

THROUGHFALL MONITORING AT 4 SITES IN THE NETHERLANDS BETWEEN 1995 AND 2001

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Abstract

During one year throughfall was measured in four Level II forest sites in the Netherlands as part of the PAN European monitoring programme for the Intensive Monitoring of Forest Ecosystems. The data for the monitoring year 2001 are reported and a canopy exchange model was applied to estimate the atmospheric deposition to these sites. The measurements made so far between 1995 and 2001 at these sites were reanalysed and the temporal variation is shown.

CONTENTS

LIST OF TABLES	4
LIST OF FIGURES	4
SUMMARY	5
1. INTRODUCTION	7
2. EXPERIMENTAL	9
2.1 Sampling and analysis	10
2.2 Quality checks	10
3. RESULTS	13
3.1 Quality checks	13
3.2 Temporal variations in throughfall fluxes	16
3.3 Annual average throughfall fluxes in 2001	16
3.4 Annual variation in throughfall fluxes	16
4. DEPOSITION ESTIMATES	18
4.1 Canopy budget model	18
4.2 Estimates of open field deposition fluxes without measurements	19
4.3 Dry, wet and total deposition estimates	20
4.4 Trends in deposition	20
4.5 Uncertainty	23
5. CONCLUSIONS	24
REFERENCES	25

LIST OF TABLES

Table 1	<i>Sites, stand characteristics their co-ordinates</i>	9
Table 2	<i>The required criteria for the ionic balance (WMO, 1992)</i>	11
Table 3	<i>Equivalent ionic conductance at 20 °C and equivalent weights for the various considered ions in deposition (de vries et al., 1999)</i>	12
Table 4	<i>Annual throughfall fluxes measured at the four sites and open field precipitation measured at Hardenberg in 2001 in mol ha⁻¹ y⁻¹</i>	16
Table 5	<i>Deposition estimates per plot in 2000 in mol ha⁻¹ a⁻¹</i>	20

LIST OF FIGURES

Figure 1	<i>Location of the throughfall monitoring sites</i>	9
Figure 2	<i>Cations versus the anions for monthly samples per year (mmol.m⁻³)</i>	13
Figure 3	<i>Calculated conductivity versus the measured conductivity (mS cm⁻¹)</i>	14
Figure 4	<i>Molar Na-Cl concentration ratio versus the deviation of the ion balance (%)</i>	14
Figure 5	<i>Temporal variations in throughfall fluxes (mol ha⁻¹ y⁻¹) and amount of throughfall (mm) in 2001</i>	15
Figure 6	<i>Annual variation in throughfall fluxes at the four sites (mol ha⁻¹ y⁻¹)</i>	17
Figure 7	<i>Comparison of annual throughfall fluxes with open field fluxes measured at Hardenberg</i>	19
Figure 8a	<i>Temporal variation in deposition measured at Dwingelo</i>	21
Figure 8b	<i>Temporal variation in deposition measured at Hardenberg</i>	21
Figure 8c	<i>Temporal variation in deposition measured at Speuld</i>	22
Figure 8d	<i>Temporal variation in deposition measured at Zeist</i>	22

SUMMARY

The Pan-European Programme for the Intensive Monitoring of Forest Ecosystems, the so-called Level II Programme of the International Co-operative Programme on Assessments and Monitoring of Air Pollution Effects on Forests (ICP Forests of UN/ECE) provides the framework in which analysis of the effects of atmospheric loads and its temporal variation is investigated. The current monitoring programme of ICP Forest at the so-called 'Intensive Monitoring' (Level II) plots in the Netherlands includes deposition measurements at four sites. Throughfall is measured by the Energy research Centre of the Netherlands at Dwingelo, Hardenberg, Speuld and Zeist. Bulk deposition is measured close to the Hardenberg site. For the other three sites bulk deposition data are obtained from the National Air Quality Monitoring Network run by the National Institute of Public Health and Environment.

This report describes the measurements made in 2001 and the results of the quality checks performed on the data. Furthermore, by application of a canopy exchange model, deposition estimates were made for the forest sites and the variation in deposition between 1995 and 2001 is shown. The total nitrogen deposition in 2000 varied between 2800 and 4100 mol ha⁻¹ y⁻¹. Highest nitrogen deposition is measured at Hardenberg, the other sites showing about the same inputs. Reduced N contributes most to the total nitrogen deposition (70%). Potential acid deposition is also highest at Hardenberg and amounts to 5900 mol ha⁻¹ y⁻¹. The other sites show inputs of 4000 – 4500 mol ha⁻¹ y⁻¹. Dry deposition is generally an order of magnitude higher than wet deposition and makes about 70% of the total deposition flux for NH₄, SO₄ and NO₃.

Throughfall and open field precipitation has been measured at the four sites in 1995-1996, 1998 - 2001. The period is too short to determine trends in deposition, because-of the uncertainty in the deposition estimates. The four sites show different features. The fluxes of sulphur and nitrogen, both total and dry, at Dwingelo and Speuld show the same temporal variation with a high correlation. At Hardenberg and Zeist this correlation is not observed. Dwingelo does not show an increase or decrease in fluxes, but at Speuld the fluxes generally increased during the measuring period. At Zeist and Hardenberg the picture is not clear, showing both decreasing as increasing fluxes and fluxes without any change. At Hardenberg the total nitrate fluxes gradually increased, whereas the total NH₄ fluxes decreased. At Zeist most of the fluxes in the recent years decreased relative to 95/96, except for the dry deposition of NH₄, which increased.

1. INTRODUCTION

The Pan-European Programme for the Intensive Monitoring of Forest Ecosystems, the so-called Level II Programme of the International Co-operative Programme on Assessments and Monitoring of Air Pollution Effects on Forests (ICP Forests of UN/ECE) provides the framework in which analysis of the effects of atmospheric loads and its temporal variation is investigated. The current monitoring programme of ICP Forest at the so-called 'Intensive Monitoring' (Level II) plots in the Netherlands includes the yearly assessment of the forest condition, foliar composition and the soil solution since 1992 at 14 sites (12 before 1995) and the five yearly assessment of a large number of more slowly changing parameters. The chemical composition of the groundwater has been measured three-monthly at the initial 12 sites during all years. In 1990 a national survey of the chemical composition of needles, litter, soil and soil solution was also conducted for 150 stands (De Vries and Leeters, 1994), which has been repeated in 1995 for 200 stands, including the 14 intensive monitoring plots. A new assessment is foreseen in the year 2000.

Throughfall measurements are attractive to use for estimation of atmospheric deposition, mainly because the measurements are easy to perform and relatively cheap compared to micro meteorological measurements. The relation between throughfall fluxes and atmospheric deposition is not always very clear. Wash-off processes from leaf and bark surfaces due to water passing through the canopy can increase concentrations relative to open field precipitation. The net-throughfall flux is determined by the net contribution of washed-off dry deposited gases and particles, interception of cloud water and re-evaporation of gases from the canopy. The kinetics of removal by wash-off may be as complex as the kinetics of dry deposition itself. Canopy interaction is, next to dry deposition, regarded as one of the most important factors influencing throughfall and stemflow composition for several ions. Both leaching from the canopy as well as canopy uptake of nutrients and gases have been found (e.g. Erisman and Draaijers, 1995). From studies on the influence of canopy exchange on the throughfall composition and studies comparing throughfall with deposition measurements it is generally concluded that for sodium and sulphur canopy exchange is negligible. Base cations and nitrogen species show large differences between throughfall and deposition as the result of canopy exchange: nitrogen is taken up whereas calcium, magnesium and potassium can be leached by the canopy. In order to determine deposition from throughfall of these components a canopy exchange model was developed, tested and refined (Draaijers and Erisman, 1996). In order to apply such a model, throughfall fluxes have to fulfil certain quality standards as described by Draaijers et al. (1996). Erisman et al. (1997) analysed the throughfall data measured between 1995 and 1996 at 14 plots, whereas Erisman et al. (2001) assessed the throughfall measurements made at four plots between 1995 and 2000. The last report focussed on the measurements made in 2000.

