DRY DEPOSITION OF ACID PRECURSORS IN THE NETHERLANDS

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ABSTRACT

A recent study indicated that the average deposition of acids and their precursors onto the Netherlands soils is probably as high as 6,000 mole per ha per year. Dry deposition amounts to approximately two thirds of this deposition.

Results of recent measurements of dry deposition fluxes in the field by gradient and eddy correlation methods are reported for NO, NO_2 , O_3 , SO_2 and aerosol particles.

Evidence for interference of chemical reaction with flux measurements for NO and NO₂, separately, is presented. Also, humidity interference on particle flux measurements is discussed.

1. INTRODUCTION

It is now generally acknowledged that acid precipitation is not limited to wet deposition, or to atmospheric deposition of acids. Instead, it is realised that the effects of acid precipitation may arise from complex reactions in the receptor soils and surface waters as a response to input from the atmosphere of a variety of compounds, acids as well as acid precursors, and trace elements [1]. The role of dry deposition of gases and aerosol particles seems to be substantial, particularly in more polluted areas.

* Division of Technology for Society TNO, P.O.Box 217, 2600 AE Delft, The Netherlands. In this paper, this substantial role is illustrated by an estimate of the "acid deposition" on the Netherland's surface area. From this estimate emerges the importance of measurements of the dry deposition of gases and particles. In the second half of the paper, we communicate some of our recent experiences with the measurement of dry deposition fluxes.

2. ESTIMATE OF ACID DEPOSITION ONTO THE NETHER-LANDS

By order of the Netherlands Ministry of Housing, Physical Planning and the Environment, TNO carried out a study to quantify atmospheric depostion onto the Netherlands of acids, acidifying compounds and nutrients [2]. Estimates of the yearly averaged atmospheric inputs of relevant compounds were made from rain water data on the one hand, and from air concentration data combined with deposition velocities from literature on the other. The compounds considered were the strong mineral acids (e.g. H_2SO_4 and HNO_3), acid precursors, such as SO_2 and NO_2 , and ammonia and ammonium ions. Although NH_3 and NH_4^+ were thought in the past to increase the pH, a recent field study has shown that atmospheric input of ammonia and ammonium ions into soils may, via the well-known process of nitrification by bacteria, lead to the formation of nitric acid [3]. Simultaneously, the strong mineral acid neutralised by ammonia in aerosols or in rain water, can be released again. This process takes place in aerated soils even at low pH-values.

The compounds selected were classified into sulphur compounds, nitrogen oxides and conversion products of the latter, and ammonia and ammonium. In T a b l e l, the dry deposition on the Netherlands is estimated of sulphur dioxide and of sulphate and sulphuric acid aerosols. Owing to its high deposition velocity, SO_2 dry deposition is dominant. In more remote areas where the ratio SO_2 to sulphate is lower, the situation may be different.

T a b l e 2 shows concentrations, deposition velocities and estimated fluxes of dry deposition for nitrogen compounds, expressed in mole/ha/year as well as in kg N/ha/year. In the relatively polluted area of the Netherlands, NO₂ probably contributes most to the dry deposition flux; in remote areas dry deposition of HNO₃ may be more important.

T a b l e 3 gives estimates for the dry deposition of ammonia and ammonium ions. Unfortunately, these data are rather uncertain, as the ranges indicate. The concentrations of these compounds were measured systematically at a few stations in the western part of the country only, whereas, however, important source areas are in the eastern and southern parts of the country. As is wellknown, the largest source of ammonia is animal manure; in our study an emission of 130 kTon/year was estimated from this source on a total of 165 kTon/year of ammonia emissions in the Netherlands. F i g u r e 1 shows the distribution of these emissions.

In T a b l e 4, yearly averaged values are given of the flux of several ions in rain water, as measured by KNMI/RIV [4].

From the data in T a b l e s 1 - 4, total fluxes can be estimated. T a b l e 5 gives nutrient fluxes. The total average input of some 50 kg N/ha/year may lead to changes in the vegatation on nutrient-deficient soils [13]. Note that dry deposition amounts to approximately two thirds of the nitrogen flux.

