands [Erisman *et al.*, 1993]. The deposition will be monitored by the micro-meteorological gradient method. This indirect method is used because monitors fast enough to be used in the eddy correlation method are not available. The deposition flux is determined from measurements of the concentration of gases at several heights above the forest and a turbulent diffusion coefficient k_z. Over low vegetation this diffusion coefficient can be determined from empirical flux-profile functions given in the literature. Because of the large roughness and the use of towers barely extending above the canopy the situation is more complex over forest. Measurements may take place in the so-called roughness layer where large deviations from classical flux-profile functions may be expected. To support calculations of the flux from the concentration gradient observed in the Speulderbos, local flux-profile functions are required.
To determine the flux-profile functions over Speulderbos an automatic system capable of measuring the flux and the concentration gradient of ozone was operated continuously in a 36 m tower for nearly eight months in 1993. From these measurements flux-profile functions for heat and ozone were derived. In this paper the experimental set up is described and the results of the measurements are reported.

In addition, the ozone fluxes observed at the site are compared with estimates of the flux using existing detailed models of the deposition process. These models are often used in large scale air pollution dispersion models to estimate dry deposition losses of ozone or deposition inputs of acidifying gases. The large dataset available from the measurements gives a unique opportunity to this comparison under a variety of conditions. To improve the comparison between modelled and observed fluxes the parameters in the model were optimized using the measurements as a reference.

In parallel with the oxone flux measurements the concentration gradients of NO (nitric oxide) and NO_x (the sum of nitric oxide and nitrogen dioxide, NO_2) was determined. The results of the flux estimates of these gases are also discussed.

2. THEORY

2.1 Measuring dry deposition fluxes over tall vegetation

The eddy correlation method is considered a reference method to measure the fluxes of trace gases to the surface. The average flux is equal to the covariance of the vertical component of the wind velocity (w) and the air concentration (c):

$$F = \overline{w \cdot c} \tag{1}$$

In order to measure the contribution of all eddies to the flux, fast response sensors are required. These are often not available for important trace gases such as sulphur dioxide and ammonia. Therefore gradient methods are often applied. Principle to the gradient method is the flux-gradient assumption. Similar to Ficks law the flux F_i of a component i is calculated from:

$$F_i = -k_z \frac{\partial c_i}{\partial z} = -\frac{k u_* z}{\Phi_c\left(\frac{z}{L}\right)} \cdot \frac{\partial c_i}{\partial z} \tag{2}$$

The deposition velocity v_d is equal to: $-F_i/c_i$ with c_i the concentration at a height $z=h-d$, h is the height above ground and d is the so-called zero displacement height.
k is von Karman's constant (taken equal to 0.4), u_* the so called friction velocity and $\Phi_c(z/L)$ is the dimensionless flux-profile relation. L is the Monin Obukhov length scale defined in [Bush, 1973]

When gas fluxes are measured the flux-profile functions are often taken equal to the flux-profile function for heat Φ_h. Empirical values for Φ_h are given in the literature [Bush, 1973]. In principle the functions for trace gases could be different to those of heat although field experiments over grassland [Droppo, 1985] showed reasonable agreement between turbulent exchange coefficients for heat and ozone. Over forest such measurements have not been reported. Especially the displacement height for gas could be different from the one for heat. Therefore the objective of this study was to determine Φ functions for a trace gas in Speulderbos.

In an earlier study carried out in 1988 and 1989 in the framework of the acidification programme local flux-profile functions (Φ_h) were used together with a displacement height of 11.5 m. These functions were derived from measurements carried out at the site [Duyzer *et*

al., 1992]. A height dependent correction factor α was used to correct the flux-profile functions Φ for heat given by Dyer and Hicks [Dyer and Hicks, 1970]:

$$L<0 \quad \Phi_c = \alpha\Phi_{(Dyer,\ Hicks)} \quad with\ \Phi_{(Dyer,\ Hicks)} = \left(1-16\frac{z}{L}\right)^{-\frac{1}{2}} \tag{3}$$

$$L>0 \quad \Phi_c = \Phi_{(Dyer,\ Hicks)} - (1-\alpha) \quad with\ \Phi_{(Dyer,\ Hicks)} = 1+\beta\frac{z}{L}\ with\ \beta = 5.2 \tag{4}$$

Since then the forest has grown by a few metres. As a consequence the values for α and the zero plane displacement height d will have changed.

2.2 Modeling the uptake of trace gases by vegetation

Processes:

In current understanding of uptake of ozone by forest canopies four pathways play a role:

1) Uptake via stomates.

It is generally believed that the uptake of ozone is largely controlled by stomatal opening (Fowler *et al.*, 1991). This implies that the uptake via stomates is the most important route. Consequently the ozone deposition rate is to a large extent determined by parameters which control stomatal uptake ie. the amount of Photosynthetically Active Radiation (PAR), water Vapour Pressure Deficit (vpd) and temperature. Bosveld *et al.*, (1993) investigated the influence of several factors on the stomatal resistance (to water vapour) of the Speulderbos. They showed that the main factor controlling stomatal resistance for Speulderbos is water Vapour Pressure Deficit. They also note that it is extremely hard to single out the effects of highly correlated parameters such as temperature, PAR, and vpd.

2) Uptake (or better, destruction) at the leaf surface.

A highly reactive gas such as ozone is easily destructed at the leaf surface. Here it will react with deposits or with the epicuticular waxes.

3) Reactions with emitted gases.

Forests are known to emit large amounts of hydrocarbons such as monoterpenes and isoprene (see for example Duyzer, 1993 and references cited therein). These gases react rapidly with ozone. The concentration of these gases is largest near the canopy. When the flux is measured above the canopy the reactions with these gases in and near the canopy

lead to an apparent downward flux. From the forest floor nitric oxide is emitted (Johanson, 1989) . The reaction rate of ozone with nitric oxide is even faster (Duyzer *et al*, 1994). Therefore the reaction with NO will also lead to a downward flux. The consequences of these reactions for the interpretation of flux measurements above the canopy will be discussed in a separate paper (Walton and Duyzer, 1995). These processes are very important for the interpretation of measurements of nitrogen oxide fluxes. The influence on the results for ozone however is probably only limited.

4) Uptake (or destruction) at the forest floor.
This process is often similar to uptake at the leaf surface. In the case of Speulderbos the floor is covered nearly completely with fallen needles. In other forests with a living, growing understorey the situation is probably completely different. On these sites stomatal conditions of the living plants may be very important.

Models
To interpret the measurements here a simple resistance layer model described by Hicks *et al.*, (1987) is used. In Walton and Duyzer (1995) a more complex, multi layer model is used to interpret measurements.
The bulk canopy resistance is derived from:

$$R_c = \frac{1}{\frac{1}{R_{stom}} + \frac{1}{(R_{inc} + R_{soil})}} \qquad (5)$$

with:

$$R_{stom} = \frac{1}{\left(\frac{G_{vpd} \cdot G_t \cdot G_D}{R_{s,raw}} + \frac{LAI}{R_{cut}}\right)}$$

$R_{inc} = \frac{8 \cdot LAI \cdot 15}{u*}$ = resistance to transfer through the canopy to the soil (according to Erisman *et al.*, 1993)

R_{soil} = resistance to uptake of ozone at the soil taken 1000 s/m.

When the surface is wet, as judged upon the value of the relative humidity $R_{stom} = 250/LAI$ (RH larger than 95%).
At night $R_{stom} = R_{cut}/\text{LAI}$ (R_{cut} is taken as 1000 s/m).

The influence of vapour pressure deficit and temperature and the difference in diffusion coefficients (D) is accounted for using the G parameters:

$$G_{vpd} = 1 - b_{vpd} \cdot vpd$$

$$GT = \left\{ \frac{T - T_l}{T_0 - T_l} \frac{T_h - T}{T_h - T_0} \right\}^{\frac{T_h - T_0}{T_0 - T_l}}$$

with T_l taken as -5°C, T_h as 35°C and T_0 as 10°C, T is the actual temperature

$$G_D = \frac{D_{O_3}}{D_{H_2O}} = \frac{.147}{.24}$$

$$R_{s,raw} = \frac{1}{\frac{LAISUN}{R_{sunlit}} + \frac{LAISHADE}{R_{shade}}}$$ with

$$R_{shade} = R_{s,min}\left(1 + \frac{b}{pardif}\right)$$

$$R_{sunlit} = R_{s,min}\left(1 + \frac{b}{pardif + parbeam}\right)$$

LAISUN and LAISHADE are calculated from:

$$LAISUN = 2 \cdot \left(1 - 2.718^{\frac{-0.5 \cdot LAI}{\cos(zenith)}}\right) \cos(zenith)$$

$$LAISHADE = LAI - LAISUN$$

pardif and *parbeam* are calculated as described in Hicks *et al.*, 1987.

Several parameters are specific for the forest in question. The LAI at Speulderbos is known from measurements carried out at the site by the Institute of Forestry and Nature Research. The variation of the leaf area index over the year is calculated from the following function (derived from Bosveld *et al.*, 1993) :

LAI= 7.8 + 0.109 x (Julianday-130) for (130<Julianday<180)
LAI= 7.8 + 0.017 x (130-Julianday) for (Julianday<130)
LAI= 13. - 0.017 x (Julianday-180) for (Julianday>180)

In practice these equations mean that the LAI is increasing in the period between May 10 and June 29 the rest of the period the leaf area index is decreasing because of needle drop.

The other parameters need to be estimated from the limited amount of literature information available. It appears that the especially information on Douglas Fir is limited.
In the sequel attempts to derive optimal parameters from the measurements carried out will be described. An important problem is that some of the parameters such as temperature, vpd and PAR which determine stomatal resistance are highly correlated.

3. METHODS

3.1 Description of the site

The measurements were carried out in a roughly 30 year old Douglas fir stand [Erisman *et al.*, 1993]. The stand is homogeneous of an area of 2.5 ha. It is surrounded by oak and larch. The stem density is nearly 800 stems per hectare. The height of the trees was about 18 to 20 metre. The one-sided leaf area index varies over the years between 10 and 17 [Jans *et al.*, 1994]. A diagram of the site is given in [Duyzer *et al.*, 1992].