The Expert Centre of the Ministry of LNV (EC-LNV) co-ordinates the Dutch contribution to ICP Forest. ECN made throughfall measurements at the 4 Level II plots in the Netherlands between January 2001 and December 2001 using the method recommended by Draaijers et al., (1996). The research was financed by the EC through EC-LNV and by the Ministry of Housing, Physical Planning and the Environment (VROM).

The aims of this investigation were i) to provide deposition estimates for the 4 plots in 2001, and ii) to show the trend in deposition estimates made at the same plots between 1995 and 2001 with the same method. Because of the canopy exchange processes it is necessary to correct the throughfall fluxes with a canopy exchange model.

This report first gives a description of the sites and the measurement methods. The results of the measurements are described in chapter 3. The report ends with conclusions and recommendations.

2. EXPERIMENTAL

The current monitoring programme of ICP Forest at the Level II plots in the Netherlands includes the yearly assessment of the forest condition, foliar composition and the soil solution since 1992 at 14 sites. At these sites throughfall gutters were installed in 1995 and for one year data were collected (Erisman et. al., 1997). In October 1997 the measurements were continued at four of the 14 sites (Erisman et al., 2001). The sites, stand characteristics, the co-ordinates and the dominant tree species are given in Table 1. Figure 1 shows the location of the sites in a map of the Netherlands. The plots are located in the main forested areas in the country: in Overijssel (1), the Utrechtse Heuvelrug (2), the Veluwe (3) and in Drenthe (4).

Table 1 *Sites, stand characteristics their co-ordinates*

No.	Plot	Locatie	Lon	Lat	Species	Distance to forest edge [m]	Tree height [m]	Crown coverage [%]	Bulk deposition site
1	106	Hardenberg-DG	06 33 00	52 32 42	Douglas fir	>100	>20	50-75	Rheezerveen
2	1040	Zeist-EI	05 13 50	52 06 32	Oak	20-40	15-20	50-75	628 Bilthoven
3	2084	Speuld-DG	05 44 17	52 16 03	Douglas fir	>100	10-15	>75	732 Speulder Veld
4	2085	Dwingelo	06 26 45	52 50 20	Scots pine	>100	15-20	>75	928 Witteveen



Figure 1 *Location of the throughfall monitoring sites*

2.1 Sampling and analysis

The sampling was done according to the descriptions in the Submanual on deposition on ICP Forests Level 2 plots (ICP Forest Expert Panel on Deposition, 1994, updated 06/1999) and data was handled according to the *Basic documents for the implementation of the intensive monitoring programme of forest ecosystems in Europe* (EC, VI/3908/95-EN). An extensive description of the methods is given in the Data Accompanying Report on Deposition Monitoring as available at the FIMCI data centre (Alterra, Wageningen) and as appendix A in Erisman et. al. (1997). Bulk deposition (open field measurements) was only made at plot 106. For all other locations bulk precipitation was obtained from wet-only measurements made by RIVM at the sites indicated in Table 1. The data from the Air Quality Monitoring Network for the years until 2001 were kindly being made available by RIVM (RIVM, 1999; 2000). For 2001 the RIVM data were not yet available, an estimate is made of the wet deposition for these years. Open field precipitation is measured as two-weekly averages, which are combined in the lab to obtain monthly samples.

At each plot 10 gutters in two parallel lines with 5 collectors each at distances of 1 - 2 m were installed. The gutters are 4 m long and have a collecting area of about 400 cm². They are placed with an angle of 150°, about 1.5 m above the surface. Sample bottles were placed below the surface and CHCl₃ was added as a preservative. The samples were kept in the dark at temperatures between 4 and 8 °C. Sample bottles were collected two-weekly and the gutters were rinsed with demi-water. Five samples were combined into one sample. Weekly samples were combined in the lab to obtain monthly samples.

In the lab the monthly sample was split, one half was acidified with HNO₃ to pH 1 for analyses of metals. These were determined by ionic chromatography by atomic absorption spectroscopy (ICP-AES). Ions determined were: K, Ca, Mg, Na, Al, Mn and Fe. The other sample was used to determine conductivity, pH (potentiometric), Cl, NO₃, SO₄ by ionic chromatography, N_{total} by Kjeldahl analysis and NH₄ by Flow Injection Analysis, FIA/conductivity. Before sending the data to FIMCI data checks were performed, as described in de Vries et. al., (1999) and outlined in the next paragraph.

2.2 Quality checks

Several criteria were met to safeguard the quality and to estimate the uncertainty. First of all the measurement set-up, conservation and handling of samples was done according to the recommendations in Draaijers et al, (1996) and the Mapping Manual (UN/ECE, 1996). Gutters were used instead of open samplers. The number of gutters was 10. Secondly, sample analysis was performed according to and with methods certified by STERLAB. Finally, samples were collected and stored in light-tight bottles at low temperatures. CHCl₃ was added as a preservative to prevent biological conversion. Additional quality checks can be done after sampling. These are described in this section.

Ion balance

The basic assumption for this quality control is that the measurements of pH, ammonium, calcium, magnesium, sodium, potassium, bicarbonate, sulphate, nitrate and chloride account almost completely for the ions present in solutions. This may not be true in the case of lake water or soil solutions with pH lower than 5, where aluminium and other trace metals may be present in ionic forms. Fluoride is in most cases negligible in terms of ionic balance. In the case of atmospheric deposition, formic and acetic acid may have a minor role in ion balance both in urban and remote areas. On the other hand ionic balance can be influenced by the presence of high amounts of organic matter. This is particularly true in the case of throughfall and stemflow deposition. The check is based on the electro neutrality of water samples: the total number of negative and positive charges must be equal. This can be checked using milli (or micro) equivalents per litre (meq l⁻¹ or µeq l⁻¹) as the concentration unit. The constants required to transform the units used in the ICP Forest research into µeq l⁻¹. The limit of acceptable errors

varies with the total ionic concentrations and the nature of the solutions. Using Σ_{cat} and Σ_{an} to indicate the concentrations ($\mu\text{eq l}^{-1}$) of cations and anions respectively, we can define percent difference as:

$$\text{PD} = 100 * (\Sigma_{\text{cat}} - \Sigma_{\text{an}}) / (0.5 * (\Sigma_{\text{cat}} + \Sigma_{\text{an}})) \quad (1)$$

where:

$$\begin{aligned} \Sigma_{\text{an}} &= \text{Alk} + [\text{SO}_4] + [\text{NO}_3] + [\text{Cl}] \\ \Sigma_{\text{cat}} &= [\text{Ca}] + [\text{Mg}] + [\text{Na}] + [\text{K}] + [\text{H}] + [\text{NH}_4] \end{aligned} \quad (2)$$

High amounts of organic matter must also be taken into consideration when present. Organic matter in general is formed by organic acids, which contribute to the anions, producing marked differences in the ion balance. Organic matter or DOC was not measured in the throughfall and bulk samples as it is only a optional parameter in the monitoring programme. The criteria for acceptance of the ion balance are given in Table 2.