In addition, some 50 kg S/ha/year is deposited; phosphorus deposition is probably small (some 0.1

The total average deposition of acids and acidifying compounds, expressed in mole-equivalents, is given in T a b l e 6. Sulphur compounds are important, but comparable contributions come from nitrogen oxides and ammonia compounds. Close to source areas, the ammonia contributions may be even more important. In the Netherlands, these source areas (intensive animal breeding) are often quite close to nutrient-deficient soils that are sensitive to acidification.

Again, dry deposition amounts to approximately two thirds of the depostion, irrespective of the chemical species group considered.

Finally, the emission and deposition of the compound groups can be compared. As T a b l e 7 shows, more acid precursors are emitted in the Netherlands than are deposited on its own surface. Part of the deposition arises from emission in the surrounding countries. Although estimates of these contributions have been only made for SO_x and NO_x so far, sufficient data for ammonia compounds are, however, lacking at the present moment.

3. MEASUREMENT OF DRY DEPOSITION FLUXES

From the study discussed in the last section, the need for adequate data on dry deposition becomes clear. Unfortunately, the data on dry deposition are rather uncertain. Deposition parameters for gases, reported in literature, show a wide range of values [5] probably due to variation in measuring methods, meteorological variables and nature of the surface. For aerosol particles, the situation is still more confusing, since measurements often show upward fluxes [6 - 8]. As we will point out, physical and chemical processes in the air may affect the measurement as well. Measuring methods for dry deposition can be subdivided into methods measuring the amount deposited, those measuring concentrations depletion in deposition boxes enclosing the surface under study, those measuring air concentrations down wind of some well-characterised source, and those measuring fluxes at some elevation above the surface [9]. Measurement of the amount deposited on natural surfaces, although principally preferable, is hardly possible except for some radio-active or fluorescent compounds and some trace elements. The validity of the use of surrogate surfaces is questionable. In box measurements, the actual ambient situation cannot be considered, since the influence of turbulence cannot be studied, and the isolation of natural soils or vegetation can lead to changes in the uptake processes. Plume dispersion experiments can give valuable results, but only at distinct and homogeneous meteorological conditions.

In the field, we preferred direct flux measurements. The disadvantage that only indirect measurements of the surface uptake are made, can be circumvented by making measurements with good fetch conditions. We used gradient as well as eddy correlation methods for the measurement of fluxes of NO, NO_2 , O_3 , SO_2 and particles.

Details of our gradient flux measurements over grass of NO, NO_2 and O_3 will be published elsewhere [10]. For the measurement of the concentration profiles, a 4 meter high mast was used, along which a sampling tube, through which air was drawn at high speed, could be moved under control of a microcomputer. A manifold in the sampling line allowed different monitors to take simultaneous samples, consecutively from typically 5 heights between 0.4 and 2.5 meter. The profile was repeatedly scanned upward and downward during the averaging period of 30 minutes.

Profiles of temperature and wind speed were mea-

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sured on a 10 meter mast.

From these profiles, fluxes were calculated by means of procedures described by Garland [11]. From our measurements over grass, it appeared that chemical reactions taking place on a time scale comparable to that of the turbulent transport, influence the fluxes of NO, NO_2 and O_3 . These fast reactions are:

1. $NO_2 + hv \rightarrow NO + O \xrightarrow{O_2} NO + O_3$ 2. $O_3 + NO \rightarrow NO_2$

During daylight conditions these reactions establish the so-called photostationary relation:

$$\frac{[\text{NO}] \cdot [\text{O}_3]}{[\text{NO}_2]} = K \tag{1}$$

where constant K is dependent on the light intensity only. Consequently, the fluxes of NO, NO_2 and O_3 are no longer independent of each other. In fact, by differentiating (1) with regard to height z one obtains

$$\frac{1}{[O_3]} \frac{d[O_3]}{dz} = \frac{1}{[NO_2]} \frac{d[NO_2]}{dz} - \frac{1}{[NO]} \frac{d[NO]}{dz}$$
(2)