3.2 Instruments

The experimental set up is schematically presented in Figure 1. Central to the instrumentation is a sonic anemometer, a Kayo Denki DAT 310 with TR61 probe mounted at the 30 metre level on a boom extending some 3 metre from the tower on the South-West side. The fast response ozone monitor [Güsten *et al.*, 1992] is mounted on a smaller boom in a way that the air inlet was located 25 cm from the sonic centre. At 24, 26.5, 30 and 35 metre above the ground high accuracy temperature sensors [Slob, 1978] are mounted on smaller booms. Relative humidity of air is obtained from a Vaisala instrument with a capacitive sensor. Radiation instruments for net radiation (Schenk 8110), Global radiation (Li-Cor) and Skye SKP 215 sensor for Photosynthetically Active Radiation (PAR) are mounted on the 30 metre level.

Air is drawn from the inlets at the same heights as the temperature sensors to a central manifold located near the instruments at the 28 m level. Using a computer controlled valve system the height from which air is drawn through the manifold can be selected. The ozone concentration is determined using a Bendix 8002 with ozone detection based upon the chemiluminescent reaction of ozone with ethylene. Nitrogen dioxide and nitric oxide concentrations were monitored using a Teco 42S chemiluminescent NO_X analyzer.

Using this set up the air concentration can be determined four times at each height within each cycle of 20 minutes. In [Duyzer, 1994] and [Weststrate and Duyzer, 1994] several tests with the set-up are described. An experiment with all tubes sampling from the same height showed that systematic differences in the concentration observed with the different tubes were not detectable and less than 0.2%. Typically this leads to maximum errors in the

\deposition velocity of 0.35 mm/s. Random fluctuations in v_d however can be as high as a few mm/s.

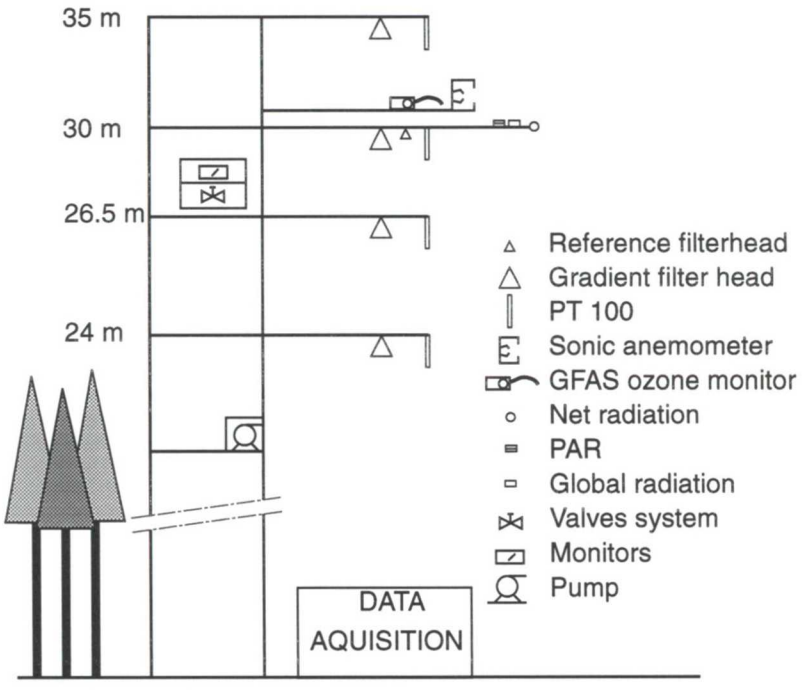

Figure 1. *Instrument set up in the meteorological tower operated by RIVM at Speulderbos.*

3.3 Calculations of the flux-profile functions from data

For every 20 minute interval the flux-profile functions Φ for heights 1 and 2 were calculated from the eddy correlation fluxes and gradients.

$$\Phi_H = -\frac{\kappa u^* z}{\overline{w\Theta}} \frac{(\Theta_2 - \Theta_1)}{(z_2 - z_1)} \tag{6}$$

$$\Phi_C = \frac{-\kappa u^* z}{\overline{wc}} \frac{(c_2 - c_1)}{(z_2 - z_1)} \tag{7}$$

with Θ_z the potential temperature calculated from the observed air temperature T as $\Theta_z = T + z \cdot \gamma$ with γ the dry adiabatic lapse rate.

In order to use only good quality data a selection procedure was applied. In addition several corrections were made to the raw data.

In Weststrate and Duyzer (1994) the various corrections which were applied to the data are described in detail. These included:

- Corrections for pressure differences in the tubes from the manifold to the individual sample intake levels.
- Correction of the heatflux for the influence of wind.
- Re-calibration of the fast response ozone monitor.
- Correction for limited time response of the ozone monitor. The ozone flux observed using the eddy correlation method was corrected for spectral response according to [Moore, 1986]. Using an experimentally determined response time for the ozone monitor of 0.1 sec the average correction was only 4% with some maximum values up to 8%.

With respect to the calculation of flux-profile functions for heat :

- Measurements obtained when the wind was blowing in the sector 315° to 45° were excluded because the measured turbulent parameters may be affected by the tower.
- Measurements during sunrise and sundown were also excluded. Moreover only cases with a monotonously increasing or decreasing temperature gradient and with the absolute value of the heatflux larger than 18 W/m^2 were considered.

The flux-profile function for ozone was only calculated in periods with significant activity of the 'sticker' which detects the ozone. Other periods were removed from the dataset. In addition the following criteria needed to be met:

- the concentration of O_3 is larger than 15 ppb.
- the flux of O_3 was larger is than 0.1 $ppb.m.s^{-1}$.
- the standard deviation in the O_3 concentration measured at one height is smaller than 5%.
- the error in v_d due to instationarity in the O_3 concentration is smaller than 5 mm/s (see Fowler and Duyzer, 1989).

The purpose of applying these additional criteria is to reduce the noise level in the calculated flux-profile functions. There is no indication in the results suggesting that the above criteria lead to a systematic bias in the results.

4. RESULTS AND DISCUSSION

All instruments were operated from December 1992 to September 1993. For several reasons a large fraction of the data obtained in the wintertime appeared to be unreliable. The data from the period April 1993 to September 1993 were most important in the analysis. Roughly 2500 successful twenty minute measurements of the eddy correlation flux were available. The gradient measurements yielded nearly 9000 successful runs for ozone and 3500 for NO_x. In Weststrate and Duyzer (1994) several statistics of the dataset are presented.

4.1 General results for ozone

Figure 2 gives a statistical overview of the data. The frequency distribution of the flux, the deposition velocity and the canopy resistance of ozone are given. The average concentration of O_3 was 34 ppb (median 28 ppb).
The average ozone flux was around 0.13 ppb m/s with a standard deviation of 0.12 ppb m/s. The average O_3 concentration during the eddy correlation measurements was 35 ppb (median value 28 ppb). The average deposition velocity was equal to 6 mm/s. The median canopy resistance calculated from the measurements was 150 s/m. A more detailed statistical treatment of the date is given in Weststrate and Duyzer (1994).

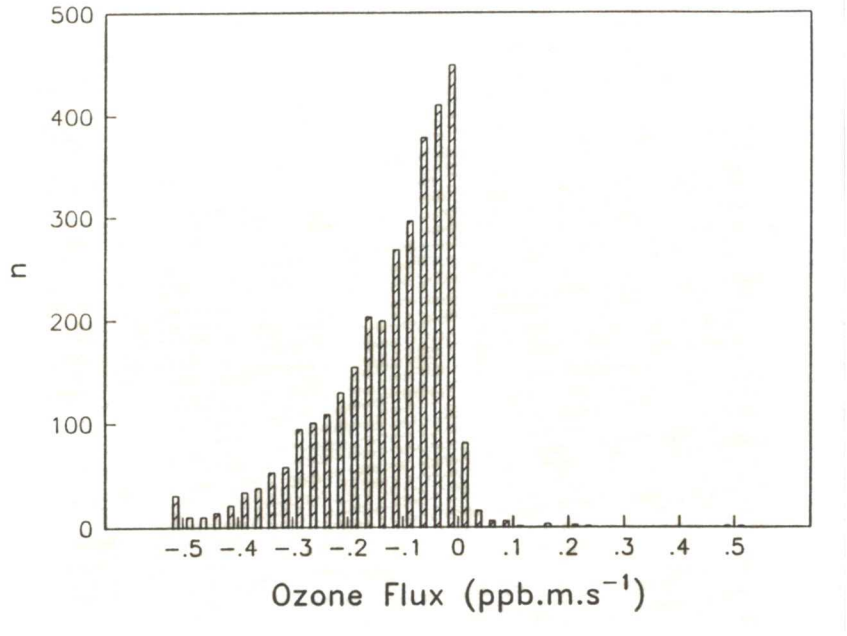

Figure 2 a. *Frequency distribution of the deposition flux of ozone as observed in 1994 by eddy correlation over Speulderbos.*

