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TNO-report

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Publication : P 89/023

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MEASUREMENTS OF DRY DEPOSITION VELOCITIES OF NH_3 OVER HEATHLAND AND FOREST

Date : 1989-05-22

Order no. : 21447

Submitted to
Journal of Geophysical Research

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SUMMARY

The dry deposition velocity of ammonia (NH_3) and particulate ammonium were determined with the aid of the micrometeorological gradient method. About 120 measurements of 1 hr duration were conducted in the Netherlands from 1984 to 1986 in different seasons, mainly over heather/purple moor grass vegetation. A relatively limited number of measurements was performed over forest.

The results show that NH_3 is deposited more rapidly than other trace gases, such as ozone, SO_2 or NO_x. An average deposition velocity of 1.9 cm/s was observed during the measurements (most of them carried out during the day-time) over all heather locations. The average flux of NH_3 during these periods was equivalent to 14.5 kg NH_3/ha/yr. The surface resistance for NH_3 over heathland appeared to be low relative to other compounds such as ozone. An average value of 0.23 $s.cm^{-1}$ is derived from a fit of all the results. The effect of several variables on the surface resistance was investigated, but only that of surface wetness was established clearly. Wet vegetation acts as an almost perfect sink for NH_3. No clear-cut difference between the various locations was found. The observed variation in the measured deposition velocities could be explained with a surface layer resistance model for some 60% on basis of fluctuations in meteorological variables, surface wetness and air temperature. The low surface resistance observed and the lack of any diurnal variation suggest that uptake via non-stomatal pathways is relevant. Although the number of measurements over forest was too small to warrant definite conclusions, it appeared that pine trees also absorb NH_3 very efficiently.

To obtain an estimate of a long term average deposition velocity of NH_3, we used a surface-layer model to account for the effect of night-time meteorology. Measurements, and calculation result in a yearly averaged 24-hour value of 1.6 cm/s.

For particulate ammonium, only one in ten measurements leads to flux values significantly higher than the detection limit of the method, owing to the low deposition velocity of particulate NH_4^+. The average flux measured is equivalent to 3.8 kg NH_4^+/ha/yr. The 24-hour yearly averaged dry deposition velocity for particulate NH_4^+ is 0.17 $s.cm^{-1}$. Under the circumstances we encountered in the Netherlands, NH_x deposition proceeded for only about 20% by dry deposition of particulate NH_4^+.

INTRODUCTION

Ammonia is the most abundant alkaline component of the atmosphere. In Western Europe, most ammonium compounds present in air originate from animal manure. Some of the ammonia released into the atmosphere is converted into particulate ammonium sulphate and nitrate. Gaseous ammonia and ammonium compounds in particles are deposited from the air both by wet deposition and by dry deposition. Nitrifying soil microbes can convert ammonia into acidic compounds by the following reaction [van Breemen et al., 1982]:

$$NH_4^+ + \frac{3}{2} O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

$$NO_2^- + \frac{1}{2} O_2 \rightarrow NO_3^-$$

Through these process NH_3 may constitutes a major contribution to the burden of acidic compounds on natural ecosystems [Duyzer et al., 1987]. Because of its fertilizing properties NH_3 may upset the biological balance of ecosystems that depend upon a paucity of nutrients. An example of such a sensitive ecosystem is the heather vegetation on peat moors. Deposition of excess nitrogen compounds from the air is likely to cause the heather to be ousted by purple moor grass.

Whereas the wet deposition flux into these ecosystems can be measured relatively easily, the dry deposition flux cannot be measured directly. The dry deposition flux can be estimated from the air concentration C at a reference height (for example 1 metre) and the deposition velocity v_d i.e. Flux = $-v_d.C$ (by convention, fluxes directed to the surface surface of the earth are taken to be negative). The dry deposition velocity, however, is known only for a few compounds and for a limited number of vegetation types.

A useful scientific tool to differentiate between the influence of the processes that play a role in the deposition process and to generalize the results of a limited number of measurements is the so-called resistance layer model. In this model a distinction is made between a turbulent layer of air extending from the reference height to very close to the the surface (represented by a resistance to transfer R_a) a laminar boundary layer, a few mm thick, in contact with the vegetation elements and represented by a resistance R_b. The final resistance to uptake by the vegetation is represented by the surface resistance (R_s). The dry deposition velocity is equal to the reciprocal of the sum of this series of resistance, viz.

$$v_d = \frac{1}{R_a + R_b + R_s}$$

Whereas values of R_a and R_b can be estimated fairly well with the aid of common micrometeorological parametrization (see, e.g., Hicks et al., 1988) much less is known about the surface resistance (R_s) specific for the combination of surface and compound.

In the measurements, described here, we used a micrometeorological method, viz, the gradient technique to measure the NH_3 flux over the surface. The flux is calculated from measurements of the vertical concentration gradient of the component in the lowest metres of the atmosphere. A turbulent diffusion coefficient k_z is estimated from measurements of the vertical gradient of the wind velocity and the air temperature. At suitable sites the flux measured in the lowest few metres of the atmosphere is representative of an area a few hundred metres upwind. From the measurements a representative surface resistance for heather/grass vegetation was calculated and used to estimate a diurnal average dry deposition velocity for NH_3 on this vegetation.

