CHAPTER 6 EVALUATION OF DEPOSITION ESTIMATES

Introduction

Probably as important as the knowledge of the deposition estimates itself, is the knowledge about the uncertainty in the estimates. It is not an easy task to do an accurate and independent uncertainty analysis. Because of the very few field experiments made to determine deposition parameters, the base for generalisation is small, and even worse is the base for evaluation of results, the latter because the same experiments must be used for derivation and evaluation of the parameters. In spite of these difficulties, the evaluation of the SO_2 dry deposition parameters has been chosen to open this chapter. For this, three long-term measurements of SO_2 gradients, over grassland, heathland and a forest in the Netherlands are used, along with a long-term eddy correlation measurement sequence over the Boden forest in Canada, to compare modelled parameters with those derived from measurements.

The only independent flux measurements which can be used for evaluating model results are throughfall measurements. However, during the past years, there has been discussion on whether throughfall measurements can actually be used to determine atmospheric deposition (Ivens et al., 1989; Johnson and Lindberg, 1990; Erisman, 1993b; Draaijers and Erisman, 1993; Draaijers, 1993). Up to now it has not been possible to quantify the impact of canopy exchange processes on throughfall deposition estimates. In the second part of this chapter, throughfall measurements are compared to flux estimates, canopy exchanges processes are quantified and a relation between the two estimates is determined.

Finally, at the end of this chapter, results of an uncertainty analysis are presented for the DEADM and the EDACS model estimates. The uncertainty analysis for the results in the Netherlands is based on a comparison of flux measurements with modelled values made in recent years in the Netherlands, on a comparison with TREND results and on an error propagation study. Since such a detailed study is not available for EDACS, a more qualitative description of the uncertainty is given.

6.1 EVALUATION OF SURFACE EXCHANGE PARAMETERS FOR SO_2

The parametrisation scheme for SO_2 surface resistance, determined for European pollution climates and receptor surfaces common in Europe (Erisman *et al.*, 1994, outlined in Chapter 4), was tested using SO_2 dry deposition measurements over a deciduous forest in Canada (Shaw *et al.*, 1988; Padro *et al.*, 1992; 1993), a coniferous forest (Erisman *et al.*, 1993a); a heathland area (Erisman 1992; Erisman *et al.*, 1993b) and a grassland area in the Netherlands (Erisman *et al.*, 1993b).

6.1.2 EXPERIMENTAL PROCEDURE

A short overview of the site characteristics, the methods used, the duration of the experiments and uncertainty estimates will be given for each dataset. The heathland and Douglas fir experiments are extensively described in Chapter 7.

Deciduous forest
As part of two Eulerian Model Evaluation Field Studies (EMEFS), measurements were taken over a deciduous forest located on the Borden Canadian Forces Base (44° 19'N, 80° 56'W). SO_2 fluxes were measured in the winter of 1990 using the eddy correlation technique (Shaw *et al.*, 1988). Fast-response SO_2 measurements were made using a modified Meloy 285 sulphur analyser with a fast-response burner block. The Meloy 285 analyser employs an FPD to sense total sulphur. The FPD is negatively sensitive to water vapour, an effect for which a correction was made. Changes in SO_2 concentrations during the half-hourly average measuring periods were accounted for by estimating the storage flux using the concentration measurements before and after the current period. The measured meteorological, concentration and deposition parameters were reported by Padro *et al.* (1993). A description of the forest and dataset of fluxes and deposition velocities can also be found in Padro *et al.* (1993). The one-sided leaf-area index (LAI) varies from 5 in summer to 1 in winter (Bark Area Density, BAI). The average height of the trees in the forest is 18 m. The measurements above the canopy were taken at 33.4 m. The number of half-hourly V_d observations for SO_2 amount to 365 for the entire measurement period between March 15, 1990 and April 29, 1990, above the leafless forest. For diurnal patterns, the standard error of the mean for each half-hour was estimated to be about ± 0.15 cm s^{-1} for V_d and $\pm 30\%$ for the flux (Padro *et al.*, 1993).

Coniferous forest
Since November 1992 continuous vertical concentration gradients of SO_2, NO_2 and NH_3 as well as relevant meteorological parameters have been measured at a Douglas fir forest site in the Netherlands. The Speulder forest site is located in the national park 'Hoge Veluwe' in the central part of the Netherlands. The measuring site consists of a homogeneous 2.5 ha monoculture of mature Douglas fir of 35 years old, with a stem density of 785 ha^{-1}. The mean

tree height is approximately 20 m. The canopy is well closed with the maximum leaf-area density at a height of 10-14 m. The one-sided LAI varies throughout the year from about 8 in early spring to 11 m at the end of the summer. The site is surrounded by a larger forested area of approximately 50 km^2; the nearest edge is at a distance of 1.5 km from the site. Directly adjacent to the site are stands of pine, mixed beech/oak, and Douglas fir and larch, with mean tree heights varying from 12 to 25 m, about roughly the same as those of the research area. A small clearing (1 ha) is situated to the north of the stand. The equipment, its performance and experiments to determine measuring errors and accuracy of the measurements are described extensively in Zwart *et al.* (1993). The standard error for each two hourly average V_d was estimated to be about ± 40%.

Grassland

A system for SO_2 based on the micrometeorological gradient technique has been developed for routine monitoring of dry deposition fluxes. The SO_2 dry deposition monitoring system has been described extensively in Mennen *et al.*, (1992) and Erisman *et al.* (1993b). The SO_2 concentrations were measured with two UV pulsed-fluorescence monitors (Thermo Environmental Instruments model 43W). One SO_2 monitor is used to measure the concentrations at four successive levels (heights of 4, 2, 1 and 0.5 m), while a second monitor continuously measures concentrations at the 4-m level. A change in SO_2 concentration during the measuring cycle can thus be detected and corrected for (Erisman *et al.*, 1993b). A measuring cycle lasts 30 min. Selection criteria have been derived to select measuring periods satisfying the demands of the flux-profile theory. Furthermore, a scheme has been developed to calculate yearly average fluxes from the selected and rejected measuring periods.

The dry-deposition monitoring system was placed at a rural site in the centre of the Netherlands from 1987 to 1989. The undisturbed fetch over the grassland is between 700 m and 1 km for the eastern, southern and western directions. The pastures surrounding the location were infrequently used for cattle grazing and irregularly spread with manure during the growing season. The grass height was maintained at 15 cm most of the time. The soil type is so-called wet-peat with an average pH ranging from 4.8 to 5.1; the soil surface was nearly always wet. Eight measuring cycles were averaged to yield 4-h average deposition parameters, in order to minimise (random) measuring errors. The standard error for each four-hourly average V_d was estimated to be about ± 50%.