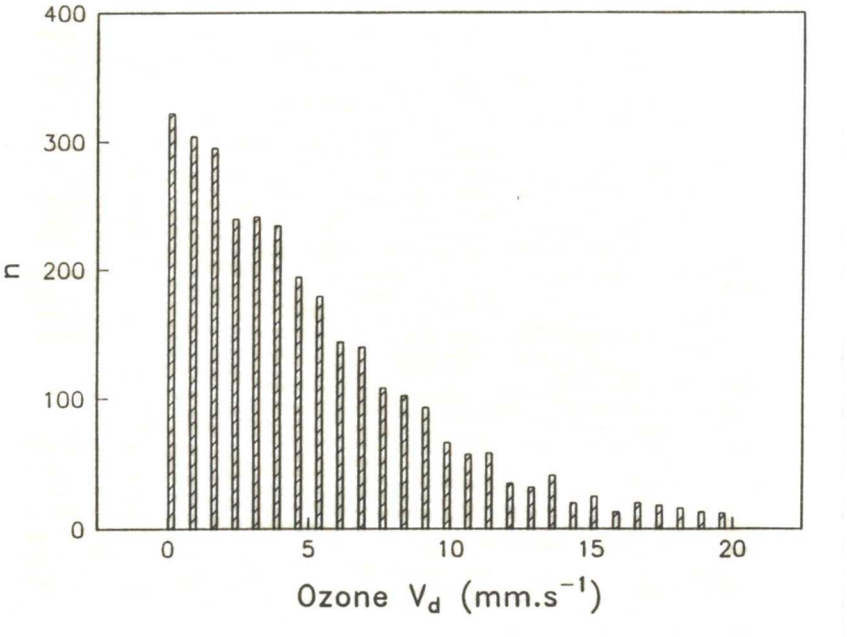

Figure 2 b. *As 2a the deposition velocity.*

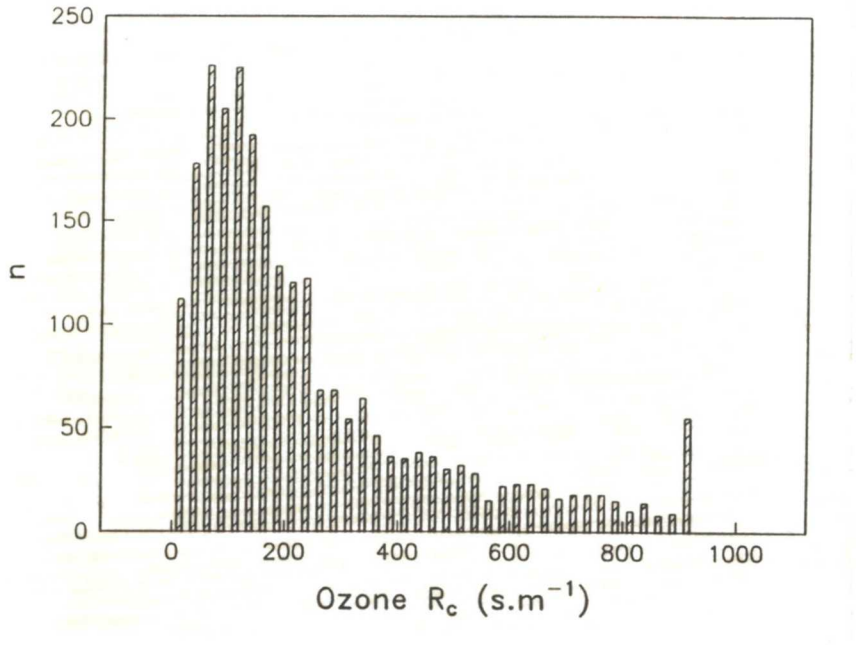

Figure 2c. *As 2a the canopy resistance.*

These results fit quite well with literature data. Greenhut (1983) reports aircraft measurements over coniferous forest in southern New Jersey with an average canopy resistance of 50 to 400 s/m. Lenshow *et al.* (1982) reports a canopy resistance of 50 s/m. Using the eddy correlation method Wesely (1983) found values varying between 150 and 400 s/m with values up to 1500 s/m at night.

Figure 3 shows a typical result of the eddy correlation measurements on July 9 and 10, 1993. A diurnal cycle of the canopy resistance R_C, calculated as in (Duyzer *et al*, 1992), is clearly detectable with values going down to around 70 s/m during the day and values of 500 s/m at night. The actual results are plotted here without any smoothing in order to give an impression of the good quality of the data. This diurnal cycle is most probably linked with uptake of O_3 by stomata.

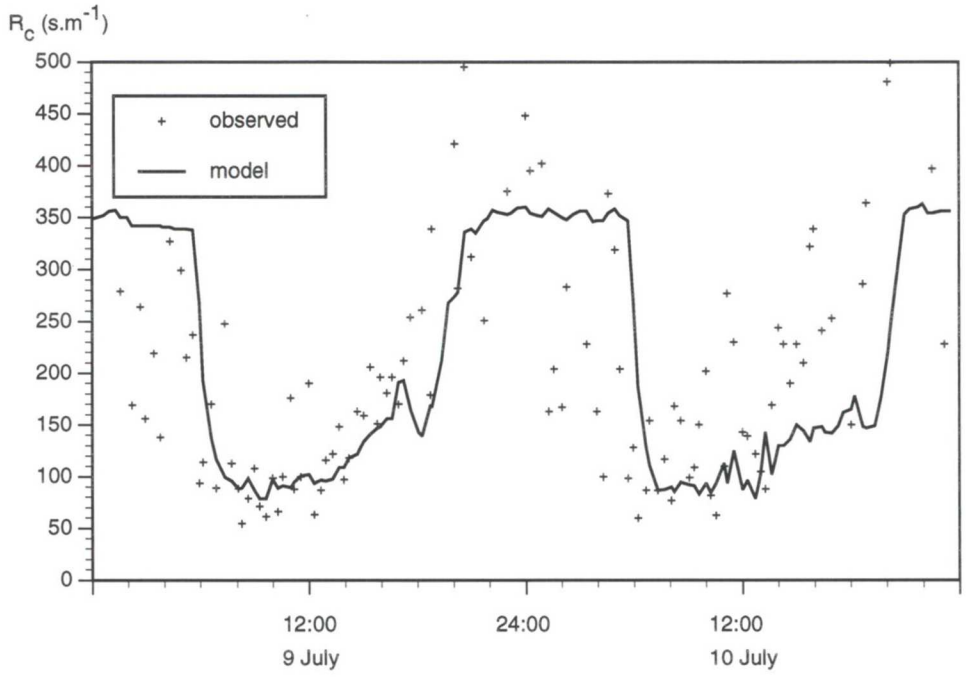

Figure 3. *The canopy resistance to uptake of O_3 calculated directly from eddy correlation measurements at Speulderbos (July 9 and 10, 1993) and the canopy resistance calculated using the model described above.*

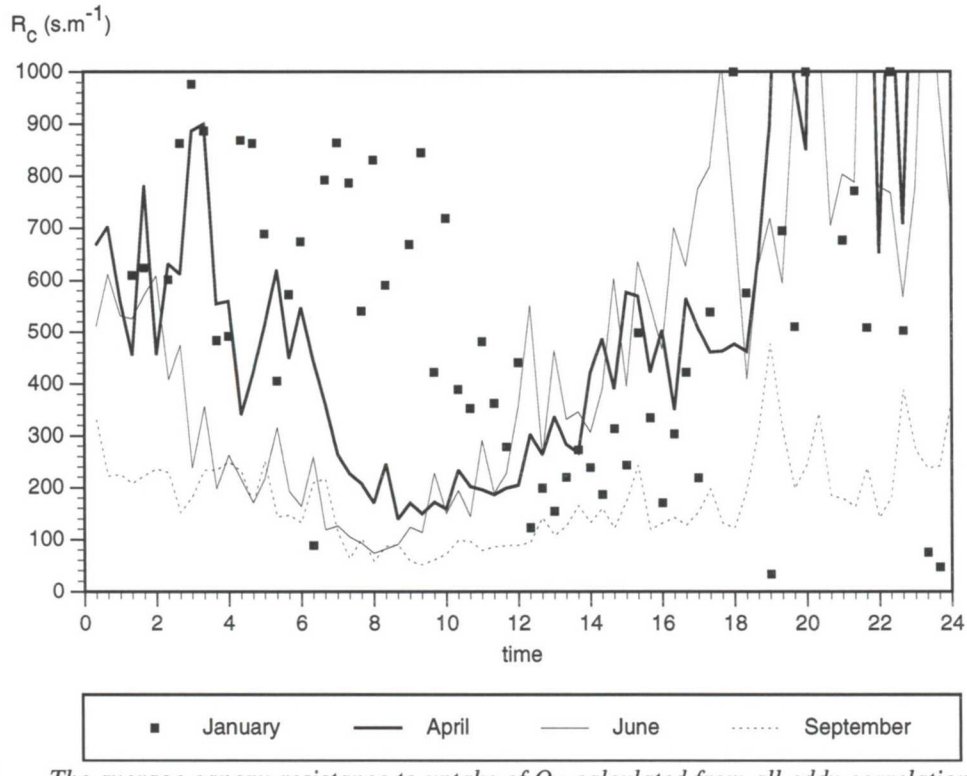

Figure 4. *The average canopy resistance to uptake of O_3 calculated from all eddy correlation measurements at Speulderbos in 1993 for different months.*

Figure 4 shows how the average canopy resistance varies over the year. Several aspects are visible:

- In January the canopy resistance R_c is only low between 11 and 16 hours whereas in September the canopy resistance is low throughout the day. This feature is probably linked with stomatal closure when the light intensity drops below a certain value in the winter. The nocturnal values of R_c observed in January are much higher. This could very well be related to differences in the uptake rate at the leaf surface. This rate is strongly related to the number of needles in the canopy (for example as expressed by the LAI) which varies considerably throughout the year. According to Bosveld *et al* (1993) the LAI, with an annual average around 11 (Posma *et al*, 1994) varies between a maximum value in June-July and a minimal value of nearly 60 % of that value in April-May. This could explain part of the differences in the nocturnal uptake. September was also a special case because the amount of rainfall was relatively high. The influence of surface wetness on the deposition rate of ozone is not clear however. The deposition rate of ozone to water surfaces is very low [Duyzer *et al.*, 1993].

The influence of several parameters on the canopy resistance was investigated. The dependency of the canopy resistance on PAR is illustrated in Figure 5a. Figure 5b and Figure 5c shows the dependency of the canopy resistance of the vapour pressure deficit and the air temperature. Especially the dependency of the vapour pressure deficit is quite strong, although it is important to realize that several cross-correlations between the air temperature, PAR and vapour pressure deficit exist. In an earlier study carried out in Speulderbos the effect of several parameters on the stomatal resistance to water vapour, calculated from eddy correlation measurements, was investigated. A strong influence of vapour pressure deficit and radiation and hardly an effect of canopy temperature was observed [Bosveld *et al.*, 1993].