EXPERIMENTAL

Measuring procedures

Measurements were conducted in campaigns lasting a week each. An individual flux measurement consisted of one hour of sampling for determination of the NH_3 flux, and two or three hours for determination of the NH_4 flux.
During the day-time, some three flux determinations, equally distributed over the day between 9 a.m. to 5 p.m., were performed for NH_3, and one or two flux determinations for NH_4 ions in particles. Every flux determination, the canopy wetness was recorded by visual and/or manual inspection. During precipitation events, sampling was stopped to prevent distortion of the NH_3 determinations by liquid water entering the tubes.
Wind speed data were measured by cup anemometers (Lambrecht 1457 S or Young 12102). The cup anemometers had starting speeds of 0.4 and 1.0 m/s respectively, and length constants of 2.7 and 5 metres. The temperature data were provided by shielded and ventilated platinum resistance thermometers. The housing of the temperature sensors was constructed as detailed by Slob [1978]. Temperature differences were measured with an accuracy of about 0.02°C. Analogue outputs of the sensors were digitized by a computer-controlled data acquisition set; averages were stored on magnetic tape every 15 minutes. Data runs were started in parallel with NH_3 sampling.
NH_3 concentrations in air were determined with the aid of oxalic acid coated denuder (50 cm long glass tubes; inner diameter 3 mm , flow rate 3 l/min). Denuders were designed and treated after sampling according to the procedures described by Ferm [1979]. Filter holders containing Whatman microfibre filters impregnated with oxalic acid were mounted in the air stream leaving the denuders. Because of their relatively low diffusion coefficient, particles will move almost undisturbed through the tubes and will be collected on the filters. To minimize particle losses by settling, the denuders were mounted vertically with their open ends pointing downwards.
The NH_3 and NH_4 samples were analysed spectrophotometrically in the laboratory directly after each campaign. The triplicate concentration measurement of the concentration at each measuring level allows calculation of the standard deviation. In Figure 1 the variation coefficient for each triplicate is shown as a function of the concentration of NH_3. The standard deviation has a small absolute component (of about 0.15 $\mu g/m^3$) and a relative component of some 5%. The standard errors of coated and sealed tubes transported

together with the sample tubes and subjected to the complete procedure were equivalent to 0.2 ± 0.1 μg/m^3 for NH_3 (1 hr sample).

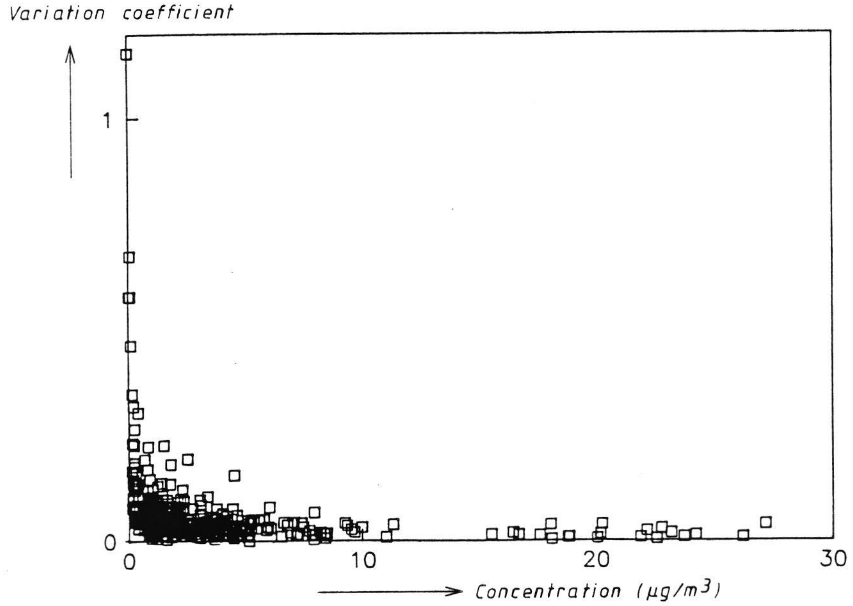

Figure 1 *Variation coefficient of NH_3 as a function of NH_3 concentration.*

The standard deviation of the NH_4^+ concentration measurement was quite high. The errors varied from less than 10% (0.6 μg/m^3) to 1 μg/m^3 or more. Typical blank values for the filters were equivalent to 0.4 ± 0.3 μg/m^3 NH_4^+.

Sensor and denuder sets were mounted on small booms extending one metre from the mast at logarithmically spaced distances between 0.6 and 7.5 m over the vegetation canopy. Each measuring level consisted of a set of three denuders operated in parallel, a temperature sensor and a cup anemometer.

During the measurements over forest, extra measurements were carried out to investigate the quality of the flux measurements, therefore the components of the heat balance of the forest (i.e. latent and sensible heat fluxes, net radiation) were measured with the aid of eddy correlation techniques and a conventional Funke type net radiometer.

Measurements were performed over short vegetation (mainly heather and purple moor grass) growing on several soil types in the Netherlands, and over two pine plantations, one in the Netherlands and one in West Germany. Figure 2 shows the location of the sites. They were selected on basis of the following criteria:

- type of ecosystem
- aerodynamic fetch (homogeneous terrain at least 500 m upwind)
- no sources of ammonia within a few kilometres.

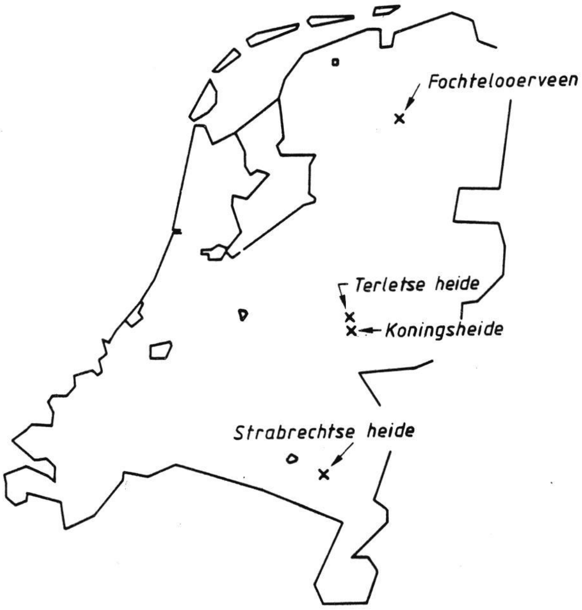

Figure 2 *Sites NH_3 deposition measurements*

Koningsheide	*pinus nigra (2.5 m), podzol*
Terletse heide	*bell heather/purple moor grass, podzol*
Fochtelooerveen	*heather/purple moor grass, peatmoor*
Strabrechtse heide	*bell heather purple moor grass, podzol*
Knesebeck (FRG)	*Pinus silvestris (18 m)*

Calculation of dry deposition fluxes

Micrometeorological parameters for calculating trace gas fluxes and surface resistance were calculated from 15-minute averages. In order to match trace gas sampling, suitable hourly or two-hourly averages were calculated from the 15-minutes averages. The higher time resolution of the micrometeorological observations allows for rejection of measurements during non-stationary situations.

