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Quality and uncertainty aspects of forest deposition estimation using throughfall, stemflow and precipitation measurements

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Preface

In order to gain a better understanding of the effects of air pollution and other stress factors on forests, a Pan-European Program for Intensive and Continuous Monitoring of Forest Ecosystems (the so-called Level II or Intensive Monitoring Program) has been implemented. In this context 858 permanent observation plots for intensive monitoring of forest ecosystems have now been selected (EC-UN/ECE, 1997), 501 in the European Union and 357 in several non-EU countries. The Pan-European Program is based on both the European Scheme on the Protection of Forests against Atmospheric Pollution (Council Regulation EEC no 3528/86) and the International Co-operative Program on Assessment and Monitoring of Air Pollution effects on Forests (ICP Forests) under the Convention of Long-Range Transboundary Air Pollution (UN/ECE). The aim of the Pan-European Program is to contribute to a better understanding of the impact of air pollution and other factors which may influence forest ecosystems. In the Program a number of surveys are executed on all plots, such as crown condition assessments, soil surveys, foliar surveys and increment studies. On a limited number of plots, deposition, soil solution and meteorological monitoring is performed. The monitoring started in 1994 and will extend over a period of at least 15-20 years. Details on sampling and analytical procedures are published in EU-Regulations and the manual of ICP Forests on methods and criteria for harmonised sampling, assessment, monitoring and analysis of the effects of air pollution on forests (UN-ECE, 1994).

Atmospheric deposition is currently monitored at 364 (in the near future at 489) intensive monitoring plots by means of throughfall, stemflow and precipitation sampling (EC-UN/ECE, 1997). The relevant EC Regulation and manual of ICP Forests (1994) give standard methods for sampling and analysis of throughfall, stemflow and precipitation. Through the Data Accompanying Report Questionnaires (DAR-Q's) the participating countries submitted information on the applied methods. In a first evaluation by FIMCI (EC-UN/ECE, 1997) a number of differences in methods have been reported. To the Expert Panel on Deposition the question has been raised on the comparability of data obtained by the different methods. This report gives information on how different measurement methods and interpretation procedures may influence the accuracy and comparability of the results. In part 1 the technical aspects of throughfall, stemflow and precipitation measurements are presented whereas the interpretation of the measurements in relation to forest deposition comes up for consideration in part 2. Potential error sources are identified and, if possible, quantified. In part 3 the uncertainty in forest deposition as determined from throughfall, stemflow and precipitation measurements is assessed by *i)* comparison with independent field and model data and *ii)* using error propagation techniques. The main objective of such an uncertainty analysis is to identify any shortcomings in the applied methods and procedures and to increase the comparability. The quality and uncertainty aspects of forest deposition monitoring described in this report are illustrated with recent results from the Speulder

forest research site in The Netherlands. Recommendations are made with respect to measurement methods, interpretation procedures and future research necessary to improve the quality and comparability of forest deposition assessment within the Intensive Monitoring Program.

This report is the outcome of research carried out by TNO Environment, Energy and Process Innovation (TNO-MEP) as part of the project 'Monitoring Dutch level II plots 1997-1999', commissioned by the National Reference Centre for Nature Management (IKC-Natuurbeheer) to TNO-MEP, ECN, SC-DLO, IBN-DLO and RIVM. Research has been financed by the Directorate Agriculture of the European Commission (DG VI/F.II.2) and IKC-Natuurbeheer.

Summary

When assessing forest deposition from throughfall, stemflow and precipitation measurements, relatively large errors may be associated with the technical aspects of the measurements (sampling strategy, sampling equipment, sample handling and analytical procedures) and the correction procedures necessary (e.g for the contribution of dry deposition to bulk precipitation fluxes and canopy exchange to throughfall and stemflow fluxes). A pre-study investigating the number of throughfall collectors needed given a certain accuracy interval and the necessity of stemflow measurements is recommended. Wet deposition should ideally be measured by means of wet-only samplers. If bulk precipitation samplers are used, short-term parallel wet-only and bulk measurements are recommended to estimate site-specific correction factors for the contribution of dry deposition onto bulk funnels. The collecting efficiency of the throughfall, stemflow and precipitation samplers should be optimized and measures should be taken to minimize sample contamination and biochemical transformations. After chemical analysis several verifying procedures have to be passed through to check the measured ion concentrations. Missing values need to be interpolated through the remaining dataset to obtain year-total throughfall, stemflow and precipitation fluxes.
For distinguishing atmospheric deposition and canopy exchange on the basis of throughfall, stemflow and precipitation fluxes several canopy budget models have been developed. In relation to the Intensive Monitoring Program, the so-called filtering approach may be considered most useful. Process-oriented research is necessary, however, to evaluate several assumptions underlying this approach. Canopy exchange and forest deposition of sulphur, sodium, chloride, magnesium, calcium and potassium can be estimated reasonably well from throughfall, stemflow and precipiation fluxes, if necessary in combination with canopy budget models. Unfortunately, up to now relatively large uncertainties are involved with the estimation of canopy uptake and dry deposition of oxidised and reduced nitrogen. Because the main goal of the Intensive Monitoring Program is to gain a better insight in the impacts of elevated deposition levels of SO_x, NO_y and NH_x on forest ecosystems, it is considered of major importance to perform additional research to improve oxidised and reduced nitrogen canopy uptake and dry deposition estimates for the Intensive Monitoring sites.
A field inter-comparison on sampling strategy, sampling equipment and sample handling is strongly recommended in order to further tune the technical aspects of the throughfall, stemflow and precipitation measurements performed within the Intensive Monitoring Program. Laboratories should regularly participate in inter-laboratory test to ensure good quality and comparability of the concentration measurements. Moreover, throughfall, stemflow and precipitation measurements should be interpreted in relation to forest deposition in a consistent manner. To enable this, guidelines for interpretation need to be developed or, otherwise, interpretation should be performed in a centralized manner. The uncertainty introduced by the use of different measurement methods, analytical procedures and interpreta-

tion methods need to be assessed in order to determine the quality and comparability of the results from the different monitoring sites. Uncertainty estimates are considered necessary for optimal interpretation of relationships derived between forest deposition and effect parameters. If state-of-the-art measurement methods, analytical procedures and interpretation procedures are used, the random and systematic error in forest deposition estimated from throughfall, stemflow and bulk precipitation data can be as low as 15-30% and 5-10%, respectively.

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PART 1 TECHNICAL ASPECTS OF THROUGHFALL, STEMFLOW AND PRECIPITATION MEASUREMENTS

Throughfall is the water dripping from leaves/needles and branches or falling through gaps in the canopy, whereas water running down tree trunks is called stemflow. Precipitation is the rain water falling in the open field. Throughfall, stemflow and precipitation water amounts and concentrations are necessary to calculate throughfall, stemflow and precipitation fluxes, respectively. Throughfall + stemflow fluxes are referred to as forest soil fluxes or forest soil loads and represent the chemical input to the forest soil. If measured using continuously open samplers, precipitation fluxes are referred to as bulk precipitation fluxes or bulk deposition fluxes. If measured using samplers which are only open to the atmosphere during precipitation events, they are referred to as wet-only deposition fluxes or just wet deposition fluxes. Wet deposition is defined as the process by which atmospheric pollutants are attached to and dissolved in cloud and precipitation droplets and delivered to the earth's surface by rain, hail or snow. Dry deposition is defined as the process where gases and particles are deposited directly from the atmosphere onto the earth's surface without the medium of hydrometeors. Cloud/fog deposition is the process where cloud and fog water droplets are directly intercepted by the earth's surface. Throughfall, stemflow and precipitation measurements can be used to estimate wet, dry and cloud/fog deposition. Procedures for this are described in part 2 of this report.

In this part of the report the technical aspects of throughfall, stemflow and precipitation measurements are discussed. These technical aspects include the sampling strategy (chapter 1.1), the collecting efficiency of the samplers (chapter 1.2), sample contamination and biochemical transformations (chapter 1.3), analytical procedures (chapter 1.4) and the interpolation of missing values (chapter 1.5). On the basis of these discussions some recommendations are made (chapter 1.6).

1.1 Sampling strategy

Throughfall

Throughfall measurements should be made in such a way that the results are representative for the site/area under consideration. This means that a sufficiently large number of samplers should be used and the samplers should be placed in such a way that the spatial variation in throughfall is covered (Beier and Rasmussen, 1989). It is generally recommended to use at least 10 randomly placed funnels with a diameter of 20 cm (Pylvänäinen, 1993; Lövblad, 1994). However, it should be realized that even in tall, homogeneous woodlands like e.g. the Speulder forest in The Netherlands, using only 10 randomly placed funnels can potentially result in an error of the throughfall flux of 15-48%, depending on the chemical component

considered (Table 1). In more open and heterogeneous forests this error will be even larger.

Table 1 *Maximum bias from the average as function of the number of throughfall funnels (in %).*

no. of funnels	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	K^+	PO_4^{3-}	HCO_3^-	H^+
24	3	2	3	3	3	2	2	1	6	3	5
23	5	4	6	5	4	3	3	3	9	5	8
22	8	5	8	8	6	5	5	4	13	7	11
21	9	6	9	10	8	6	6	5	17	8	14
20	10	7	10	11	9	8	8	6	20	10	17
19	11	7	11	12	10	9	10	7	23	12	20
18	12	8	12	12	11	10	11	8	25	14	23
17	13	9	13	13	11	10	12	10	28	16	25
16	14	9	14	14	12	11	13	11	30	18	27
15	15	10	15	15	13	12	14	12	32	20	28
14	16	11	16	16	14	13	15	13	34	22	30
13	17	12	17	17	15	14	15	14	36	24	31
12	18	13	19	18	16	15	17	15	39	26	34
11	20	14	21	20	18	17	18	17	43	28	38
10	23	15	23	22	20	18	21	18	48	30	43
9	25	16	26	25	22	20	23	19	53	34	48
8	28	18	28	28	24	22	25	20	59	34	53
7	31	20	31	32	27	25	28	22	65	37	60
6	35	23	35	36	31	28	31	24	72	38	64
5	40	27	40	42	35	31	32	25	79	40	69
4	47	31	47	50	41	33	33	27	87	42	75
3	56	38	58	56	44	36	34	29	95	48	81
2	60	41	64	60	49	37	34	33	108	56	90
1	63	42	76	67	62	40	35	34	141	61	110

Note: The reference values are the averages obtained with 25 funnels. Measurements were performed at the Speulder forest (The Netherlands) on a weekly basis in the period between October 1992 and August 1993. The Speulder forest research site consists of a 2.5 ha homogeneous monoculture of Douglas fir (Pseudotsuga menziessii), 35 year old with a stem density varying between 785 and 1250 trees ha^{-1} and a mean tree height of 21.5 m. The canopy is well closed with a one-sided LAI varying from 9 in early spring to 12 at the end of the summer. The forest is growing on a dry, sandy, podzolic soil.

Although throughfall is usually collected by means of funnels, throughfall gutters have the preference because they integrate over a larger canopy area yielding more representative estimates of the throughfall flux (e.g. Beier and Rasmussen, 1989; Van Ek and Draaijers, 1991). At the Speulder forest, smaller coefficients of variations were found for throughfall fluxes measured using 25 gutters in combination to throughfall fluxes measured using 25 funnels, Na^+, Cl^- and Mg^{2+} throughfall fluxes being the only exceptions (Table 2). Gutters will especially be beneficial to use in heterogeneous (species, tree age, canopy coverage) forests of relatively low stature. Another advantage of using gutters over funnels is that they are probably less vulnerable to bird droppings. At the Speulder forest, concentrations known to

be influenced by bird droppings, i.c. K^+, PO_4^{3-}, HCO_3^-, NH_4^+ and pH (Asman *et al.*, 1982), were found significantly smaller (t-test, one tailed; $p<0.05$) when throughfall was collected by gutters, NH_4^+ being the only exception (Table 2). NH_4^+ concentrations in throughfall were probably too high to be significantly altered by bird droppings.

Throughfall sampling at the Speulder forest by means of funnels and gutters.

Table 2 *Mean and standard deviation of throughfall fluxes (in mol ha^{-1}) measured at the Speulder forest using 25 funnels and 25 gutters, respectively.*

		SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	K^+	PO_4^{3-}	HCO_3^-	H^+
gutters	x	312.5	261.5	741.4	229.8	271.1	40.7	49.1	128.6	1.2	16.6	9.7
	s.d.	70.4	41.9	165.7	60.1	63.4	8.3	9.7	22.4	0.6	3.2	4.2
funnels	x	308.1	276.9	736.4	233.8	278.1	42.2	49.0	138.4	1.9	33.0	7.2
	s.d.	77.0	50.6	191.8	59.2	60.9	7.9	10.1	24.2	0.9	9.9	3.1

Note: Measurement period: October 1992 - February 1993. The collecting area of individual funnels and gutters amounted to 0.032 and 0.057 m^2, respectively. Funnels and gutters had no protection against birds sitting on top of them. A detailed description of the Speulder forest is given in the footnote to Table 1.

Stemflow

The contribution of stemflow to the total flux to the forest floor varies with tree species as well as with chemical component. The variability in stemflow contributions between tree species is caused to a large extent by differences in bark structure and the inclination of branches (Janssen, 1991). Johnson and Lindberg (1992) also found a major impact of stem density on the contribution of stemflow to the total flux to the forest floor. Within forest stands the tallest trees usually turn out to

supply the largest stemflow fluxes (Ivens, 1990; Janssen, 1991). In general, stemflow contributes less than 10% to the total flux to the forest floor, but for e.g. beech and dense pine stands the stemflow contribution may be considerably larger, i.e. up to 40% (Nicholson *et al.*, 1980; Alcock and Morton, 1981; Ivens, 1990). The contribution of stemflow was found strongly dependent on rain intensity and duration (Spranger, unpublished data). Stemflow can cause extreme soil acidification in the immediate surrounding of tree trunks (e.g. Skeffington, 1983; Wolfe *et al.*, 1987). For effect-related studies it may therefore be very useful to include stemflow measurements.
Stemflow can be measured by attaching spiral cords or collars around the base of tree stems. Considering the very large inter-tree variability of stemflow fluxes usually observed within forest stands (Parker, 1983; Spranger, 1992), stemflow should be measured from a large number of trees to obtain area representative estimates. The minimum number of 5 to 10 trees mentioned by Lövblad (1994) most probably needs to be considered as a rather conservative estimate in this respect.

Precipitation
Wet deposition onto a specific forest should be measured using wet-only samplers situated in a clearing near the forest to avoid systematic differences in meteorology and/or pollution climate. Wet-only samplers are funnels which are only open to the atmosphere during precipitation events. Continuously open funnels are often used to collect precipitation because wet-only samplers are expensive, require a power source which is not always available, and their rain sensors are relatively sensitive for disturbances (Graham *et al.*, 1988). The total flux to such open funnels is called bulk precipitation flux, and consists of wet deposition and dry deposition onto the funnels. Average correction factors for the contribution of dry deposition onto the funnels have been derived from parallel measurements with bulk samplers and wet-only samplers (Table 3). A considerable variability in the ratios between wet-only deposition and bulk precipitation fluxes can be observed. The amount of dry deposition onto bulk precipitation funnels will depend on local gas and aerosol concentrations, turbulence intensities and the collection efficiency of the samplers (Draaijers and Erisman, 1993; Van Leeuwen *et al.*, 1996). Gauger and Koeble (1998) found differences between wet-only deposition and bulk precipitation fluxes mainly related to sampler type, location and meteorological circumstances.