Heathland

A three-year experiment involving several research groups was conducted at the Elspeetsche Veld for the determination of deposition fluxes on heathland. Micrometeorological measurements of SO_2, NH_3 and NO_2 were made using different techniques. Furthermore, throughfall and bulk precipitation fluxes of SO_4^{2-}, NH_4^+ and NO_3^- were also measured. The experiment was carried out from 1989 to 1992 at a heathland nature reserve in the central part of the Netherlands: i.e. the 'Elspeetsche Veld' (52° 16' N, 5° 45' E) near the village of Elspeet.

The heathland is located in a region with moderate ambient concentrations of SO_2 (6 $\mu g\ m^{-3}$) and NOx(20 ppb) (RIVM, 1989). The ammonia emission density in this area is about equal to the average NH_3 emission in the Netherlands (Erisman, 1989). The standard error for each two-hourly average V_d was estimated about 30%.

6.1.3 MODELLED V_D COMPARED WITH MEASUREMENTS

For the comparison of modelled deposition parameters with those obtained from measurements, only data satisfying theoretical constraints and well above detection limits were employed. Data were rejected for wind speeds below 1 m s^{-1}, and for wind directions with no ideal fetch, when one of the measured parameters was below the detection limit and when the concentration changes during a measuring cycle were too large (Padro *et al.*, 1993; Erisman *et al.*, 1993a; 1993b; 1993c). These selection criteria had little influence on the Canadian data. The Speulder forest dataset was reduced by about 50%, mainly as a result of the detection limit of the SO_2 monitors and because of technical problems. It has not been estimated whether this has resulted in a systematic bias in the dataset. For Zegveld and Elspeet about 70-80% of the data were rejected, mainly due to a poor fetch and the detection limit of the SO_2 monitors used. It was found that for the Zegveld and Elspeet, data selection did not lead to a systematic bias in deposition parameters. The conditions in the remaining dataset were found to be representative for the whole measuring period (Erisman *et al.*, 1993b).

The remaining dataset comprised 364 half-hourly averaged deposition parameters for the deciduous forest, 652 two-hourly averaged data for the coniferous forest, 1391 two-hourly averaged data for heathland and 821 four-hourly averaged data for grassland. For each measuring period, R_c values were calculated according to the parametrisation given in Chapter 4. Furthermore, R_c values were calculated using parametrisations given by Wesely (1989) for comparison. The aerodynamic resistance R_a and the quasi-laminar layer resistance R_b were estimated according to the equations given in Erisman *et al.* (1994, see Chapter 4). The inverse of the sum of the three resistances is the dry deposition velocity V_d. In Figures 6.1 A to 1 D, modelled V_d values are compared to those obtained from measurements for the deciduous forest, coniferous forest, heathland and grassland, respectively. In these figures, average modelled values and their standard deviation for each class of measured V_d are plotted against class averages. Classes are formed by placing combinations of measured and modelled V_d values in increasing order of measured deposition and averaging the combinations over an equal number of data. The standard deviation is given as a measure for the variation in each class. This cannot be considered as a measure of the uncertainty in class averages. In Table 6.1, minimum, maximum and average values of some measured parameters are given. This table also gives average deposition parameters and the standard deviation. The correlation coefficient of the modelled V_d against the measured values, and the standard error are also presented here. Averages, standard deviations and correlation coefficients between

measured and modelled V_d obtained with the parametrisation by Wesely (1989) are also given.

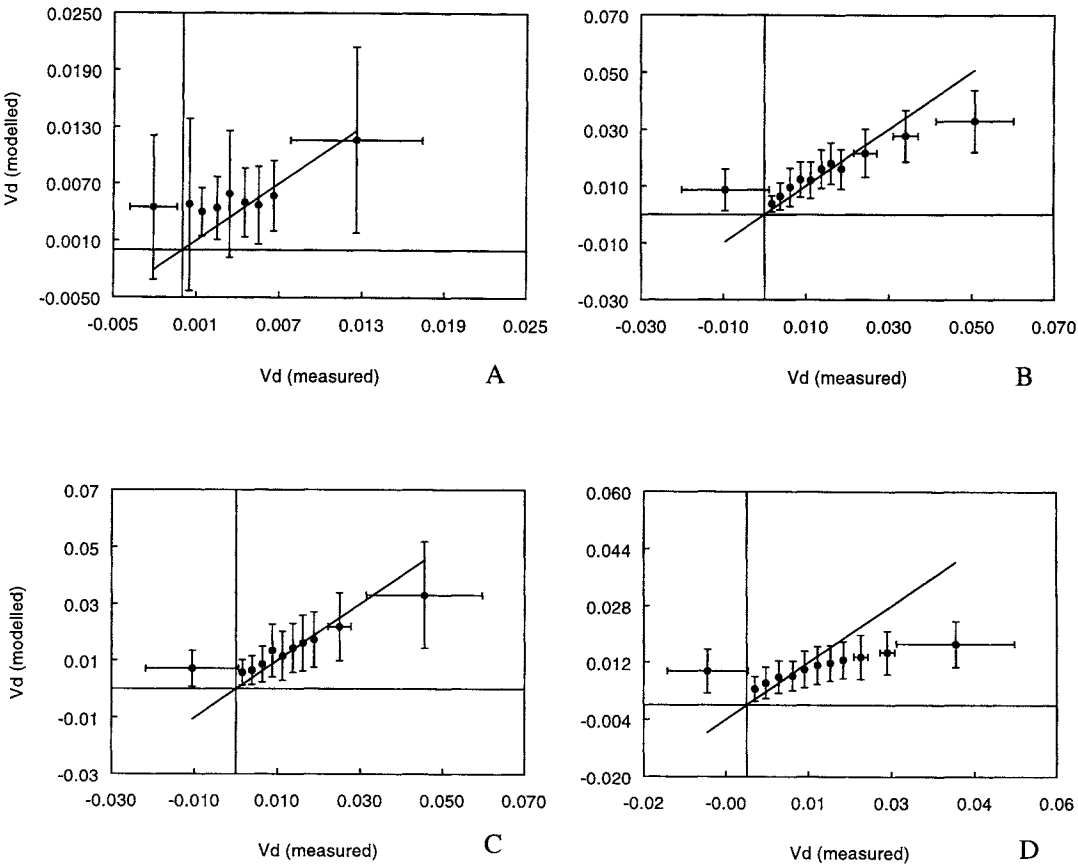

FIGURE 6.1 Comparison of modelled V_d (m s^{-1}) with V_d obtained from measurements: A. Deciduous forest; B. Coniferous forest; C. Grassland and D. Heathland. Solid dots represent average modelled values for class-average measured values. The line represents the 1:1 ratio. Small overbars represent measured class averages ± SD, while large overbars represent modelled averages ± SD.