Table 2 *The required criteria for the ionic balance (WMO, 1992)*

Cations+anions ($\text{mmol}_c \text{ m}^{-3}$)	Acceptable difference (%)
≤ 50	≤ 60
50 - 100	≤ 30
100 - 500	≤ 15
≥ 500	≤ 10

Comparison between measured and calculated conductivity

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the type and concentrations of ions and on the temperature of measurement. It is defined as:

$$\text{K} = \text{G} * (\text{L}/\text{A}) \quad (3)$$

where G = is the conductance (unit: ohm^{-1} or Siemens), defined as the reciprocal of resistance; A (cm^2) is the electrode surface area, L (cm) is the distance between the two electrodes. The units of K are $\mu\text{S cm}^{-1}$. Conductivity depends on the type and concentration (activity) of ions in solution; the capacity of a single ion to transport an electric current is given in standard conditions and in ideal conditions of infinite dilution by the equivalent ionic conductance. A careful, precise conductivity measurement is a further means of checking the results of chemical analyses. It is based on a comparison between measured conductivity (CM) and the conductivity calculated (CE) from individual ion concentrations (c_i), multiplied by the respective equivalent ionic conductance (λ_i) at 20 °C:

$$\text{CE} = \Sigma \lambda_i c_i \quad (4)$$

The ions are those considered in the ionic balance; the values of λ_i for the different ions are given in table 3, referring to 20 and 25°C. As the concentrations are expressed in $\mu\text{eq l}^{-1}$, λ_i is given as $\text{kS cm}^2 \text{ eq}^{-1}$, to get conductivity in $\mu\text{S cm}^{-1}$. The percent difference, CD, is given by the ratio:

$$\text{CD} = 100 * |(\text{CE}-\text{CM})|/\text{CM} \quad (5)$$

At low ionic strength (below 0.1 meq l^{-1}) of atmospheric deposition samples, the discrepancy between measured and calculated conductivity should be no more than 2% (Miles and Yost

1982). Ionic strength (I_s), in meq l^{-1} , can be calculated from the individual ion concentrations as follows:

$$I_s = 0.5 \sum c_i z_i^2 / w_i \quad (6)$$

where:

c_i = concentration of the i -th ion in mg l^{-1} ;
 z_i = absolute value of the charge for the i -th ion;
 w_i = gram molecular weight for the i -th ion.

For ionic strength higher than 0.1 meq l^{-1} and lower than 0.5 meq l^{-1} the Davies correction of the activity of each ion can be used (see ICP manual):

$$y = 10^{-0.5\{\sqrt{I_s}/(1+\sqrt{I_s})-0.3I_s\}} \quad (7)$$

Finally, corrected conductivity may be calculated as:

$$C_{\text{Ecorr}} = y^2 \quad CE = y^2 \sum \lambda_i c_i \quad (8)$$

The plot of measured and calculated conductivity is useful in the routine data checking of a set of analyses; the departure of some results from linearity may suggest the presence of analytical or some other kind of errors.

The Technical Report 1999 gives ranges for acceptance of differences between measured and calculated conductivity (de Vries et. al., 1999). According to WMO, the discrepancy between measured and calculated conductivity should be no more than 20% at a measured conductivity above $30 \mu\text{S cm}^{-1}$. At low ionic strength, the acceptable differences are higher, a maximum difference of 30% is generally required.

Sodium to chloride ratio

The sodium to chloride ratio in open field precipitation and in throughfall is expected to follow that of sea water, especially in areas close to the sea as is the case in the Netherlands. Assuming that seasalt is the dominant source of both Na and Cl, its concentration ratio mostly varies between 0.7 and 1.0 in annual bulk deposition and throughfall, with a median value resembling the seawater ratio of about 0.84. This ratio is used as criteria to check the data.

Table 3 *Equivalent ionic conductance at 20 °C and equivalent weights for the various considered ions in deposition (De Vries et al., 1999)*

Element	Equivalent ionic conductance ($\text{kS cm}^2 \text{ eq}^{-1}$)	Equivalent weight (g eq^{-1})
H	0.3151	1
Ca	0.0543	20
Mg	0.0486	12
K	0.0670	39
Na	0.0459	23
NH ₄ -N	0.0670	14
NO ₃ -N	0.0636	14
SO ₄ -S	0.0712	16
Cl	0.0680	35.5
Alk	0.0394	1

3. RESULTS

In this chapter the results of the monitoring of throughfall and bulk precipitation at the four sites are given. First the results of the quality checks are discussed. Then the results of the year 2001 are given followed by the last section describing the data between 1995 and 2001.

3.1 Quality checks

The quality checks were used to check the data on inconsistencies. In general about 20% of the data show discrepancies from the acceptable ranges in ionic balances, conductivity and/or Na-Cl ratio. Errors could be identified based on the interpretation of the three criteria and in most cases corrected. Examples of errors that were encountered were: Na contamination, dilution factor not taken into account, missing values. Samples were reanalysed or, if no explanation could be found, only one of the duplo samples was taken into account. The data after corrections are shown in Figure 2 to 4. These Figures show the comparison of the cations versus the anions (2), the measured versus the calculated conductivity (3) and the Na-Cl ratio versus the deviation of the ionic balance (4).

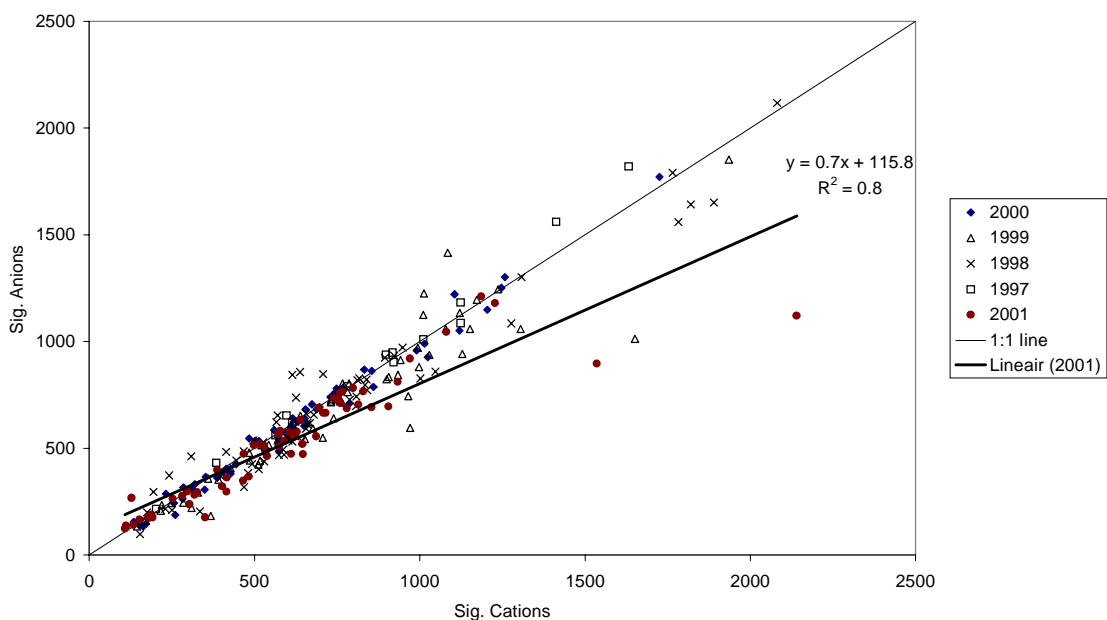


Figure 2 Cations versus the anions for monthly samples per year (mmol.m^{-3})