Table 3 *Annual mean ratio of wet-only deposition and bulk precipitation fluxes as measured at several locations in The Netherlands, Germany, Sweden, Italy and the United Kingdom.*

Location	Reference	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	K^+	PO_4^{3-}	H^+
Vredepeel, Netherlands	KNMI/RIVM (unpubl.)	0.83	0.83	0.77	0.82	0.80	0.72	0.80	0.34	n.a.	n.a.
Leiduin, Netherlands	KNMI/RIVM (unpubl.)	0.72	0.72	0.66	0.63	0.63	0.63	0.63	0.67	n.a.	n.a.
Biddinghuizen, Netherlands	KNMI/RIVM (unpubl.)	0.88	0.90	0.92	0.86	0.88	0.82	0.88	0.91	n.a.	n.a.
Witteveen, Netherlands	KNMI/RIVM (unpubl.)	0.87	0.88	0.83	0.92	0.92	0.85	0.92	0.68	n.a.	n.a.
De Bilt, Netherlands	Ridder et al. (1984)	0.74	0.78	0.77	0.77	0.83	0.65	0.45	0.71	n.s.	1.2
Arnhem, Netherlands	Ruijgrok et al. (1990)	0.81	0.88	0.78	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.17
Den Helder, Netherlands	Slanina et al. (1990a)	0.82	0.82	0.73	0.73	0.75	0.65	0.69	0.64	n.a.	1.16
Speulder forest, Netherlands	Van Leeuwen & Bleuten (1994)	0.88	0.89	0.98	0.91	0.94	0.84	0.71	0.74	n.a.	0.83
Bornhoved, Germany	Spranger (1992)	0.88	0.87	0.86	n.s.	n.s.	n.s.	0.74	0.49	n.s.	2.52
Waldhof, Germany	Gauger and Koeble (1998)	0.94	0.94	1.14	1.16	1.05	0.76	0.58	0.70	n.a.	1.02
Zingst, Germany	Gauger and Koeble (1998)	0.96	0.94	0.96	1.11	1.04	0.85	0.39	0.80	n.a.	1.45
Brotjackelriegel, Germany	Gauger and Koeble (1998)	1.08	0.97	1.03	1.07	1.18	0.97	1.04	0.53	n.a.	0.83
Deuselbach, Germany	Gauger and Koeble (1998)	1.03	0.91	1.00	0.95	0.98	0.62	0.55	0.59	n.a.	1.36
Schauinsland, Germany	Gauger and Koeble (1998)	0.78	0.71	0.68	0.78	0.77	0.44	0.49	0.28	n.a.	0.95
Neuglobsow, Germany	Gauger and Koeble (1998)	1.04	1.01	0.95	1.17	1.14	1.04	0.85	0.59	n.a.	1.09
Schmücke, Germany	Gauger and Koeble (1998)	1.00	0.93	0.99	0.89	0.90	0.97	0.89	0.77	n.a.	0.88
Rotenkamp, Germany	Gauger and Koeble (1998)	0.79	0.79	0.79	0.82	0.84	0.60	0.69	0.56	0.71	n.a.
Braunschweig-Völkenrode, Germany	Gauger and Koeble (1998)	0.73	0.76	0.77	0.77	0.76	0.53	0.53	0.69	0.65	n.a.
Neuenkirchen, Germany	Gauger and Koeble (1998)	0.77	0.72	0.82	0.66	0.80	0.61	0.71	0.86	0.63	n.a.
Erkerode, Germany	Gauger and Koeble (1998)	0.86	0.81	1.00	0.83	0.77	0.83	0.85	0.94	n.a.	n.a.
Elmwarte, Germany	Gauger and Koeble (1998)	0.86	0.84	0.95	0.86	n.a.	0.70	0.61	0.81	n.a.	n.a.
Drachenberg, Germany	Gauger and Koeble (1998)	0.76	0.79	0.80	0.92	0.79	0.54	0.58	0.46	0.65	n.a.
Lelm, Germany	Gauger and Koeble (1998)	0.71	0.66	0.87	0.65	0.76	0.47	0.59	0.64	0.70	n.a.
Wester-+Brunsbüttel, Germany	Gauger and Koeble (1998)	0.75	0.76	0.66	0.69	0.75	0.90	0.60	0.50	n.a.	n.a.
Bornhoved-2, Germany	Gauger and Koeble (1998)	0.92	0.83	0.71	0.86	0.91	0.80	0.60	0.49	n.a.	n.a.
Lübeck-Schönb., Germany	Gauger and Koeble (1998)	0.91	0.86	0.78	0.81	0.85	0.79	0.43	0.47	n.a.	n.a.
Britz, Germany	Gauger and Koeble (1998)	0.85	0.86	0.89	0.77	0.8	0.60	0.60	0.80	0.44	n.a.
Westerland, Germany	Gauger and Koeble (1998)	0.71	0.70	0.80	0.74	0.72	0.68	0.35	0.58	n.a.	1.03
Lake Gardsjon, Sweden	Grennfelt et al. (1985)	0.95	0.83	0.80	0.68	0.71	0.88	1.67	0.77	n.a.	n.a.
Pallanza, Italy	Mosello et al. (1988)	0.92	0.89	0.94	0.93	0.90	0.76	0.76	0.84	n.a.	1.02
Leeds, United Kingdom	Clark & Lambert (1988)	0.92	0.95	0.93	0.85	0.87	0.86	0.80	0.83	n.a.	0.99
Eskdalemuir, United Kingdom	Stedman et al. (1990)	0.91	0.98	0.97	0.82	0.82	0.82	0.76	0.77	n.a.	1.02
Stoke Ferry, United Kingdom	Stedman et al. (1990)	0.90	0.91	1.04	0.82	0.86	0.84	0.73	0.84	n.a.	0.91
Ludlow, United Kingdom	Stedman et al. (1990)	0.57	0.52	0.63	0.37	0.38	0.38	0.38	0.53	n.a.	0.65
Lough Navar, United Kingdom	Stedman et al. (1990)	0.85	0.95	1.34	0.81	0.80	0.81	0.68	0.85	n.a.	0.96
Barcombe Mills, United Kingdom	Stedman et al. (1990)	0.62	0.65	0.84	0.63	0.63	0.66	0.48	0.55	n.a.	0.69
Yarner Wood, United Kingdom	Stedman et al. (1990)	0.87	0.83	1.16	0.98	0.99	1.00	0.79	0.98	n.a.	0.78
High Muffles, United Kingdom	Stedman et al. (1990)	0.83	0.79	0.89	0.72	0.75	0.73	0.60	0.67	n.a.	0.85
Strathvaich Dam, United Kingdom	Stedman et al. (1990)	0.75	0.84	1.40	0.60	0.59	0.66	1.04	0.77	n.a.	0.62
Glen Dye, United Kingdom	Stedman et al. (1990)	0.72	0.74	0.83	0.53	0.56	0.56	0.63	0.59	n.a.	0.71
	Average	0.84	0.83	0.89	0.81	0.82	0.73	0.69	0.67	0.63	1.03
	Standard deviation	0.11	0.10	0.17	0.17	0.16	0.16	0.23	0.16	0.10	0.38
	Coefficient of variation (%)	13	12	19	20	19	22	34	24	16	37
	Minimum	0.57	0.52	0.63	0.37	0.38	0.38	0.35	0.28	0.44	0.62
	Maximum	1.08	1.01	1.40	1.17	1.18	1.04	1.67	0.98	0.71	2.52

Note: The large wet-only to bulk ratios sometimes observed by Stedman *et al.* for NH_4^+ could be explained by biochemical transformations in the bulk samplers (Stedman *et al.*, 1990). n.s. = no significant differences between wet-only and bulk samplers; n.a. = not analysed.

Wet deposition estimated from samplers located in the vicinity of each other usually shows small variability. Slanina *et al.* (1990b) found for major ions the annual wet deposition flux of one wet-only sampler deviating 2-13% at most from the mean of eight wet-only samplers (Table 4). Only for K^+ a larger bias was found which was explained by biochemical disturbances. It is recommended to install at least two parallel samplers, in order to decrease the risk of losing data due to contamination, and to obtain a larger quantity of solution for analysis during relatively dry periods (Lövblad, 1994). Another advantage may be that by acidification of one sample, heavy metals may be detected separately from the other chemical compounds. If possible, precipitation sampling should be performed in several clearings in order to minimize systematic errors. Spranger (1992) analyzed the spatial variability of bulk deposition fluxes at seven sites 50-2500 m apart, with two samplers each. The total variability was highest for PO_4^{3-}, Mn^{2+}, H^+, K^+ and Ca^{2+}, and lowest for Na^+, Cl^-, SO_4^{2-} and NO_3^-. The temporal variability of the differences between sites was found an indicator of the non-systematic variability due to shower pattern, sampling and chemical analysis. It was shown that these non-systematic variability's were highest for PO_4^{3-}, Mn^{2+}, K^+ and H^+, whereas Ca^{2+}, Mg^{2+}, K^+ and Mn^{2+} showed consistent differences between sites and were therefore strongly influenced by adjacent sources (e.g. road dust for Ca^{2+} and Mg^{2+}; vegetation for K^+ and Mn^{2+}).

Table 4 *Average bias from the average as function of the number of wet-only precipitation collectors (in %).*

no. of funnels	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	K^+	PO_4^{3-}	HCO_3^-	H^+
8	0.80	0.60	2.40	1.40	0.90	1.40	2.90	7.00	n.a.	n.a.	0.20
7	0.60	0.50	2.10	1.10	0.50	1.10	2.30	5.30	n.a.	n.a.	0.20
6	0.70	0.50	1.80	1.00	0.50	1.10	1.70	5.70	n.a.	n.a.	0.40
5	0.80	0.60	1.90	1.50	0.70	1.40	2.00	6.60	n.a.	n.a.	0.40
4	1.10	0.80	2.30	2.20	1.10	1.80	3.20	7.80	n.a.	n.a.	0.30
3	2.10	0.90	4.30	3.20	2.30	3.50	6.60	24.80	n.a.	n.a.	-0.30
2	5.20	1.60	9.40	7.70	6.30	9.70	13.30	65.50	n.a.	n.a.	-1.20
1	5.30	1.80	9.60	7.60	6.20	9.70	13.10	66.70	n.a.	n.a.	-1.10

Note: The reference values are the averages obtained with 8 collectors. Measurements were conducted at Lelystad (The Netherlands) on a weekly basis in the period between March 1983 and December 1985 (after Slanina *et al.*, 1990b). n.a. = not analysed.

In many areas, for example in northern Europe and at high altitudes, it may be necessary to sample snow as well. Especially in the open field it has been found very difficult to perform representative snow sampling (Sevruk, 1993). Relatively large uncertainties are associated with the estimation of precipitation amounts, especially at high wind speeds. Recently, however, special equipment has been designed for snow sampling under these circumstances (Lövblad, 1996). The concentration of pollutants in snow is possible to determine by sampling of the snow column, before any melting takes place.

1.2 Collection efficiency of the samplers

The amount of water collected by a sampler will be determined by its collection efficiency which, in turn, depends on the splashing and wetting loss as well as on its aerodynamic characteristics. Splashing loss may be important during high intensity rainfall and hail and can be minimized by using samplers with high rims and sufficiently steep funnel slopes, i.e. at least 45° (WMO, 1971). Wetting loss is caused by water adhering to the walls of the collector which subsequently evaporates. Allerup and Madsen (1980) estimated the wetting loss from bulk funnels on average 2-5% of the total precipitation amount, depending on funnel design and climatic conditions. In general, wetting loss from throughfall collectors will be small compared to the wetting loss from precipitation collectors. Precipitation collectors present an aerodynamic blockage causing air flow streamlines to divert away from the collector opening so that the trajectories of falling hydrometeors are displaced, leading to reduced catch. Wet-only collectors tend to be more massive than simple bulk collectors and generally suffer from poorer catch due to greater aerodynamic blockage (Lövblad *et al.*, 1993). The undercatch increases with windspeed and decreases with hydrometeor falling velocities, and thus is worst for snow in windy conditions. Sevruk *et al.* (1994) estimated the loss as a result of aerodynamic blockage 3-25% for rain and up to 100% for snow, depending on the shape of the precipitation collector and orifice rim, the thickness of the orifice rim, wind speed, and, most of all, on the situation of the collector in the open field. Wet-only collectors may be equipped with rain sensors which are not good enough to detect fine drizzle, leading to underestimation of precipitation amounts.
To minimize losses, the opening of the precipitation collector should ideally be placed at ground level, surrounded by an anti-splash grid (Sevruk and Hamon, 1984). For snow, a double-fence precipitation gauge can be used (Sevruk, 1993). Placing collectors at ground level, however, makes them less usable for collecting water for chemical analysis. For precipitation collection, wind shielded locations near the forest site are recommended (WMO, 1971). Grassland surrounded by trees seems most suitable for this purpose. However, one should take into account that near-by obstacles may have a certain impact on the air flow around the funnels and, consequently, on their collection efficiency. For this reason, funnels should be positioned at a distance of at least 4 times the height of the nearest porous obstacle and at a distance of at least 8 times the height of the nearest vast obstacle (WMO, 1971; Allerup and Madsen, 1980).
Due to relatively low wind speeds usually observed beneath forest canopies, the aerodynamic design of the throughfall sampler is less critical, except in case of very open stands. When using gutters for throughfall sampling, however, their collection efficiency should be compared to the collection efficiency of the funnels used for precipitation sampling. Throughfall gutters should be placed at an angle of at least 25° to horizontal to ensure good water discharge and to minimize wetting losses (Van Ek and Draaijers, 1994). Corrals or spiral cords used to collect stemflow should be made such that water overflow at high intensity rainstorms is prevented. Moreover, they must be firmly attached to the stem to prevent leakage. At

places where the cord/collar does not cling to the stem, the small gaps should be filled with silicone kit. Stemflow corrals should not be made too 'wide' to prevent the collection of a significant proportion of thoughfall (Rasmussen and Beier, 1986).

1.3 Sample contamination and biochemical transformations

When used to collect water for chemical analysis, precipitation samplers and throughfall gutters/funnels should be placed higher than 0.5m above the ground surface to prevent soil splash and to minimize dry deposition of blown-up soil dust. A 'bird ring' is recommended in order to prevent birds sitting on the top of the collector through which excrement's (droppings) may enter the sample. To avoid contamination by e.g. coarse litter fragments, insects and pollen, throughfall, stemflow and bulk precipitation should be filtered before entering a reservoir. A filter with a minimum mesh width of 250 µm is recommended, as smaller mesh widths most probably will significantly reduce the collecting efficiency due to evaporation (Ridder *et al.*, 1985; Slanina *et al.*, 1987). Mentioned contaminants are potentially subject to adsorption and/or desorption processes (Peden and Skowron, 1978). Binding to litter debris was mentioned as a possible cause of reducing N concentrations during storage (Ferm, 1993), whereas mineralization of organic matter was suggested to cause increasing concentrations (Slanina *et al.*, 1990a; Van Leeuwen and Bleuten, 1994). Branding (1995), however, found no significant differences between throughfall sampled by means of funnels and litter traps. Experiments performed by e.g. Doskey and Ugoagwu (1989) and Draaijers (1993) suggest that in spring pollen may have a measurable impact on throughfall composition. K^+, PO_4^{3-} and SO_4^{2-} concentrations were found increased most. Annual throughfall fluxes, however, were not significantly influenced by pollen deposition (Van Ek and Draaijers, 1994).
Using wet-only throughfall samplers will prevent contamination by litter fragments, micro-organisms and pollen as well as dry deposition directly onto the sampling device. Richter and Lindberg (1988) found in a Chestnuk oak forest in a remote area in the USA, however, negligible differences in SO_4^{2-}, Ca^{2+} and K^+ concentrations between continuously open and wet-only throughfall funnels. Surprisingly, significantly smaller H^+ and NO_3^- concentrations were observed in the bulk funnels. Biochemical transformation in the sample bottles seems the major cause for this as differences were especially distinct in the summer period, and wet-only samples were collected immediately after each precipitation event and bulk samplers at 5-weekly intervals (Richter and Lindberg, 1988). Slanina *et al.* (1990a) found in a Douglas fir forest near Kootwijk (The Netherlands) no significant differences between SO_4^{2-}, NO_3^- and NH_4^+ fluxes measured with continuously open and wet-only throughfall funnels. Similar results were obtained by Van Leeuwen and Bleuten (1994) at the Speulder forest using bulk and wet-only gutters. This suggests that sample contamination and dry deposition onto the sample device is of

no or only limited importance for the throughfall composition. However, the representativity of mentioned investigations may be questioned.
Results from experiments performed by Ridder *et al.* (1985), Draaijers (1993) and Buijsman (1994) indicate that concentrations may change during storage. Concentrations of NH_4^+, NO_3^- and PO_4^{3-} in throughfall (Draaijers, 1993), and NH_4^+ and PO_4^{3-} in precipitation (Ridder *et al.* 1985; Buijsman, 1994), were found significantly lowered, most probably as a result of algae present in the sample bottles. Algae take up nitrogen and phosphorus for their growth. Bacteria present in the sample bottles may cause nitrification through which part of the NH_4^+ is transformed to NO_3^- and H^+ is produced, as well as denitrification through which NO_3^- is transformed to N_2 and N_2O which subsequently degas. Especially N compounds seem vulnerable to transformation during storage. Both increasing and decreasing concentrations can be found, depending on what kind of algae, bacteria and litter fragments are present in the sample bottles. Also the amount of oxygen (aerobic or anaerobic circumstances) in the sample bottles seems relevant. Cool sample bottles protected from direct sunlight will to a large extent prevent the growth of algae and bacteria. This can be achieved by storing the sample bottles in a pithole and covering them by e.g. aluminium foil, and/or by using a dark tube below the funnel (Block and Bartels, 1984; Spranger, 1992). The use of preservatives can diminsh biochemical transformation. An effective, non-volatile preservative should be used, which does not interfere with the analysis of any ion of interest, e.g. HgI_2. When using such a preservative samples should be treated like chemical waste.
Material used for sampling must be chemically inert, i.e. must not chemically react with the water sample. Throughfall gutters, stemflow corrals, precipitation funnels, snow collectors, sample bottles, filters etc. should be cleaned after each sampling period by repeated washing (at least three times) by means of de-ionized water (Ridder *et al.*, 1985; Slanina *et al.*, 1990b). If heavy metals are studied, pre-rinsing of the sample bottles with diluted nitric acid (0.1M) is recommended. To minimize biochemical transformations by algae and bacteria, contamination by bird droppings as well as evaporation from the sample bottles and snow collecting gauges, samples should be stored in the field no longer than one week (Slanina *et al.*, 1990a).