TABLE 6.1 Average, minimum and maximum measured parameters, and measured and modelled V_d, F and R_c values, with correlation coefficients between modelled and measured values, as well as SD (in parentheses

Parameter	Deciduous forest	Coniferous forest	Grassland	Heathland
C SO_2 average	3.1	11.7	13.9	7.2
min	1.0	4.0	3.0	0.5
max ($\mu g\ m^{-3}$)	27.9	81.1	76.2	12.0
T average	10.5	6.4	9.7	9.6
min	-6.9	-10.4	-3.3	-10.1
max (°C)	28.2	25.2	24.3	30.1
u average	3.1	4.1	4.8	3.7
min	1.0	1.0	1.1	1.0
max ($m\ s^{-1}$)	7.8	9.5	13.2	9.1
Q average	190	78	115	145
min	0	0	0	0
max ($W\ m^{-2}$)	900	860	790	810
rh average	59	82	80	85
min	27	20	33	10
max (%)	100	100	99	100
No. wet hours	105	487	440	1013
No. dry hours	261	426	381	378
Periods	March 15 - April 29, 1990	November 1992-June 1993	November 1987-September 1989	November 1989-Augusts 1992
No. measurements	365, half-hourly averages	652, two-hourly averages	821, four-hourly averages	1391, two-hourly averages
Measured V_d[a]:	0.0028 (0.0056)	0.0165 (0.0193)	0.0148 (0.0100)	0.0115 (0.0135)
Modelled V_d[a]:	0.0066 (0.0067)	0.0168 (0.0152)	0.0110 (0.0061)	0.0134 (0.0100)
Wesely (1989): ($m\ s^{-1}$)	0.0010 (0.0001)	0.0020 (0.0009)	0.0056 (0.0021)	0.0071 (0.0034)
modelled versus measured V_d:				
Correlation coeff.:	0.39	0.66	0.46	0.64
Standard error:	0.007	0.011	0.010	0.010
Wesely (1989) versus measured V_d:				
Correlation coeff.:	0.39	0.17	0.30	0.21
Standard error:	0.0001	0.0009	0.011	0.013
Measured F[a]:	-0.012 (0.034)	-0.196 (0.239)	-0.199 (0.175)	-0.065 (0.100)
Modelled F[a]: ($\mu g\ m^{-2}\ s^{-1}$)	-0.021 (0.032)	-0.205 (0.207)	-0.140 (0.109)	-0.074 (0.081)
Measured R_c[a]:	4 (6580)	70 (335)	20 (195)	55 (185)
Modelled R_c[a]: ($s\ m^{-1}$)	185 (115)	130 (770)	50 (85)	60 (120)

[a] The estimates have been presented in more significant figures than consistent with their accuracy for intercomparison.

The results in Figures 6.1A to D show that modelled V_d correlate well with the measurements taken in the coniferous forest and heathland, where 44 and 41%, respectively, of the variance was accounted for. The correlation between modelled and measured velocities for the deciduous forest and grassland is lower. Only 15 and 21% , respectively, of the variance was accounted for. The datasets are too large to use statistical tests to test the hypothesis to see if overall averages or variances of measured and modelled values are equal. This can be done for subsets e.g. for each class in Figures 6.1A to D. These results can be roughly extracted from the figures. It can be seen that for the coniferous forest and heathland measurements, averages are about equal for each class except for negative values. For the grassland, average measured values are significantly higher. For the deciduous forest, the lowest modelled values are higher than those measured, whereas the larger values are equal. For each class, Wesely's parametrisation yields significantly lower values than measured or obtained from the parametrisation presented here. Wesely's parametrisation implies too large a value of R_c. The correlation between modelled and measured values is lower for Wesely's R_c parametrisation than that given here (Table 6.1).

It is more interesting to see whether modelled and measured values agree for the periods dominated by certain processes than just to compare class averages. Four periods were selected where different resistances are expected to dominate: (1) daytime dry conditions (R_{stom}), and (2) wet conditions (R_{ext}), (3) night-time dry conditions (R_{inc}) and (4) wet conditions (R_{ext}). Results of averages and correlation between modelled and measured values for these four periods are presented in Table 6.2.

The results presented in Table 6.2 show the same general features as those obtained for class averages. The modelled V_d values for the deciduous forest are generally higher than those measured. The modelled V_d values for the coniferous forest and heathland are generally in good agreement with measurements. Grassland V_d values agree well for wet periods. However, for dry conditions in daytime and night-time, modelled values are too low. It is not clear from these results which resistance from Eqn. 4.3 is modelled better.

TABLE 6.2 Average dry deposition velocities (m s^{-1}) and correlation coefficients between modelled and measured V_d for dry/wet and daytime and night-time periods, with SD in parentheses.

	Daytime		Night-time	
	Dry conditions	Wet conditions	Dry conditions	Wet conditions
Deciduous forest				
Measured V_d[a]	0.003 (0.006)	0.006 (0.007)	0.001 (0.003)	0.001 (0.006)
Modelled V_d[a]	0.006 (0.007)	0.011 (0.010)	0.003 (0.001)	0.006 (0.010)
Cor. coeff.	0.10	0.83	0.32	0.26
Std. error	0.007	0.005	0.001	0.010
Number	195	59	85	26
Coniferous forest				
Measured V_d[a]	0.007 (0.016)	0.023 (0.020)	0.007 (0.008)	0.025 (0.020)
Modelled V_d[a]	0.006 (0.004)	0.024 (0.014)	0.006 (0.005)	0.026 (0.016)
Cor. coeff.	0.47	0.57	0.56	0.60
Std. error	0.004	0.012	0.004	0.013
Number	167	142	123	220
Grassland				
Measured V_d[a]	0.014 (0.010)	0.015 (0.010)	0.013 (0.011)	0.017 (0.013)
Modelled V_d[a]	0.007 (0.003)	0.015 (0.006)	0.007 (0.004)	0.014 (0.006)
Cor. coeff.	0.42	0.49	0.60	0.58
Std. error	0.009	0.009	0.009	0.011
Number	260	268	121	173
Heathland				
Measured V_d[a]	0.008 (0.011)	0.014 (0.015)	0.009 (0.011)	0.012 (0.013)
Modelled V_d[a]	0.008 (0.005)	0.019 (0.010)	0.007 (0.006)	0.015 (0.010)
Cor. coeff.	0.38	0.65	0.58	0.81
Std. error	0.005	0.012	0.006	0.008
Number	403	507	148	333

[a]The estimates have been presented in more significant figures than consistent with their accuracy, for intercomparison.

Figures 6.2A to D give examples of time series of measured and modelled V_d values for the four types of vegetation. These figures illustrate comparisons of the diurnal cycles between the model and measurement under different conditions. Again, the model seems to overpredict over the deciduous forest.