Each of these three terms is proportional to the deposition velocity v_d of one of the three substances, since for instance:

$$v_{d 0_3} = \frac{F_{0_3}}{[0_3]} = \frac{-K_z \frac{d[0_3]}{dz}}{[0_3]}$$

where F is the flux and K_z is the vertical turbulent diffusivity. Indeed we found rather high correlations ($\rho = 0.7$) in our data between the quantities on both sides of equation (2). F i g u r e 2 shows results from 16 half-hour averages obtained on three different days. As a result of these interactions, the concepts of a deposition velocity and of a surface resistance cannot be used for the individual components. In contradistinction, the quantities NO_x (NO + NO_2) and oxidant ($NO_2 + O_3$), which are conserved in reactions 1 and 2 can be characterised by a deposition velocity. Equation (2) can be rearranged to express component gradients in terms of gradients of these conservative quantities. So, for instance, we obtain for NO:

$$\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}z} = \frac{([\mathrm{NO}] + \mathrm{K})}{([\mathrm{O}_3] + [\mathrm{NO}] + \mathrm{K})} \frac{\mathrm{d}[\mathrm{NO}_x]}{\mathrm{d}z} - \frac{[\mathrm{NO}]}{([\mathrm{O}_3] + [\mathrm{NO}] + \mathrm{K})} \frac{\mathrm{d}[\mathrm{O}_x]}{\mathrm{d}z}$$

This expression shows that, owing to air chemistry, upward fluxes of NO may be observed even if fluxes of both oxidant and NO $_{\rm v}$ are downward.

In T a b l e 8, we show some of the results of our measurements over grass. Often, deposition velocities of NO_x and oxidant are comparable in size. On some days, upward fluxes are measured for NO_x , probably as a result of advection from local sources. On two days in December 1982, at a temperature of approximately 0°C, values of the deposition velocities were found below the detection limit of approximately 0.1 cm.s⁻¹. Only on these days some SO₂ deposition measurements were carried out simultaneously. The deposition velocities found were below the detection limits as well. We continue our gradient measurements for different surfaces and different meteorological conditions.

For particles, we carried out some eddy correlation measurements. Vertical wind speed was measured by a two-head sonic anemometer built at our laboratory. The concentration of particles in the size range of 0.4-5 μ m was measured with an optical particle counter, equipped with a rate meter. Particles were sampled from air from between the heads of the anemometer in a sampling tube causing a delay of approximately 0.1 sec. Both instruments had response times below 0.1 s and were sampled at

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10 Hz simulateneously. By averaging the product of the fluctuating parts of vertical wind speed w and concentration c, flux F can be obtained:

$$F = w' \cdot c'$$

where the primes indicate the fluctuating components.

Averages of three minutes were taken in order to subtract non-fluctuating components, typically 5-10 of such measurements were combined to obtain 15 or 30 minute averages.

Although our measurements have so far been too limited to allow for quantitative conclusions with regard to the deposition velocity of particles, one aspect of our results merits attention. This is the effect on the flux of heating the sampling inlet.

It is well-known that the size of particles in ambient air may change appreciably when relative humidity changes as a result of water vapour condensation, and that these changes can take place fairly rapid, in the order of a second or less [12]. Consequently, humidity gradients may give rise to spurious fluxes since the particle counter counts all particles above a certain threshold size, and the size distribution is very steep in this region of particle size [6]. Since humidity normally decreases with increasing height during the day, spurious fluxes would be direct upward.

In an attempt to eliminate these effects, we heated the sampling inlet in order to dry the particles, as suggested by Slinn. Up to now we have found that fluxes were consistently more upward in the absence of inlet heating. Usually, the deposition velocities of the dried aerosol seem to be very small. As an illustration, T a b l e 9 shows some data obtained at an agricultureal field, before crop growth. These data were obtained from successive measurments where the heating was

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turned off part of the time. Note also the effect of heating on the concentration. Although the evidence is still poor, these results indicate that attention should be paid to these effects.

4. CONCLUSIONS

We showed estimates of deposition of acids and acidifying compounds onto the Netherlands. Dry deposition amounts to approximately two thirds of this depostion, which is about 6,000 mole/ha/year. In addition we pointed out that rapid chemical and physical processes may interact with dry deposition flux measurements in the field. In particular, such effects are to be expected from the reactions between NO, NO₂ and O₃, and from the condensation of water vapour on hydrophylic aerosol particles.