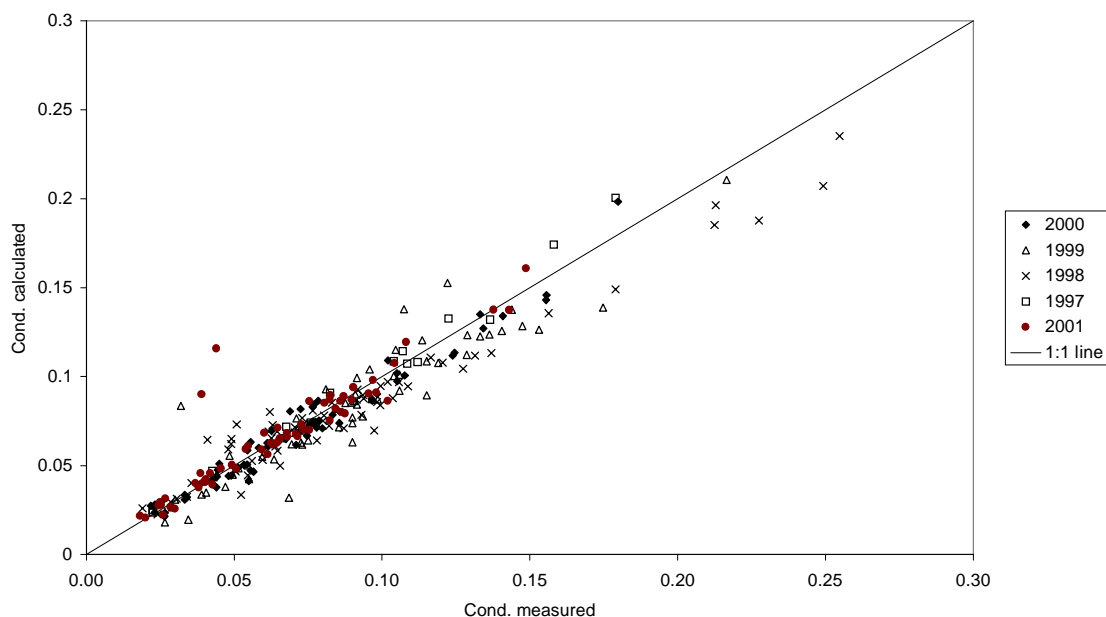


Figure 3 Calculated conductivity versus the measured conductivity ($mS\ cm^{-1}$)

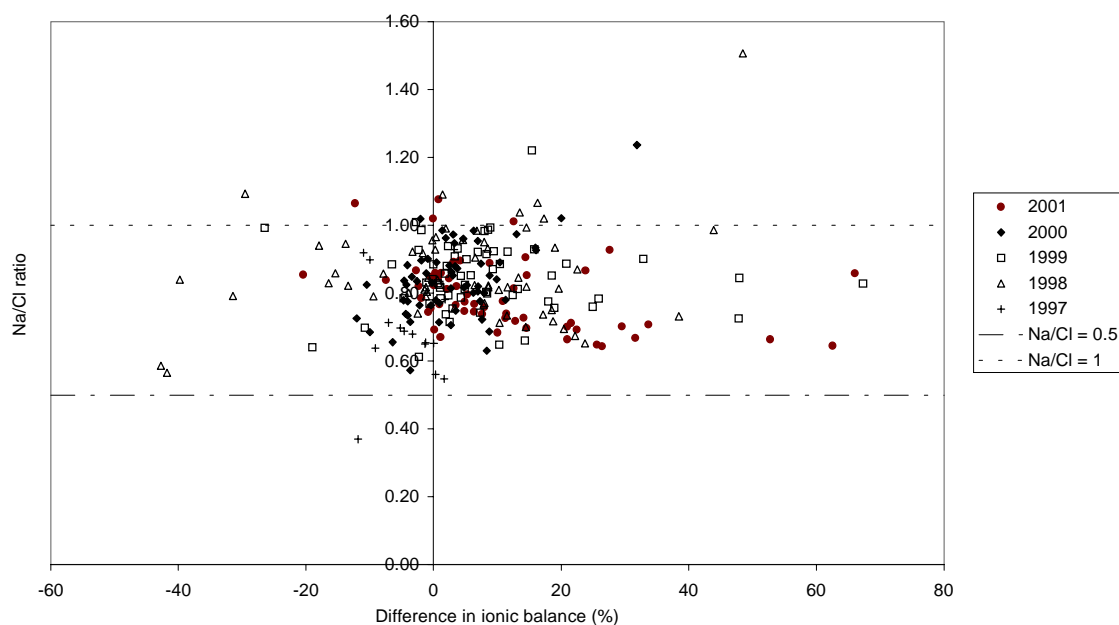


Figure 4 Molar Na-Cl concentration ratio versus the deviation of the ion balance (%)

As can be seen from the figures, most of the data fall within the acceptable ranges. However, several data are rejected when using the FIMCI software to evaluate the data using the above described data checks. For the 2001 data this was especially related to the ionic balance: the alkalinity appeared to be high in about 5 samples, combined with relatively high pH values (> 6). Carbonates of organic nitrogen compounds might also cause the data that are outside the limits.

Annual fluxes were calculated by averaging the concentrations for those periods, which fulfilled either the ion-balance or conductivity criteria, or both. This concentration was multiplied by the total amount of throughfall or precipitation over the whole year, including also the rejected periods.