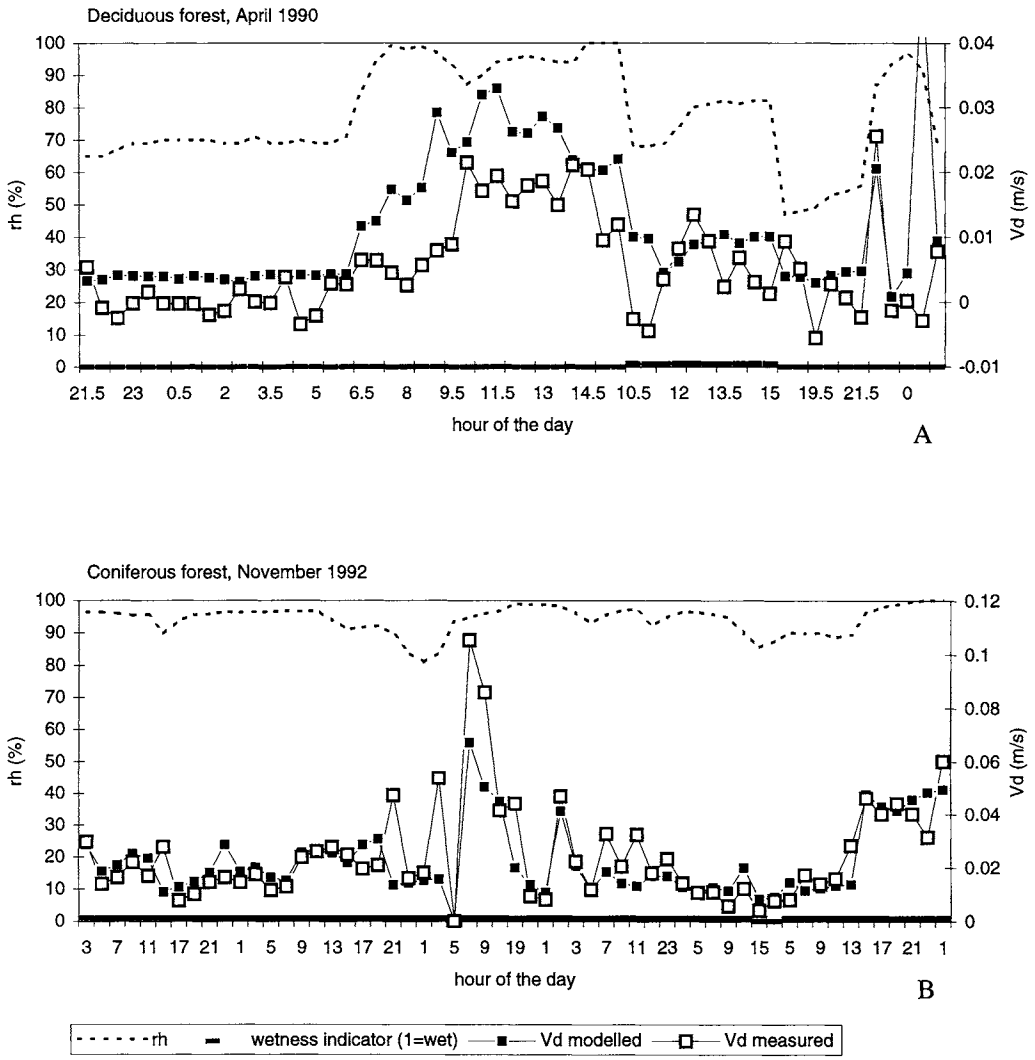

FIGURE 6.2. Examples of time series of modelled and measured V_d: A. Deciduous forest; B. Coniferous forest.

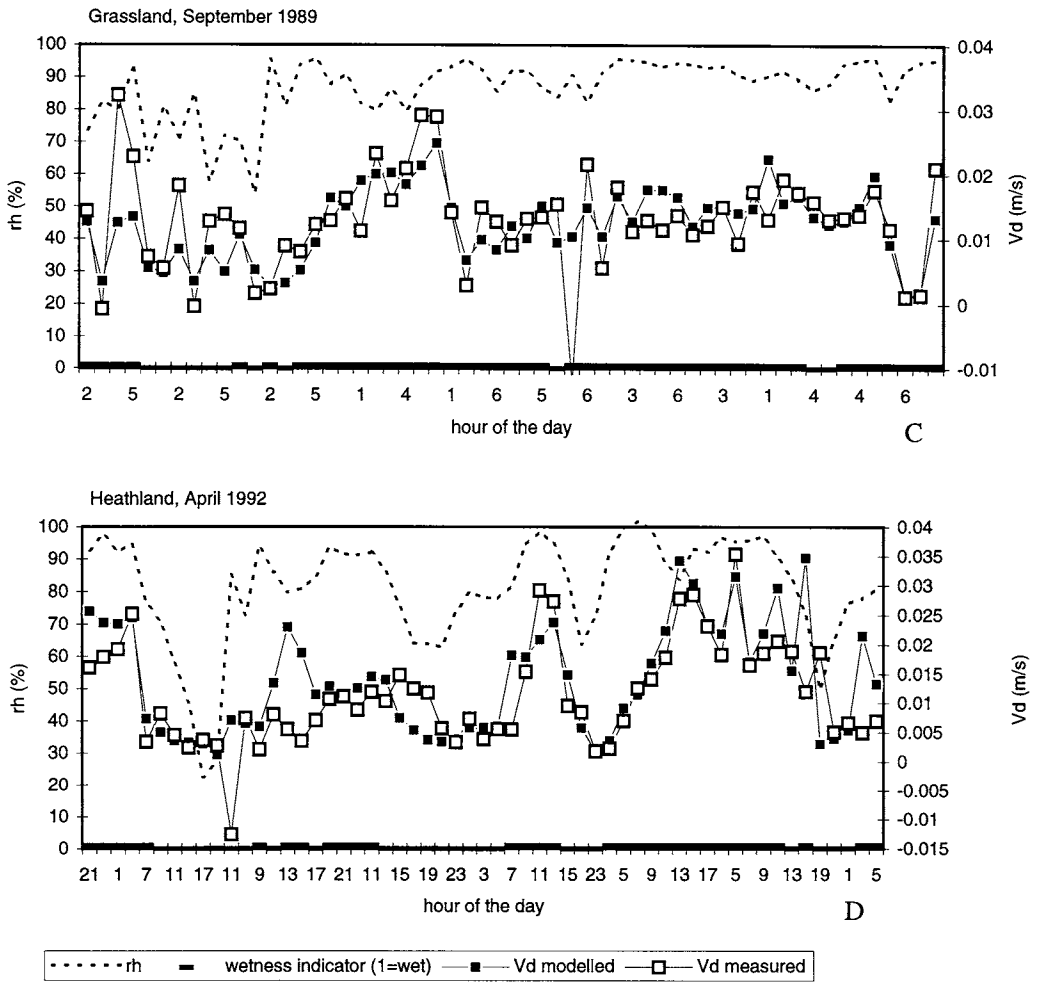

FIGURE 6.2 (*continued*). Examples of time series of modelled and measured V_d: C. Grassland and D. Heathland.