The concentration gradient is calculated, assuming a logarithmic profile, viz. $\frac{dc}{d \ln z}$ rather than $\frac{dc}{dz}$, with the aid of a linear unweighted least-square analysis. The relative standard deviation in $\frac{dc}{d \ln z}$ is estimated from

$$\sigma = \sqrt{\frac{1/\rho^2 - 1}{n - 2}} * 100\% ,$$

where ρ is the correlation coefficient between c(z) and ln (z), and n the number of points used in the calculation (normally 12). From a Student T test, gradients are considered significantly different from zero when σ is less than 45%. Under normal conditions the error in the determination of the concentration gradient dominates the total error, and therefore the total error in the flux determination is considered to be equal to the error in the gradient. The average flux F can be calculated from:

$$F = \frac{-k u_*}{\phi_h} \frac{dc}{d \ln z}$$

where k is the von Kármàn's constant. The friction velocity u_* and ϕ_h are calculated from the measured wind speed and temperature gradients according to Berkowicz and Prahm [1982]. The dimensionless flux profile relation for heat according to Dyer and Hicks [1970] were used. The fluxes over forest were calculated with a Bowen ratio technique involving actual heat fluxes measured with sonic anemometers. The additional measurements of heat fluxes showed that the components of the heat balance of the forest could be measured with sufficient accuracy over these sites. The experimental set-up during the measurements over forest and the calculation procedures are described in more detail in Duyzer et al. [1987].

The deposition velocity at a reference level of 1 metre over the canopy is calculated from

$$v_d = \frac{-F}{c\,(1\ \mathrm{m})}$$

RESULTS

About 120 individual hourly flux measurements were carried out. Owing to analytical errors, technical faults during the measurements, instationarity or rainfall, 17% of the NH_3 flux measurements were rejected, and about half of flux measurements gave values below the detection limit of the method (some 1-10 $ng.m^{-2}.s^{-1}$). For NH_4^+, only 10% of the measured fluxes were above the detection limit. In case of a flux measurement below the detection limit the uncertainty of the value obtained for the flux is very high and it is not clear whether there is deposition or even a small emission flux. In these cases, no values for deposition velocity and surface resistance were calculated. It is important to know whether the rejection of v_d and R_s under these conditions introduces important systematic errors in the averaged values.

In the case of NH_3 the main cause for fluxes below the detection limit is clearly that the concentrations are too low to allow a vertical gradient to be measured accurately. The average concentration during periods when significant gradients were found was 5 $\mu g.m^{-3}$, whereas during periods where non-significant gradients were found, the average concentration was 1 $\mu g.m^{-3}$. Non-significant gradients were also detected at relatively lower wind speeds (and so lower v_d). This difference is, however, far less pronounced, and will cause only a minor systematic shift to a somewhat higher average value for v_d.

Horvath [1982] suggests the occurrence of a compensation point in the air concentration of NH_3. At air concentrations under this compensation point the vegetation will emit NH_3. At concentrations slightly higher than the compensation point, deposition velocities will be very low. In the total data set there are several instances of high deposition velocities associated with low concentrations, and three instances of emission fluxes. Therefore a compensation point over Dutch heathland vegetation is likely to be as low as a few tenth of a $\mu g.m^{-3}$.

Figure 3 shows the observed dry deposition flux of NH_3 gas over heathland. The number of non-significant fluxes at low NH_3 concentration is relatively high but even at these concentrations high deposition velocities are found.

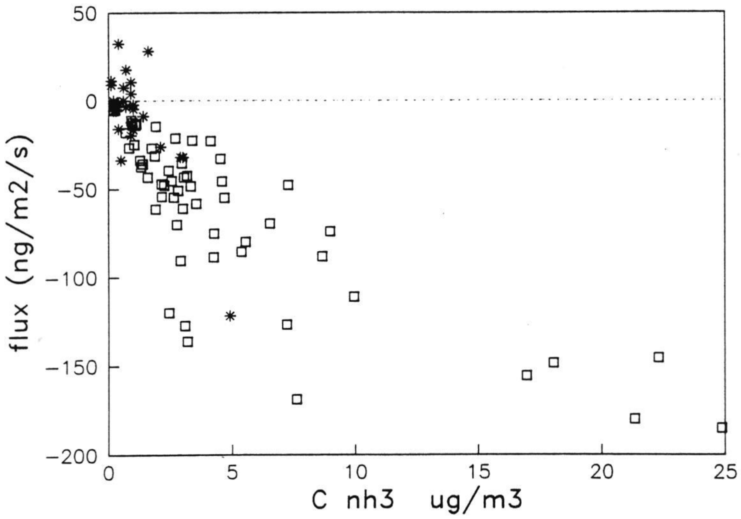

Figure 3 *Observed deposition fluxes of NH_3 as a function of NH_3 concentration.*
** indicate measured fluxes not significantly different from zero.*

Table 1 lists the averages per location. For the calculation of the average fluxes of both NH_3 and NH_4^+, all the measurements were used (so including those fluxes not significantly different from zero). The high relative errors are of minor importance here, because the absolute errors are small. Taking into account all measurement therefore, gives an unbiased average flux (the average flux for significant gradients was 64 $ng.m^{-2}.s^{-1}$, whereas for non-significant gradients it was 2.5 $ng.m^{-2}.s^{-1}$). In view of the small number of flux measurements above the detection limit for NH_4^+, the average value of v_d is calculated as $\overline{vd} = -\overline{F} / \overline{c}$. This gives a reasonable estimation of the average value for v_d, because there is no correlation between the flux measurements on one hand and the concentration measurement on the other.

The small differences in surface resistance for the different ecosystems (especially different in soil type) show that NH_3 is absorbed very efficiently by all different heather/purple moor grass vegetation soil types. The surface resistance is (not significantly) higher on the Strabrechtse Heide resulting in a lower deposition velocity. This location is surrounded by important sources of NH_3. The NH_3 flux over this location was still very high because of the high concentration of NH_3. The maximum average (1 hr) flux of the whole project was encountered here (58 kg ha^{-1} yr^{-1}).