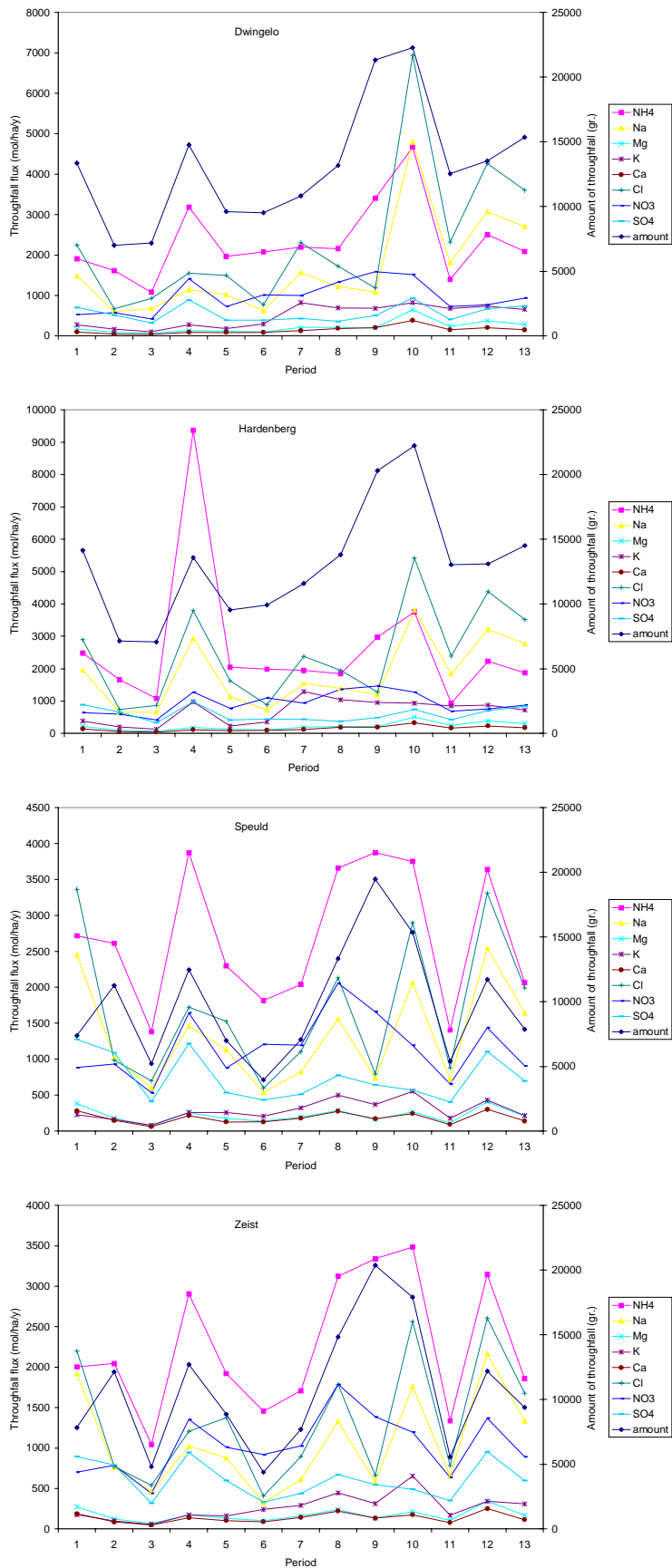


Figure 5 Temporal variations in throughfall fluxes ($\text{mol ha}^{-1} \text{y}^{-1}$) and amount of throughfall (mm) in 2001

3.2 Temporal variations in throughfall fluxes

The temporal variation as monthly averages in throughfall fluxes of K^+ , Ca^{2+} , Mg^{2+} , Na^+ , NH_4^+ , Cl^- , NO_3^- and SO_4^{2-} is plotted in Figure 5 for the four sites. Generally the throughfall fluxes display the same pattern for all components. The temporal variation is primarily determined by the amount of precipitation for each month. Fluxes are low when the amount of precipitation is low. Generally the correlation between the temporal variation is strongest between the sites closest to each other: Zeist and Speuld and Hardenberg and Dwingelo. All sites show a distinct peak in the forth period of the year and in autumn, as the result of high rainfall intensities.

3.3 Annual average throughfall fluxes in 2001

The fluxes of throughfall and open field precipitation were calculated by multiplying the concentration with the amount of water and make the necessary conversions to express the flux in $mol\ ha^{-1}\ y^{-1}$. Table 4 gives the fluxes for the year 2001. Annual average fluxes were calculated as the sum of monthly fluxes. The total nitrogen flux is calculated as the sum of nitrate and ammonium fluxes, whereas the potential acid flux is estimated according to:

$$Potential\ acid = NH_4^+ + NO_3^- + 2\ SO_4^{2-} \quad (9)$$

Table 4 *Annual throughfall fluxes measured at the four sites and open field precipitation measured at Hardenberg in 2001 in $mol\ ha^{-1}\ y^{-1}$*

site:	NH_4	Na	Mg	K	Ca	Cl	NO_3	SO_4	Tot N	Po. Acid
Dwingelo	2475	1750	220	150	570	2385	950	575	3420	4570
Hardenberg	2495	1205	195	165	270	1525	1115	680	3610	4970
Speuld	1840	1000	145	130	245	1260	830	600	2670	3870
Zeist	1100	975	240	215	925	1375	470	515	1570	2595
bulk-Hardenberg	490	300	45	45	35	365	530	155	1210	1570

Throughfall fluxes of total nitrogen are, just like the years before, lowest at Zeist, a plot relatively far away from livestock breeding areas. The northern sites show about the same nitrogen loading of 44 – 55 $kg\ N\ ha^{-1}$. Speulder forest is in between the Northern sites and Zeist. The potential acid fluxes are highest in Hardenberg (5000 $mol\ ha^{-1}\ y^{-1}$) and lowest in Zeist (2600 $mol\ ha^{-1}\ y^{-1}$). These values are about the same as in 2000.

Base cation fluxes are high in the north, probably because of the impact of sea salt deposition, as can be derived from the Na and Cl fluxes. Furthermore, high potassium fluxes are measured at Dwingelo.

3.4 Annual variation in throughfall fluxes

Throughfall fluxes have been measured since 1995 at the four plots. For 1.5 year, between 1996 and 1997, no measurements were made. Figure 6 shows the annual variation in throughfall fluxes. The general variation in fluxes at the four sites is similar, with lowest Na and highest NH_4 in 1995 and similar fluxes during the other years. Remarkable is the increase in NO_3 fluxes at Hardenberg between 1995 and 2001. In the next chapter deposition fluxes corrected for canopy exchange will be given, providing more information about trends in atmospheric inputs.

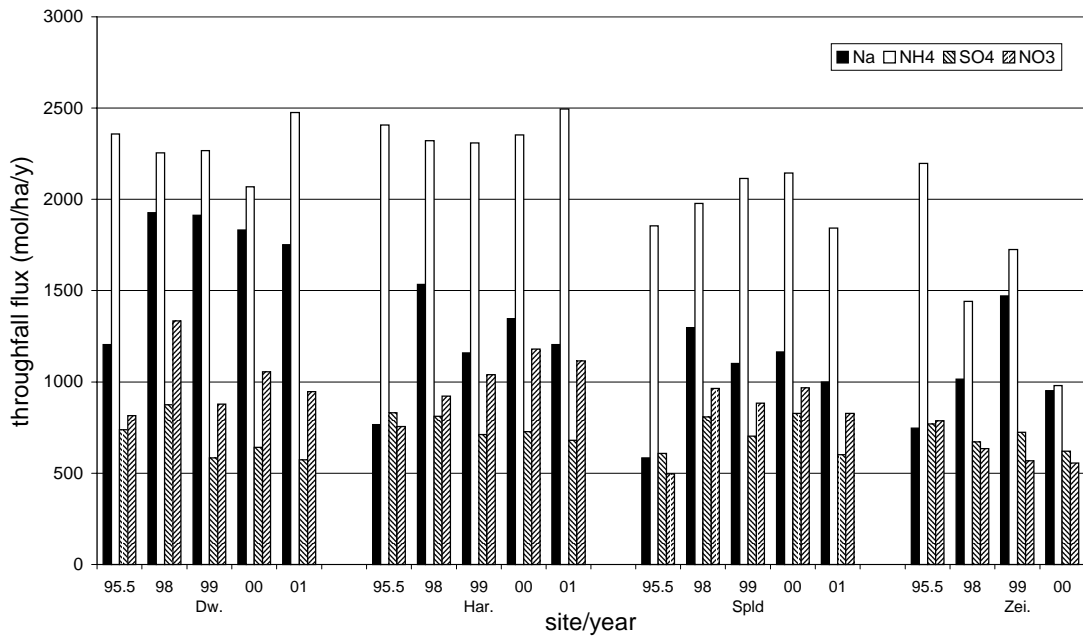


Figure 6 Annual variation in throughfall fluxes at the four sites ($\text{mol ha}^{-1} \text{y}^{-1}$)

4. DEPOSITION ESTIMATES

Deposition estimates can be made using a canopy exchange model. Such a model is described in the first section. The next section describes the results of the model followed by a description of deposition trends at the different plots.