1.4 Analytical procedures

For satisfactory sample preservation, samples should be stored in the laboratory in darkness below 4 °C until analysis (Ridder *et al.*, 1985). The storage period should be kept as short as possible and certainly less than one week. Preferably, samples should be analyzed for acidity and electric conductivity in the field or within 24 hours of sampling. Ion concentrations should be measured within one week of sampling (Slanina *et al.*, 1987). Directly after chemical analysis, measured ion concentrations should be verified by *i)* checking the balance between the sum of all anions and cations, respectively, *ii)* comparing measured conductivity's with those calculated from ion concentrations and ion-specific activity coefficients, and *iii)*

checking for extreme values and discrepancies in the covariation between ions, samplers and between stations. First two verifying procedures will only give a reliable indication of the data quality if all major constituents are measured. If necessary, chemical analysis must be repeated as soon as possible.
Parameters for analysis within throughfall monitoring programs usually include conductivity, pH, alkalinity (if median pH > 5), SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Cl^-, Mg^{2+}, Ca^{2+}, K^+ as well as Kjehldahl-N which gives the sum of inorganic and organic nitrogen. PO_4^{3-} is often analyzed because it indicates contamination due to bird droppings. Sometimes also parameters such as Al^{3+}, Fe^{2+}, Mn^{2+} and heavy metals like Cu^{2+}, Zn^{2+}, Hg^{2+}, Pb^{4+}, Cd^{2+}, Co^{3+} and Mo^{4+} are analyzed (Lövblad, 1994; Lindberg *et al.*, 1994). The laboratory should use well defined sample treatment and analytical procedures according to European standards for good laboratory practice. The regular analysis of reference samples is recommended. Short-term repetition of analysis in the same laboratory, using the same sample treatment and analytical method, shows that the analytical error for major ions is usually less than 5% (Diederen, 1988). Concentrations are found less reliable, i.e. repeatable, when they are close to the detection limit of the analyzing equipment. In that case analytical errors up to 20% may arise (Diederen, 1988; Draaijers, 1993).
To ensure good quality of the concentration measurements, the laboratory should also regularly participate in inter-laboratory tests. In Table 5 results are presented of inter-laboratory tests performed by Diederen (1988) and Mosello *et al.* (1994). Samples A and B in the study of Diederen (1988) have concentrations more or less similar to those usually observed in throughfall in The Netherlands. Concentrations observed in samples C and D of Diederen's study and in samples A and B of Mosello's study may be considered representative for precipitation in large parts of Europe. As might be expected, differences between laboratories increase with decreasing concentrations. For throughfall concentrations, the maximum deviation between laboratories is generally found less than 20%, whereas for precipitation concentrations deviations up to 90% are observed. Accurate analysis seems especially difficult for alkalinity and sodium, chloride and magnesium concentrations.

Table 5 *Results from an inter-laboratory test in which 8 Dutch laboratories participated (after Diederen, 1988) and results from an inter-laboratory test in which altogether 98 laboratories participated: 53 from Italy, 10 from Spain, 5 each from Switzerland and France, 4 each from Austria and Uruguay, 3 each from Argentina and the Czech Republic, 2 from Portugal, 1 each from Albania, Great Britain, Greece, Eire, Norway, Russia, Slovene, Finland and Poland (after Mosello et al., 1994).*

	Cond.	pH	Alk.	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	K^+
Diederen (1988)											
Average concentration (n=8)											
sample A	n.a.	n.a.	n.a.	1577	1207	3089	1007	1210	239	186	817
sample B	n.a.	n.a.	n.a.	641	331	1121	421	442	82	56	279
sample C	n.a.	n.a.	n.a.	150	82	252	114	99	17	12	66
sample D	n.a.	n.a.	n.a.	55	29	112	24	36	8	4	22
Max. dev. between laboratories (%)											
sample A	n.a.	n.a.	n.a.	6	14	12	9	17	17	16	6
sample B	n.a.	n.a.	n.a.	6	10	8	10	12	12	29	7
sample C	n.a.	n.a.	n.a.	13	11	9	9	27	9	14	10
sample D	n.a.	n.a.	n.a.	42	10	9	21	74	29	19	13
Mosello et al. (1994)											
Average concentration (n=98)											
sample A	98	3.7	0.17	153	16	76	30	55	16	26	11
sample B	24	4.4	0.07	36	2	22	8	27	7	9	5
Max. dev. between laboratories (%)											
sample A	9	1	60	7	13	7	9	24	26	8	9
sample B	13	2	90	11	17	13	22	32	61	11	19

Note: Besides the average concentration of the samples, the maximum deviation between laboratories with 95% confidence interval is presented. The latter is calculated as (UCL95-LCL95)/AVG, where UCL95 and LCL95 represent the upper and lower 95% confidence limit, respectively, and AVG the average concentration. Electric conductivity (Cond.) in $\mu S.cm^{-1}$; alkalinity and ion concentrations in $\mu mol.l^{-1}$.
n.a. = not analysed.

Results of an interlaboratory test on heavy metals in precipitation samples performed within the framework of the HELCOM, PARCOM, EMEP and AMAP monitoring Programs are presented by Winkler and Roider (1997). In total 15 laboratories from different countries participated and depending on component between 500 and 800 samples were analysed. Even when outliers were excluded, the scatter between the participant was found very large. Only 30-60% of all the samples analysed was falling in the range of ±25% of the mean and 1-13% of the samples had deviations larger than 100%. Largest deviations were found for chromium and nickel which was traced back to the reduced solubility of these heavy metals. Somewhat better comparability was observed for arsenic, cadmium, copper, lead and zinc.

1.5 Missing values

In every throughfall, stemflow and precipitation monitoring program some data will be missing e.g. as a result of damaged collecting equipment due to vandalism (humans and/or animals) or gales, or will not be usable due to bird droppings. If samples are not pooled, missing values can be interpolated through the remaining data set by using the strong spatial correlation's usually observed between collectors situated in the vicinity of each other in the same stand (Draaijers, 1993; Van Leeuwen and Bleuten, 1994). Seasonal variations in these correlation's should be taken into account.

1.6 Recommendations

When starting throughfall monitoring at a forest site, a pre-study should be carried out to find the number of throughfall collectors needed given a certain uncertainty interval. Throughfall can be sampled for one or two months by means of a large number of collectors (e.g. 25 or more depending on the height, openness and homogeneity of the forest stand), placed randomly. During such a pre-study, throughfall fluxes need to be determined for each collector individually. For monitoring "representative" throughfall collectors need to be selected. It is recommended that a pre-study determining the amount of throughfall collectors needed, also includes investigating the need of stemflow measurements in the final sampling program and, if so, how many and which trees need to be sampled. A first indication if stemflow contributes significantly to the total flux to the forest floor may be obtained by measuring, in addition to throughfall fluxes, stemflow fluxes from several relatively tall trees during rainfall events with high intensity and/or duration. For monitoring stemflow a selection of "representative" (not only the tall) trees need to be made. Stemflow measurements are definitely needed in beech and dense pine forests. It is recommended to measure wet deposition by means of two parallel wet-only samplers placed in a wind shielded location near the forest site. If bulk samplers are used short-term parallel wet-only and bulk measurements are recommended to estimate site-specific correction factors for the contribution of dry deposition onto the funnels.
The collecting efficiency of the throughfall, stemflow and precipitation samplers should be optimized and measures should be taken to minimize sample contamination and biochemical transformations during storage. When using gutters for throughfall sampling their collection efficiency should be compared to the collection efficiency of the funnels used for precipitation sampling. To avoid soil splash and to minimize dry deposition of blown-up soil dust, samplers should be placed higher than 0.5 m above the ground surface. To avoid contamination with litter fragments, insects etc., throughfall, stemflow and precipitation should be filtered before entering a reservoir. A filter with a mesh width of 250 μm is recommended. To prevent the growth of algae and bacteria, samples should be stored in a pithole covered by e.g. aluminum foil and/or by using a dark tube below the funnel. It is

recommended to store samples in the field no longer than one week to avoid the necessity of using preservatives. In the laboratory samples should be stored in darkness below 4 °C until analysis which should take place within one week of sampling. The laboratory should use well defined sample treatment and analytical procedures according to European standards for good laboratory practice, and should regularly participate in inter-laboratory tests to ensure good quality of the concentration measurements. Directly after chemical analysis, measured ion concentrations should be verified by *i)* checking the balance between the sum of all anions and cations, respectively, *ii)* comparing measured conductivities with those calculated from ion concentrations and ion-specific activity coefficients, and *iii)* checking for extreme values and discrepancies in the covariation between ions, samplers and between stations to detect for example bird droppings. If necessary, chemical analysis must be repeated as soon as possible. To obtain year-total fluxes, missing values (both concentrations and amounts) should be interpolated through the remaining dataset by using the strong spatial correlation usually observed between collectors situated in the vicinity of each other, taking into account seasonal variations in these correlations.

PART 2 PROCEDURES FOR ESTIMATING DEPOSITION

After interpolation of missing values, precipitation fluxes for each sampling period can be calculated by multiplying rainfall concentrations with rainfall amounts. Similarly, throughfall fluxes can be calculated by multiplying throughfall concentrations with throughfall volumes, and stemflow fluxes by multiplying stemflow concentrations with stemflow amounts. Bulk precipitation fluxes should be corrected for dry deposition onto the collectors to obtain wet deposition amounts. Net throughfall fluxes can subsequently be estimated by subtracting wet deposition amounts from throughfall and stemflow fluxes. The contribution of canopy exchange to net throughfall must be quantified to obtain and estimate for dry and fog/cloud deposition. Adding wet to dry+fog/cloud deposition gives an estimate for the total deposition to the forest. Following guidelines mentioned in the so-called Mapping Manual (TFM, 1996) total deposition of potential acid, $[TD_{pa}]$, can subsequently be calculated according to (in mol ha^{-1} yr^{-1}):

$$[TD_{pa}] = 2*[SO_4^*] + [NO_3] + [NH_4] - 2*[Mg^*] - 2*[Ca^*] - [K^*]$$

where $[SO_4^*]$ denotes the total deposition of sulphur compounds corrected for the contribution of sea salt, $[NO_3]$ the total deposition of oxidised nitrogen compounds and $[NH_4]$ the total deposition of reduced nitrogen compounds. $[Mg^*]$, $[Ca^*]$ and $[K^*]$ represent the total deposition of magnesium, calcium and potassium corrected for the contribution of sea salt. Sea salt correction factors based on the composition of sea water have been derived by Asman *et al.* (1982). With respect to soil acidification it is assumed that 1 mol of SO_4 is forming 2 moles of H^+, and 1 mol of NO_3 and NH_4 each 1 mol of H^+. NH_4 is assumed to contribute fully to soil acidification through the process of nitrification in the soil (Van Breemen *et al.*, 1982). Under the influence of oxygen, nitrifying bacteria may transform reduced nitrogen compounds in the soil into nitrate and acid. If NH_4 is completely nitrified and leached from the ecosystem the potential acid load equals the actual acid load. The contribution of HCl, HF, PAN and organic acids to the total deposition of potential acid is assumed negligible.

In this part of the report first the theory of canopy exchange is given (chapter 2.1) followed by an overview of available canopy budget models to distinguish canopy exchange and atmospheric deposition on the basis of throughfall, stemflow and precipitation measurements (chapter 2.2). In chapter 2.3 a very useful model (the so called 'filtering approach') is described in more detail. The estimation of canopy uptake and dry deposition of nitrogen is dealt with in chapter 2.4. The possible contribution of dry deposition directly to the forest floor and understorey vegetation is discussed in chapter 2.5. Chapter 2.6 presents recommendations for forest deposition estimation from results of throughfall, stemflow and precipitation measurements.

2.1 Canopy exchange processes

Throughfall fluxes are found to be influenced by passive diffusion and ion exchange between the surface water and the underlying apoplast of canopy tissues. Passive diffusion is found to be the major cause of elevated anionic concentrations in throughfall while both diffusion and ion exchange contribute to cationic concentrations in throughfall (Schaefer & Reiners, 1990). The rate of canopy exchange depends on tree species and ecological setting. For example, during the growing season deciduous tree species tend to lose more nutrients from the crown foliage through leaching than coniferous tree species. Conifers, however, stay green all the year round and continue to lose nutrients throughout the dormant season (Smith, 1981). The age distribution of leaves and soil nutrient status also affect the magnitude of leaching to a large extent. Young immature leaves/needles tend to lose much more nutrients compared to older ones (except when they are hydrophobic; Parker, 1990), and fertilisation is found to enhance canopy leaching considerably (Matzner *et al.*, 1983). Biotic stresses like insect plagues may initiate large canopy leaching. Bobbink *et al.* (1990) monitored throughfall in a heather vegetation and observed a marked increase of canopy losses occurring simultaneously with an outbreak of a heather-beetle plague. Furthermore, abiotic stresses like drought and temperature extremes are found to enhance canopy leaching (Tukey & Morgan, 1963). The presence of certain pollutants may also be of importance. Large concentrations of ozone, for example, were found to enhance the permeability of cell membranes in canopy foliage, thereby increasing ion leakage (Evans & Ting, 1973). Moreover, the amount and timing of precipitation is found to be relevant with respect to canopy leaching. Relatively long residence times during drizzle account for relatively high leaching rates compared to short rain periods with large rainfall intensities. Large rain amounts may deplete leachable pools within the canopy, thereby inhibiting ion leaching (Lovett & Lindberg, 1984). Losses from leachable pools within the canopy are believed to be replenished within 3-4 days after a large storm by increased root uptake or translocation from other parts of the tree (Parker, 1983).

Sulphur compounds

SO_2 may be taken up by the stomata. If a significant part of the SO_2 is retained in the foliage and translocated from the canopy to the roots, this would result in an underestimate of sulphur deposition by measuring throughfall. Gay & Murphy (1989) found that up to 70% of the SO_2 absorbed by foliage during short-term experimental exposures could not subsequently be removed by washing. However, Schaefer & Reiners (1990) and Granat & Hällgren (1992) conclude that essentially all of the dry deposited sulphur dioxide is eventually extracted out of the apoplast pools (i.e. aqueous layer on the outside of cell membranes) by rain and appears in throughfall.

Fowler & Cape (1983) and Cape *et al.* (1987) compared net throughfall measurements in a Scots pine stand with estimates of SO_2 dry deposition using eddy correlation techniques. For a 71-day spring period, SO_2 dry deposition appeared to be

equal to the net throughfall flux of sulphate. For a 84-day autumn period, SO_2 deposition only accounted for 8% of the sulphur flux in net throughfall. The latter observation led Fowler & Cape (1983) to the conclusion that canopy leaching is a major component of the net enrichment in throughfall. According to Ivens (1990), this large difference between both estimates in the autumn period can also be explained by the omission of dry particulate sulphur deposition which can make up 30% of the total sulphur deposition (Lindberg *et al.*, 1986), and by sulphur leaching from senescent leaves, which also has been observed by Meiwes & Khanna (1981). Based on a comparison of throughfall data with deposition measurements of SO_2 and particulate sulphate on a large number of sites throughout the Unites States (Integrated Forest Study, IFS), Lindberg *et al.* (1990) and Johnson & Lindberg (1992) conclude that foliar leaching of SO_4^{2-} contributed maximally 15% to the net throughfall flux of sulphate.

Several radioactive $^{35}SO_4^{2-}$ studies have been conducted to evaluate the applicability of the throughfall method to estimate sulphur deposition (Garten *et al.*, 1988; Lindberg & Garten, 1989; Cape *et al.*, 1992; Wyers *et al.*, 1994). Garten *et al.* (1988) added radiolabelled SO_4^{2-} through single-stem well injection into the internal nutrient store of two Red Maple and two Yellow Poplar trees and analysed the amount of radiolabelled SO_4^{2-} and total sulphate present in throughfall. During a 104-day period in the growing season, less than 10% of the net throughfall flux of sulphate could be accounted for by foliar leaching. Similar experiments with several individuals of Loblolly pine trees led to the same conclusion (Lindberg & Garten, 1989). Because the experiments conducted by Garten *et al.* (1988) and Lindberg & Garten (1989) were performed on isolated trees or trees situated at forest edges, the contribution of canopy leaching to net throughfall fluxes measured by these experiments may be larger in forest interiors (Fowler *et al.*, 1992).

Cape *et al.* (1992) applied radioactive sulphate to the soil below a closed Scots pine forest canopy during a four month period in summer. Results suggest (assuming rapid equilibrium of $^{35}SO_4^{2-}$ with sulphate in the soil) that root-derived sulphate contributed approximately 3% of sulphate in net throughfall and that dry deposition of SO_2 and sulphate particles contributed 97% to the total net throughfall flux of sulphate. However, there were some indications that equilibrium could not be safely assumed. For this reason, the possibility of a significant contribution of soil-derived sulphate to sulphate deposition in net throughfall could not be ruled out on the basis of this experiment (Cape *et al.*, 1992).

At catchments at Lake Gardsjön on the Swedish west coast forested with Norway spruce, the deposition and watershed output has been studied during a period of 10 years by means of throughfall, precipitation and runoff measurements (Hultberg, 1985; Hultberg & Grennfelt, 1992). Runoff and throughfall sulphate fluxes were found to be very similar, suggesting uptake of sulphur by tree roots and transport to the tree canopy being of minor importance. Moreover, sulphate fertilisation in several catchments did not enhance sulphate throughfall fluxes significantly, supporting the hypothesis that sulphate throughfall provides a reasonable good measure for sulphur (SO_2 + SO_4^{2-} aerosol) deposition (Hultberg & Grennfelt, 1992). Similar

conclusions were drawn by Likens *et al.* (1990) for catchments covered with deciduous forest at Hubbard Brook (USA).

Nitrogen compounds

Present knowledge on canopy exchange of nitrogen compounds is limited due to the complexity of the exchange processes involved. Up to now, leaching of inorganic nitrogen from forest canopies has not been reported in the literature. On the contrary, numerous reports indicate that inorganic nitrogen may be taken up by canopy foliage, stems, epiphytic lichens or other microflora. Canopy foliage has been demonstrated experimentally to be capable of absorbing and incorporating gaseous NO_2 , HNO_3 and NH_3 as well as NO_3^- and NH_4^+ in solution (Reiners & Olson, 1984; Bowden *et al.*, 1989). In laboratory experiments, NH_4^+ in solution was found to be exchanged with base cations present in leaf tissues (Roelofs *et al.*, 1985). Epiphytic lichens were also shown to be active absorbers of NO_3^- and NH_4^+ in solution (Lang *et al.*, 1976; Reiners & Olson, 1984).