The latter authors conclude that because of the high aerodynamic roughness of the forest the strong *vpd* response of the stomates acts to keep transpiration at a constant value of 200 W/m^2 in the absence of other limiting factors.

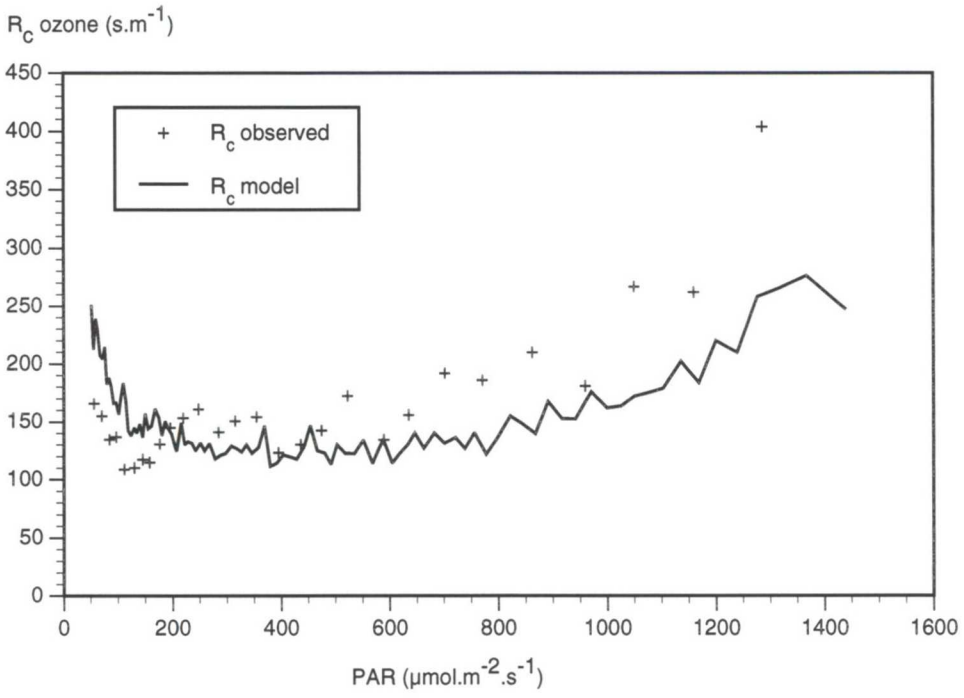

Figure 5a. *The average canopy resistance of O_3 calculated from eddy correlation measurements above Speulderbos as a function of Photosynthetic Active Radiation. The canopy resistance calculated using the model described above is also plotted.*

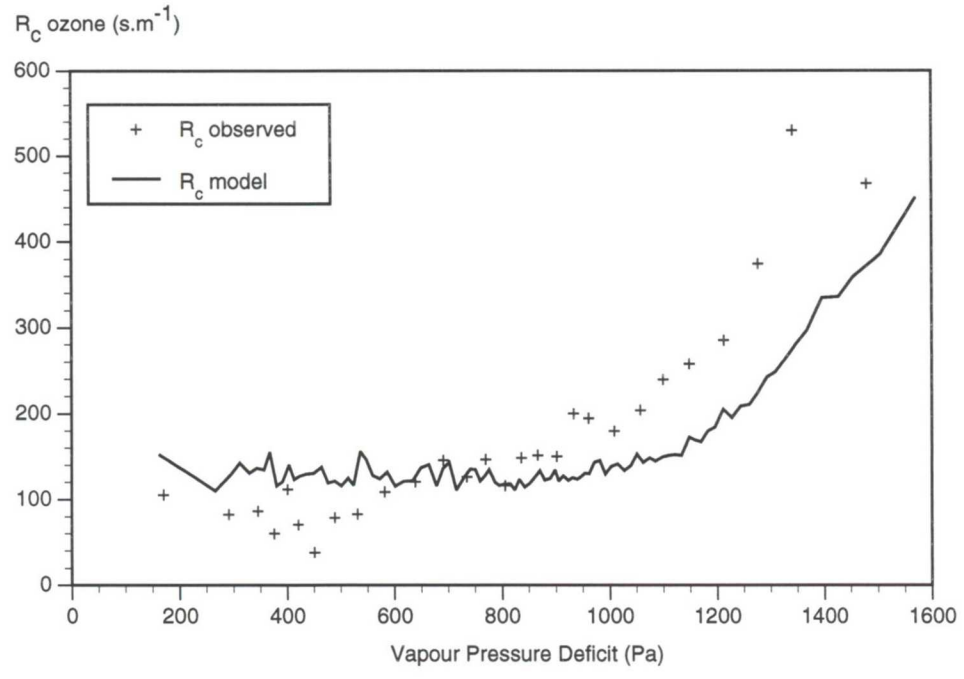

Figure 5b. *As 5a for vapour pressure deficit (only daytime results).*

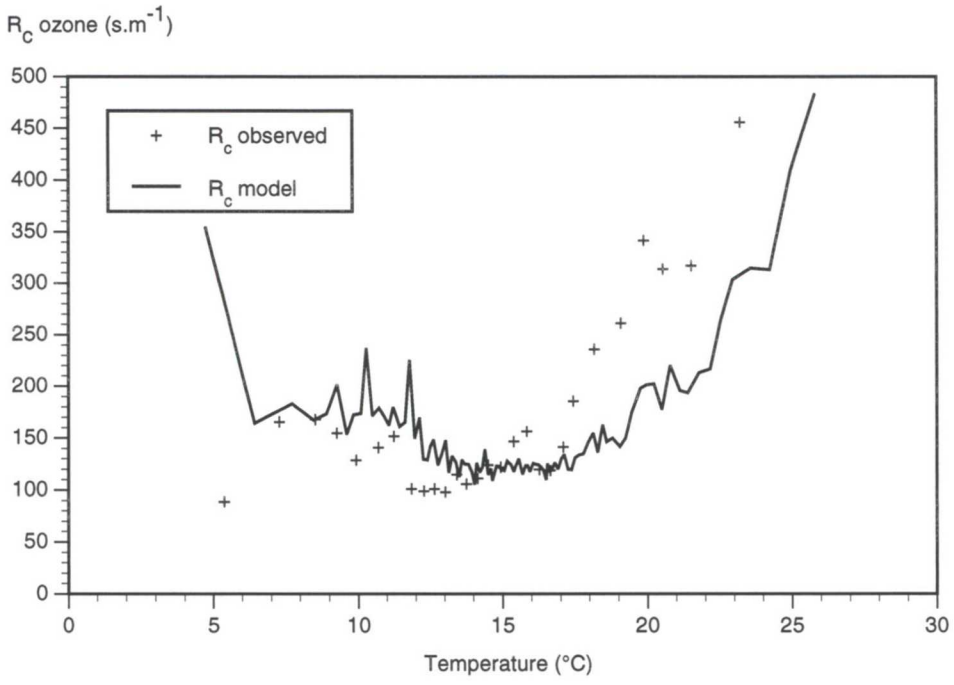

Figure 5c. *As 5a for air temperature.*

The measurement results were compared with the model described above. Several parameters however were unknown. Optimal values were derived using a Simplex search method. A number of combinations of different parameters in the model can be found which compare equally good with the measurements. Therefore the optimisation procedure has only a limited absolute value. This phenomen was also reported by Bosveld *et al*, 1993. A good fit can be obtained for example using the values given in table 1. It was tried to leave as many parameters constant as possible. The relative variance of the difference between the modelled values of the canopy conductance ($1/R_c$) and the observed values decreased from 200% with the literature values to 78%.

In Figure 3 the results performance of the model can be compared with the results of the actual measurements on these days. The comparison is good on July 9. On July 10 the calculated values of R_c are significantly lower. This deviation is probabaly related to limitations in the model description in which the effect of water-stress is not incorperated. At the moment there is no data available on waterstress. July 10 was a warm and dry day so it seems logical to assume some waterstress.

In Figure 5 the measurements are presented together with the parameterised results. It is relevant to stress that optimal results can not be found when literature values are used.

Table 1 *Optimal values of model parameters derived from a comparison between the observed individual values and estimates using the model described in chapter.*

Parameter	value	lit. value *)	unit
Rsmin	273	232	s m^{-1}
b	25	25	W m^{-2}
bvpd	0.62	0.0026	kPa^{-1}
T_l	-5	-5	°C
T_o	10	9	°C
T_h	35	35	°C
R_{cut}	2600	2600	s m^{-1}
R_{soil}	1000	1000	s m^{-1}

*) value derived from Jarvis *et al.* (1976). These values are all given for spruce.

4.2 Flux-profile functions

A specific averaging procedure was used to calculate flux-profile functions. After all selection procedures around 500 twenty minute cases were left. The arithmetic average of these Φ functions for ozone in a certain stability interval z/L shows too much scatter. The large scatter is caused by the magnitude of the concentration gradient as well as the magnitude of the fluxes. Especially at (near) neutral conditions (windy, overcast) when the ozone concentration is low the deposition flux becomes very small. Only between 24 and 35 metre the difference can be observed well above the detection limit.

In order to reduce the large effect of outliers a robust statistical treatment is required. Therefore several averaging procedures were compared [Weststrate and Duyzer, 1994]. The larger temperature data set showed less scatter and was used as a database to test these procedures. Best results were obtained using a robust statistical method proposed by the Analytical Methods Committee (1989). With this method the average is calculated on the basis of the 50 and 75 percentile values thereby minimising the influence of outliers. For heat the difference in the results obtained using the various procedures appears to be small. For O_3 only the robust methods gave useful results. Based on the similarity in transport mechanisms it was assumed that the procedures used for heat could be applied for O_3 with confidence as well.