Table 1 *Average day-time results for NH_3 for different locations. Values in parenthesis are the absolute standard deviations.*

Location	**n**	**$\overline{v}_d$ (cm s^{-1})**	**$\overline{R}_s$ (s cm^{-1})**	**n**	**$\overline{F}$ (kg ha^{-1} yr^{-1})**	**$\overline{c}$ (µg .m^{-3})**
Terletse Heide	21	1.8 (0.74)	0.30 (0.27)	29	11 (10)	2.5 (2.4)
Fochtelooerveen	24	2.3 (1.3)	0.36 (0.41)	35	13 (12)	2.6 (1.6)
Strabrechtse Heide	7	1.0 (0.39)	0.64 (0.26)	9	35 (24)	13 (9.5)
Koningsheide (forest 2.5 m)	3	2.3 (0.40)	0.27 (0.03)	14	10 (15)	1.6 (2.1)

Table 2 lists the average results for all heather locations. The results of the measurements over forest do not differ significantly from the ones over heather. Although the number of fluxes significantly different from zero is too low for definite conclusions the results indicate a strong absorption of NH_3 by this forest.

Table 2 *Average day-time results for NH_3 and NH_4 over heather locations. The standard deviation is given in parentheses.*

		NH_3	**n**	**NH_4^+**	**n**
$\overline{v}_d$	(cm/s)	1.9 (1.1)	51	0.18 (0.54)	71
$\overline{R}_s$	(s/cm)	0.38 (0.36)	51	-	
$\overline{F}$	(kg/ha/yr)	15 (15)	73	3.8 (11)	71
$\overline{c}$	(µg.m^{-3})	3.9 (5.1)	73	6.6 (6.4)	71

The surface resistance for NH_3 on heather/grass vegetation is very low, and the dry deposition velocity is correspondingly high. For O_3 over the same and comparable locations, the surface resistance was some 3-4 s/cm [Duyzer and Bosveld, 1988]. For NH_4 the deposition velocity is much lower than for NH_3, as might have been expected from the physical and chemical properties of the two species. Because of the large standard errors in the measurements, it makes no sense to calculate average data for the different locations. To investigate the dry deposition of NH_4^+, more measurements over forest and other terrains have to be made with more sensitive methods.

It is also relevant to note that 80% of the total ammonium dry deposition is by gaseous NH_3. This result is probably typical for deposition of ammonium compounds in regions with such intensive livestock breeding as large parts of the Netherlands. In more remote regions of Europe the relative contribution of particulate ammonium will be higher.

MODELING NH_3 DRY DEPOSITION

In order to widen the applicability of the results, the surface-layer model can be used to estimate an average R_s. For many trace gases, such as SO_2 and O_3, the arithmetic mean surface resistance is calculated from the measurements. This figure is also presented for NH_3 in Table 2. However, introducing a long-term average value of R_s in a surface layer model, and calculating the aerodynamic resistances from short-term meteorological data, should give a correct value for the long-term dry deposition velocity. The arithmetic mean of R_s for NH_3 does not afford a useful long-term average for a surface-layer model, because:

$$\overline{v_d} = \overline{\frac{1}{R_a + R_b + R_s}} \neq \overline{\frac{1}{R_a + R_b + \overline{R_s}}}$$

For gases such as SO_2, $R_a + R_b$ is much smaller than R_s (so $v_d \approx R_s^{-1}$) and, therefore, the differences between the two averages are very small. For NH_3, however, the quantities $R_a + R_b$ and R_s are of the same order of magnitude. The strong influence of the windspeed related parameters R_a and R_b on the deposition velocity of NH_3 can be seen in Figure 4 where v_d is shown to be an increasing function of the windspeed measured at 7 meter. Such a strong relationship is not found for gases such as SO_2 were the value of v_d is determined by the value of the surface resistance (see for example Hicks et al., 1985). An iteration procedure was used to calculate a representative fixed value for the long-term 'average' surface resistance. This value (R_s') applied to all the measurements gives the best fit to all the individual hourly measurements and renders:

$$\overline{v_d} = \frac{1}{\overline{R_s' + R_a + R_b}} = \overline{\frac{1}{R_s' + R_a + R_b}}$$

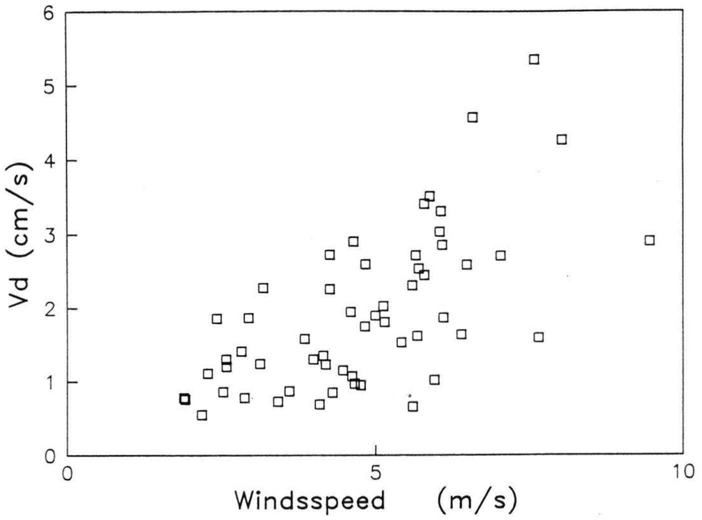

Figure 4 *The dry deposition velocity of NH3 as a function of the windspeed measured at 7 m.*

Using this approach for all measurements, we calculated a value for R_s' of 0.23 $s.cm^{-1}$. It is interesting to calculate the deposition velocity from the observed aerodynamic (R_a + R_b) resistances and this fixed value R_s'. A comparison of these estimates with the actual measured deposition velocities affords an insight into the quality of this formulation of the surface layer model for NH_3. Using a fixed value for all measurements of course creates a systematic bias of the estimated v_d; the surface-layer model will estimate relatively high deposition velocities at low observed v_d, and relatively low deposition velocities at high deposition rates. In Figure 5 the estimated deposition velocity for each measured deposition velocity is plotted for $R_s' = 0.23$ $s.cm^{-1}$. Although the average deposition velocities is well estimated it is clear that the observed variation in the deposition can only be explained to a small degree (some 32%). To obtain a better figure for the accountable variance we investigated the influence of other parameters, using only the measurements above the detection limit. Table 3 lists the factors investigated together with their ranges during the measurements. The signs indicate whether there is a clear-cut dependence of v_d or R_s on the variable in question.