Based on information available in the literature, Ivens (1990) suggested the above ground uptake of total inorganic nitrogen by forests to be between 150 and 350 $eq.ha^{-1}.yr^{-1}$, not clearly related to tree species. Within the Integrated Forest Study, Johnson & Lindberg (1992) measured throughfall and stemflow fluxes of NO_3^- and NH_4^+ in several forest stands scattered over the United States. Simultaneously, dry deposition amounts of NO_2, NO, HNO_3, HNO_2, NO_3^-, and NH_3 and NH_4^+, respectively, were estimated. Moreover, wet and cloud water deposition fluxes of nitrate and ammonium were determined. Canopy retention of inorganic nitrogen was estimated by total deposition (dry + wet + cloud water) minus soil flux (throughfall + stemflow). It was concluded that, on average, 40% of all inorganic nitrogen input to forests was retained by the vegetation, whereas 60% was found back in the throughfall as NO_3^- and NH_4^+. (Johnson & Lindberg, 1992). Total inorganic nitrogen uptake amounted up to 850 $eq.ha^{-1}.yr^{-1}$, with a strong positive relationship between deposition and uptake for spruce and spruce-fir stands. Other tree species showed a rather constant inorganic nitrogen uptake (200-300 $eq.ha^{-1}.yr^{-1}$), with only little response to deposition amount (Johnson & Lindberg, 1992).

In the same study, part of the inorganic nitrogen retained by the canopy was supposed to be converted into organic substances and subsequently leached. Total nitrogen (organic + inorganic) in throughfall and stemflow was about 84% of the total inorganic nitrogen deposition (Johnson & Lindberg, 1992). Microbes were assumed to play an important role in the conversion of inorganic to organic N, if it occurs. However, it was recognised that organic N in throughfall also arises from internal pools and surfaces of plants and lichens, and from microparticulate detritus and pollen (Johnson & Lindberg, 1992). Atmospheric deposition of organic nitrogen compounds is estimated to be small, i.e. < 100 $eq.ha^{-1}.yr^{-1}$ (Beringen *et al.*, 1992). Carlisle *et al.* (1966) reported for a *Quercus petraea* stand an organic nitrogen throughfall flux of ± 350 $eq.ha^{-1}.yr^{-1}$. Similar or somewhat larger throughfall fluxes of organic nitrogen were measured by Alenäs & Skärby (1988) in *Picea abies* forest stands.

More insight has been gained on nitrogen uptake by tree canopies by performing experiments with radiolabelled ^{15}N. Bowden *et al.* (1989), for example, simulated cloud water deposition by fumigating *Pinus rubens* seedlings with a fine water spray. Essentially, they conclude that the total uptake of NH_4^+ and NO_3^- ions from cloud water is small compared to the amount of nitrogen required to create new growth. Foliar retention of $^{15}NH_4^+$ appeared to be larger compared to uptake of $^{15}NO_3^-$. Garten & Hanson (1990) applied radiolabelled NH_4^+ and NO_3^- to *Acer rubrum* and *Quercus alba* through simulated rain. They concluded that $^{15}NO_3^-$ deposited to deciduous tree leaves is easily removed by washing with water, while $^{15}NH_4^+$ is retained and presumably assimilated into the leaf. Experiments with radiolabelled ^{15}N made by Vose *et al.* (1989) show that foliar uptake of dry deposited HNO_3 is small.

Sodium and chloride

Although Fassbender (1977) reported some sodium uptake by young spruce trees during his laboratory experiments, sodium and chloride are normally considered to be more or less conservative elements showing only minor canopy exchange (Parker, 1983). In Germany, Bredemeier (1988) found a clear downwards gradient with increasing distance from the North Sea in sodium and chloride in bulk precipitation as well throughfall, indicating a major contribution of sea-salt particles to these fluxes. Ivens (1990) found a strong correlation between sodium and chloride in both bulk precipitation and throughfall samples, respectively, compiled from all over Europe. Sodium and chloride were found to occur in the same molar ratio as in sea water, i.e. 0.86. Moreover, sodium in throughfall was linearly related to sodium in bulk precipitation with an intercept of the regression line not significantly different from zero, suggesting nil canopy exchange (Ivens, 1990). Based on a comparison of throughfall data with deposition measurements on a large number of sites in the United States, Johnson & Lindberg (1992) also conclude that Na^+ in throughfall may be considered as solely derived from atmospheric deposition. All these studies show the inertness of Na in the canopy.

Magnesium, calcium, potassium and phosphate

A substantial part of magnesium, calcium and potassium in throughfall is normally caused by canopy leaching (Parker, 1983). These ions are leached in association with foliar excretion of weak organic acid anions (Tukey, 1980; Hoffman *et al.*, 1980) or through exchange with H^+ and NH_4^+ in leaf tissues (Roelofs *et al.*, 1985). K^+ is found to be relatively more susceptible to canopy leaching compared to Mg^{2+} and Ca^{2+} because it is not so tightly bound in structural tissues or enzyme complexes (Wood & Bormann, 1975). A literature compilation made by Parker (1990) indicates that it is not clear to which degree these base cations present in throughfall originate from atmospheric deposition and foliar leaching, respectively. Canopy leaching contributed between 10% and 80% to the total flux of these base cations reaching the forest floor. At coastal forest sites, magnesium in throughfall was predominantly caused by atmospheric deposition of sea-salts (Parker, 1983). Johnson & Lindberg (1992) suggest that calcium in throughfall may be enhanced at

sites located in areas with calcareous soils or near calcium fertilised arable land. Observations done by White & Turner (1970), Abrahamson *et al.* (1976) and Alcock & Morton (1981) suggest that magnesium and calcium may also be irreversibly retained within the canopy. Ivens (1990) hypothesises that canopy uptake may occur if tree canopies suffer from base cation deficiencies due to limited cation supplies from the soil.
Negligible amounts of phosphorus in ambient air suggest that canopy leachates contribute more than 90% to throughfall phosphate (Parker, 1983). Minor amounts of phosphate in throughfall may originate from soil dust, especially in forests situated near fertilised arable land. Furthermore, bird droppings may contribute to phosphate in throughfall (Van der Maas *et al.*, 1990; Ivens, 1990).

Hydrogen
Deciduous stands in regions remote from acid precipitation are usually found to have a higher throughfall pH in comparison to incident precipitation indicating canopy retention of protons (Parker, 1983). There are, however, a number of exceptions to this rule, especially at high acid deposition rates (e.g. Künstle *et al.*, 1981; Skeffington, 1983). For coniferous stands, reports of higher throughfall pH (e.g. Abrahamsen *et al.*, 1976; Miller, 1984) are as common as reports of lower pH (Parker, 1983).
In polluted areas remote from ammonia emission sources, throughfall is generally more acid than bulk precipitation (Georgii *et al.*, 1986; Bredemeier, 1988). In The Netherlands, the proton flux under the forest canopy is found to be smaller than in the open field (Van Breemen *et al.*, 1982; Houdijk, 1990; Ivens, 1990). This is attributed to canopy uptake of protons through exchange with cations like magnesium, calcium and potassium, and to the neutralising effect of dry deposition of ammonia onto the water layers present on the tree surface (Ivens, 1990).

Bicarbonate and organic compounds
Bicarbonate in throughfall is usually found in regions away from acidified precipitation where it originates from atmospheric CO_2 (Cronan, 1978). In such regions, bicarbonate may even be the dominant anion because leachate cations commonly transfer as bicarbonate salts (Tukey, 1970). Partly, bicarbonate in throughfall may originate from canopy leaching of carbon or bird droppings (Parker, 1983).
A variety of organic compounds including sugars, amino acids, organic acids, hormones, vitamins, pectic and phenolic substances are probably leached from the canopy but difficult to measure due to their low stability in throughfall water and their high volatility (Parker, 1990).

2.2 An overview of canopy budget models

Several models have been developed to estimate canopy exchange and atmospheric deposition solely on the basis of throughfall and precipitation measurements. For

example, monitoring throughfall and precipitation fluxes on an event basis allows the application of the regression model developed by Lovett and Lindberg (1984). This empirical model is based on the calculation of a multiple regression using event net throughfall (NTF) as the dependent variable and the duration of the antecedent dry period (DDP) and precipitation amount (P) as independent variables:

$$NTF = b_1 * DDP + b_2 * P.$$

The regression coefficients (b_1 and b_2) represent the mean dry deposition and canopy exchange rate, respectively. If information on the total duration of dry periods and the annual rainfall amount is available, these coefficients can be used to calculate yearly mean dry deposition and canopy exchange amounts. The model has proven very valuable for estimating canopy exchange and atmospheric deposition in forests situated in areas with convective storms and extended dry weather periods (e.g. Lovett and Lindberg, 1984; Puckett, 1990), but was found less useful in areas characterized by frequent low-intensity rainfall and relatively short dry periods (Lindberg *et al.*, 1990; Ivens, 1990; Draaijers *et al.*, 1994b).
An alternative to regression modeling is application of the canopy budget model developed by Ulrich (1983) which was extended by Bredemeier (1988) and Van der Maas and Pape (1991). This model allows a discrimination between canopy exchange and atmospheric deposition using long-term throughfall and precipitation fluxes. Dry deposition and canopy leaching of Ca^{2+}, Mg^{2+} and K^+ is computed by means of the so-called 'filtering approach', assuming a fixed relationship between wet and dry deposition of particles and taking Na^+ as a tracer (Ulrich, 1983). The total canopy uptake of H^+ and NH_4^+ is taken equal to the total canopy leaching of Ca^{2+}, Mg^{2+} and K^+ taking place via ion exchange. Based on experiments in the laboratory (Van der Maas *et al.*, 1991), it is assumed that H^+ has per mol an exchange capacity six times larger than NH_4^+. Canopy exchange of SO_4^{2-} and NO_3^- is assumed negligible. A more detailed description of the model is presented by Draaijers *et al.* (1994b) and Draaijers and Erisman (1995) as well as in chapter 2.3.1 of this report. For the Speulder forest and other Dutch forests, the combination of throughfall measurements and application of the model resulted in deposition estimates which were similar to deposition estimates derived from micrometeorological measurements and inferential modeling, deposition of NO_y being the only exception. The discrepancy found for NO_y could in part be explained by the (probably wrong) assumption that canopy uptake of oxidized nitrogen compounds is negligible. Up to now, several basic assumptions in the model are not properly evaluated for different environmental conditions (tree species, ecological setting, pollution climate) which limits its application (Draaijers *et al.*, 1994b; Draaijers & Erisman, 1995).
The major weakness of the 'filtering approach' is the assumed relation between wet and dry deposition of particles. To overcome this weakness a new approach was formulated by Beier *et al.* (1992), using Na^+ to base cation ratios in fractions originating from the same process, i.e. dry deposition. Their approach can be used if throughfall and stemflow measurements are made both inside and near the edge

of the forest stand ('forest edge approach'). The fraction of dry deposition to leaching inside the stand is estimated based on the assumptions that only <10% of the throughfall flux of Ca^{2+} and Mg^{2+} under the edge trees and >95% of K^+ inside the stand are caused by leaching. The calculations of Beier *et al.* (1992) show that, especially for Ca^{2+} and Mg^{2+}, the influence of this choice is relatively small. However, process-oriented studies are necessary to obtain more precise knowledge on these properties for different environmental conditions.
Mayer and Ulrich (1974) took thoughfall to precipitation flux ratios in winter to estimate dry deposition in summer, assuming canopy exchange only takes place in the summer period and trees have the same dry deposition catching efficiency in summer and winter. Miller *et al.* (1976) and Lakhani and Miller (1980) proposed to calculate canopy leaching from the intercept of the regression of bulk precipitation versus throughfall, assuming a functional relationship between wet deposition and dry deposition, and furthermore canopy exchange to be independent of wet and dry deposition. Considering present knowledge on canopy exchange and deposition processes, the assumptions underlying the approaches of Mayer and Ulrich (1974) and Miller *et al.* (1976) may be regarded questionable (Spranger, 1992; Erisman and Draaijers, 1995). For distinguishing canopy exchange and atmospheric deposition on the basis of throughfall and precipitation measurements, the 'multiple regression approach', 'filtering approach' and 'forest edge approach' can be considered much more reliable.

2.3 The filtering approach

2.3.1 Model description

Model assumptions and a short overview of the calculation scheme of the "filtering approach" are presented below. The following abbreviations are used: TF = throughfall flux, SF = stemflow flux, DD = dry deposition flux, BP = bulk precipitation flux, CL = canopy leaching, CU = canopy uptake, wa = weak acids, cat = total cations, an = total anions, bc = sum of base cations Ca^{2+}, Mg^{2+} and K^+. DDF = dry deposition factor and EF = excretion factor. An appropriate time step for running the model is 0.5-1 year but, in principle, monthly data can be used as well. In the model, Na^+ in throughfall is assumed not to be influenced by canopy exchange. Furthermore, particles containing Ca^{2+}, Mg^{2+}, K^+, Cl^- and PO_4^{3-} are assumed to have the same mass median diameter as Na^+ containing particles. Dry deposition of Ca^{2+}, Mg^{2+}, K^+, Cl^- and PO_4^{3-} can subsequently be calculated according to (Ulrich, 1983):

$$DD = DDF * BP$$

The dry deposition factor equals:

$$DDF = (TF_{Na}+SF_{Na}-BP_{Na})/BP_{Na}$$

Canopy leaching of these ions is calculated according to:

$$CL = TF+SF-BP-DD.$$

Canopy leaching computed for Cl^- is regarded as deposition of HCl(gas) as Cl^- leaching is generally assumed negligible (Draaijers, 1993). The total canopy uptake of H^+ and NH_4^+ is assumed to equal the total canopy leaching of Ca^{2+}, Mg^{2+} and K^+ minus canopy leaching of Ca^{2+}, Mg^{2+} and K^+ associated with foliar excretion of weak acids (canopy uptake should always balance canopy leaching). To calculate the latter, Van der Maas and Pape (1991) define an excretion factor equal to:

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

where CL_{wa} is computed according to:

$$CL_{wa} = TF_{wa}+SF_{wa}-BP_{wa}-DD_{wa}.$$

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 (Van der Maas and Pape, 1991; Draaijers, 1993). TF_{wa} is assumed equal to TF_{cat}-TF_{an}, SF_{wa} equal to SF_{cat}-SF_{an} and BP_{wa} to BP_{cat}-BP_{an} (e.g. Guiang *et al.*, 1984). Dry deposition of weak acids is assumed equal to bulk precipitation of weak acids (Van Locht and Van Aalst, 1988). The canopy leaching of base cations through exchange with H^+ and NH_4^+ is computed according to:

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

Canopy uptake of H^+ and NH_4^+ is subsequently calculated from the sum of exchanged ions of Ca^{2+}, Mg^{2+} and K^+ where it is assumed that, based on experiments in the laboratory (Van der Maas *et al.*, 1991), H^+ has an exchange efficiency (= exchange activity) six times larger than NH_4^+:

$$CU_H = CL_{bc} / (1+ (1 / 6*(TF_H/TF_{NH4})))$$

$$CU_{NH4} = CL_{bc} - CU_H$$

Knowing their canopy uptake, the dry deposition flux of H^+ (from H_2SO_4, $(NH_4)HSO_4$, 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 (Van der Maas and Pape, 1991).

2.3.2 A combined field and laboratory experiment to determine the ratio between the uptake efficiency of H^+ and NH_4^+

The ratio between the uptake efficiency of H^+ and NH_4^+ used in the "filtering approach" (chapter 2.3.1) will depend on tree species and ecological setting of the forest stand. In this chapter a combined field and laboratory experiment is described to determine this ratio for a specific forest stand.

Method description
Six first-order branches need to be collected from different trees using a branch cutter. The branches need to be transported to the laboratory in plastic bags immediately after cutting. The first order branches are subsequently cut into pieces through which several sub-samples are obtained. In case of coniferous trees, the different year classes of needles need to be represented in proportion to the amount present in the forest. The wounds resulting from cutting need to be connected to parafilm to prevent leakage of plant sap. About 80g fresh plant material is put in plastic 1*l* bottles with a wide opening. The material is shaked for one hour with 900 ml destilled water to remove dry deposition from the branches. Subsequently the branches are shaked for
24 hours (with a speed of about 60 rpm) with 900 ml 100 µM and 1000 µM NaCl, HCl and NH_4Cl solution, respectively (in total six different solutions). For each solution at least 4 replicates are performed. Moreover, for each treatment two blanks are taken along, i.e. the same procedure is followed as described above but than without branches/plant material. Solutions are analyzed for all major ions.