6.1.4 DISCUSSION

The comparison analysis was conducted for dry deposition velocities instead of surface resistances, as it is the most important parameter and because R_c values show large scatter with no general distribution, making comparison difficult. Furthermore, R_c values are very

sensitive to measurement errors, especially at small V_d's. Small V_d's are the result of either large values of R_a+R_b or a large resistance to surface uptake. Small measurement errors might result in very large positive or negative values of R_c, introducing enormous scatter in the dataset. Measurement errors lead to a normal distribution of errors in V_d, but to an unknown distribution in R_c (see section on uncertainties below). By only comparing modelled with measured V_d values there is the danger of ignoring differences between modelled and measured values. These differences can result from surface processes occurring during periods showing very high values of R_a+R_b (i.e. stable conditions), which yield low V_d. In general, these processes do not influence agreement between model and measurements and may therefore be ignored. However, in cases where they dominate, this can introduce a large systematic bias.

Uncertainties

The measured and modelled deposition parameters are subject to several uncertainties. During periods when the fluxes or concentrations are small, measurements usually show a high uncertainty due to the relative high error in the concentration gradient. Systematic errors are excluded as much as possible through the selection procedure. However, a random measurement error can lead to random errors in V_d, which might lead to negative values. These might be interpreted as emission rather than small deposition. On the other hand, at zero resistance to uptake at the surface (R_c~0), random errors can yield V_d values that are larger than the maximum possible V_d. Large random errors cause frequency plots of measured V_d to look like normal distributions (the distribution of the random error), while the 'real' distribution of V_d is logarithmic. Figures 6.3 A to D give the frequency distributions of measured and modelled V_d. As expected from the results presented in Figure 6.1, the modelled and measured distributions of V_d over the coniferous forest and heathland are similar. Moreover, the distributions approach the logarithmic form, as expected. Thus, measured V_d is not influenced to a large extent by a random error.

The distribution for the grassland is logarithmic, but the peaks for the modelled and measured distributions are different, suggesting an incorrect R_c parametrisation. An investigation of individual measurements, revealed that by using 4-h averages, the surface wetness parametrisation yielded an underestimate of the time the surface was wet (see also Table 6.2). It was observed in the field that the surface was wet nearly all of the time, whereas results in Table 6.1 suggest that this was only true for about 50% of the cases.

The distribution for the deciduous forest follows the shape of a normal distribution. This suggests that the measurement results are dominated by a random error. Concentrations during the measurements are relatively low, with an average value of 3.1 $\mu g\ m^{-1}$ (Table 6.1). The lower the concentration, the higher the error in the concentration gradient as a result of random errors. This can be seen by introducing an extra selection criterion on concentration. If

measurements at concentrations below 2 μg m^{-1} are rejected, the shape of the frequency distribution becomes logarithmic. Furthermore, the correlation coefficient between modelled and measured values increases to 0.6 (36% of variance accounted for), with no systematic differences between the averages. Also, comparison between modelled and measured values for dry/wet conditions during daytime and night-time shows improvement.

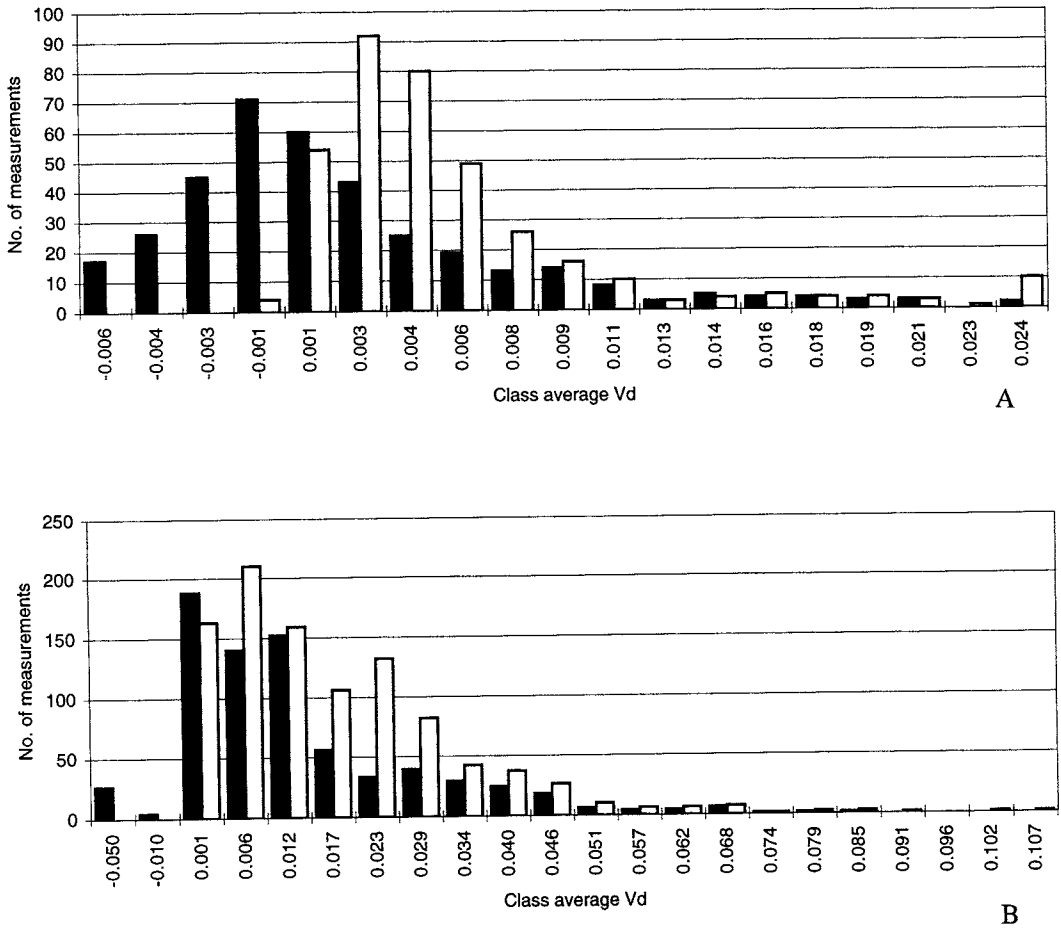

FIGURE 6.3 Histograms of modelled (open columns) and measured (dark columns) V_d (m s^{-1}): A. Deciduous forest; B. Coniferous forest.