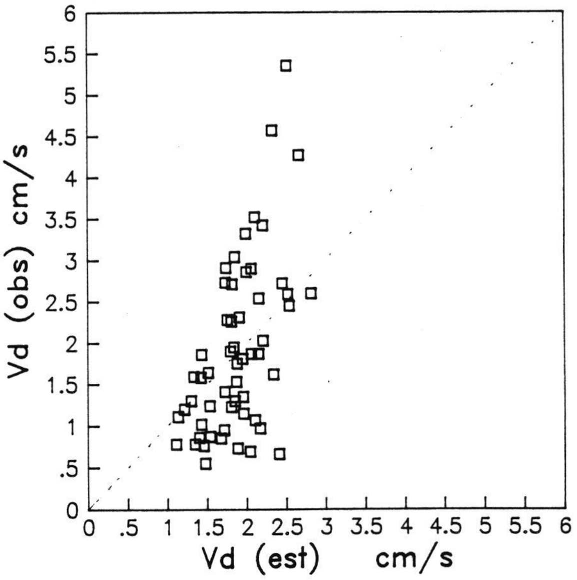

Figure 5 *Observed deposition velocity of NH_3 as a function of the estimated deposition velocity using a fixed value of 0.23 $s.cm^{-1}$ for R_s.*

Table 3 *Influence of some parameters on dry deposition velocity (v_d) and surface resistance R_s, and their ranges of variation (+) = clear positive correlation, (o) no significant correlation, (-) clear negative correlation, * no significant effect in the complete dataset. The signs in parenthesis account for the observed effect under dry conditions.*

Factor	**Range**	**v_d**	**R_s**
season	day number: 73-338	o	o
time of day	10-17 hrs	o	o
air temperature	3-23°C	o (o)	o (+)*
friction velocity	10-70 $cm.s^{-1}$	+	o
NH_3 concentration	0-25 $\mu g/m^3$	o	o
surface wetness	dry...wet	+	-

Figure 6 shows the measurement performed over heather as a function of day number for different locations. The measurements are sufficiently distributed over the year, and no significant influence of seasonal variation or location can be established.

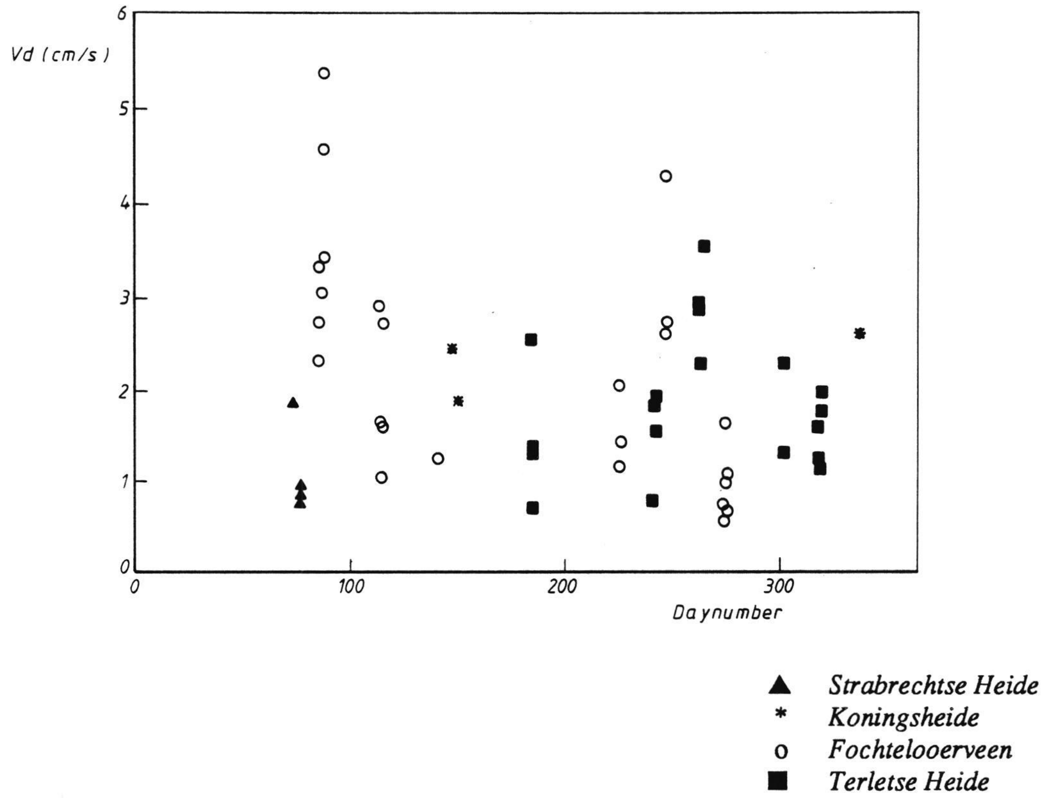

Figure 6 *NH_3 dry deposition velocity (v_d) as a function of day number for different locations.*

During the measurements the wetness of the vegetation-surface was assessed by visual and manual inspection. The usual causes of wetness of vegetation were rain or drizzle so the observations were very easy. In the dry cases however the problem remains that a surface that is visually dry can still be wet on a microscale, and absorb gases as a wet surface. Nevertheless a strong dependence of v_d and R_s on surface wetness was found. Figure 7 shows the surface resistance during the wet and dry measurements as a function of time of day. Clearly, the surface resistance of wet vegetation is practically zero, as might have been expected from the high solubility of NH_3 in water. Table 4 shows the average surface resistance for wet and dry periods. Even during dry periods the surface resistance for NH_3 is very low. In measurements performed over the same locations in 1985 and 1986 we found surface resistances for water vapour of 2 to 4 s/cm [Duyzer and Bosveld, 1988]. In many cases the surface resistance found for NH_3 was much lower. These low values cannot be explained by stomatal uptake alone.