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LEGENDS OF FIGURES

Figure 1. Emission density of NH₃ in the Netherlands for emission from animal manure. Data of E. Buysman, IMOU, the Netherlands.

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Figure 2. Relative gradients of 0_3 vs (NO₂-NO) where

 $X = \frac{1}{[NO_2]} \frac{d[NO_2]}{dlnz} - \frac{1}{[NO]} \frac{d[NO]}{dlnz} \text{ and}$

$$Y = \frac{1}{[0_3]} \frac{d[0_3]}{dlnz}$$

Data from 9, 15 and 29 September 1982. The dashed line is a representation of equation (2).

LEGENDS OF TABLES

Table 1. Yearly averaged (around 1980) concentration, deposition velocity and deposition flux for dry deposition of SO_2 and sulphates in the Netherlands. Concentration variations over the Netherlands are indicated between brackets.

Table 2. Concentration, deposition velocity and deposition flux (in mole/ha/year, and in kg N/ha/year) by dry deposition of nitrogen oxides and their transformation products, in the Netherlands around 1980. The variations over the Netherlands are indicated in brackets.

Table 3. Yearly averaged (around 1980) concentration, deposition velocity and flux for dry deposition of ammonia and ammonium ions to the Netherlands.

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Table 6. Deposition of acid and acidifying components (mole/ ha/year) in the Netherlands. About 1980.

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Table 8. Meteorological variables (friction velocity u^* (cm.s⁻¹) and Monin Obukhov length L (m) and calculated deposition velocities v_d (cm/s)¹⁾ for NO_x and Ox.

Table 9. Influence of heating of the sampling tube on the deposition velocity of particles $(0.4 - 5 \ \mu m)$ over an agricultural field from eddy correlation measurements.



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Data from 9, 15 and 29 September 1982. The dashed line is a representation of equation (2).

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Table 1. Yearly averaged (around 1980) concentration, deposition velocity and deposition flux for dry deposition of SO₂ and sulphates in the Netherlands. Concentration variations over the Netherlands are indicated between brackets.

Component	Concentration (µg/m ³)	Deposition velocity (ms ⁻¹)	(mole/ha/year)	
$SO_2 = (incl. H_2SO_4)$ H_2SO_4	25 (10-40) 12 2	8. 10^{-3} 1-4. 10^{-3} 1-4. 10^{-3}	<pre>830 (340-1340) 40-160 ≅ 100 6- 26 ≅ 16</pre>	

Table 2. Concentration, deposition velocity and deposition flux (in mole/ha/ year, and in kg N/ha/year) by dry deposition of nitrogen oxides and their transformation products, in the Netherlands around 1980. The variations over the Netherlands are indicated in brackets.

Component	Concentration	Deposition	Flux of deposition			
	(µg/ m)	(ms ⁻¹)	mole/ha/year	kg N/ha/year		
		2				
NO	12 (5-25)	1. 10^{-3}	130 (50-270)	1.8 (0.7-3.8)		
NO2	27 (20-45)	3. 10 ⁻³	550 (410-910)	7.7 (5.7-12.7)		
hno ₃	4 (< 5)	6. 10 ⁻³	120 (< 150)	1.7 (< 2.1)		
PAN	2 (1.5-2.5)	2.5 10 ⁻³	13 (10-16)	0.2 (0.14-0.23)		
NO ³	7 (3-8)	14. 10 ⁻³	36-142 (15-162)	0.5-2.(0.2-2.2)		
			Total	12.7 (7-21)		

Table 3. Yearly averaged (around 1980) concentration, deposition velocity and flux for dry deposition of ammonia and ammonium ions to the Netherlands.

Component (Conc.	Deposition velocity (ms ⁻¹)	Flux of deposition				
	(µg/m°)		mole/ha/year	"average"	kg N/ha/year	"average"	
NH3	~ 7	5-10.10 ⁻³	650-1300	975	9.1-18.2	13.7	
NH ₄ ⁺	~ 4	1-4 .10 ⁻³	70- 280	175	1 - 3.9	2.5	
				Total	10 -22	16.2	

Table 4. Yearly averaged (1978-1981) wet depositon of some ions in the Netherlands (KNMI/RIV [4]).