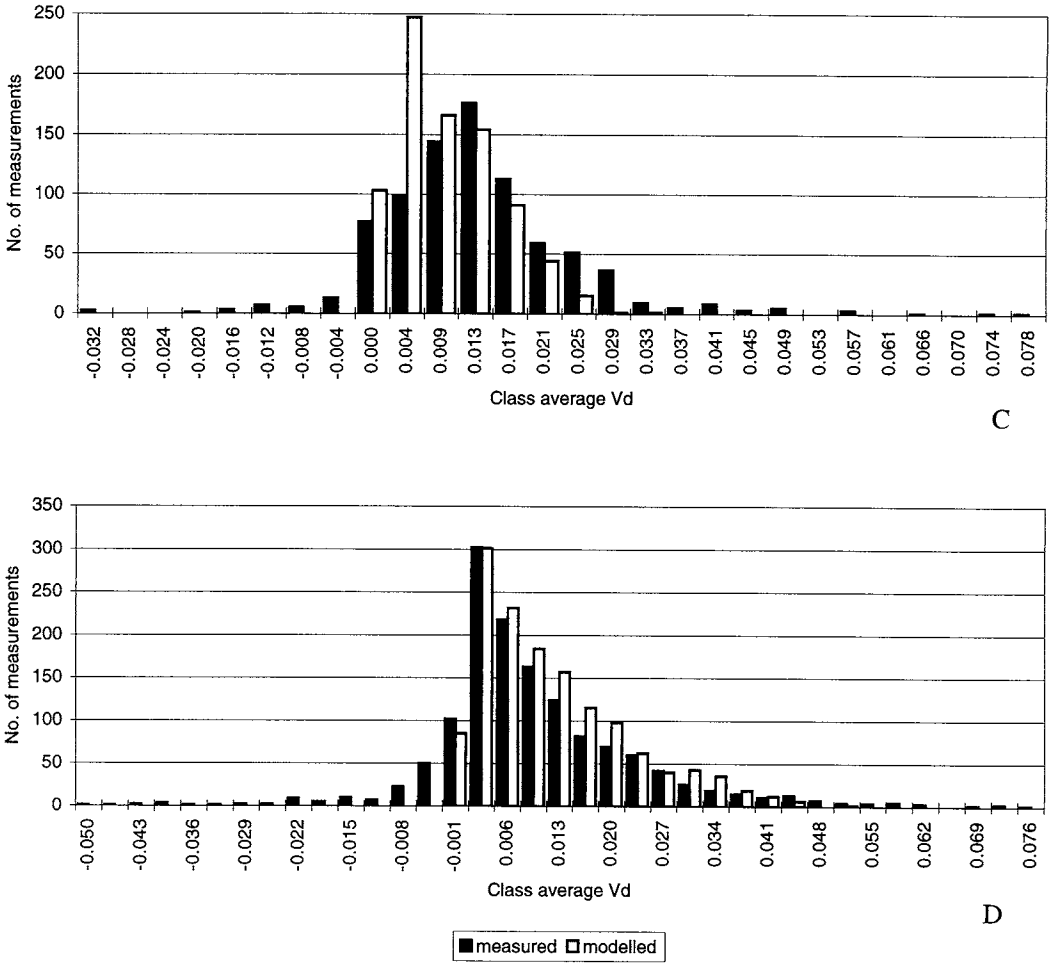

FIGURE 6.3 (*continued*) Histograms of modelled (open columns) and measured (dark columns) V_d (m s^{-1}): C. Grassland and D. Heathland

Comparison with other parametrisations

Much early work done on parametrisation of the surface resistance to gaseous dry deposition comes from the USA (Hicks *et al.*, 1987; 1989; Wesely, 1989), the UK (Garland, 1977; 1978; Fowler, 1978; 1985) and Canada (Voldner *et al.*, 1986; Padro *et al.*, 1993). Wesely (1989) recently derived a scheme for the RADM model representative for North American conditions (see Section 4). Padro *et al.* (1993) used this scheme and the scheme presently used in the ADOM model to compare SO_2 V_d values with those obtained from measurements in the Borden forest, the same dataset as used here. They found that ADOM's estimates were much larger than the measured values, whereas Wesely's parametrisation yielded smaller estimates than were measured. These results are comparable to those found in the present study. Wesely's parametrisation yields much lower V_d values than measured for each of the four types of vegetation. This is mainly caused by the surface resistance description for periods during or after rain. Wesely assumes that R_c values increase during or after rainfall as a result of sufficient S(IV) saturation of the rain, which prevents further uptake of SO_2. This assumption is based on unpublished measurements by the Argonne National Laboratory (Wesely, 1989). Before Wesely's parametrisation is used, this assumption must be tested since it will have serious implications, especially in those areas where the surface is frequently wetted by rain. It could lead to an underestimate of the surface uptake of SO_2 by a of factor of 2 (low vegetation) to 8 (forests)! Testing the assumption on S(IV) saturation can be done using short-term precipitation measurements of S(IV), base cations and pH, as well as ambient NH_3 and base cation concentrations.

Representativeness of parametrisation for European pollution climates

As the surface resistance parametrisation is derived from the measurements made at the heathland site of Elspeetsche Veld (Erisman *et al.*, 1993c), it might only be representative for the Dutch pollution climate. This pollution climate is different from other climates common in Europe, and might therefore not be useful for models used to estimate deposition in Europe. However, from Table 6.1 it is obvious that the measured parameters (*C*, *T*, *u*, *Q* and *rh*) cover a very wide range, representative for large areas in Europe. The ratio of hours for which vegetation was assumed to be wet to those for which the vegetation was assumed to be dry is larger than for most areas in Europe because of the Dutch marine climate. However, there were sufficient measurements made during very dry periods to allow a valid study of the parametrisation under such conditions. In any case, during these periods deposition velocities and fluxes tend to be very low and therefore not too important.

A major concern in the Netherlands is the relatively high neutralisation capacity caused by large ammonia emissions from intensive livestock breeding. This is not representative for large areas of Europe (and USA, see discussion on comparison to Wesely's parametrisation), where NH_3 emissions and concentrations are much lower (Buijsman *et al.*, 1987; Asman and Van Jaarsveld, 1992). In the Netherlands the annual average ammonia concentration is about

equal to that of SO_2: 5 ppb and 4 ppb, respectively. This is also the case at the three Dutch measuring sites. It has been suggested that the presence of ammonia enhances sulphur deposition (Van Breemen *et al.,* 1982; Adema *et al.,* 1986). However, Erisman and Wyers (1993) showed that this so called co-deposition is important only in extreme conditions, i.e. when there is a very high ratio of NH_3 concentration to that of SO_2. They found that surface wetness was most important for enhancing dry deposition, but they did not demonstrate that NH_3 does not play a role under wet conditions.

6.2.5 SYNTHESIS

This section has described the testing of a surface resistance parametrisation for surface uptake of SO_2 using eddy correlation measurements over a deciduous forest in Canada and vertical gradient measurements over a coniferous forest, a grassland and a heathland in the Netherlands. The surface resistance parametrisation includes the stomatal resistance, the resistance for wet surfaces caused by precipitation and relative humidity, the resistance to in-canopy aerodynamic transport, and the resistance to soil and to snow-covered surfaces. It is concluded that the modelled V_d compare reasonably well with the measurements, yielding no systematic differences for the coniferous forest and heathland (more than 40% of variance accounted for). There is much less agreement with the measurements for the deciduous forest and grassland, where systematic differences are shown. However, it was concluded that the errors were not due to the surface resistance parametrisation, but rather to possible random errors in the (low) concentration measurements over the deciduous forest and for the grassland measurements to underestimating the time the surface was assumed wet. The parametrisation was tested for four different classes (dry and wet conditions for day and night). No systematic error could be detected from this comparison other than what is described above.