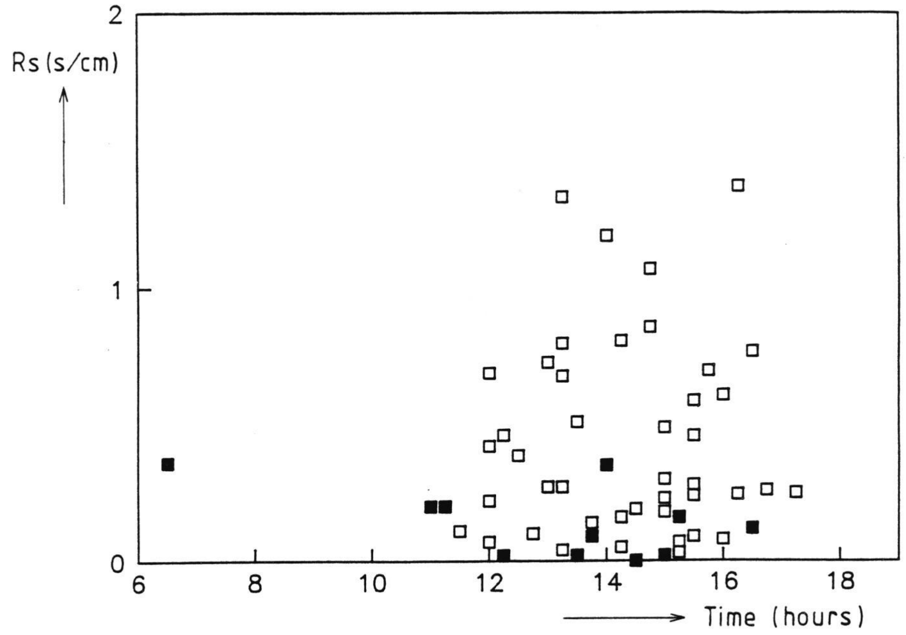

Figure 7 *Surface resistance of heather for NH_3 as a function of time of day. Filled squares indicate visually wet vegetation.*

Table 4 *Average and standard deviation of the surface resistance for NH_3 over heather and iteratively deduced long-term values of R_s' for periods when the vegetation was either visually wet or not.*

	n	R_s s/cm	R'_s s/cm
wet	9	.12	.09
dry	42	.43	.28
all periods	51	.38	.23

In any case it follows from Figures 6 and 7 that for heather purple/moor grass vegetation diurnal and seasonal dynamics are not very relevant to the NH_3 uptake. Likewise, the results of the few measurements performed during the night (surface resistances practically zero) did not differ significantly from the day-time results. A possible explanation for this lack of correlation might be the efficient absorption of NH_3 directly on the plants surface masking the less relevant stomatal pathway.

No influence of air temperature could be discovered in the complete data set. If only dry periods are considered, it is interesting to note that high surface resistances are always observed at temperatures higher than 20°C. A plausible explanation for this observation would be the lower solubility of NH_3 gas in water at higher temperatures. On the other hand it might simple be the extension of the surface wetness effect viz. only at higher temperatures (say, over 20°C) the vegetation is really dry. More measurements are needed to investigate this aspect further. In this context it is worth noting that grasslands in the Netherlands have recently been found to be wet 200 nights a year [Römer et al., 1988].

Using the parametrization found for surface wetness, we investigated the performance of the model once more. In Figure 8 the observed deposition velocities are plotted as a function of those predicted by the model. For surface wetness we used the parametrization of Table 4, viz. $R_S = 0.09$ s.cm^{-1} during wet periods. For dry periods, we used a simple parametrization derived from our measurements, viz. R_S = Temperature x 0.02 s.cm^{-1} (temperature in ° centigrade). The improvement is significant, the accountable variation increasing to 68% (51% if only the wetness parametrization is used).

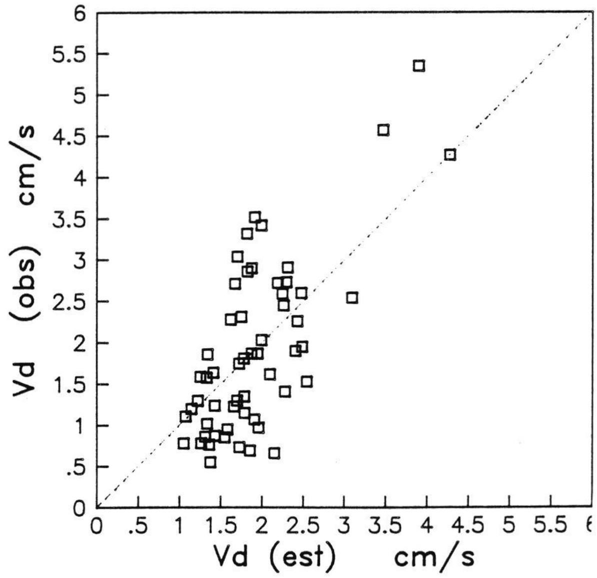

Figure 8 *Observed deposition velocities of* NH_3 *as a function of the estimated deposition velocity using a fixed value of 0.09 s.cm*$^{-1}$ *for* R_s *during wet periods and a temperature dependency during dry periods as described in the text.*

ESTIMATES OF A 24 HR AVERAGE ANNUAL DEPOSITION VELOCITY

Scientifically several questions remain with respect to the processes that play a role in the dry deposition of NH_3. Nevertheless there is a need for a defendable deposition velocity that can be used in large scale air pollution models. These models are used to estimate the deposition fluxes over sensitive areas and play a role in discussions concerning the effects of air pollutants on sensitive ecosystems such as forest.