Figure 6a shows the flux-profile functions calculated for heat for the heights 30 to 35 m. A displacement height of 15 m was assumed as 75% of the height of the trees [Jarvis *et al.*, 1976]. It is important to realise that the zero displacement height was now chosen to be 15 metre rather than the 11.5 metre chosen earlier. This difference is related to the growth of the forest over this period the forest which was between 0.6 to 0.9 m per year and therefore some 3 m over these years [Jans *et al.*, 1994]. It appears that the functions can be described

quite well with small corrections to the existing flux-profile functions. The values of the Φ_h function calculated using classical equations (3) and (4) with α equal to 0.9 are also plotted. It was noted that a slightly better comparison between the observations and the functions could be obtained when the coefficient β in the flux-profile functions was taken to be 7 rather than 5. Similar results are also reported by Bush (1973).

Table 1 shows the data for the other height intervals as well. The correction factors compare quite well with the results found in the earlier study [Duyzer *et al.*, 1994]. As was observed earlier the deviation from the original functions increases when the canopy is approached.

Table 1 *Values of* α *to correct flux-profile functions as in equations (3) and (4) for heat for different height intervals* h_1 *and* h_2. *Assuming a displacement height of 15 m the effective height* z_{eff} *for which the* Φ *is valid is calculated from:* $z_{eff} = \sqrt{z_1 \cdot z_2}$

Interval h_2-h_1	z_{eff}	α
24 - 26.5	10.2	0.75
26.5 - 30	13.1	0.8
30 - 35	17.3	0.9
24 - 35	13.4	0.75

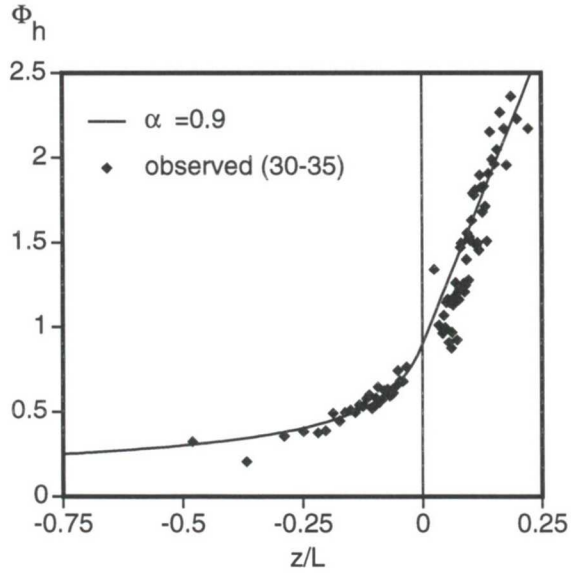

Figure 6a. *Flux-profile functions* Φ_h *observed over Speulderbos. The lines indicate the classical functions according to equations (3) and (4) using a value of 0.9 for the correction factor* α.

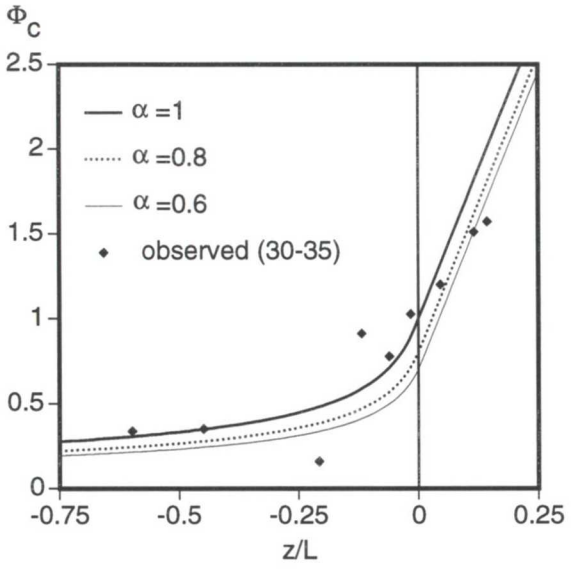

Figure 6b *Flux-profile functions Φ_C over Speulderbos. The drawn line indicates classical functions according to equations (3) and (4) using indicated values for α.*

The results for ozone for the 30–35 m interval are displayed in Figure 6b. The results for this height interval compare reasonably well with the results for this interval for heat. The uncertainty due to scatter however is much larger. For the other height intervals the scatter is even worse. For the interval 24–35 metre the comparison between heat and ozone is quite good. For both O_3 and heat an α factor of 0.75 gives a reasonable fit to the data. It is therefore concluded that there is no significant difference between the functions for heat and those for ozone.

In order to test this assumption further the ozone flux was calculated using the gradient method and compared with fluxes measured by the eddy correlation method. To calculate the gradient flux the flux-profile functions derived for heat (given in Table 1) were used for each of the three height intervals.

The results of this comparison are presented in Figure 7 where the average of the three height intervals is compared with the eddy correlation flux. The observed fluxes compare quite well over a range of a factor of ten. This gives confidence in the flux-profile functions chosen for the analysis. The flux calculated according to the so called modified Bowen ratio method was also compared with the eddy correlation flux. The fluxes calculated for several height intervals also compared very well with the eddy correlation flux [Weststrate and Duyzer, 1994].

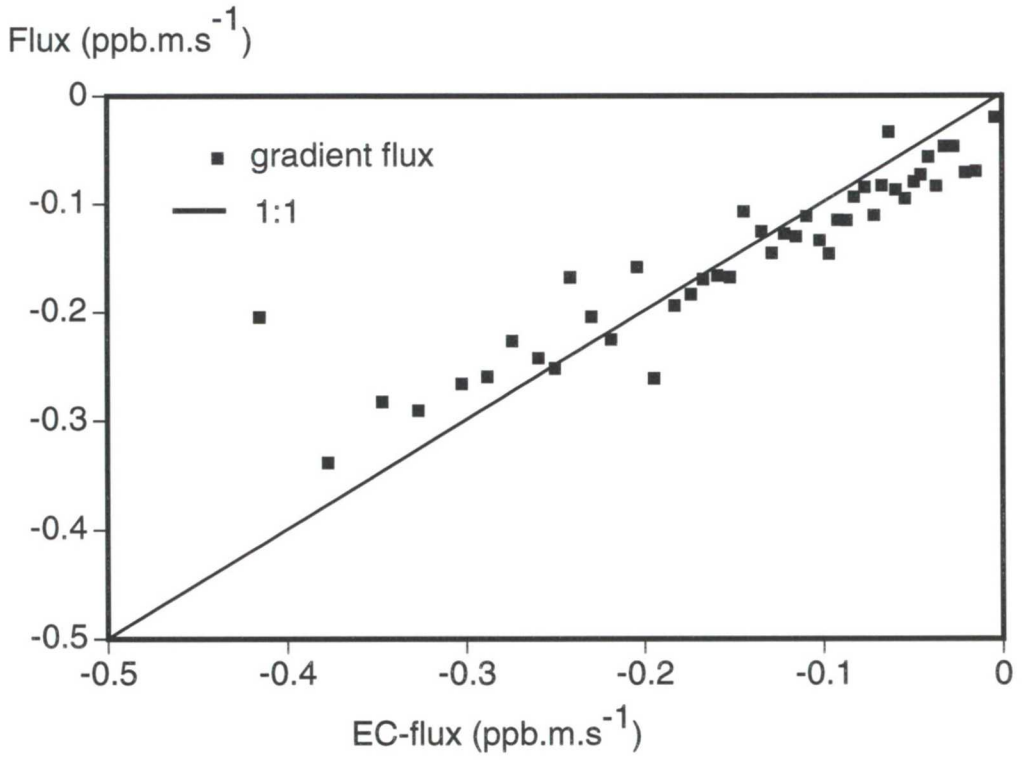

Figure 7. *The flux of O_3 to the Speulderbos calculated using the gradient method against the flux observed using the eddy correlation flux.*

4.3 Constant flux layer

The Speulderbos area is relatively inhomogeneous. This may severely limit the possibility to do good quality flux measurements. To test the validity of the constant flux assumption over the forest several additional measurements were carried out in a three week campaign in June 1993 [Walton *et al.*, 1995]. The ozone flux was measured by eddy correlation at the 25 m and at 35 m level. No significant differences could be detected between the fluxes of momentum, heat and ozone observed at two levels [Choularton *et al*, 1994]. During this campaign the ozone flux was recorded simultaneously at a second tower (the 'Aerosol' tower) located some 50 m away from the one described here. The fluxes at both towers did not deviate significantly either. This result is shown in Figure 8. Both observations endorse the assumption that a fairly homogeneous flux field exists over Speulderbos.

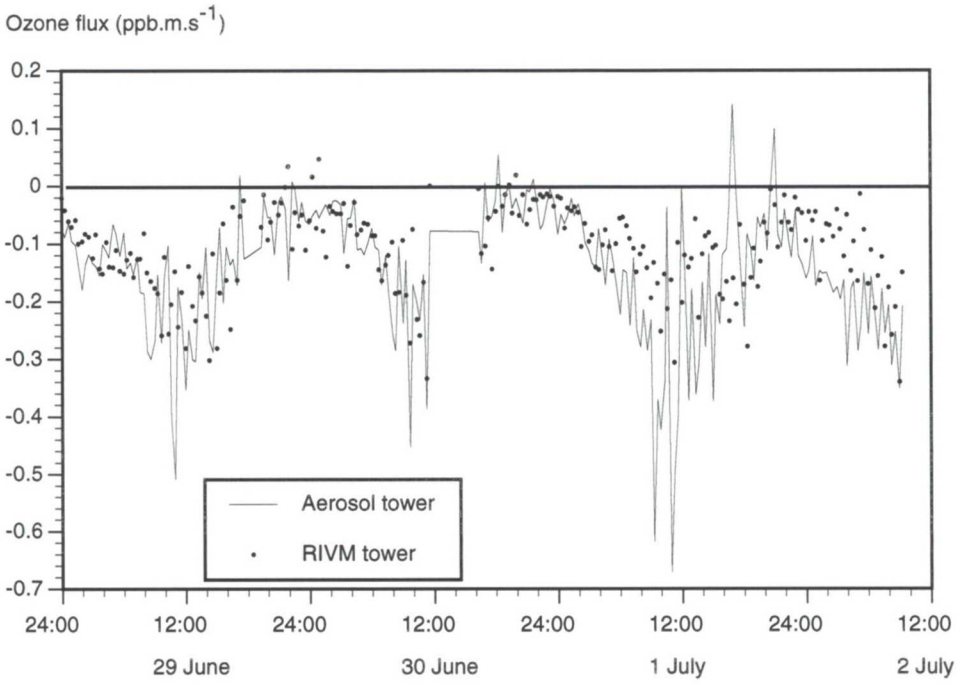

Figure 8. *Ozone flux measured at the RIVM tower at Speulderbos and at the 'Aerosol tower' some 50 metres away from the RIVM tower.*