Results for the Speulder forest (The Netherlands) and discussion
Results of such combined field and laboratory experiment performed at the Speulder forest by Van der Maas et al. (1991) are presented in Table 6.
Shaking with 100 µM NaCl caused a significant release of K^+, Ca^{2+}, Mg^{2+} and Mn^{2+}, amounting to 0.0663 $mmol_c$ cations. 100 g $branches^{-1}$. 24 $hours^{-1}$. However, there was no significant uptake of Na. With a 1000 µM NaCl solution a significant uptake of Na (0.0288 $mmol_c$. 100 g $branches^{-1}$. 24 $hours^{-1}$) was measured, while the release of other cations was similar to that from branches shaken with 100 µM NaCl.
The experiment with 100 µM HCl resulted in a significant uptake of 0.0709 $mmol_c$ H^+. 100 g $branches^{-1}$. 24 $hours^{-1}$, which was counteracted by a cation release of 0.1025 $mmol_c$ 100 g $branches^{-1}$. 24 $hours^{-1}$. With 1000 µM HCl an H^+ uptake of 0.1470 and cation release of 0.3022 $mmol_c$. 100 g $branches^{-1}$. 24 $hours^{-1}$ was measured.
Shaking with 100 µM NH_4Cl caused a significant NH_4^+ uptake (0.0091 $mmol_c$. 100 g $branches^{-1}$. 24 $hours^{-1}$) associated with a base cation release of 0.0849 $mmol_c$. 100 g $branches^{-1}$. 24 $hours^{-1}$. With 1000 µM NH_4Cl, NH_4^+ uptake and cation release increase to respectively 0.0374 and 0.1148 $mmol_c$. 100 g $branches^{-1}$. 24 $hours^{-1}$. Release and uptake of anions by the branches was very low. Generally, only organic anions were released. Uptake of Cl^- was significant only in case of the

1000 µM HCl treatment. Significant but very low uptake of NO_3^- and SO_4^{2-} was found with the 100 µM NaCl treatment.
The results show that removal of cations from branches increases with increasing concentrations of treatment solutions. The removal of anions is very low. Because incomplete removal of salts and acids from the branch and needle surfaces during shaking with pure water seems unlikely, most of the removal must be explained by excretion by plant tissue. The very high removal of cations with 1000 µM HCl is due mainly to releases of Mn^{2+} and Fe^{2+}. From throughfall data it is clear that Mn^{2+} leaching is normally lower than K^+, Ca^{2+} and Mg^{2+} leaching, while Fe^{2+} leaching hardly occurs. The unrealistic high rates of Mn^{2+} and Fe^{2+} leaching may result from dissolution of terrestrial dust associated with the leaves, or from injuries to the leaf tissue caused by high acidity.
H^+ induced the highest exchange at both concentration levels. The exchange rates found for NH_4^+ were much lower. Significant uptake of Na^+ was only found with 1000 µM, while the release of cations remained relatively low. The release of H^+ was invariably higher than that of NH_4^+ and Na^+. Release of NH_4^+ and Na^+ was always very low or insignificant. It can be concluded that H^+ is much more active as an exchanger than NH_4^+ and Na^+, while NH_4^+ is a stronger exchanger than Na^+. Based on these data, it is assumed that H^+ and NH_4^+ control the canopy exchange reactions and that the exchange activity of H^+ is 6 times higher than of NH_4^+. The factor 6 is calculated from the ratios of H^+ and NH_4^+ uptake for the two concentration levels. Na^+ is assumed to have no exchange activity.

Table 6 *Release (+) or uptake (-) of ions by Douglas fir branches from the Speulder forest after shaking with a NaCl, HCl or NH_4Cl solution (in $mmol_c$. 100 g $branches^{-1}$. 24 $hours^{-1}$). * denotes significant at $p<0.05$ (t-test) (after Van der Maas et al., 1991).*

Treatment	H^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	Al^{3+}	Fe^{2+}	Mn^{2+}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	HCO_3^-
100 µM NaCl	0.0026	0.0295	-0.0023	0.0122	0.0073	0.0004	0.0057	0.0147	0.0000	0.0000	-0.0009	-0.0032	0.0000	0.0045
	*	*		*	*			*			*	*		
1000 µM NaCl	0.0026	0.0172	-0.0288	0.0163	0.0084	0.0004	0.0011	0.0181	0.0000	0.0039	0.0000	0.0017	0.0000	0.0050
	*	*	*	*	*			*						*
100 µM HCl	-0.0709	0.0368	-0.0003	0.0262	0.0112	0.0012	0.0041	0.0283	0.0000	0.0004	-0.0010	-0.0007	0.0000	0.0007
	*	*		*	*			*						
1000 µM HCl	-0.1470	0.0612	0.0015	0.0853	0.0245	0.0056	0.0245	0.0996	0.0007	-0.0247	0.0000	-0.0017	0.0001	0.0000
	*	*	*	*	*	*	*	*	*	*				
100 µM NH_4Cl	0.0062	0.0371	0.0023	0.0155	0.0080	0.0001	0.0027	0.0181	-0.0091	0.0036	0.0003	0.0007	0.0004	0.0045
	*	*		*	*			*	*				*	*
1000 µM NH_4Cl	0.0114	0.0385	0.0007	0.0220	0.0110	0.0005	0.0051	0.0261	-0.0374	-0.0112	0.0000	-0.0001	0.0004	0.0024
	*	*	*	*	*		*	*	*				*	*

2.4 Estimation of canopy uptake and dry deposition of nitrogen

As discussed in chapter 2.3 canopy exchange and dry deposition of sulphur, sodium, chloride, magnesium, calcium and potassium can be estimated reasonably well using throughfall, stemflow and precipitation measurements, if necessary in

association with canopy budget models. Unfortunately, up to now canopy uptake and dry deposition of nitrogen can not be properly estimated. The 'filtering approach' may provide an estimate of canopy uptake and dry deposition of reduced nitrogen, only if the site-specific ratio between uptake efficiency of H^+ and NH_4^+ is determined from a combined field and laboratory experiment as described in chapter 2.3.2.
An estimate for canopy uptake of oxidised and reduced nitrogen can be obtained by using results of the Integrated Forest Study (IFS) reported by Johnson and Lindberg (1992). Johnson and Lindberg (1992) found for 12 sites in the USA the above ground uptake of inorganic nitrogen, CU_N, significantly related to the total deposition of inorganic nitrogen, TD_N, according to:

$$CU_N = 0.41 * TD_N + 54.2 \qquad (r^2 = 0.66) \qquad [1]$$

For the same sites, the throughfall + stemflow flux of inorganic nitrogen, TF_N+SF_N, was significantly related to TD_N, according to:

$$TF_N+SF_N = 0.59 * TD_N - 54.2 \qquad (r^2 = 0.80) \qquad [2]$$

Combining equation [1] and [2] provides the relationship between the canopy uptake and the throughfall + stemflow flux of inorganic nitrogen (in eq ha^{-1} yr^{-1}):

$$CU_N = 0.69 * (TF_N+SF_N) + 91.9 \qquad [3]$$

Johnson and Lindberg (1992) made their measurements at sites situated in areas with relatively low air concentrations of N compounds in comparison to those found in certain areas in Europe. Throughfall + stemflow fluxes of inorganic nitrogen in the IFS ranged between 100 and 1000 eq.ha^{-1} yr^{-1}. Equation [3] therefore may only be applied for this range of inorganic nitrogen fluxes. It is not clear if uptake rates will increase linearly at higher throughfall + stemflow fluxes because nitrogen saturation in the canopy might be expected. Another restriction for using equation [3] is made by Johnson and Lindberg (1992) themselves. In their study the relationship between uptake and deposition appeared to be quit strong for spruce and spruce-fir forests but was found much less pronounced for other tree species. Canopy uptake of nitrogen will not only be governed by deposition amount but also by numerous other factors as was already explained in chapter 2.1. Process-oriented research on canopy uptake of nitrogen in relation to these factors is therefore recommended. While TF_N+SF_N gives a minimum estimate for nitrogen deposition, $TF_N+SF_N+CU_N$, with CU_N estimated according to equation [3], provides a more realistic estimate for nitrogen deposition to forests.
For estimating stomatal uptake of gaseous nitrogen compounds (NO_2, NO, HNO_3, HNO_2 and NH_3) a model developed by Bouten and Bosveld (1992) can be applied. This model uses air concentrations and meteorology as input data. Stomatal conductance is described as a product of response functions for water vapor deficit, global radiation, temperature, soil moisture status and leaf area index. To obtain

realistic values for stomatal uptake of nitrogen compounds from the model of Bouten and Bosveld (1992), results from air concentration measurements made at or near the forest site under consideration need to be used. Passive samplers may be useful for measuring air concentrations due to the low costs involved and no need for electricity. Air concentration data representative for the large scale pollution climate (as collected e.g. within the framework of the EMEP Program) are of limited value for use at specific sites. Especially concentrations of reduced nitrogen compounds have been found subject to considerable small scale variability as they are strongly influenced by local sources. Meteorological measurements should ideally be performed at the site as well, but meteorological data can also be obtained from nearby sites part of a routine network.

Additional information on canopy uptake of nitrogen may be obtained by performing experiments with radiolabelled ^{15}N (see e.g. Bowden *et al.*, 1989; Garten and Hanson, 1990; Vose *et al.*, 1989) or surface wash experiments using real and artifical twigs. Results from surface wash experiments performed at the Speulder forest are presented in chapter 3.1.3.

Inferential deposition models like DEADM (Erisman, 1992) and EDACS (Erisman and Draaijers, 1995) which are generally used to estimate atmospheric deposition on regional scales, also provide the possibility to estimate dry deposition to specific forest sites. In inferential models, dry deposition is calculated by multiplying air concentrations with dry deposition velocities. Dry deposition velocities are calculated from land-use and meteorological information using detailed parametrizations of the dry deposition process. To estimate dry deposition of nitrogen to specific forest sites, information is necessary on *i)* site characteristics (location, main tree species and tree height), *ii)* local air concentrations (NO_2, NO, HNO_3, HNO_2, NO_3, NH_3 and NH_4) and *iii)* local meteorology (wind speed, temperature, dew point temperature or relative humidity, cloud cover and precipitation amount). Dry deposition estimates will improve if also information on canopy coverage, leaf area, tree density and/or distance to forest edges is available. Erisman (1992) used the DEADM model for estimating dry deposition to specific forest sites in The Netherlands. More recently, the EDACS model has been applied to estimate dry deposition to forest sites in Germany (Van Leeuwen *et al.*, 1996) and Europe (Draaijers *et al.*, 1996).

Micrometeorological measurements also have been used to estimate dry depostion to specific forest sites (Erisman *et al.*, 1996). The dry deposition flux is either derived from measurements of the vertical component of the wind velocity and the gas concentration with the most direct of these methods, the so-called *eddy correlation method*; or from air concentration measurements at different heights above the receptor surface and several meterological parameters, the so-called *gradient method*. Detailed descriptions of both methods are presented by a.o. Erisman and Draaijers (1995). Other micrometeorological techniques consist of Bowen ratio approaches, variance and a variety of so-called conditional sampling techniques. Information on these techniques can be found in e.g. Businger (1986), Hicks *et al.* (1986), Baldocchi *et al.* (1988) and Fowler and Duyzer (1990). Compared to throughfall, stemflow and precipitation measurements, micrometeorological meas-

urement techniques are expensive when used on a routine basis. Recently, some progress has been made in developing cheaper micrometerological measurement methods (Erisman *et al.*, 1996). Results from micrometeorological measurements performed at the Speulder forest are presented in chapter 3.1.2.

2.5 Contribution of dry deposition directly to the forest floor

The amount of dry deposition to the forest floor will largely depend on the below-canopy air concentration, wind speed (turbulence intensity), and the structure and wetness of the forest floor and understorey vegetation. This flux is expected to be small because of the low wind speeds usually observed beneath forest canopies (Fowler, 1979; Lovett and Lindberg, 1992). Moreover, the total surface area of the understorey vegetation is generally small in comparison to the surface area of the canopy. However, transport of gases and aerosols to the forest floor may be substantial in very open forest stands, in forest edges and in deciduous forests during the winter period when gusts penetrate deeply through the canopy (Meyers and Baldocchi, 1988). Up to now no reliable estimates are available for the amount of dry deposition to the forest floor under these circumstances.

2.6 Recommendations

To estimate atmospheric deposition from throughfall, stemflow and precipitation fluxes several corrections have to be made. To obtain an estimate for wet deposition, the bulk precipitation flux needs to be corrected for dry deposition directly onto the collector by using wet-only to bulk ratios derived from parallel wet-only and bulk measurements made at the measurement site or, if not available, by using average wet-only to bulk ratios derived from literature (Table 3). To estimate dry + fog/cloud deposition, the net throughfall flux (i.e. throughfall flux + stemflow flux - wet deposition flux) needs to corrected for canopy exchange (uptake or leaching). From literature, it can be derived that, in general, stomatal uptake of SO_2 will be balanced by leaching of SO_4^{2-}. However, significant stomatal uptake of NO_2, HNO_2 and NH_3 has been found as well as uptake of H^+ and NH_4^+ from water layers covering the tree surface. Several experiments also indicate uptake of NO_3^- in solution. Canopy uptake of H^+ and NH_4^+ is generally assumed to be equal to leaching of K^+, Ca^{2+} and Mg^{2+} via ion exchange processes. Additional leaching of K^+, Ca^{2+} and Mg^{2+} takes place along with weak organic acids. Canopy exchange of Na^+ and Cl^- is usually considered insignificant. Canopy exchange strongly depends on tree species, ecological setting and pollution climate. Information on canopy exchange for a specific throughfall site can be obtained e.g. by the use of tracers (e.g. Wyers *et al.*, 1994), specific surface wash experiments (e.g. Van der Maas *et al.*, 1991; Ibrom, 1993; Römer and Te Winkel, 1994), detailed throughfall sampling in both time and space (e.g. Hansen *et al*, 1994; Hansen, 1994) and by comparisons of throughfall sampling techniques with micrometeorological methods and inferential

modelling (e.g. Lovett *et al.*, 1992; Draaijers and Erisman, 1993; Spranger *et al.*, 1994). Results of such experiments performed at the Speulder forest research site are described in chapter 3.1.

For distinguishing canopy exchange and atmospheric deposition on the basis of throughfall, stemflow and precipitation measurements several canopy budget models have been developed. The 'multiple regression approach', 'forest edge approach' and 'filtering approach' can be considered most useful in this respect. The 'multiple regression approach' can be used if throughfall, stemflow and precipitation fluxes are monitored on an event basis and has proven reliable in areas with convective storms and extended dry weather periods. The 'forest edge approach' can be used if throughfall and stemflow measurements are made both inside and near the edge of the forest stand. In most studies, however, throughfall and stemflow fluxes is only measured on a weekly (i.e non-event) basis and inside the forest stand (i.e. not near the forest edge). In this case the 'filtering approach' can be used which has proven valuable for estimating canopy exchange and forest deposition in The Netherlands, Germany, Denmark and Sweden. Process-oriented research is recommended, however, to evaluate several basic assumptions of the 'filtering approach' (e.g. the ratio between the uptake efficiency of H^+ and NH_4^+) in relation to specific environmental conditions (climate, tree species etc.).

Canopy exchange and forest deposition of sulphur, sodium, chloride, magnesium, calcium and potassium can be estimated reasonably well using throughfall, stemflow and precipitation measurements, if necessary in association with above mentioned canopy budget models. Unfortunately, up to now canopy uptake and dry deposition of nitrogen can not be properly determined. The 'filtering approach' can be used to estimate canopy uptake of reduced nitrogen, only if the site-specific ratio between uptake efficiency of H^+ and NH_4^+ is determined from a combined field and laboratory experiment. In low N pollution areas, an estimate for canopy uptake of oxidised and reduced nitrogen can be obtained by using a relationship between canopy uptake and throughfall + stemflow flux derived from measurements made in the USA within the framework of the Integrated Forest Study (Johnson and Lindberg, 1992). For estimating stomatal uptake of gaseous nitrogen compounds (NO_2, NO, HNO_3, HNO_2 and NH_3) a model developed by Bouten and Bosveld (1992) can be applied. To estimate dry deposition of nitrogen (and other components) to specific forest stands, inferential models like EDACS (Erisman and Draaijers, 1995) have been found useful. Micrometeorological measurements can also be used to estimate dry deposition but are up to now quit expensive in comparison to throughfall, stemflow and precipitation measurements (Erisman *et al.*, 1996).

Dry deposition to the forest floor and understorey vegetation is not taken into account in throughfall and stemflow studies. This type of dry deposition can potentially be substantial in very open forest stands, in forest edges and in deciduous forests during the winter period. Process-oriented research on the amount of dry deposition to the forest floor and understorey vegetation under these circumstances is recommended.

PART 3 UNCERTAINTY ANALYSIS

The uncercertainty in atmospheric deposition determined from throughfall, stemflow and precipitation measurements can be assessed by *i)* comparison with independent field and model data and *ii)* by using error propagation techniques. Canopy exchange is usually considered a major source of uncertainty when using throughfall and precipitation measurements for atmospheric deposition assessment. For this reason, in chapter 3.1 field experiments and model excersises are described that can be used to study the impact of canopy exchange on differences observed between atmospheric deposition and throughfall fluxes. Results of such experiments and model excersises performed at the Speulder forest (The Netherlands) are presented. In chapter 3.2 the theory of error propagation is described. The theory has been applied to determine the uncertainty in atmospheric deposition assessed from throughfall and precipitation flux measurements at the Speulder forest. In chapter 3.3 some recommendations with respect to uncertainty analysis are presented.

3.1 Comparison with independent field and model data

To obtain more insight in canopy exchange processes, and to quantify them, throughfall and precipitation fluxes were measured at the Speulder forest research site in The Netherlands. Two canopy exchange models were applied to test assumptions on canopy exchange processes (Van Leeuwen and Bleuten, 1994). Information on canopy exchange was provided by comparing throughfall flux estimates with deposition estimates from micrometeorological measurements and inferential modelling (Erisman *et al.*, 1994b), and by comparing deposition estimates from surface wash experiments using real and artificial twigs, respectively (Römer and Te Winkel, 1994). The canopy uptake of gases through stomata was estimated using measured air concentrations and a stomatal conductance model developed by Bouten and Bosveld (1992). Specific information on canopy leaching of root-derived sulphate was provided by a ^{35}S tracer experiment (Wyers *et al.*, 1994).