4.1 Canopy budget model

A canopy budget model developed by Ulrich (1983) was used to estimate the impact of canopy leaching on throughfall and stemflow fluxes of Mg^{2+} , Ca^{2+} and K^+ . Draaijers and Erisman (1995) present an extensive description and uncertainty analysis of the model. In the model, Na^+ is assumed not to be influenced by canopy exchange. Therefore dry deposition of Na^+ can be calculated by subtracting wet deposition from the throughfall + stemflow flux. Particles containing Mg^{2+} , Ca^{2+} and K^+ are assumed to have the same mass median diameter as Na^+ containing particles. Dry deposition of Mg^{2+} , Ca^{2+} and K^+ can subsequently be calculated according to:

$$DD_x = (TF_{Na} + SF_{Na} - BP_{Na})/BP_{Na} * BP_x \quad (10)$$

where DD, TF, SF, and BP represent dry deposition, throughfall, stemflow and bulk precipitation flux, respectively and x denotes Mg^{2+} , Ca^{2+} or K^+ . In equation [10] $(TF_{Na} + SF_{Na} - BP_{Na})/BP_{Na}$ represents the so-called 'dry deposition factor'. Canopy leaching of these ions is calculated according to:

$$CL = TF + SF - BP - DD \quad (11)$$

Canopy leaching computed for Cl^- leaching is generally assumed negligible (Draaijers, 1993). The total canopy uptake of H^+ and NH_4^+ is assumed to equal the total leaching of Mg^{2+} , Ca^{2+} and K^+ minus canopy leaching of Mg^{2+} , Ca^{2+} and K^+ associated with foliar excretion of weak acids (canopy uptake should always balance canopy leaching). To calculate the latter an excretion factor is defined:

$$EF = CL_{wa}/(CL_{Mg} + CL_{Ca} + CL_K) \quad (12)$$

where Cl_{wa} is computed according to:

$$Cl_{wa} = TF_{wa} + SF_{wa} - BP_{wa} - DD_{wa} \quad (13)$$

It is assumed that all organic acids are leached in a neutral salt form. For the calculation of the excretion factor it is very important that all ions significantly contributing to the cation-anion balance are measured, and also with the highest possible accuracy (Draaijers, 1993). Tf_{wa} was assumed to equal $TF_{cat} - TF_{an}$, SF_{wa} equal to $SF_{cat} - SF_{an}$ and BP_{wa} equal to $BP_{cat} - BP_{an}$. Dry deposition of weak acids is assumed equal to bulk precipitation of weak acids. The canopy leaching of base cations through exchange with H^+ and NH_4^+ is computed according to:

$$Cl_{bc} = (CL_{Mg} + CL_{Ca} + CL_K) * (1 - EF) \quad (14)$$

Canopy uptake of H^+ and NH_4^+ is subsequently calculated from the sum of exchanged ions of Mg^{2+} , Ca^{2+} and K^+ where it is assumed that, based on experiments in the laboratory, H^+ has an exchange efficiency six times larger than NH_4^+ :

$$\begin{aligned} CU_H &= Cl_{bc} / (1 + (1 / [6 * (((TF_H / TF_{NH4} + (BP_H / BP_{NH4}))) / 2])) \\ CU_{NH4} &= Cl_{bc} - CU_H \end{aligned} \quad (15)$$

Knowing their canopy uptake, the dry deposition flux of H^+ (H_2SO_4 , $(NH_4)_2SO_4$, HNO_3 and HCl) and NH_4^+ (NH_3 and NH_4^+ aerosol) can be computed from $TF + SF + CU - BP$. Finally, it is assumed that canopy leaching of SO_4^{2-} and NO_3^- is zero allowing the calculation of dry deposition of SO_4^{2-} (SO_2 and SO_4^{2-} aerosol) and NO_3^- (NO , NO_2 , HNO_2 , HNO_3 and NO_3^- aerosol) according to $TF + SF - BP$.

In this study annual mean throughfall, stemflow and bulk precipitation fluxes are used through which differences in dry deposition factor caused by seasonal changes in pollution climate and canopy characteristics are neglected. The assumption that Mg^{2+} , Ca^{2+} and K^+ containing particles are deposited with equal efficiency as Na^+ containing particles introduces an error, as the particle size distribution of these constituents is not necessarily the same (Milford and Davidson, 1985). There will be a shift in the size distribution towards particles with smaller radii with increasing distance to source areas and/or lower relative humidity (Fitzgerald, 1975).

4.2 Estimates of open field deposition fluxes without measurements

For the application of the canopy exchange model it is necessary to have data on wet deposition measurements. At Hardenberg ECN measures the wet deposition using bulk samplers in a nearby open field. For the other three sites, so far, data from the National Monitoring Network (RIVM, 2000) were obtained (Erisman et al., 2001). These results will only become available in May 2002 because of validation. Therefore, an estimate was made of the wet deposition fluxes, using the strong relationship between wet deposition and throughfall (see e.g. Erisman et al., 2001). These results only serve as a first estimate. When the RIVM data will become available, these will be used to update the trend data.

Figure 7 shows a scatterplot of annual throughfall fluxes versus open field fluxes measured at Hardenberg between 1995 and 2001, for the different components. The bulk deposition measurements were corrected for dry deposition on the samplers using correction factors listed in van Leeuwen et al. (1995). A linear relation for all components is plotted ($R^2 = 0.70$). The slope of this equation is used to calculate wet deposition fluxes for the other sites using the measured throughfall data. These wet deposition estimates are used in the canopy exchange model to estimate the dry deposition and canopy uptake.

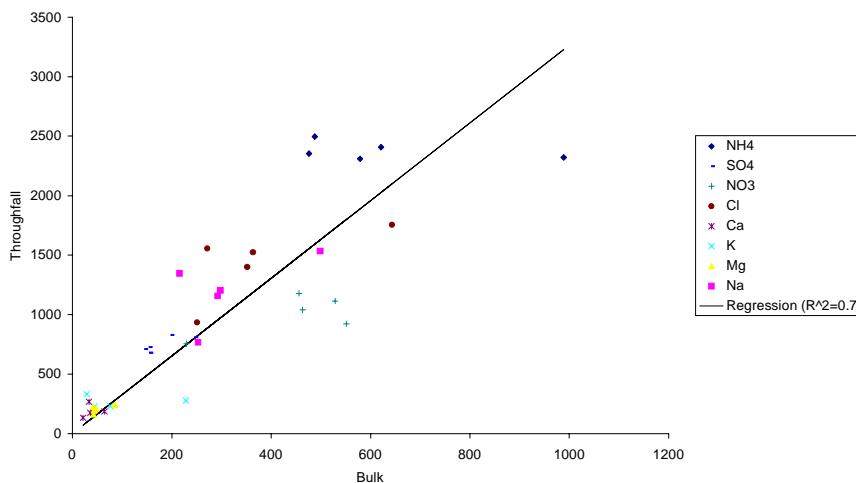


Figure 7 Comparison of annual throughfall fluxes with open field fluxes measured at Hardenberg

4.3 Dry, wet and total deposition estimates

Dry deposition fluxes in 2000 calculated with this model, together with the wet deposition data measured at Hardenberg and derived in the previous section, and the total deposition is given in Table 5. Dry deposition is generally an order of magnitude higher than wet deposition and makes about 70% of the total deposition flux for NH_4 , SO_4 and NO_3 . The total nitrogen deposition varies between 1600 and 3400 mol $\text{ha}^{-1} \text{y}^{-1}$. Highest nitrogen deposition is measured at Dwingelo, the same holds for the potential acid deposition. This is in line with the throughfall data presented in Table 4, but the deposition estimates are somewhat higher because of the correction for the canopy uptake. Note that these calculations are based on estimated wet deposition, instead of measured wet deposition data!