4.4 General results for NO_x

For NO and NO_2 only gradient measurements are available. Only during the large experiment in June 1993 eddy correlation measurements of NO_2 were carried out. It is a well recognized fact that fluxes and profiles of NO and NO_2 are affected by chemical reactions (Duyzer *et al.* 1995). Correction methods however have only recently been developed and have hardly been validated. From the calculations described in Walton and Duyzer (1995) it also appears that the flux divergence above the canopy is relatively small. So although the profiles of NO_2 and especially NO above the canopy are probably influenced by chemical reactions in air they are used here without corrections. Therefore the results for NO and NO_2, individually, need to be treated with care. With respect to chemical reactions NO_x (NO + NO_2) is to a large extent a conserved quantity. In the complex mixture of reactions taking place in air NO_x is not always conserved (for example PAN and HNO_3 are formed) but the losses are relatively small. The situation is even more complex because NOx monitors usually measure not only NO and NO_2 but also PAN and HNO_2 and some nitrates quantitatively. It is not clear wether or not HNO_3 is measured with the NOx monitor. Probably losses in the intake tubing are large and HNO_3 will not be measured. In any case to estimate the input of nitrogen into forest it seems, as a first estimate, justifiable to use the NO_x-flux.

The measurements for NO_x show that net fluxes to the forest are extremely small the median flux is –2.5E-3 ppb m/s or 0.5 kg N/ha/yr (and a standard deviation of 7 ppb m/s. This means in any case that the input of NO_x from the atmosphere is small. From a scientific point of view and because of the difference in effects of NO and NO_2 and the different impact on atmospheric chemistry it is more interesting to look into NO and NO_2 fluxes separately.

In an earlier study carried out in Speulderbos in 1988 and 1989 by the Agricultural University of Wageningen unexpected results were found (Duyzer *et al.*, 1994). The flux of NO_2 was, especially during the day, often directed upwards. The NO flux during the day, was often directed towards the surface. At night NO fluxes were away from the surface whereas NO_2 fluxes were often small but directed towards the surface. Very little other measurements of NO or NO_2 fluxes over forest have been described in the literature. Hicks *et al.* (1983) report measurements over coniferous forest but finds the results hard to interpret. Fluxes were very noisy and bidirectional in some periods

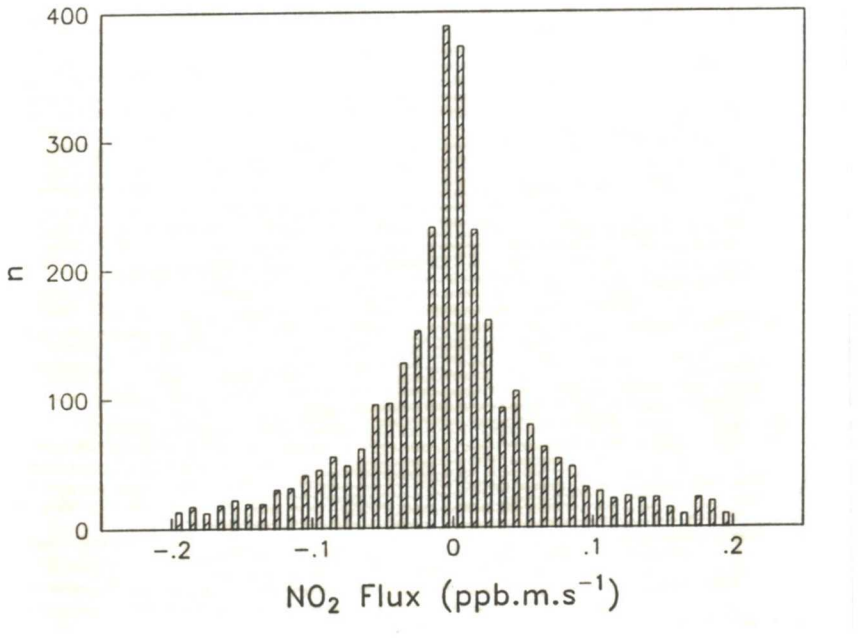

Figure 9a. *Frequency distribution of the flux of NO_2 as observed in 1993 by the gradient method correlation over Speulderbos.*

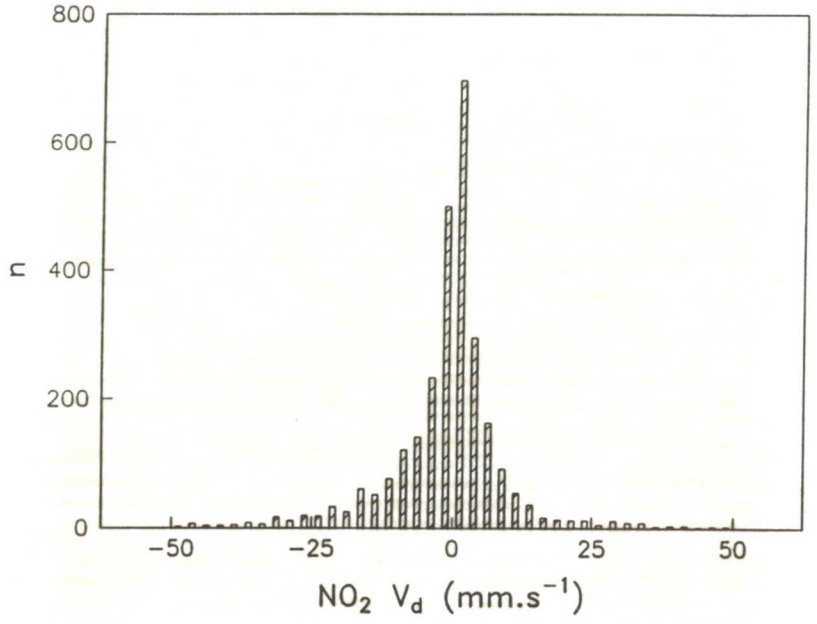

Figure 9b. *As 9a but the deposition velocity.*

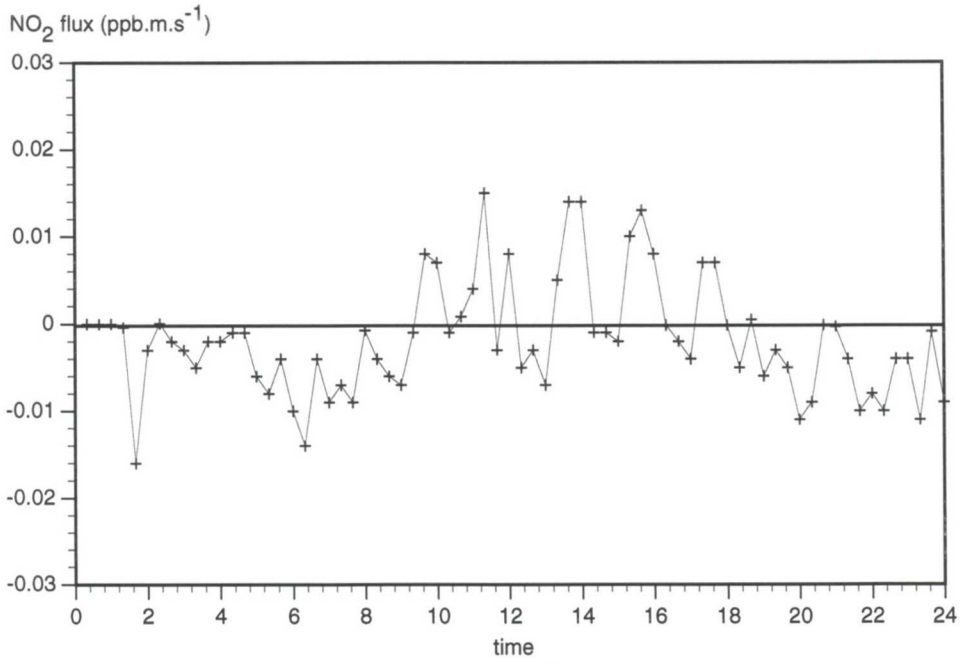

Figure 9c *Diurnal cycle of the NO_2-flux averaged over all measurements.*

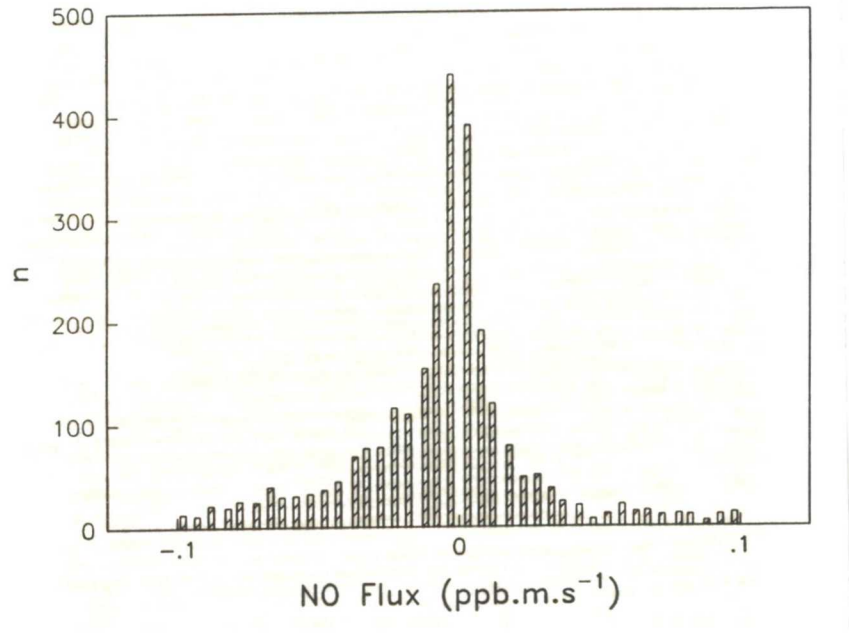

Figure 10a. *Frequency distribution of the flux of NO as observed in 1993 by the gradient method correlation over Speulderbos.*