3.1.1 Precipitation and throughfall measurements and application of canopy budget models

Precipitation and throughfall fluxes at the Speulder forest were measured continuously on a weekly basis between October 1992 and July 1993. Bulk precipitation was sampled in a clearing approximately 300 m from the Speulder forest site by means of four continuously open funnels. Two of these funnels were connected to a mechanical sequential sampler after March 1993. During several months wet-only precipitation was measured to estimate the contribution of dry deposition onto the funnels and to derive bulk to wet-only correction factors. Throughfall was

sampled weekly by 25, 4m long gutters. Throughfall was additionally sampled on an event basis by two gutters connected to a tipping bucket rain gauge and a sample changer. Division between events was made when the time lapse between two tips of the recording tipping bucket was larger than two hours.
Wet deposition was estimated by correcting bulk precipitation fluxes for dry deposition to the funnels. The stemflow ion flux was estimated from literature to be on average 6% of the throughfall ion flux (Van Leeuwen *et al.*, 1994). By subtracting the wet deposition flux from the throughfall+stemflow flux (= net throughfall) and assuming nil canopy exchange for sulphate, nitrate, chloride and sodium, an estimate for dry and fog deposition was obtained. All fluxes presented in this paper are expressed as annual averages, unless stated otherwise. Annual fluxes were scaled by time.
Continuous monitoring of throughfall and precipitation fluxes at the Speulder forest allowed the application of the canopy budget model developed by Ulrich (1983) which was extended by Van der Maas and Pape (1991) described in chapter 2.3.1 (filtering approach). Throughfall and bulk precipitation were also sampled on an event basis allowing the application of the regression model of Lovett and Lindberg (1984) described in chapter 3.3.1 (multiple regression approach).
Table 7 presents results of the filtering approach applied for the Speulder forest. If foliar leaching is expressed as percentage of net throughfall, values for K^+, Ca^{2+} and Mg^{2+} equal 89, 46 and 29%, respectively. Minor canopy uptake of phosphate was calculated. About 88% of the total proton deposition and approximately 9% of the total NH_x deposition was taken up by the canopy.
The filtering approach is built on assumptions which are sometimes questionable. When a particular assumption is not valid this propagates into successive calculations through which an accumulation of errors may arise. For instance, the assumption that Mg^{2+}, Ca^{2+}, Cl^- and K^+ containing particles are deposited with equal efficiency as Na^+ containing particles will certainly introduce an error as the particle size distribution of these constituents is not the same. At the Speulder forest mass median diameters (MMDs) of Ca^{2+} (7.7 µm) and to a lesser extent Mg^{2+} (5.9 µm) were found to be larger than those of Na^+ (5.1 µm) while the MMD of K^+ (2.6 µm) was considerably smaller (Ruijgrok *et al.*, 1996). As a result dry deposition of Ca^{2+} and to a lesser extent Mg^{2+} containing particles will be underestimated by the model and dry deposition of K^+ containing particles will be overestimated. Based on these dry deposition values, canopy leaching of Mg^{2+}, Ca^{2+} and K^+ is computed which, in turn, is used to calculate canopy uptake of H^+ and NH_4^+. The ratio of canopy uptake efficiency between H^+ and NH_4^+ is obtained from foliar extraction experiments with small Douglas-fir twigs in the laboratory (Van der Maas *et al.*, 1991). Whether these results may be extrapolated to field situations remains uncertain. The model assumes nil canopy exchange of SO_4^{2-} and NO_3^-. This assumption is probably valid for SO_4^{2-} but invalid for NO_3^-. Uncertainties associated with the computation of the excretion factor include the incompleteness of the ion balance (e.g. Mn^{2+}, Fe^{2+} and Al^{3+} were not measured in this study, probably resulting in an underestimation of the excretion factor) and the assumption that the dry deposition of weak acids equals the bulk precipitation flux of weak acids. Addi-

tionally, the computation of the excretion factor is also very sensitive for possible analytical errors (Draaijers and Erisman, 1995).

Table 7 *Results of the filtering approach applied on throughfall measurements performed between November 1992 and May 1993 at the Speulder forest research site (eq. ha^{-1} a^{-1}). TF = throughfall + stemflow; BP = bulk precipitation, WD = wet deposition, DD = dry deposition, TD = total deposition, CL = canopy leaching, $SO_4^{2-}s$ = sea salt sulphate and wa = weak acids*

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCl(g)	PO_4^{3-}	H^+	NH_4^+	NO_3^-	SO_4^{2-}	$SO_4^{2-}s$	wa
dry deposition factor = 1.27; excretion factor = 0.12													
TF	1153	322	396	392	1379		7	24	2452	697	2563	138	77
BP	507	23	110	137	614		2	167	739	340	716	61	8
WD	461	17	78	115	577		2	139	724	303	630	55	19
DD	646	29	140	174	765	15	3	38	1968	357	1847	78	8
TD	1107	46	218	289	1357		5	177	2692	660	2477	133	27
CL	0	270	146	81	0		2	-181	-255	0	0	0	61

Note: A detailed description of the Speulder forest is given in the footnote of Table 1.

Table 8 presents results of the multiple regression approach applied for the Speulder forest. The use of this model requires independent throughfall collections. For this reason rain events larger than 15 mm were used to separate between deposition periods. In this way, all dry deposition washed-off was assumed to belong to the antecedent dry period (Van Leeuwen and Bleuten, 1994). Only for K^+ and H^+ significant relationships ($p<0.05$) were found between event net throughfall on the one hand and the duration of antecedent dry period and precipitation amount on the other hand. This means that only the leaching part of net throughfall of K^+ and H^+ could be determined. By multiplying mean canopy leaching rates (b_2) presented in Table 2 with annual rainfall amounts (842 mm), canopy leaching for K^+ can be estimated to be 190 (±43) $eq.ha^{-1}.a^{-1}$ and canopy uptake of H^+ 200 (±40) $eq.ha^{-1}.a^{-1}$. Model results with respect to dry deposition are discussed in Van Leeuwen and Bleuten (1994).

Although the simple formulation of the model was found subject to a number of caveats (extensively discussed in Lovett and Lindberg, 1984), the model has proven very valuable in areas with convective storms and extended dry weather periods (e.g. Lovett and Lindberg, 1984; Puckett, 1990). However, at the Speulder forest events are characterised by extended periods of low-intensity rainfall and short antecedent dry periods. This will have important implications for canopy exchange and dry deposition processes. Long-duration, low-intensity rainfall is conducive to accelerated foliar leaching of plant nutrients (Schaefer and Reiners, 1990), and wetness on vegetation may reduce the resistance to dry deposition, leading to higher fluxes of SO_2 and NH_3. Moreover a wet canopy during 'dry periods' may facilitate canopy leaching. The climatic conditions in The Netherlands and other European areas with similar climate (i.e. at least NW Europe, Scandinavia) thus do not favour the application of the model which may be the reason for the small amount of significant relationships observed (Table 8). Another reason for this may be the small number of independent throughfall collections (8) which could be distinguished.

Table 8 *Dry deposition rates (b_1) (in $mmol.m^{-2}.hr^{-1}$), canopy leaching rates (b_2) (in $meq.m^{-2}.mm\ rainfall^{-1}$), number of observations (n) and coefficients of determination (r^2) for the no-intercept regression equations between event net throughfall of K^+ or H^+ on the one hand and the duration of antecedent dry period and precipitation amount on the other hand. Regression equations for all other ions were not significant ($p>0.05$), and are for this reason not presented. n.s. = not significant*

	b_1		b_2		n	r^2
	mean	st.dev.	mean	st.dev		
K^+	0.0037	0.001	0.0225	0.0051	8	0.84
H^+	n.s.	n.s.	-0.024	-0.005	8	0.85

3.1.2 Micrometeorological measurements and inferential modelling

Information on canopy exchange can be obtained by comparing throughfall deposition estimates with estimates from micrometeorological measurements and inferential modelling. Between November 1992 and May 1993 the dry deposition flux of SO_2, NH_3 and NO_2 was estimated using the gradient technique (Mennen *et al.*, 1994; Erisman *et al.*, 1994b). In the same period dry deposition of HNO_3, HNO_2 and HCl was inferred from measured air concentrations and parametrized dry deposition velocities (Erisman *et al.*, 1994b). A model describing stomatal conductance as a product of response functions for water vapour deficit, global radiation, temperature, soil moisture status and leaf area index (Bouten and Bosveld, 1992) was used to estimate gaseous uptake through stomata. Dry deposition of acidifying aerosols (SO_4^{2-}, NO_3^-, NH_4^+ and Cl^-) and base cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) was inferred using results of air concentration measurements performed by Römer and Te Winkel (1994), and a parametrization of the deposition velocity according to Slinn (1982) modified by Ruijgrok *et al.* (1994). During two campaigns in December 1992 and February 1993, respectively, fog deposition was estimated by measuring the turbulent water flux of fog droplets using the eddy correlation technique (Vermeulen *et al.*, 1994). The fog water flux through sedimentation depends on the fog droplet radius and was estimated using Stoke's law. The fog droplet size distribution was measured using a FSSP measuring device. Fog deposition fluxes of SO_4^{2-}, NO_3^- and NH_4^+ were obtained by multiplying total fog water fluxes with the average chemical composition of the fog droplets which was measured by Römer and Te Winkel (1994) using a string collector (Daube *et al.*, 1987). Fog deposition estimates were extrapolated to the whole measurement period on the basis of fog duration measurements from a nearby meteorological station (Vermeulen *et al.*, 1994).

Summed for the period November 1992 - May 1993, the dry and fog deposition estimate for NO_y is approximately twice as large as the net throughfall flux of NO_3^- (Table 9). Net throughfall fluxes of SO_4^{2-}, NH_4^+, Na^+, Cl^- and Mg^{2+} are not significantly different from corresponding dry and fog deposition estimates (paired t-test, one tailed, $\alpha = 0.05$). For K^+ and Ca^{2+}, net throughfall fluxes are significantly

higher (89% and 36%, respectively) than corresponding dry and fog deposition estimates. This is probably the result of the contribution of canopy leaching to the net throughfall flux of K^+ and Ca^{2+}. If net throughfall fluxes of base cations are corrected for canopy exchange using the filtering approach, very reasonable agreement is found with dry and fog deposition estimates (Table 9). Corrected net throughfall fluxes of Ca^{2+} and Mg^{2+} were somewhat smaller than corresponding dry and fog deposition estimates (Table 9), which is probably due to the overestimation of the contribution of canopy leaching to the net throughfall fluxes of Ca^{2+} and Mg^{2+} by the budget model.

Observed differences between net throughfall fluxes on the one hand and dry and fog deposition estimates from micrometeorological measurements and inferential modelling on the other hand can not be regarded exclusively due to canopy exchange but may also be the result of measuring artefacts. Dry deposition estimates from micrometeorological measurements and inferential modelling are uncertain through errors in the air concentration measurements (Arends *et al.*, 1994), their sometimes small time coverage (Erisman *et al.*, 1996) and the uncertainties associated with the parametrization of the dry deposition velocities (Ruigrok *et al.*, 1994).

The uncertainty in annual mean dry deposition of gaseous sulphur, reduced nitrogen and oxidized nitrogen compounds derived from micrometeorological measurements and inferential modelling made at the Speulder forest was estimated by Erisman *et al.* (1996) to amount 40%, 30% and 60%, respectively. The uncertainty in annual mean dry deposition of aerosols was estimated to amount 40%. Uncertainties in fog deposition are associated with the estimation of water fluxes and the measurement of the average chemical composition of the fog droplets (Vermeulen *et al.*, 1994). The uncertainty in annual mean fog water deposition is expected to be at least 100%. Using the gas, aerosol and fog water deposition estimates presented in Table 9, the uncertainty in dry + fog deposition at the Speulder forest can be estimated to amount 25-40%, depending on component. Uncertainties associated with the throughfall method when used for estimating dry and fog deposition are extensively discussed in chapter 3.2. Results for the Speulder forest are presented in Table 12.

Table 9 *Dry and fog deposition estimates for the Speulder forest derived from micro-meteorological measurements and inferential modelling for the period November 1992 - May 1993 (in mol.ha^{-1}.a^{-1}). Moreover, net throughfall fluxes (net TF) and net throughfall fluxes corrected for canopy (net TFcor) are presented.*

	SO_x	NO_y	NH_x	Na	Cl	Ca	K	Mg
gas	663	356	1443	0	0	0	0	0
aerosol	216	414	645	599	885	101	34	118
fog water	34	23	96	2	4	1	1	0
dry + fog	913	793	2184	601	889	102	35	118
	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Ca^{2+}	K^+	Mg^{2+}
net TF	924	394	1728	692	802	159	305	138
net TF cor	924	394	1983	692	802	86	35	98

3.1.3 Surface wash experiments using real and artificial twigs

Between November 1992 and May 1993 several surface wash experiments were performed at the Speulder forest using Douglas-fir twigs and artificial twigs (Römer and Te Winkel, 1994). The artificial twigs had similar geometrical characteristics as the Douglas-fir twigs and were chemically inert. Measurements with Douglas-fir twigs were performed at 11, 15, 17 and 19 m above the forest floor, while measurements with artificial twigs only took place at 15, 17 and 19 m height. After exposure to dry deposition for a few days, the twigs were rinsed with demineralised water (Römer and Te Winkel, 1994). The rinsing water was analysed for all major components. Deposition on the twigs was extrapolated to the whole canopy using the ratio between twig leaf area and the corresponding canopy stratum leaf area as measured by Steingröver and Jans (1994). Information on canopy exchange was obtained by comparing deposition to real and artificial twigs, respectively (Römer and Te Winkel, 1994).

From laboratory experiments it was concluded that the rinsing method used removed on average 89% and 86% of the accumulated material from the Douglas-fir and artificial twigs, respectively (Römer and Te Winkel, 1994). Rinsing should ideally be performed after dry periods of several days, but only three such periods could be distinguished. In the seven other measurement periods needle wetness occurred as a result of (light) drizzle and/or fog (Römer and Te Winkel, 1994). Generally, the amount of material accumulated on the twigs was found to increase with height in the canopy (Römer and Te Winkel, 1994). Significant relationships ($p < 0.05$) are found between the amount rinsed from Douglas-fir twigs and artificial twigs, K^+ being the only exception (Figure 1). Averaged over all measurement periods and integrated over the whole canopy (using LAI per canopy stratum), the amount of K^+ and Ca^{2+} rinsed from Douglas-fir twigs is 52% and 23%, respectively, larger than the amount rinsed from artificial twigs (Figure 2a). For all other ions no significant differences are found between the amount rinsed from Douglas-fir and from artificial twigs (paired t-test, one tailed, $\alpha = 0.10$). When only the three measurement periods with dry conditions are considered, for all ions (except

Ca^{2+}) significantly larger amounts are rinsed from Douglas-fir twigs in comparison to artificial twigs (Figure 2b). For the seven measurement periods with drizzle and/or fog, significantly larger amounts of K^+ and Ca^{2+} and significantly smaller amounts of SO_4^{2-}, NO_3^-, NH_4^+, Na^+ and Cl^- are rinsed from Douglas-fir twigs (Figure 2c).

During dry periods, the migration of substances in the transpiration stream may result in an accumulation on the surface of Douglas-fir needles. Under dry circumstances gaseous deposition will mainly (except for HNO_3) be controlled by stomatal uptake (Erisman *et al.*, 1994) which will only be relevant for real twigs. The fate of gases adsorbed to foliar tissues is uncertain as they may be permanently retained (through incorporation into amino-acids and/or translocation to other parts of the tree), leached (through diffusion and/or ion-exchange) or re-emitted to the atmosphere. When gases are permanently retained or re-emitted to the atmosphere, they will not be measured in the rinsing solution of Douglas-fir twigs. Particle deposition may differ as a result of differences in wettability, stickiness and/or surface geometry of Douglas-fir and artificial twigs, respectively. However, the amount of material rinsed from artificial twigs during measurement periods with dry conditions corresponded very well with modelled dry deposition (Ruijgrok *et al.*, 1994), suggesting that under these circumstances artificial twigs represent real Douglas-fir twigs reasonably well.

During periods with needle wetness, canopy leaching will be relatively intense (Schaefer and Reiners, 1990), explaining the large amounts of K^+ and Ca^{2+} rinsed from Douglas-fir twigs in comparison to artificial twigs (Figure 2c). Moreover, some uptake of NH_4^+ and probably NO_3^- in solution may be expected. Gaseous deposition will mainly take place in the water layer covering the surface (although it may be argued that for some gases stomatal uptake is large even if the external surfaces are wet) and, for this reason, will not be different for Douglas-fir and artificial twigs unless their wettability differs or the chemistry of the water layer is different. Gaseous deposition will be influenced by the pH of water layer. In contrast to artificial twigs, the pH of the water layer on Douglas-fir twigs may be influenced or even regulated by canopy exchange. Field observations showed that after fog, rain or dew formation artificial twigs remained wet for a considerably longer time period than did Douglas-fir twigs. As a consequence gaseous deposition amounts on artificial twigs will be relatively large, which may explain the relatively large accumulation of acidifying compounds on artificial twigs in comparison to Douglas-fir twigs during periods with drizzle and/or fog. Moreover, the retention of (sea salt) particles will be more efficient on artificial twigs, which may explain the relatively large amounts of Na^+ and Cl^- rinsed from artificial twigs. For Mg^{2+}, increased leaching from Douglas-fir twigs probably counterbalanced the more efficient retention of Mg^{2+} containing particles on artificial twigs, resulting in no significant difference between the amount rinsed from Douglas-fir and artificial twigs, respectively, during periods with drizzle and/or fog (Figure 2c).

The rinsing experiments had a time coverage of only 25% and were made mainly in the winter period when the vegetation is physiologically less active and usually covered with a water film. Differences between real and artificial twigs may there-

fore not be representative for the whole year or even the measurement period. They are probably (much) larger in summer.