Representativeness of the sample

If all relevant meteorological and biological parameters have the same distribution in the measurements as they normally have over the year, then the average of the measurements is a good representation of the yearly average over natural terrains. It is interesting to see how representative our dataset is for the conditions that occur over the year in the Netherlands. In the above it was shown that the deposition velocity of NH_3 is a strong function of the wind speed. Therefore we investigated the representativeness of our dataset with respect to wind speed.

Figure 9 shows the cumulative frequency distribution of the wind speed during the 84 hourly measurements and a year average cumulative plot of four locations in the Netherlands (taken from [Wieringa and Rijkoort, 1983]. For purposes of comparison, the wind speed has been converted into the so-called potential wind speed*. The measured distribution most resembles the curve for Eindhoven (near the Strabrechtse Heide) which is the farthest inland of the four locations and probably the most representative for our measuring sites. As expected the number of high wind speed observations is somewhat lower than normal over the year, leading to a slight underestimation of the average deposition velocity (less than 10%). From this graph and the information in table 3 it follows that this set of measurements is a good sample of the situations (with respect to wind speed) encountered normally over the year in the Netherlands. The observed average deposition velocity of NH_3 therefore is a good estimate, applicable to day-time conditions in the Netherlands.

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* The potential wind speed is the wind speed that will be measured in an undisturbed environment and is calculated from the wind speed measured at 7 metres with the formula

$U_p = U_7 (0.764 \ln (60/0.06)/\ln (7/0.06))$

U_p = potential wind speed, U_7 = observed wind speed at 7 m, z_0 is taken to be equal to 7 cm (typical for the values observed during this study).

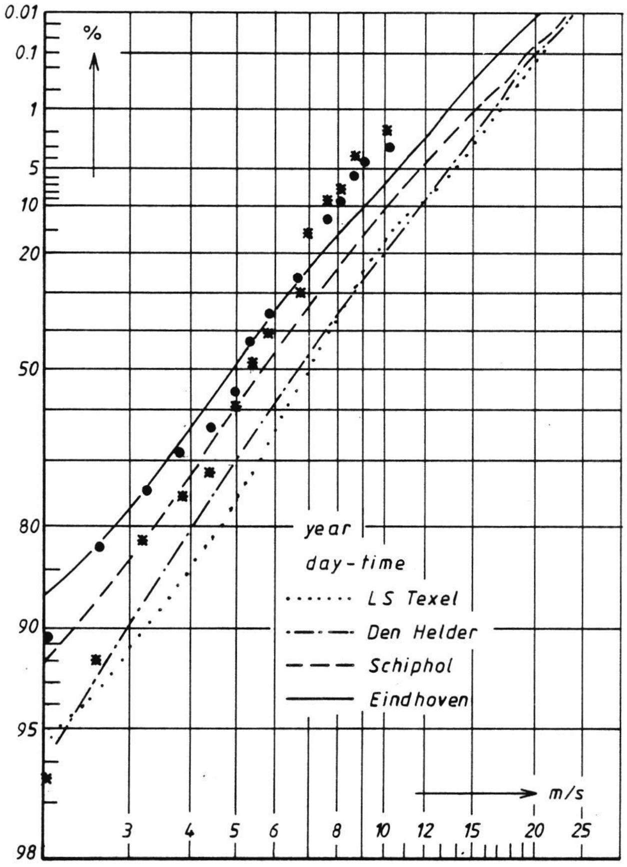

Figure 9 *Frequency distribution for day-time hourly potential wind speed for the year (from Wieringa and Rijkoort (1983)). The points represent the values calculated from the measurements over heathland.*

. *all measurements*

* *flux measurements above detection limit only*

Errors in long term estimates

An average deposition flux (F) over a period T can be formally estimated from

$$\overline{F} = \frac{1}{T} \int_0^T v_{d,t} \cdot c_t dt$$

Since meteorological variables are not likely to change dramatically within an hour, a reasonable averaging time is about one hour, and the flux might be computed from:

$$\overline{F_1} = \frac{1}{n} \sum_{j=1}^{n} v_d(j) \cdot c(j)$$

if hourly observations of the dry deposition velocity and air concentrations were available. Because mostly no hourly average v_d values, but only average concentrations are available, the flux has to be estimated from:

$$\overline{F_2} = \overline{v_d} \cdot \overline{c}$$

with a much longer averaging time (up to a year). The fractional error in this flux due to interdependence of v_d and c is:

$$\frac{F_1 - F_2}{F_1} = \frac{\sigma_{v_d}}{\overline{v_d}} \cdot \frac{\sigma_c}{\overline{c}} \cdot \rho$$

where ρ is the correlation coefficient between v_d and c. In the measurements described here no significant correlation between v_d and c was found, so the error in F_2 is probably relatively low for NH_3. The magnitude of the correlation between v_d and c cannot easily be predicted for several reasons. Moreover the correlation will be different for each gas. The concentration on one hand depending on emissions, meteorology, the deposition velocity on the other hand depending on biological processes and meteorology. On a qualitative basis one could expect high concentrations and high deposition velocities of NH_3 during the day-time. Hicks et al. [1985] discuss these effects and estimate a typical error of some 20% in the actual deposition flux for SO_2 when using weekly averaged deposition data rather than hourly averages. Meyers and Yuen [1987] used different averaging strategies to calculate dry deposition fluxes for O_3 and SO_2. They found errors of up to 40% when using weekly average deposition velocities and concentrations to calculate the deposition flux for O_3. For SO_2 the errors were much smaller. In a separate project we measured NH_3 concentration together with meteorological parameters, over heathland in the Netherlands. A strong correlation between the air temperature and the NH_3 concentration was found [Duyzer et al., 1989]. Together with the high surface resistance observed at high temperatures this example may lead to a bias in a yearly estimate using average values for v_d and R_s. The data were used to estimate the average dry deposition flux of NH_3 to the vegetation. From a sensitivity analysis we concluded that the bias in estimates using yearly average values for NH_3 is typically less than 30%.