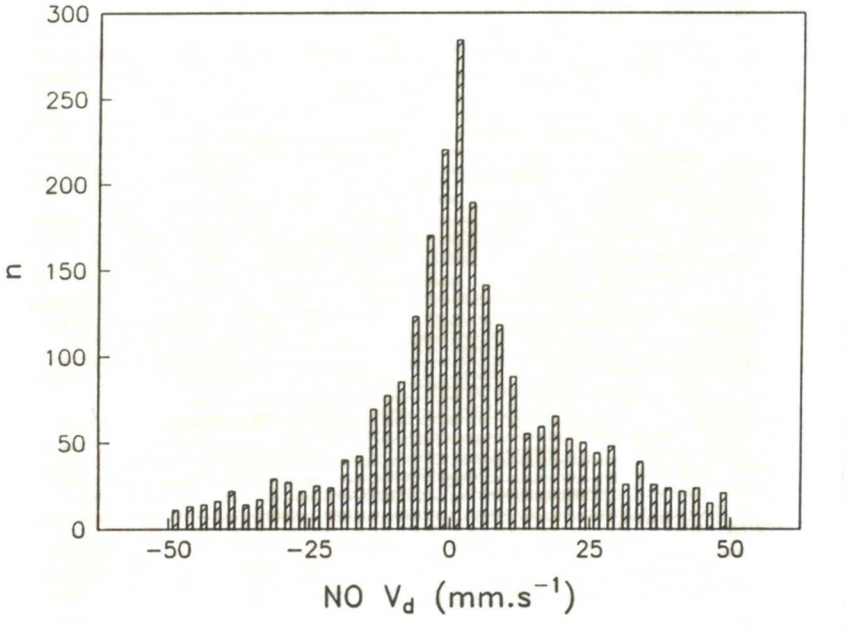

Figure 10b. *As 10a but the deposition velocity.*

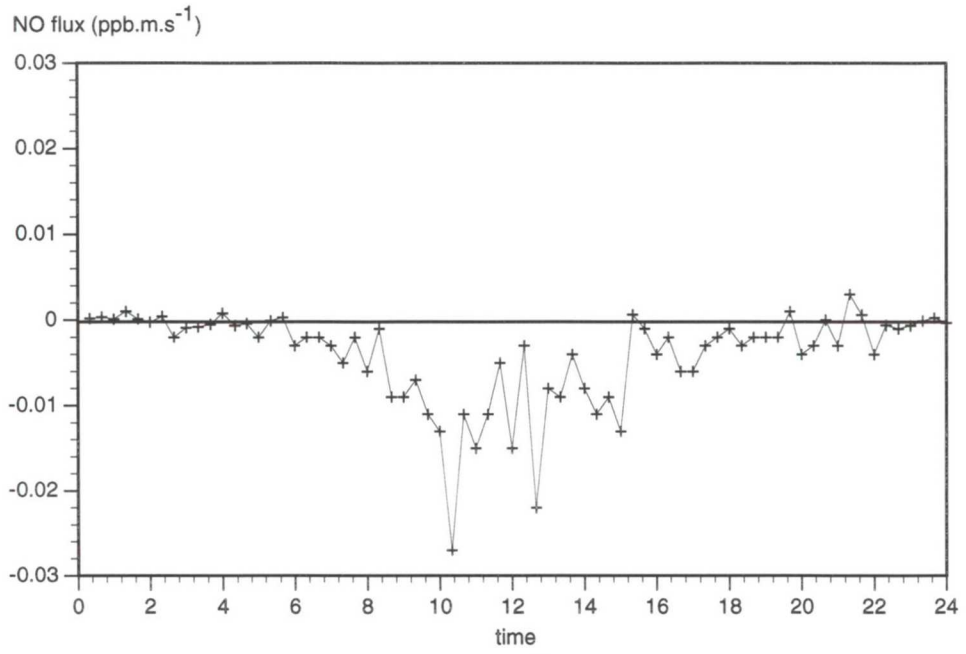

Figure 10c. *Diurnal cycle of the NO-flux averaged over all measurements.*

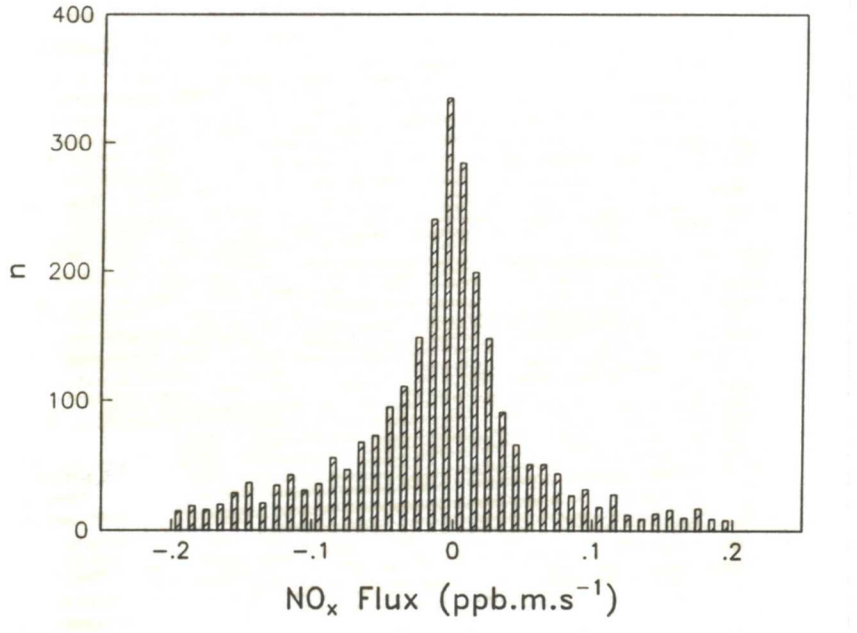

Figure 11a. *Frequency distribution of the flux of NO_x as observed in 1993 by the gradient method correlation over Speulderbos.*

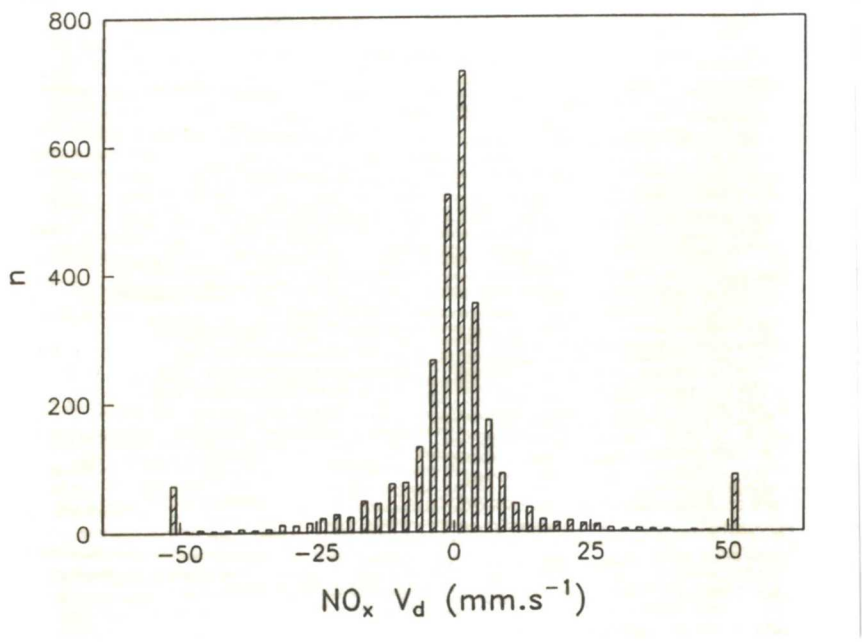

Figure 11b. *As 11a but the deposition velocity.*

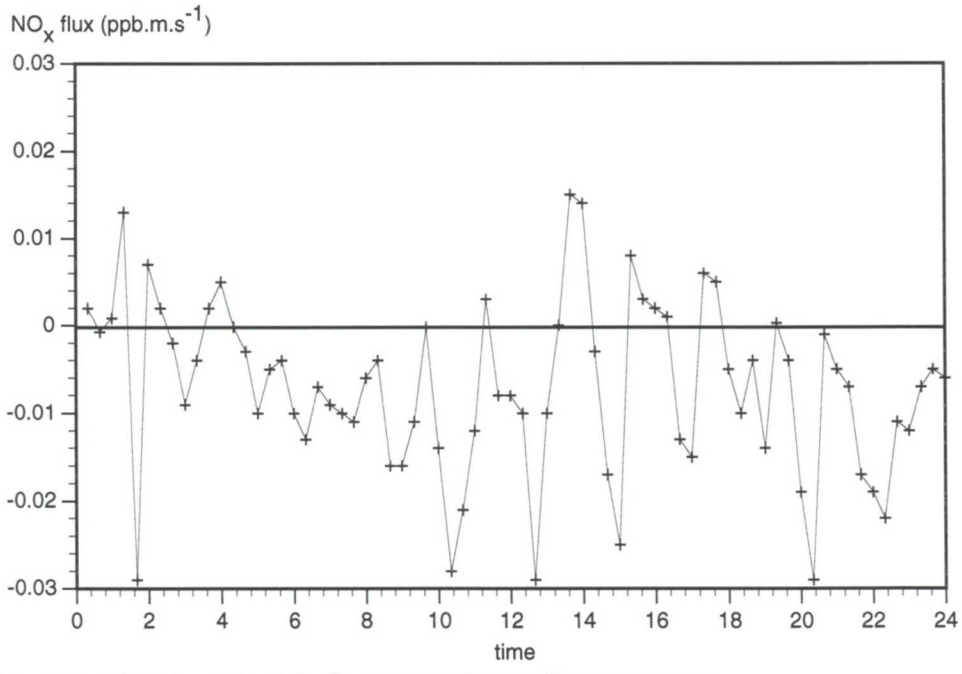

Figure 11c. *Diurnal cycle of the NO_X-flux averaged over all measurements.*

The average concentration of NO over the whole dataset was approximately 1.6 ppb (median 0.8) and the NO_2 concentration was around 9 ppb (median 7.3). Figure 9 gives an overview of the results for NO_2. It is clear that there is a considerable noise component in the measurements. Nevertheless the general picture is similar to the earlier observation that

the flux of NO_2 is away from the surface in the daytime. At night the flux is small and directed towards the surface. For NO presented in Figure 10 the results are also simular to those found in previous studies. The NO flux is towards the surface during the day and near zero at night. Figure 11 shows the results for NO_x. As expected these results are a combination of the individual results for NO and NO_2.