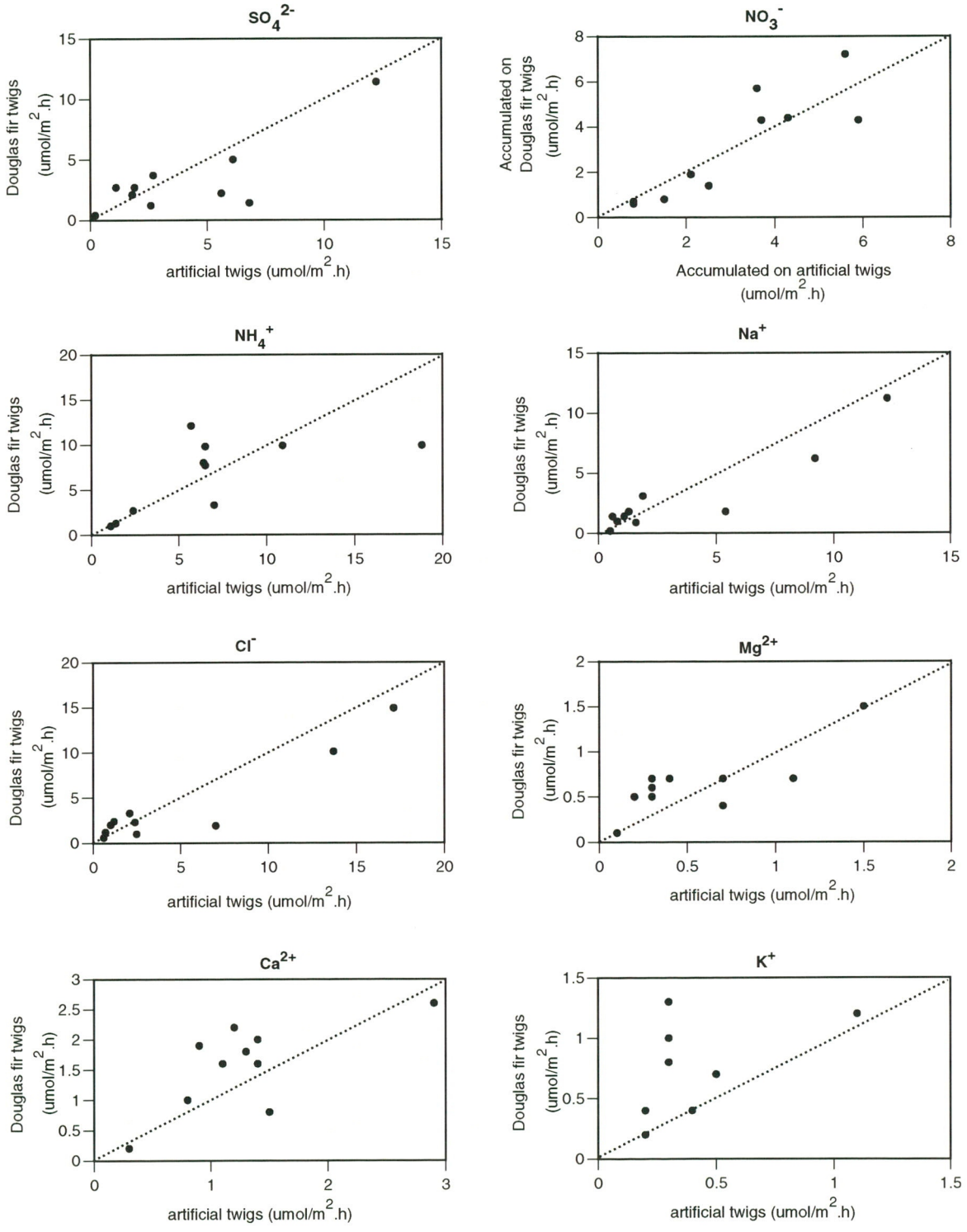

Figure 1 *Relationship between the amount rinsed from Douglas-fir and artificial twigs, respectively. Amounts are integrated over the whole canopy (in µmol/m^2 ground area. hour). The dashed line represents the 1:1 relationship.*

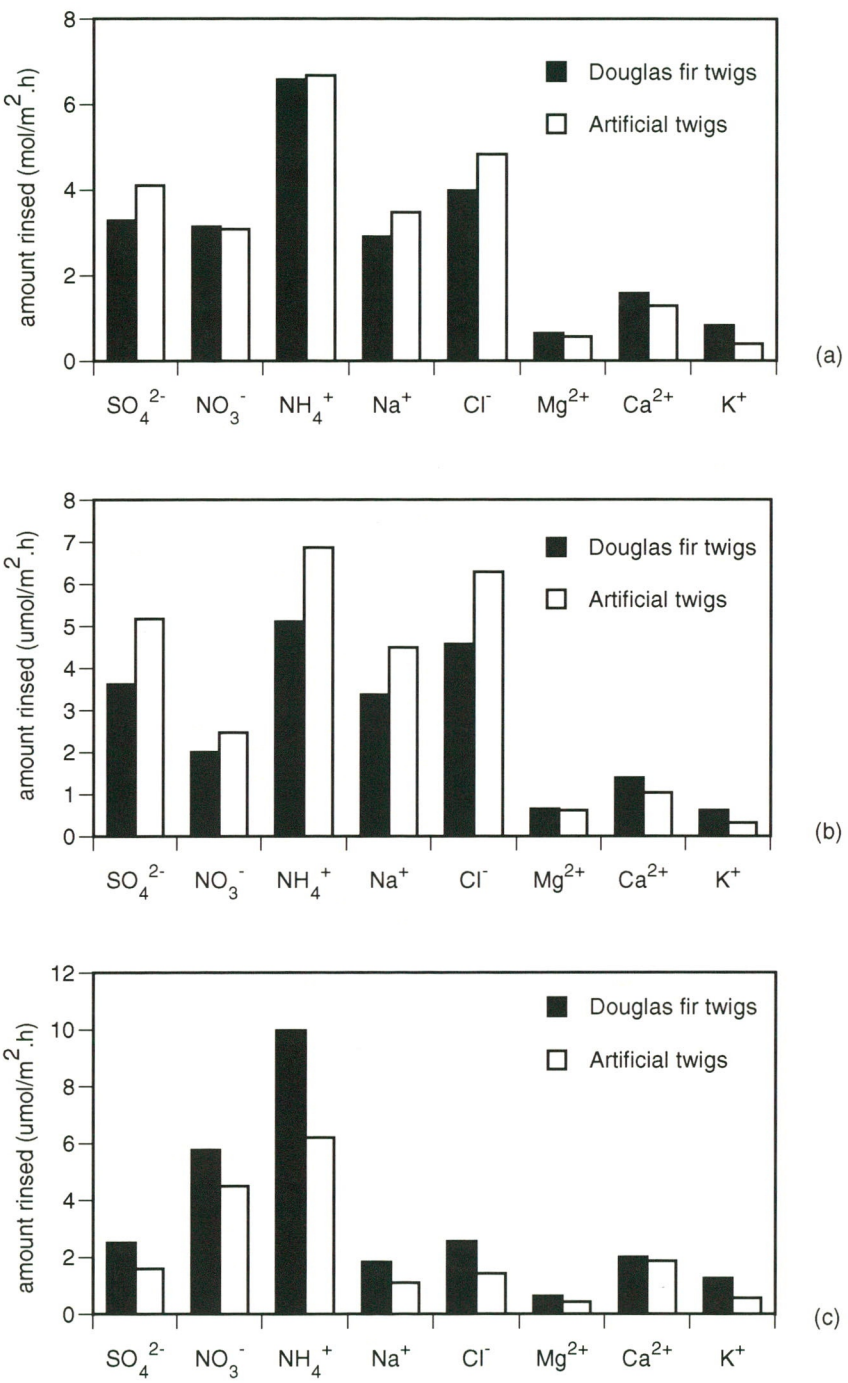

Figure 2 *The amount rinsed from Douglas-fir and artificial twigs, respectively, averaged for (a) all measurement periods, (b) averaged for periods with dry conditions and (c) averaged for periods with light drizzle and/or fog. Amounts are integrated over the whole canopy (in µmol/m² ground area. hour).*

3.1.4 ^{35}S tracer experiments

To estimate the amount of sulphate in throughfall originating from root-derived canopy leaching, a ^{35}S tracer experiment was performed from June 1993 to April 1994 (Wyers *et al.*, 1994). Two plots (containing 5 and 7 trees, respectively) were fertilised each month with an artificial rain water solution containing radioactive $(NH_4)_2{}^{35}SO_4$. Fertilisation took place by means of a drainage system installed at a depth of 10 cm in the mineral soil. One plot (plot 1) received an amount equal to the yearly mean deposition of ammonium and sulphate. The other one (plot 2) was fertilised with twice this amount. Specific activity was measured in the soil, needles and throughfall water on a monthly basis. Every month, freshly collected needles were soaked in water for 24h, and the portion of root-derived sulphur leached from the needles was obtained. The relative contribution of foliar leaching of root-derived sulphate to sulphate in throughfall was calculated by the ratio of the ^{35}S specific activity of sulphate and the water-leachable sulphur from the canopy (Wyers *et al.*, 1994).
The specific activities of needles and water-leachable sulphur were found about equal and showed similar trends with time (Wyers *et al.*, 1994). This indicated that isotopic equilibrium was obtained, i.e. that the specific radioactivity was about equal for the total and the water-leachable sulphur pool in the needles. The relative contribution of foliar leaching of root-derived sulphate to sulphate in throughfall calculated from the ratio of the ^{35}S specific activity of sulphate and the water-leachable sulphur from the canopy amounted on average approximately 3%. Only during one occasion (November 1993), the relative contribution is found larger than 10%. These results are similar to those obtained for Red Maple and Yellow Poplar trees in the USA (Garten *et al.*, 1988) and Scots pine trees in Scotland (Cape *et al.*, 1992). No significant effect of doubling of the annual deposition of ammonium sulphate on root-derived sulphur leaching was found (Wyers *et al.*, 1994).
It was assumed that by soaking freshly collected needles for 24h in water, the 'leachable' portion of root-derived sulphur was extracted from the needles (Wyers *et al.*, 1994). Most likely, the water extract will also contain some dry deposited SO_2 and SO_4^{2-} aerosols, resulting in some dilution of the root-derived ^{35}S labelled 'leachable' sulphate with unlabelled dry deposited sulphur. If so, the specific activity of sulphate measured in the extract is not representative for the root-derived leachable sulphate. This effect will increase if sampling of needles is preceded by long dry periods. The calculated relative contribution of foliar leaching to sulphate in throughfall should therefore be regarded as an upper limit for leaching of root-derived sulphur.

3.1.5 Comparison of results for the Speulder forest

No significant differences were found between the dry and fog deposition estimates of SO_x and the net throughfall fluxes of SO_4^{2-}. Moreover, no significant dif-

ferences were found between the amount of SO_4^{2-} rinsed from Douglas fir and artificial twigs, respectively. The S^{35} tracer experiment indicated that leaching of soil-derived sulphur contributed about 3% (80 mol.ha^{-1}.a^{-1}) to the throughfall flux of SO_4^{2-} at the Speulder forest. Using a stomatal uptake model developed by Bouten and Bosveld (1992), stomatal uptake of SO_2 was estimated to constitute 5% (36 mol.ha^{-1}.a^{-1}) of the total dry deposition of SO_2 (Erisman *et al.*, 1994b). When compared with the total atmospheric deposition of sulphur, it may be concluded that at the Speulder forest sulphur behaves more or less conservatively, with on an annual basis SO_2 uptake balancing leaching of soil-derived sulphur (Table 10).
Differences found between NO_y dry and fog deposition estimates and NO_3^- net throughfall fluxes would suggest that approximately 50% (399 mol.ha^{-1}.a^{-1}) of the total NO_y deposition is irreversibly retained within the canopy (Table 10). Canopy foliage, stems, epiphytic lichens or other microflora are, in principle, able to absorb and incorporate gaseous NO_2, HNO_2 and HNO_3, as well as NO_3^- in solution (e.g. Lang *et al.*, 1976; Johnson and Lindberg, 1992; Lovett and Lindberg, 1993). At the Speulder forest, stomatal uptake as estimated with the model of Bouten and Bosveld (1992) was found to constitute 100%, 11% and 0% of the total NO_2, HNO_2 and HNO_3 dry deposition, respectively (Erisman *et al.*, 1996b). The sum of the stomatal uptake of these compounds equalled 128 mol.ha^{-1}.a^{-1}. No significant differences were found between the amount of NO_3^- rinsed from Douglas-fir and artificial twigs, respectively, indicating uptake of NO_3^- in solution of no or only little importance. This leaves an inexplicable gap of 270 mol.ha^{-1}.a^{-1} between the NO_y dry and fog deposition estimate and the NO_3^- throughfall flux. Binding to litter debris was mentioned as a possible cause of reducing NO_3^- concentrations in throughfall during storage (Ferm, 1993), but was expected to be insignificant in this study (Van Leeuwen and Bleuten, 1994).
Differences found between the dry and fog deposition estimates of NH_x and the net throughfall fluxes of NH_4^+ were statistically not significant. According to the canopy budget model, canopy uptake of NH_4^+ at the Speulder forest amounts to 255 mol.ha^{-1}.a^{-1}. This is larger than the amount of NH_3 estimated to deposit through stomatal uptake, 139 mol.ha^{-1}.a^{-1}, i.e. 10% of the total dry deposition of NH_3 (Erisman *et al.*, 1994b). The difference (116 mol.ha^{-1}.a^{-1}) is assumed to be due to uptake of NH_4^+ in solution although results from the rinsing experiments indicate that at the Speulder forest this process is of limited importance: no significant differences were found between NH_4^+ amounts rinsed from Douglas-fir and artificial twigs, respectively. However, it must be noted once again that the rinsing experiments had only a small time coverage and were performed in the winter period when the vegetation is physiologically less active.
Dry and fog deposition estimates of Na^+, Cl^- and Mg^{2+} were found not significantly different from corresponding net throughfall fluxes. Moreover, no significant differences existed between the amounts of Na^+, Cl^- and Mg^{2+} rinsed from Douglas-fir and artificial twigs, respectively. The canopy budget model suggests that Mg^{2+} leaching equals 41 mol.ha^{-1}.a^{-1} but the model is assumed to slightly overestimate the real leaching amount of Mg^{2+} at the Speulder forest. In all, it may be concluded

that at the Speulder forest canopy exchange of Na^+ and Cl^- is negligible and canopy leaching of Mg^{2+} small (< 40 mol.ha^{-1}.a^{-1}) (Table 10).
K^+ is usually found to be relatively more susceptible to canopy leaching compared to Mg^{2+} and Ca^{2+} because it is not so tightly bound in structural tissues or enzyme complexes (Wood and Bormann, 1975). At the Speulder forest leaching of K^+ is considerable. A comparison with dry and fog deposition estimates has revealed that 89% (270 mol.ha^{-1}.a^{-1}) of the net throughfall flux of K^+ results from canopy leaching. This is in good agreement with the leaching of K^+ calculated with the canopy budget model (270 mol.ha^{-1}.a^{-1}). Somewhat lower K^+ leaching was calculated with the multiple regression model (190 mol.ha^{-1}.a^{-1}), perhaps the result of the exudation of K^+ which appears as dry deposition in the model. Surface wash experiments indicate a K^+ leaching amount of only 104 mol.ha^{-1}.a^{-1}. This large deviation from the other estimates (around a factor of 2.5) is probably due to the relatively small time coverage of these experiments through which results are not representative for the whole measurement period.
Comparing dry and fog deposition estimates with net throughfall fluxes has revealed that 36% (57 mol.ha^{-1}.a^{-1}) of the net throughfall flux of Ca^{2+} may be the result of canopy leaching. This corresponds reasonably well with the Ca^{2+} leaching amount calculated with the canopy budget model (73 mol.ha^{-1}.a^{-1}), especially taking into account that this model slightly overestimates the real leaching amount of Ca^{2+} at the Speulder forest. As for K^+, the Ca^{2+} leaching amount calculated from surface wash experiments (30 mol.ha^{-1}.a^{-1}) is probably too low. Canopy leaching of Ca^{2+} at the Speulder forest may then be assumed to range between 50 and 75 mol.ha^{-1}.a^{-1}.
Canopy retention of H^+ as estimated with the budget model (181 mol.ha^{-1}.a^{-1}) agrees well with the H^+ canopy uptake calculated with the multiple regression model (200 mol.ha^{-1}.a^{-1}).
Comparing results given in Table 9 with canopy exchange rates presented in Table 10, it becomes apparent that at the Speulder forest differences observed between soil loads and deposition fluxes are to a major extent the result of canopy exchange. For closing the gap between the soil load of NO_3^- and the deposition flux of NO_y, however, additional research is necessary. Further knowledge on canopy exchange may be obtained by e.g. using tracers (^{15}N) in ecosystem studies. For this to be useful, NO_2, HNO_2, HNO_3 and NO_3^- dry deposition estimates from micrometeorological measurements and inferential modelling need to be improved, too (Erisman *et al.*, 1994b).
Field experiments at the Speulder forest were mainly performed in the winter period (November until May) when the vegetation is physiologically less active and frequently wet. By scaling measurement results to one year (Table 10), stomatal uptake is probably underestimated. The effect of measuring only in the winter period on uptake and leaching in solution is more difficult to assess. The more frequent occurrence of water films in the winter period may to some extent have counterbalanced the effect of the low physiological status of the vegetation. During the measurement period no episodes with winter smog, frost, drought or an insect plague occurred. Such stress factors may intensify canopy exchange processes con-

siderably. Canopy exchange rates for the Speulder forest can not directly be considered representative for other forests. Canopy exchange will strongly depend on tree species and ecological setting (Van Ek and Draaijers, 1994).
The climatic conditions during the measurements did not favour the application of the multiple regression model. In contrast, the canopy budget model has proven to be a useful tool for determining the impact of canopy exchange on throughfall fluxes at the Speulder forest. The combination of throughfall measurements and this model resulted in deposition estimates which were similar to deposition estimates derived from micrometeorological measurements and inferential modelling. Unfortunately, several basic assumptions in the budget model are not properly evaluated under different environmental conditions (ecological setting, pollution climate). This limits the models usability up to now to forest stands growing on dry and sandy, nutrient poor podzolic soils under current air pollution levels (Draaijers and Erisman, 1995). The model probably can be improved by using wet deposition instead of bulk precipitation fluxes in the calculation procedure. This will be subject of further study.