The surface resistance parametrisation developed by Wesely (1989) was also tested using the same dataset. Results show a systematic underestimation of V_d values when compared to measured values. The underestimate is mainly the result of the parametrisation of R_c during and after precipitation. Wesely assumes an increase in R_c, whereas measurements show a decrease to values close to zero. This can lead to an underestimation of V_d SO_2 by a factor of 2 for low vegetation to a factor of 8 for forests.

The parametrisation demonstrated for the Netherlands may be representative for large parts of Europe. Other types of vegetation can be modelled by adjusting the stomatal resistance. The parametrisation might not be representative for those areas which have a completely different pollution climate from that occurring during the measurements. This might be the case for very dry areas or areas where ammonia concentrations are negligibly low compared to those for SO_2. Unfortunately, there is a lack of long-term measurements for such areas. It is

therefore recommended to perform such measurements over these areas to evaluate and/or improve surface resistance parametrisations.

6.2 RELATION BETWEEN ATMOSPHERIC DEPOSITION AND SOIL LOADS

Introduction
There are no long-term micrometeorological measurements of other components available than those for SO_2. It is therefore not possible to do similar tests of the parametrised deposition parameters with measurements. Modelled fluxes might be tested with throughfall measurements. However, the relation between throughfall fluxes and atmospheric deposition is not in all cases very clear. Wash-off processes from leaf and bark surfaces due to water passing through the canopy can increase concentrations relative to open field precipitation. The net-throughfall flux is determined by the net contribution of washed-off dry deposited gases and particles, interception of cloud water and re-evaporation of gases from the canopy. The kinetics of removal by wash-off may be as complex as the kinetics of dry deposition itself. Canopy interaction is, next to dry deposition, regarded as one of the most important factors influencing throughfall and stemflow composition for several ions. Both leaching from the canopy as well as canopy uptake of nutrients and gases have been found (Parker, 1983).

In several attempts to compare throughfall fluxes with atmospheric deposition estimates, large differences between the two estimates for deposition were found (e.g. Ivens, 1990, Draaijers and Erisman, 1993; Erisman, 1993b). Establishing a link between the two is useful because it provides a way to estimate soil loads from atmospheric deposition estimates and allows the use of the relatively simple and cheap throughfall method to determine atmospheric deposition. The link between atmospheric deposition and soil loads is important because critical loads refer to soil loads and atmospheric deposition estimates provide a link with emissions. Thus if critical load exceedances are used to estimate emission reductions, the relation between atmospheric deposition and soil load should be known.

The data used in published comparisons between the two are of varying quality, for both atmospheric deposition estimates and throughfall estimates. Ivens (1990), Draaijers (1993) and Beier and Rasmussen (1989) have addressed the uncertainty in throughfall measurements and proposed sampling methods, which should reduce most of it. Furthermore, Erisman (1993a) provided a method to estimate atmospheric deposition on the required scale (stand level), which enabled a good comparison. Draaijers and Erisman (1993) compared throughfall estimates with atmospheric deposition estimates of SOx for 30 different forest stands on the Utrechtse Heuvelrug in the Netherlands. They assessed the uncertainty in the two methods and found that by changing the surface resistance parametrisation of SO_2 in the inference model to that derived from more recent dry deposition measurements in the Netherlands (Erisman *et al.*, 1994), the agreement between the two estimates was reasonable without any systematic differences. This would mean that canopy exchange of sulphur species is negligible in the long term (one year).

In this section throughfall measurements and deposition estimates will be compared on two levels: at the site, using experiments done at the Speulder forest in the Netherlands (described in section 7.3) and on the national level (The Netherlands), using throughfall measurements made at 51 sites throughout the Netherlands for several years. First, some theoretical considerations on canopy exchange processes will be given.

6.2.1 THEORETICAL CONSIDERATIONS ON CANOPY EXCHANGE

Draaijers *et al.* (1994) provide a literature overview of field and lab experiments on canopy exchange. The most important factors determining canopy exchange are listed. Here, only a summary of the most important processes will be given.

Concentrations in water layers covering leaves and needles are found to be influenced by passive diffusion and ion exchange between the surface water and the underlying apoplast of canopy tissues (i.e. aqueous layer outside cell membranes). Diffusion is found to be the major cause of elevated (leached) anionic concentration in throughfall, while both diffusion and ion exchange contribute to (leached) cationic concentrations in throughfall (Schaefer and Reiners, 1990). Diffusion is controlled by the (ion-specific) resistance of the cuticle and epicuticular wax, and by the concentration gradient between leaf-surface water and apoplast (Reiners and Olson, 1984). Ion exchange can take place for both anions and cations, but cuticular anion exchange sites are far fewer in number than cation exchange sites. Cations, especially those abundant in the foliar apoplast, are released from cuticular ionic binding sites in exchange for hydrogen or ammonium ions retained by the foliage (Roelofs *et al.*, 1985; Parker, 1990). Cations can also be released from foliage along with weak organic acid anions, or along with inorganic anions (Cronan and Reiners, 1983). Canopy uptake of gases through stomata is governed by gas concentrations and ion equilibrium concentrations in the apoplast, the dissolved gas in apoplast liquid and stomatal opening.

The rate of canopy exchange depends on tree physiology, pollution climate and ecological setting. As deciduous trees are leafless in winter, canopy exchange is little during this season. Coniferous trees stay green all year and continue to lose or gain nutrients throughout the dormant season. In general, however, deciduous trees tend to lose more nutrients than coniferous trees (Smith, 1981). The age distribution of leaves also affects the magnitude of leaching; young immature needles tend to lose fewer nutrients compared to older ones (Parker, 1990). Senescent leaves lose more nutrients than green leaves. Leaf wetness is important as the liquid on the outside of the foliage comprises the medium for canopy exchange. The wettability of foliage is found to differ considerably among tree species (Boyce *et al.*, 1991). Moreover, an increasing rate of foliar wax degradation caused by, for example, exposure to air pollutants is thought to lead to a decrease in water repellency, which in turn will lead to longer retention of moisture (Cape, 1983). Biotic stresses such as insect plagues

and diseases may initiate canopy leaching (Bobbink *et al.*, 1990). The same holds for abiotic stresses such as drought and temperature extremes (Tukey and Morgan, 1963). Soil fertilisation is found to increase canopy leaching (Cape, 1983). The presence of pollutants might enhance canopy leaching; concentrations of, for example, ozone might enhance the permeability of cell membranes in foliage, thereby increasing ion leakage (Evans and 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 fluxes compared to short rain periods with large rainfall intensities.