There could be several explanations for this phenomenon. In Walton and Duyzer (1995) a mechanism which could explain these results is discussed. The picture is as follows :
NO is emitted from the soil at rates of up to 10 and 30 ng N m^{-2} s^{-1} (average 18 ng N m^{-2} s^{-1} or 0.03 ppb m s^{-1} or 6 kg N ha^{-1} yr^{-1}) These fluxes were observed at the site during the large field campaign in June 1993 (Walton *et al*, 1995). Two dynamic enclosures were used to measure NO_2 and NO fluxes at the forest floor. The air in the enclosures covering an area of nearly 0.5 m^2 were stirred with electric fans. To limit the influence of the enclosure on soil processes the lid was placed on the enclosure only ten minutes before the measuring cycle was started the lid. During the measurement the concentration of NO and NO at the inlet and the outlet of the enclosure was determined using a TECO 42 A. During the measurements carried out on June 29 and 30 and July 1 the concentration of NO detected at the inlet was near the detection limit of the instrument and the NO_2 concentration varied between 5 and 10 ppb. The resistance of the forest floor to NO_2 uptake was typically 500 s/m.

It is assumed that all NO emitted from the forest floor is converted to NO_2 in the trunk space by reaction with O_3 before it enters the canopy. When the flux of this NO_2 which enters the canopy from below is higher than the amount of NO_2 that is being taken up in the canopy the flux observed above the canopy is away from the surface. When the NO flux from the soil and the amount of NO_2 formed from it is lower than the possible uptake in the canopy the flux of NO_2 observed above the canopy will be towards the canopy. The following qualitative relation would then hold for the NO_2 flux observed above the canopy.

$$F_{NO_2}\text{ (above canopy)} \approx F_{NO}\text{ (soil)} + F_{NO_2}\text{ (Canopy)}$$

The amount of NO_2 taken up by the canopy (F_{NO_2} (Canopy)) can be derived from the NO_2 concentration and the canopy resistance R_c.
The dataset was inspected for facts to endorse the above mechanism. This evaluation however is severly hindered by the large noise component in the flux.

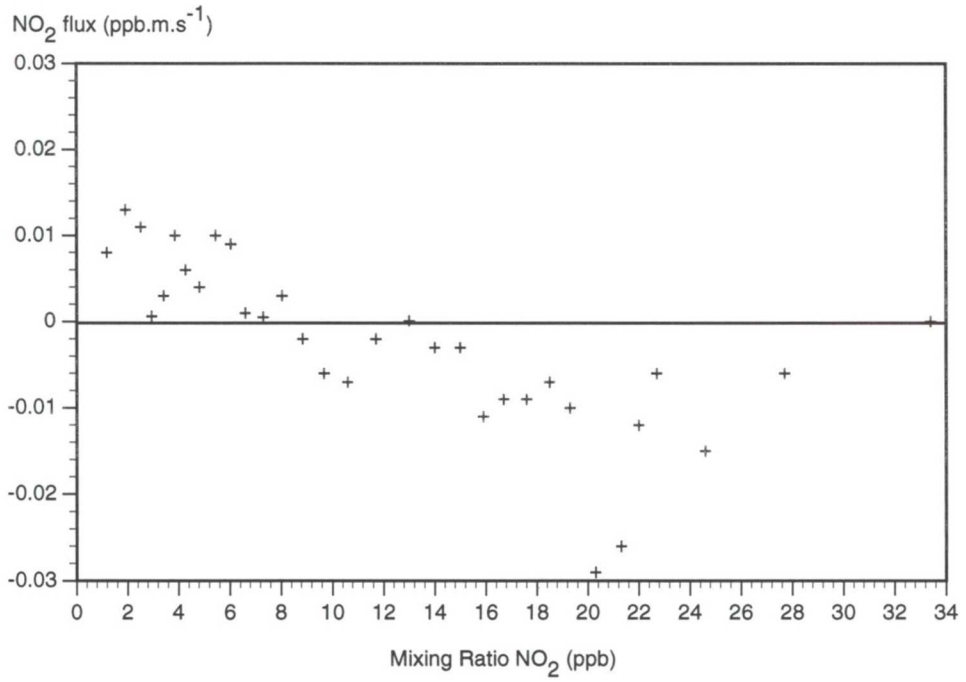

Figure 12. *The flux of NO_2 calculated from the gradients above the forest as a function of the NO_2 concentration.*

Figure 12 shows the NO_2 flux as a function of the concentration of NO_2. The results support the above mechanism. The flux is away from the surface (positive sign) when the concentration is low. Similar support is found when the NO_2 flux is plotted as a function of the deposition velocity observed for ozone. The deposition velocity of ozone could represent the canopy uptake of NO_2. Upward fluxes are correlated with low deposition velocities of ozone. It has often been shown that soil emission rates are a function of soil temperature (Meixner, 1994 and references therein). In the dataset there is correlation between air temperature and the NO_2 flux. It appears that no emission occurs at temperatures below 15° C. Again because of the strong correlation between air temperature and other relevant parameters conclusions based on correlations have to treated with great care. Nevertheless there seems to be considerable support for the above mechanism in the dataset.

5. CONCLUDING REMARKS

The dry deposition flux of ozone to Speulderbos was measured continuously at a height of 30 meters for several months between December 1992 and September 1993 using a new fast response ozone sonde. In the same period the concentration of ozone, nitric oxide and the sum of nitrogen dioxide and nitric oxide (NO_x) was measured at four heights (between 20 and 36 m) above the canopy. In addition a large number of meteorological parameters were measured continuously. From these measurements flux profile functions for heat and ozone were determined. It appears that the new flux profile functions for Speulderbos can be described quite well with small modifications to classical functions described in literature.

The homogeneity of the flow and deposition field over Speulderbos was studied during a three week campaign. From simultaneous measurements carried out at two separate towers and at two different heights above the forest it was concluded that for ozone there are hardly indications of a flux divergence.

The experiments shown here form evidence that the gradient method (and the Bowen ratio method) can be used over forest for ozone. It seems reasonable to assume that this conclusion is also valid for other trace gases with sinks in the canopy such as sulphur dioxide or ammonia. This conclusion however may not be valid for gases with sources and sinks at the forest floor such as nitrogen oxides. Apart from that the results of this study are an important scientific basis for flux monitoring at Speulderbos.

The influence of several parameters on the deposition flux was investigated. There appears to be a strong correlation between the canopy resistance to uptake of ozone and water vapour pressure deficit and photosynthetically active radiation. The measurement results were compared with estimates based on a model described in the literature. This exersize showed that these estimates may differ from the observations by more than a factor of two on the average. An attempt was made to improve the model by parameter optimization. The poor behaviour of the model described in literature is in contrast with recent comparisons described in literature for SO_2 and NH_3 [Erisman *et al.*, 1995]. This is very much related to the fact that for the latter gases the dry deposition is to a large extent controlled by the atmosperic resistance R_a and R_b. The atmospheric resistances can be modelled quite well. The uptake of ozone is largely controlled by stomatal conditions and therefore harder to model. Experience with estimates of ozone deposition rates is much poorer (Padro, 1991)

The average anual flux of NO_x to Speulderbos is small, the medium flux equals 0.5 kg N/ha/yr. This value can be compared with the dry deposition of NO_2 to the Speulderbos which was recently estmated to be 2.7 kg/ha/yr [Erisman *et al.*, 1995]. The reason

for this difference is the emission of NO from the forest floor which is not accounted for in the model estimates.

Continous measurements of the NO_2 gradient above the canopy often indicate fluxes away from the canopy. NO gradients indicate usually fluxes towards the canopy. These observations can be understood quite well using a detailed multilayer canopy model (described in Walton and Duyzer, 1995) which includes chemical reactions in air between NO, NO_2 and O_3. The observed emission of NO_2 above the canopy is caused by a strong emission of NO from the forest floor. The NO is converted by O_3 to NO_2 in the trunkspace where photolysis of NO_2 is less eficient. An important fraction of the formed NO_2 is taken up in the canopy. The fraction of NO_2 which is not taken up will leave the canopy as NO_2. This NO_2, emitted from the canopy is not in equilibrium with the photochemical processes occuring in the layers of air aloft, further away from the above. Further away from the canopy more NO_2 will be photolyzed. This leads to a additional decrease with height of the NO_2 concentration above the canopy. The photolysis of NO_2 leads to formation of NO and consequently to an increased concentration of NO at higher layers. This gradient is easily mis-interpreted as deposition of NO.
In any case the forest seems to emit NO_2 rather than absorb it which is in constrast with current understanding. There is a need to improve parameterization of NO_2 deposition fluxes to forest. This process may have a significant effect on regional ozone formation.

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J.H. Duyzer	Project leader
Hilbrand Weststrate	Research worker

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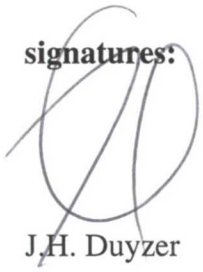

J.H. Duyzer
Project leader
Date: 31 maart 1995

Ir. H.P. Baars
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