Table 10 *Canopy exchange rates for the Speulder forest derived from different field experiments and canopy exchange models performed during the period November 1992 and May 1993 (in mol.ha^{-1}.a^{-1}). '+' denotes leaching, '-' denotes uptake.*

	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	K^+	H^+
Model of Van der Maas & Pape (1991)	x	x	-255	x	x	41	73	270	-181
Model of Lovett & Lindberg (1984)	x	x	x	x	x	x	x	235	-196
Model of Bouten & Bosveld (1992)	-36[1]	-128[2]	-139[3]	x	x	x	x	x	x
Dry+fog dep. versus net throughfall	n.s.	-399	n.s.	n.s.	n.s.	n.s.	57	270	x
Rinsing experiments	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	30	104	x
^{35}S experiment	80	x	x	x	x	x	x	x	x

1 stomatal uptake of SO_2
2 stomatal uptake of NO_2, HNO_2 and HNO_3
3 stomatal uptake of NH_3

x = no information
n.s. = not significant

3.2 Error propagation

Experiments should have an accuracy which corresponds to the goal aiming at. Usually a number of primary variables need to be measured to obtain the final results. For example, to estimate the throughfall flux both throughfall amounts and its chemical composition need to be determined. The uncertainty in the primary variables (in this case throughfall amount, chemical composition) determines the uncertainty in the final result (throughfall flux). The different primary variables

usually do not contribute to the same extent to the uncertainty in the final result. When estimating the uncertainty in atmospheric deposition estimated from throughfall fluxes also the uncertainty associated with the estimation of the stem-flow contribution, canopy exchange, wet deposition and dry deposition directly to the forest floor need to be taken into account.
Uncertainties in the deposition estimates are the result of random and systematic errors. Random errors are the result of a certain variability in measured quantities and parameters due to e.g. measuring errors, correcting procedures or parametrizations. Random errors in the deposition estimates will be a function of averaging time and spatial scale. Systematic errors result from neglecting processes or variables for which knowledge is insufficient. Systematic errors will only partly be reduced as a result of averaging in time and space. Whereas random errors lead to variability around an average value, systematic errors may result in serious bias in the deposition estimates. The difference between random and systematic errors is not always very clear. Certain assumptions can lead to both types of errors (Erisman, 1992).
The overall uncertainty in deposition estimates can be determined by using error propagation techniques. The most difficult part when applying such a method is the definition of the uncertainty ranges in the basic measurements or theoretically derived parameters. Lack of reference or validation measurements often necessitates assumptions on uncertainty ranges. Often the standard deviation is taken as a measure of the uncertainty. However, also the maximum deviation from the average can be used in this respect. Poor understanding of physical, chemical and biological processes related to atmospheric deposition often introduces extra uncertainty. For the determination of the overall uncertainty (U_c), the absolute (random or systematic) uncertainties for individual variables (e.g. U_a and U_b) need to be squared and added. The square root of the result is the overall uncertainty. This is only valid if no correlation between the variables exists. If variables show a significant correlation an extra term needs to be added, namely $2*r*U_a*U_b$, where r is the correlation coefficient between the variables:

$$U_c = (U_a^2 + U_b^2 + 2*r*U_a*U_b)^{0.5}$$

This procedure holds when the variables are added or subtracted. When variables are multiplied or divided essentially the same procedure is followed, however, relative rather than absolute uncertainties are considered (Erisman, 1992; Janssen *et al.*, 1990). In Table 11 the procedures of error propagation is elucidated for different relationships possible between the primary variables. As for many cases the correlation coefficient between variables is unknown, ideally two cases need to be considered: first a propagation of errors without correlation (conservative case), and second, a propagation with full positive correlation (worst case).

Table 11 *The overall uncertainty (U_c) of a variable c as function of the relation between the primary variables a and b assuming no correlation between the primary variables (Squires, 1972).*

Relation between primary variables	Procedure to calculate uncertainty in case r=0
$c = a + b$	$U_c = ((U_a)^2 + (U_b)^2)^{0.5}$
$c = a - b$	$U_c = ((U_a)^2 + (U_b)^2)^{0.5}$
$c = a * b$	$U_c = (((U_a/a)^2 + (U_b/b)^2)^{0.5}) / c$
$c = a / b$	$U_c = (((U_a/a)^2 + (U_b/b)^2)^{0.5}) / c$
$c = a^n$	$U_c = (n*(U_a/a)) / c$
$c = \ln(a)$	$U_c = U_a / a$
$c = e^a$	$U_c = U_a * c$

When examining the procedures in Table 11 it becomes clear that raising to the square means that some errors can be neglected. For example, in the case of $c = a + b$ and taking $U_a = 2$ and $U_b = 1$, U_c becomes $(2^2 + 1^2)^{0.5} = 2.24$. Although U_b still equals $0.5*U_a$ this actually means that by neglecting U_b and taking $U_c=U_a=2$, the error in U_c only amounts 12% (this is true if there is no correlation between a and b. If there is high correlation (r=1), then $2*r*U_a*U_b$ has to be added. U_c then becomes $(2^2 + 1^2 + 4)^{0.5} = 3$. In this case the error in U_c amounts 50%!). If c is the sum of more variables, the neglecting of uncertainties which are less then half of the largest uncertainty may seem rather crude. However, neglecting all uncertainties smaller then one third of the largest error can be justified. Similarly, when variables are multiplied or divided, it is allowed to neglect relative errors smaller than one third of the largest relative error.

The random and systematic errors in the annual deposition estimates from throughfall and bulk precipitation measurements at the Speulder forest have been determined using the procedures of error propagation described above. Both random and systematic errors were determined. Results are presented in Table 12. Uncertainty estimates are presented as percentages (x%) reflecting the maximum deviation possible. Uncertainty estimates are in many cases uncertain themselves and for this reason they have been rounded to the nearest number of five. Uncertainty estimates are only presented for the conservative case because no or only small correlation between the primary variables is expected. Besides the uncertainties in throughfall and bulk precipitation flux determined from uncertainties in their primary variables (amounts, chemical composition), the uncertainty of several other parameters necessary for forest deposition estimation are presented. From the uncertainties in throughfall fluxes, bulk precipitation fluxes and other parameters, the uncertainties in wet, dry and total deposition have been calculated.

Table 12 *The random and systematic error in throughfall and bulk precipitation fluxes and their primary variables as well as the random and systematic error in other parameters necessary to estimating the error in wet, dry and total deposition. Numbers hold for the Speulder forest in The Netherlands and reflect the maximum possible error.*

Uncertainty sources	Random error	Systematic error
Throughfall flux		
Amount		
Sampling strategy	10-15 [1]	0
Collecting efficiency of samplers	0	<5 [2]
Measuring volumes	<5 [3]	0
Missing values	<5 [4]	0
Amount *total*	10-15	0-5
Chemical composition		
Sampling strategy	10-15 [1]	0
Sample contamination and		
Biochemical transformations	<5 [5]	0
Analytical procedures	<5 [6]	5-10 [6]
Missing values	<5 [4]	0
Chemical composition *total*	10-20	5-10
Throughfall flux	15-25	5-10
Bulk precipitation flux		
Amount		
Sampling strategy	5-10 [7]	0
Collecting efficiency of samplers	0	<5 [2]
Measuring volumes	<5 [3]	0
Missing values	<5 [4]	0
Amount *total*	5-10	0-5
Chemical composition		
Sampling strategy	5-10 [7]	0
Sample contamination and		
Biochemical transformations	<5 [5]	0
Analytical procedures	<5 [6]	5-10 [6]
Missing values	<5 [4]	0
Chemical composition *total*	5-15	5-10
Bulk precipitation flux	5-20	5-10
Other parameters		
Ratio bulk - wet-only	<5 [8]	0
Stemflow flux	100 [9]	0
Soil flux	20-30 [10]	5-10 [10]
Canopy exchange rate	50-200 [11]	0
Dry deposition directly to forest floor	0	<5 [12]
Atmospheric deposition		
Wet deposition	5-20	5-10
Dry deposition	20-45 [13]	5-20 [13]
Total deposition	15-30 [14]	5-10 [14]

Notes Table 12

1) At the Speulder forest throughfall was sampled using 25 randomly placed gutters. The error in throughfall amount and chemical composition introduced by non-representative sampling is therefore believed to be rather small, i.e. 10-15% depending on component. It must be realized that if for example only 10 randomly placed funnels would have been used the random error would have been much larger (15-50%, see chapter 1.1)

2) The collecting efficiency of the throughfall gutters and precipitation funnels was compared to that of a standard rain gauge recommended by WMO (1971). Only very small differences were found.

3) Throughfall and precipitation volumes were measured using a calibrated measuring jug. A comparison was made with volumes measured by weight. Only very small differences were found.

4) Missing values were interpolated through the remaining data set by using the strong spatial correlation's observed between collectors situated in the vicinity of each other, taking into account seasonal variations in these correlation's.

5) At the Speulder forest several experiments were performed to quantify the impact of sample contamination and biochemical transformations on annual throughfall and bulk precipitation fluxes (Van Leeuwen and Bleuten, 1994; Van Ek and Draaijers, 1994). N and P compounds were found relatively vulnerable to biochemical transformations during storage but the impact on annual throughfall and precipitation fluxes measured was always found less than 5%. The influence of binding to litter debris, mineralization of organic matter, dry deposition directly onto throughfall gutters and pollen deposition was found insignificant (see chapter 1.3).

6) Inter-laboratory test have shown that the error associated with analytical procedures can potentially be very large in throughfall studies (see chapter 1.4). For the Speulder forest research, the laboratory used well defined sample treatment and analytical procedures according to European standards for good laboratory practice. Moreover, the laboratory regularly participated in inter-laboratory tests. Therefore it was believed that the errors associated with analytical procedures were quit low.

7) Precipitation was sampled using 2 bulk samplers placed in a clearing 300 m away from the Speulder forest. Annual mean precipitation amounts and concentrations were compared to those of a wet-only sampler located in the same clearing and to those of a bulk sampler situated on top of a measuring tower above the forest (Van Leeuwen and Bleuten, 1994). Relatively small differences were found, i.e. 5-10% depending on component. The error estimates presented here are in line with those presented by Slanina et al (1990b).

8) The ratio of wet-only and bulk precipitation flux was measured directly at the Speulder forest. The error in the annual mean ratio is therefore considered relatively small. If no simultaneous wet-only and bulk measurements are performed and the mean ratio derived from literature would have been used (see Table 3), the error in wet-only to bulk ratio will be much larger (30-150% with the largest potential errors for H^+, Ca^{2+} and K^+).

9) Stemflow was not measured directly at the Speulder forest because it was expected to contribute only to a small extent to the total soil flux. Measurements in similar Douglas fir forest stands in The Netherlands indicate that stemflow equals about 6% of the throughfall flux (Van Breemen et al, 1992). This percentage was also applied for the Speulder forest to estimate stemflow fluxes. Thus derived stemflow fluxes are expected to have relative large potential error (100%).

10) Soil flux is defined as throughfall + stemflow flux. To calculate the uncertainty in the soil flux, the stemflow flux is taken 6% of the throughfall flux. The uncertainty in soil flux at the Speulder forest is mainly determined by the uncertainty in throughfall flux, despite the large uncertainty in stemflow flux.

11) Several experiments were performed and models applied to estimate canopy exchange rates at the Speulder forest (see chapter 3.1). An overview of experimental and model results is presented in Table 10. Estimated canopy exchange rates for individual compounds show strong variability in relation to method used to derive them, with maximum deviations from the average of 50-200% depending on component. Canopy exchange of sulphur, sodium and chloride was considered insignificant.

12) Dry deposition directly to the forest floor strongly depends on below-canopy air concentrations, turbulence intensity, and the structure and wetness of the forest floor and understorey vegetation. At the Speulder forest dry deposition directly to the forest floor is expected to be very small due to the very dense canopy (one-sided LAI = 9-12) and absent understorey vegetation.

13) Dry deposition is calculated from the throughfall flux - wet deposition - canopy leaching. The uncertainty in dry deposition is estimated using throughfall fluxes and wet deposition amounts presented in Table 7 and average canopy exchange rates derived from Table 10. Fog deposition is assumed to be included in the dry deposition estimate. Dry deposition directly to the forest floor is assumed insignificant at the Speulder forest. Numbers presented hold for SO_x, NO_y, NH_x, Na, Cl, Mg and Ca. The random and systematic error in dry deposition of K amounts 115-180% and 35-70%, respectively.

14) Total deposition is defined as dry deposition + wet deposition. Fog deposition is assumed to be included in the dry deposition estimate. Numbers presented hold for SO_x, NO_y, NH_x, Na, Cl, Mg and Ca. The random and systematic error in total deposition of K amounts 85-130% and 25-50%, respectively.

For the Speulder forest the random and systematic error in annual mean total deposition, estimated from throughfall and bulk precipitation measurements in combination with additional measurements on wet-only to bulk precipitation ratios and canopy exchange rates, amounts 15-30% and 5-10%, respectively. These values hold for SO_x, NO_y, NH_x, Na, Cl, Mg and Ca. The random and systematic error in annual mean total deposition calculated for K is found much larger, i.e. 85-130% and 25-50%, respectively. This is caused by the large contribution of canopy leaching to the throughfall flux of K (80%). At the Speulder forest random errors are thus larger compared to systematic errors. The random error in total deposition is found dominated by the random error in dry deposition. The latter, in turn, is dominated by the random error in throughfall flux and for K by the random error associated with the estimation of the canopy exchange rate. The random errors associated with the estimation of the bulk precipitation and stemflow flux are found less critical. The random error in throughfall and bulk precipitation flux mainly results from non-representative sampling. The systematic error in throughfall and bulk precipitation fluxes arises from uncertainties associated with analytical procedures and the collecting efficiency of the samplers.
Error estimates made for forest deposition at the Speulder forest may not be considered representative for other forests in Europe. At the Speulder forest state-of-the-art measurement and analytical techniques have been used with a sufficiently large number of replicate samplers. In throughfall studies, usually a much smaller number of throughfall replicate samplers is used through which the potential error due to non-representative sampling will be much larger. When bulk samplers are used for collecting precipitation, the uncertainty in wet deposition will be much larger. Moreover, interlaboratory tests have shown that the errors associated with analytical procedures can be much larger than the ones considered valid for the Speulder forest. Canopy exchange rates are likely to be subject to much larger uncertainty if less extensive canopy exchange research is performed as done at the Speulder forest. The uncertainties associated with the estimation of the stemflow flux will become more important in beech or dense pine forests where the contribution of stemflow to the soil flux is expected to be much larger. Similarly, the uncertainties associated with the estimation of dry deposition directly to the forest floor will be more important in case forest deposition is to be estimated for deciduous forest, very open forest stands, or forest edges. In all, it can be concluded that the uncertainty estimates made for the Speulder forest are lower-limit values and that for other throughfall and bulk precipitation studies usually larger random and systematic errors hold than those presented in Table 12.

3.3 Recommendations

Deposition estimates should always be verified by comparison with independent field and model data. Moreover, when assessing forest deposition from results of throughfall and precipitation measurements, an extensive uncertainty analysis should be made including all the different steps in the monitoring program. Based on the results of the analysis, the main shortcomings in the applied methods and procedures should be assessed and, if required, additional research initiated. Relatively large errors may be associated with the sampling strategy, analytical procedures and the estimation of wet-only to bulk ratios, stemflow fluxes, canopy exchange rates and dry deposition directly to the forest floor and understorey vegetation. When interpreting forest deposition data in relation to e.g. soil acidification or health effects, the uncertainty in deposition estimates should be taken into account. Random and systematic errors in forest deposition estimated from throughfall, stemflow and bulk precipitation data generally will be larger than those calculated for the Speulder forest, i.e. 15-30% and 5-10%, respectively.
Within the framework of the Pan-European Program for Intensive and Continuous Monitoring of Forest Ecosystems, throughfall, stemflow and precipitation measurements are made at a large number of sites throughout Europe. The relevant EC Regulations and manual of ICP Forests (1994) give standard methods for the sampling and analysis of the throughfall, stemflow and precipitation. Through the Data Accompanying Report Questionnaires (DAR-Q's) the participating countries submitted information of the applied methods. In a first evaluation by FIMCI (EC-UN/ECE, 1997) a number of differences in methods have been reported. The countries involved in the Program generally use their own specific sampling strategy, sampling equipment, sampling handling and analytical procedures and interpretation methods. For this reason, a field inter-comparison of sampling strategy, sampling equipment and sampling handling should be performed as soon as possible in order to further harmonize the technical aspects of the measurements. Laboratories should regularly participate in inter-laboratory test to ensure good quality of the concentration measurements. Moreover, throughfall, stemflow and precipitation measurements should be interpretated in relation to forest deposition in a consistent manner. To enable this, guidelines for interpretation need to be developed or, otherwise, interpretation should be performed in a centralized manner.
The uncertainty introduced by the use of different measurement methods, analytical procedures and interpretation methods need to be assessed in order to determine the quality and comparability of the results from the different monitoring sites. It should be stressed, however, that even using one single measurement method, analytical procedure and interpretation method cannot prevent systematic errors (e.g. introduced by not taking into account dry deposition to the forest floor and understorey vegetation). Only the comparability on a relative basis will be improved. Field and laboratory inter-comparisons will enable researchers to identify the most accurate sampling strategy, sampling device, sampling handling and analytical procedure and will at the same time promote knowledge transfer among the

participants. Permanent efforts to improve quality assurance and keep it at a high level are necessary to yield credibility in the data sets obtained.

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