Ion	Flux of wet deposition				
1011	mole/ha/year	kg N/ha/year			
H ⁺	455 (216 - 599)	-			
so ₄ =	576 (481- 748)	-			
NH4 ⁺	766 (502- 972)	10.7 (7.0-13.6)			
N0 ₃ -	474 (421- 559)	6.6 (5.9 - 7.8)			
NH4 ⁺ +NO3 ⁻	1240 (1004-1483)	17.4 (14.1-20.8)			

Table 5. Flux of anorganic nitrogen (in kg N/ha/year) by dry and wet deposition of nitrogen compounds, averaged for the Netherlands. Variation over the Netherlands is indicated between brackets. Yearly average about 1980.

	NOx	$NH_3 + NH_4^+$	Total
Dry deposition	12.7 (7-21)	16.2	28.9
Wet deposition	6.6 (5.9-7.8)	10.7 (7-13.6)	17.4 (14.1-20.8)
Total	19	27	46

Table 6. Deposition of acid and acidifying components (mole/ha/year) in the Netherlands. About 1980.

	NOx	$NH_3 + NH_4^+$	so _x	Total
Dry deposition	800	1320	1690	3800 (66%)
Wet deposition Total	420 1220 (21%)	680 2000 (34%)	890 2580 (45%)	2000 (34%) 5800 (100%)

Table 7. Deposition and emission of acid and acidifying compounds (in 10⁹ mole/year) in the Netherlands. About 1980.

Component	Deposition	Emission	
NO_{x}	4.9	12.0	
NH ₃ + NH ₄ ⁺	8.0	9.7	
SO _x	10.3	14.8	
Total	23.2	36.5	

Table 8. Meteorological variables (friction velocity u* (cm.s⁻¹) and Monin Obukhov length L (m) and calculated deposition velocities v_d (cm/s)¹⁾ for NO_x and Ox.

date		u*	L	$v_d(NO_x)$	$v_{d}^{(0x)}$	date		u*	L	$v_d(NO_x)$	v _d (0x)
8 Sept	I	34	8000	- 2.0	0.8		IV	24	- 20	0.6	0.6
	II	29	- 300	- 1.1	1.1	29 Sept	I	23	- 50	- 0.5	-
	III	30	- 70	- 1.5	0.4		II	22	- 100	0.7	0.4
	IV	30	- 70	-	0.8		III	16	100	0.2	0.0
	V	24	- 40	- 1.2	-		IV	11	20	0.1	0.1
	VI	29	- 90	- 1.7	0.8	24 Nov	I	43	300	- 2.6	0.7
9 Sept	I	9	- 30	0.4	0.3		II	45	400	1.5	-
	II	11	190	0.2	0.4		III	32	100	0.6	0.0
	III	13	70	0.0	0.3	1 Dec	I	24	- 400	- 0.3	-
	IV	16	-1200	0.7	0.7		II	24	120	- 0.2	0.0
	V	23	130	0.6	0.6		III	26	60	0.0	0.6
	VI	20	60	0.4	0.6	2 Dec	Ι	10	200	0.0	0.0
	VII	15	30	0.1	0.3		II	9	120	0.0	0.0
15 Sept ²⁾	I	2	-	0.0	0.3		III	9	40	0.1	0.0
	II	6	- 1	0.7	-		IV	10	30	0.0	0.0
	III	11	- 3	0.0	0.6		V	10	20	0.1	0.0

1) Negative deposition velocities result from upward fluxes.

*

2) Values of micrometeorological variables uncertain due to low wind speeds.

Table 9. Influence of heating of the sampling tube on the deposition velocity of particles (0.4 - 5 μ m) over an agricultural field from eddy correlation measurements.

Heating	ConcentrationDeposition(arbitraryvelocityunits)(cm s ⁻¹)		σ	N 2)
ON	17	- 0.20	0.33	10
ON	13	- 0.06	0.17	10
OFF	15	- 0.26	0.19	10
ON	11	+ 0.14	0.10	5
OFF	15	- 0.25	0.08	5
ON	10	+ 0.04	0.21	5
ON	11	- 0.09	0.06	5

1) negative values refer to upward fluxes

2) number of 3-minute-measurement.