Estimate of a night-time deposition velocity for NH_3

In the above, it is argued that the day-time measurements of NH_3 deposition velocities yield a reasonable estimate of the yearly averaged day-time dry deposition velocity. For long-term modelling purposes, a representative value of the night-time deposition velocity has to be estimated. Only a few measurements were carried out at night, and their interpretation was hampered by rapidly changing weather. Their number was too small for yearly average night-time values of v_d or R_s to be deduced from them. During day-time measurements, no relation of R_s with time of day was found. From the few night-time measurements it cannot be concluded that the night-time surface resistance differs widely from the day-time value. It is only for lack of information that the night-time surface resistance for NH_3 is assumed to be equal to that during day-time (viz. 0.23 s/cm).
The aerodynamic resistances (R_a+R_b) can be calculated from routine observations of wind speed and atmospheric stability. Table 5 lists the occurrence of night-time (18.00 to 06.00 hrs) stability classes for Cabauw, the Netherlands. Data are from the network operated by the Dutch National Institute of Public Health and Environmental Hygiene (R.I.V.M.).

Table 5 *Occurrence of night-time Pasquil stability classes, observed wind speed (at 10 m), calculated wind speed (5 cm roughness length), Monin-Obukhov length, aerodynamic and boundary layer resistances and deposition velocity.*

Pasquil class		D1	Dm	Dh	E	F
U_{10}	(m/s)	2.0	4.8	7.7	3.2	1.3
L	(m)	1000	1000	1000	43	12
R_a	(s/m)	50	21	13	39	155
R_b	(s/m)	37	15	19	28	100
v_d	(cm/s)	0.91	1.8	2.2	1.1	0.4
Occurrence	(%)	36	25	15	8	17

These values are calculated from the wind speed measured at 10 m, with a roughness length of 5 cm, and a Monin-Obukhov length estimated for each stability class. The Monin-Obukhov lengths are estimated according to Duym and van Aalst [1984]. From these figures the aerodynamic and boundary layer resistances per stability class have been calculated, and an average deposition velocity for each stability class can be derived. This approach is somewhat better than an estimate, where averaged night-time values for R_a and R_b are used. The frequency-weighted average night-time dry deposition velocity for NH_3 over heathland calculated with the aid of the above surface-layer model is 1.26 cm/s.

24 Hr average deposition velocities for NH_3 and NH_4^+

Averaging the calculated night-time value with the observed day-time value of 1.9 cm/s leads to a long-term average dry deposition velocity of 1.6 cm/s.

For NH_4^+ a correction for night-time stability is hardly possible, because the measurements do not provide an accurate surface resistance. However, since the surface resistance is very high, the correction for night-time meteorology is probably very small. A day-time dry deposition velocity for NH_4^+ particles of 0.18 cm/s gives a rough estimate of the surface resistance of 5.6 s/cm/. This surface resistance, together with the data from Table 8, leads to a night-time dry deposition velocity of 0.17 cm/s. Because of the large uncertainty in the deposition velocity, this correction is not significant and the best estimate for a yearly average value for v_d is 0.18 cm/s.

DISCUSSION

Only a few measurements of the dry deposition of NH_3 are reported in the literature. Table 6 lists some results, most of which were obtained with the aid of enclosure techniques.
A number of striking differences between these results and our results are found. Several authors report emissions and compensation points. In our study, we found hardly any emission from the soil. Even at low concentration, absorption appeared to be very efficient.

Table 6

Reference	Species	Results
Hutchinson et al. 1972	several crops	v_d = 0.22 - 0.65 (per unit of LAI) Strong influence of light intensity
Denmead et al., 1978	corn	R_s = 0.2 - 0.5 (emission when moist)
Lemon et al., 1980	quack grass, alfalfa	deposition, emission
Horvath, 1982	short grass	v_d concentration dependent $v_d = 1.04 - 0.082 / NH_3$
Aneja et al., 1986	several agricultaral crops	strong influence on light intensity
Van Hove et al., 1987	snap bean	no internal resistance to transport
Porter et al., 1972	corn	strong absorption

*) v_d and R_s in $cm.s^{-1}$ and $s.cm^{-1}$, NH_3 in $\mu g.m^3$
Horvath and Denmead et al. use a micrometeorological method. The other authors all used enclosure techniques.
Porter et al. use a radioactive tracer.

This difference is probably due to our measurements having been conducted in nature reserves, which never received any artificial fertilization. Our results therefore cannot be used to estimate dry deposition fluxes over agricultural areas where nitrogen fertilization has been applied.
Another interesting difference between our field measurements and those reported elsewhere is the lack of any diurnal or even seasonal influence on the surface resistance.
This may have to do with the typical growing behaviour of the heather vegetation but the strong influence of surface wetness may also mask the less pronounced influence of stomatal uptake etc. This strong effect, possibly even causing a related temperature effect

leads to a model of NH_3 uptake by heather at our latitudes where cuticular uptake is at least as important as stomatal uptake. This mechanism is supported by the large number of observations of surface resistances lower than those measured for water vapour over these sites. Denmead et al. [1978] also found surface resistances of NH_3 over corn too small to be explained by stomatal uptake alone.

Although the mechanisms that play a role in NH_3 deposition are not completely clarified, it is from an environmental management point of view important to have a representative dry deposition velocity of NH_3 over sensitive ecosystems. From our measurements it appears that even with a limited dataset a defendable, representative average value can be derived. The error associated with the use of yearly avarge values is probably limited to 30%. The lack of night-time data can, at least in first order, be overcome using the surface layer model to account for night-time meteorology.
For forests the present situation is less satisfactory. More measurements are necessary to show that observed similarity with NH_3 deposition to heather is systematic. If the latter is the case NH_3 may be an important source of nitrogen for forest ecosystems in some regions in Europe. The results of our measurements of particulate ammonium fluxes are not satisfying from a scientific point of view. Nevertheless it is clear that the dry deposition velocity of particulate ammonium is less than 0.3 cm/s and that only some 20% of the total load with NH_x into heathland in the Netherlands relates to particulate ammonium.

ACKNOWLEDGEMENT

We thank the wardens of Fochtelooerveen, Strabrechtse Heide, Terletse Heide, Koningsheide and Knesebeck Forest for permission to carry out measurements on their premises. The research described here was funded by the Commission of the European Community, the Dutch Ministry of Housing, Physical Planning and the Environment, and the TNO Division of Technology for Society.

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