Table 5 *Deposition estimates per plot in 2000 in mol $\text{ha}^{-1} \text{a}^{-1}$*

Location	Dry deposition ²			Wet deposition ²			Total deposition ²			Tot. Nitrogen ²	Potential Acid ²
	NH_4	SO_4	NO_3	NH_4	SO_4	NO_3	NH_4	SO_4	NO_3		
Dwingelo	1715	398	657	759	176	291	2474	574	948	3422	4570
Hardenberg ¹	917	525	585	488	156	529	1405	681	1114	2519	3880
Speuld	1277	417	574	565	184	254	1841	601	827	2669	3870
Zeist	761	356	326	337	157	144	1097	513	470	1568	2593

¹Data for Hardenberg are different to a large extent from those reported in Erisman et al. (2001) for 2000, because here wet deposition measurements were corrected for dry deposition onto the samplers.

²These are preliminary estimates, because wet deposition was calculated and not (yet) obtained from RIVM.

4.4 Trends in deposition

Throughfall and open field precipitation has been measured at the four sites in 1995-1996, 1998, 1999, 2000 and 2001. From these data the temporal variation can be determined. Figures 8a to 8d show the temporal variation in deposition estimates for the four sites as derived from throughfall measurements and bulk deposition data after application of the canopy exchange model. The period is too short to determine trends in deposition, because of the uncertainty in the deposition estimates (see next section). The four sites show different features. The fluxes of sulphur and nitrogen, both total and dry, at Dwingelo and Speuld show the same temporal variation with a high correlation. At Hardenberg and Zeist this correlation is not observed. The fluxes at Dwingelo and Speuld do not show an increase or decrease in fluxes during the measuring period. At Hardenberg the picture is also not clear, showing both decreasing as increasing fluxes and fluxes without any change. At Zeist most of the fluxes in the recent years decreased relative to 95/96, except for the dry deposition of NH_4 , which increased.

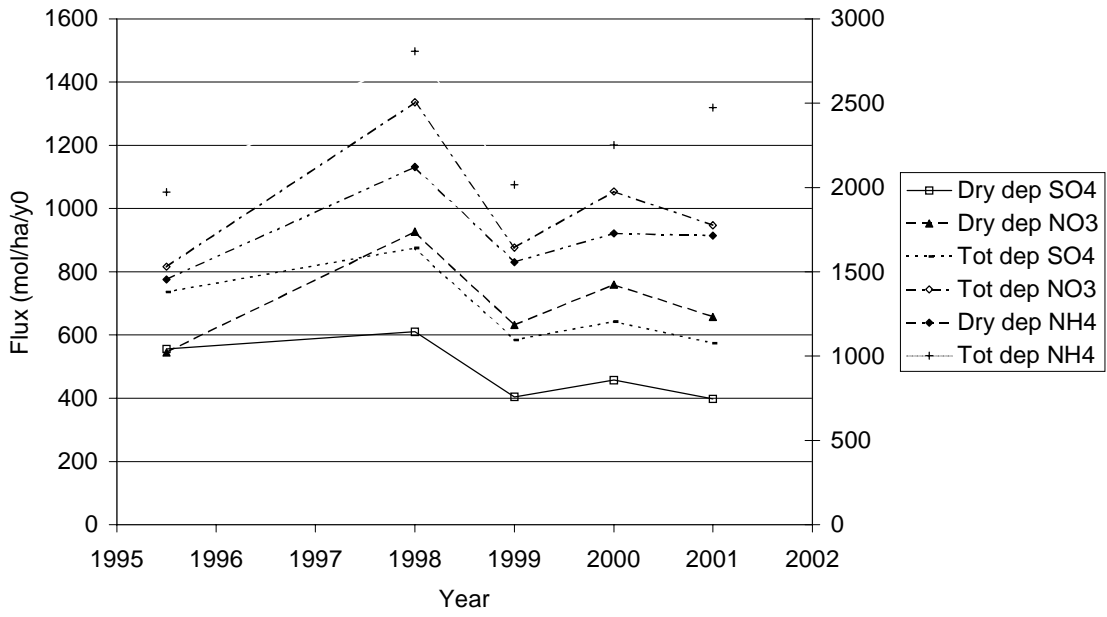


Figure 8a Temporal variation in deposition measured at Dwingelo

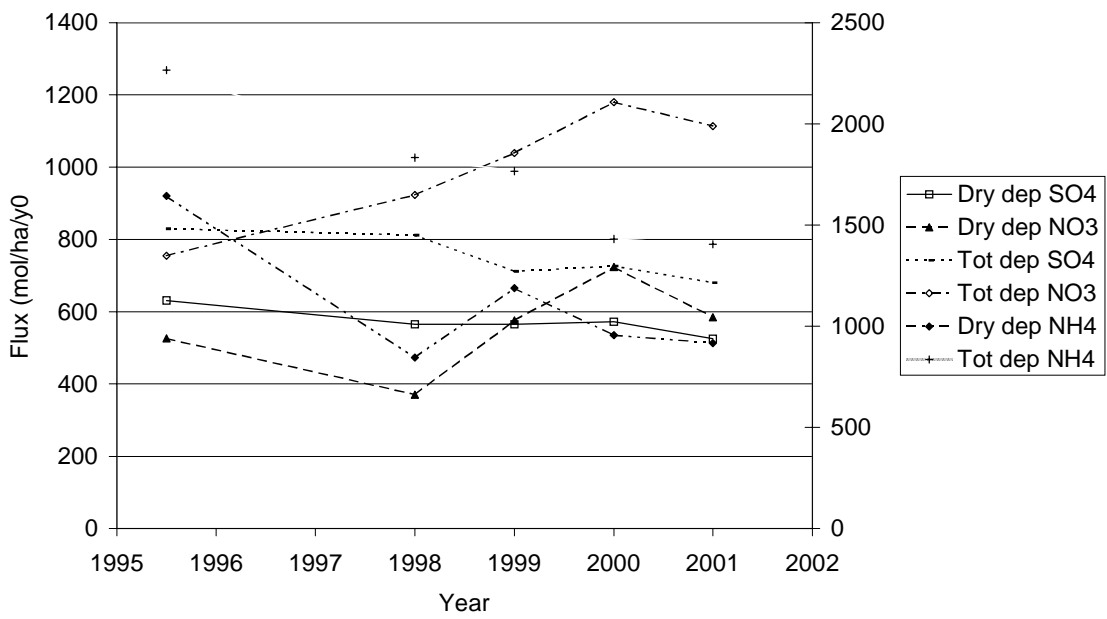


Figure 9b Temporal variation in deposition measured at Hardenberg

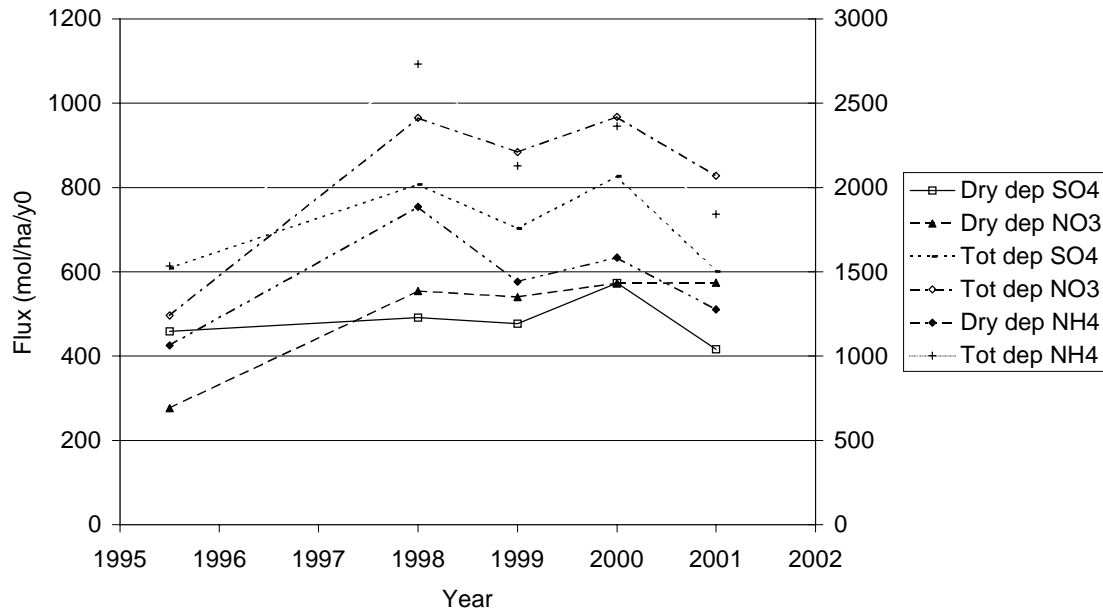


Figure 10c Temporal variation in deposition measured at Speuld

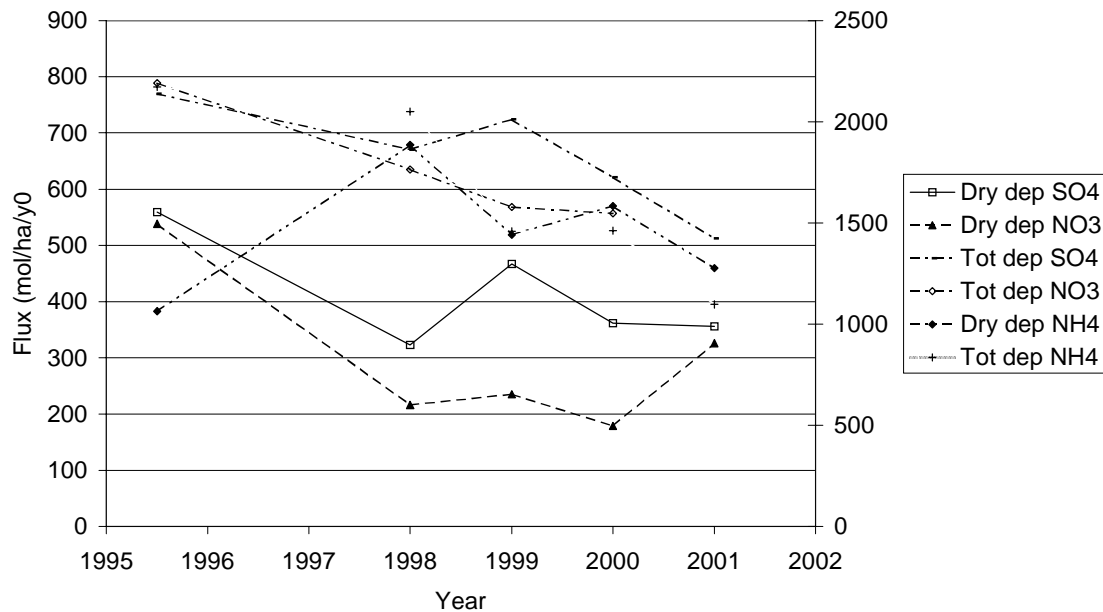


Figure 11d Temporal variation in deposition measured at Zeist

There are several drawbacks, which should be taken into account before drawing conclusions about trends in deposition from these data. First of all the growth rate is about half a meter per year. An increase in forest height and biomass leads generally to an increase in dry deposition. Secondly, throughfall is an indirect measure for atmospheric deposition. The difference between throughfall and micro meteorological measurements have been discussed in length, see e.g. Erisman and Draaijers (1995) for an overview. Apart from the accuracy of the two methods, comparison between the two methods is hampered by i) canopy exchange processes, especially relevant for nitrogen compounds and base cations, ii) representativity of the data, i.e. throughfall measurements are representative for a small canopy area 'above' the gutters, whereas micro meteorological measurements are representative for an area of about 100 times the measuring

height, an area with a radius of about 4 km in the case of Speulder forest; ii) throughfall measurements represent the flux to the stems and canopy, whereas micro meteorological fluxes represent the flux to the whole surface, including the surface below the canopy, and iv) throughfall fluxes are compound totals, whereas micro meteorological fluxes include both gaseous and particle fluxes. Several studies revealed that if both the micro meteorological measurements and the throughfall measurements are made with much care and fulfilling the most important demands regarding sampling, representativity and accuracy, and the throughfall fluxes are corrected for canopy exchange processes (Draaijers *et al.*, 1996), both methods yield similar annual average fluxes within 20%, except for nitrogen compounds (see Erisman and Draaijers, 1995). Finally, it must be emphasised that the wet deposition fluxes at Speuld, Dwingelo and Zeist were calculated instead of derived from RIVM measurements.

4.5 Uncertainty

Stemflow was not measured at the sites. The contribution of stemflow to the total flux to the forest floor varies with tree species as well as with chemical component. In general, the contribution is less than 10% of the total flux to the surface (Ivens, 1990; Draaijers *et al.*, 1996). The deposition estimates from throughfall measurements are therefore underestimated.

Draaijers *et al.* (1996) estimated that the uncertainty in throughfall fluxes used for deposition estimates, when made under ideal circumstances with the best available techniques is about 40%. The uncertainty of the fluxes reported here will be in that order of magnitude.

There are two ways in which on the short term the uncertainty in deposition estimates from throughfall measurements can be reduced. First the measurement of DOC, which is optimal in the programme, should be made manual. By measuring DOC the quality checks can be used much better and biased data can be separated from the data that are rejected because of high DOC concentrations. Furthermore, the canopy exchange model will give more accurate outcomes because a correction for weak acids can be applied. Secondly, a comparison between the micro meteorological measurements made at Speulder forest and the throughfall measurements will improve the quality of the canopy exchange model by improving the estimates of empirical parameters.

5. CONCLUSIONS

During one year between January and December 2001 throughfall measurements were made at 4 ICP Level-II plots in the Netherlands. The measurements were made with 10 gutters per plot, sample bottles were stored in light protected bottles at low temperatures, all to assure high quality results. Most of the fluxes could be used to estimate atmospheric deposition after the application of several quality checks. For the estimate of atmospheric deposition a canopy exchange model was applied and dry and wet deposition fluxes were calculated.

The deposition estimates from throughfall measurements show that there is an influence of forest characteristics, such as tree height and crown coverage, on the dry deposition flux. The higher the trees the higher the dry deposition flux. Dry deposition is higher for those components for which deposition depends mostly on the receptor surface and its roughness, such as sodium and ammonia. For the gases, which are not ideally absorbed at the canopy surface, such as SO₂ and NO_x the roughness effect is much less.

No hard evidence was found for strong reductions in deposition between 1995 and 2001 based on the deposition estimates derived from throughfall measurements. Because of the large uncertainties in the throughfall measurements long time series are needed or very big changes between the years are necessary to determine trends. The accuracy of the data can be improved by measuring DOC concentrations and by improving the canopy exchange model. A way to improve the model is to compare the years of throughfall measurements made at Speulder forest with the micro meteorological measurements done at the tower above the forest.

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