6.2.2 RESEARCH RESULTS FROM THE SPEULDER FOREST SITE

Throughfall fluxes at the Speulder forest

During the experiments in the Speulder forest, the same throughfall method was used as that by Draaijers (1993) for the comparison reported in Draaijers and Erisman (1993) (see also section 7.3). The number of samplers (gutters) was increased to 25 in order to determine the optimum for deducing a soil-load flux representative for the whole forest stand (Van Leeuwen *et al.*, 1994). The results of the throughfall measurements have been reported in Van Leeuwen *et al.* (1994) and in Draaijers *et al.* (1994). Stemflow was not measured in the Speulder forest. It is expected that stemflow fluxes for Douglas fir are negligible compared to throughfall fluxes, accounting for a maximum of 6% of the total flux (Van Leeuwen *et al.*, 1994). Net throughfall fluxes are calculated for 30 different periods. Not all periods ended with showers with enough precipitation to wash off all the dry deposited material from the canopy. It was estimated that this would take about 15 mm of precipitation (Van Leeuwen *et al.*, 1994). This occurred only in four periods, thus the November '92-May '93 period was split in four periods. This, however, represents a small base for statistical analysis when comparing with atmospheric deposition estimates. Therefore another 12 periods were selected in which it is supposed that at least most of the dry deposited material was washed off and thus the whole period could be split into 16 periods. The net throughfall fluxes averaged over the period of 23 November 1993 to 10 May 1993 are listed in Table 6.3. The estimated uncertainty is given in parentheses. The contribution of canopy exchange to net throughfall was estimated using the Ulrich model (1983), as outlined in Draaijers *et al.* (1994).

Atmospheric deposition at the Speulder forest

Wet deposition is measured on a routine basis at the Speulder Veld, about 3 km from the Speulder forest site. Wet deposition data for 1993 are given in Table 6.3. As it is not possible to determine atmospheric deposition solely with micrometeorological measurements, the resistance analogy is used as supplement. Dry deposition fluxes are inferred from measured concentrations (gases and particles) and estimated dry deposition velocities for those periods in which gradient measurements could not be used for estimating deposition. V_d is estimated using meteorological measurements and a component specific surface resistance. This surface

resistance is determined using a parametrisation outlined in Chapter 4. The resistance analogy is applied to determine gas, particle and fog deposition for the period that throughfall was measured in order to compare throughfall fluxes with atmospheric deposition (see section 7.3).

TABLE 6.3 Average net throughfall fluxes, and dry and fog deposition estimates for the Speulder forest, along with wet deposition at Speulder Veld (mol $ha^{-1}a^{-1}$)

Component	Net throughfall	Dry deposition based on net throughfall and model results (Draaijers *et al.*, 1994)	Dry deposition based on concentration and meteorological measurements	Wet deposition Speulder Veld	Difference between net throughfall and atmospheric deposition (%)[a]
SO_2			660 (30)		
Fog			35 (30)		
SO_4^{2-} aerosol			215 (60)		
SOx	925(30)	925 (30)	910 (40)	270 (20)	-1
NH_3			1440 (40)		
Fog			100 (30)		
NH_4^+ aerosol			645 (60)		
NHx	1730 (30)	1980 (40)	2185 (50)	680 (25)	10
HNO_2			105 (40)		
HNO_3			135 (40)		
NO_2			115 (40)		
Fog			25 (30)		
NO_3^- aerosol			410 (60)		
NOy	395 (30)	395 (40)	790 (40)	290 (25)	67
Cl^-	800 (30)	800 (30)	890 (50)	535 (20)	10
K^+	305 (30)	35 (50)	35 (50)	40 (30)	0
Na^+	690 (30)	690 (30)	600 (50)	465 (20)	-14
Ca^{2+}	160 (30)	85 (40)	100 (50)	45 (30)	17
Mg^{2+}	140 (30)	100 (40)	120 (50)	65 (30)	19

[a] Calculated as $[(AD-NT)/(AD+NT)]*200\%$; *AD*=atmospheric deposition; *NT*= dry deposition based on net throughfall and a model by Van der Maas *et al.* (1991). Estimated uncertainty (expert judgement) is given in parentheses in %.

Gas deposition

The dry deposition of SO_2, NO_2 and NH_3 was estimated using the gradient technique (Erisman *et al.*, 1993; Wyers *et al.*, 1993). The performance of the SO_2 and NO_2 instruments used and the monitoring system as a whole are extensively described in Zwart *et al.* (1994). First, data were selected to meet theoretical demands and to reduce errors in deposition parameters. Second, a parametrisation of the surface resistance for the different gases was derived from the selected data and tested. Finally, meteorological and concentration measurements and

estimated surface conditions for the rejected periods were used, together with the surface resistance parametrisation and the resistance analogy, to estimate fluxes for individual periods that throughfall measurements were available. Results are reported in Draaijers *et al.* (1994). In the same period, dry deposition of HNO_3, HNO_2 and HCl was inferred from measured air concentrations and parametrised V_d values (Erisman *et al.*, 1994). Gas deposition estimated for the total throughfall measuring period is given in Table 6.3. Estimates of the uncertainty from expert judgement (Zwart *et al.*, 1994; Mennen *et al.*, 1995) are given in parentheses. Part of the uncertainty is the result of low-time coverage of the measurements: for example, only 48% of the time measurements for NH_3 and 42% for NO_2 are available. For SO_2, a relatively large time coverage of 79% was obtained. The average dry deposition velocities over the period November 1992 to May 1993 are 1.8 ± 2.5 cm s^{-1} for SO_2, 2.6 ± 8.0 cm s^{-1} for NH_3, and 0.1 ± 1.4 cm s^{-1} for NO_2.

Particle input

Dry deposition of acidifying aerosols and base cations was inferred from measured air concentrations and the model described in Chapter 4. The input was estimated using the continuous aerosol concentration measurements and an integrated dry deposition velocity over the size distribution of the components (Ruijgrok *et al.*, 1994). The average fluxes for the November 1992 to May 1993 period are listed in Table 6.3. The uncertainty in the fluxes is taken from Ruijgrok *et al.* (1994). The time coverage of the flux estimates was about 70% due to technical problems.

Fog input

Deposition of fog to the Speulder forest was estimated by Vermeulen *et al.* (1994). Input by fog was estimated by parametrisation of *LWC* on visibility measurements and a parametrisation of V_d based on u_*^2 (see section 7.3). It was found that the water flux measured with throughfall was larger than that measured using the eddy correlation method. This is probably due to the cut-off diameter used by the droplet spectrum measurements (45 μm). This means that periods with drizzle are not taken into account in the fog deposition estimates using micrometeorological methods. The chemical composition of fog droplets was measured by Römer and Te Winkel (1994) using a CWP string collector. Concentrations in fog are taken as the average over a number of samples obtained in the Netherlands over several years (Van Aalst and Erisman, 1991; Vermeulen *et al.*, 1994) because of lack of measured data representative for the six months. Vermeulen *et al.* (1994) concluded that the SO_4^{2-} and NH_4^+ fluxes estimated with the two methods did not differ by more than a factor of two. Differences were higher for NO_3^-.

The total fog deposition estimated for the November 1992 to May 1993 period is given in Table 6.3. The contribution of fog to the total dry deposition in this period is very low: 4% for SOx, 5% for NHx and 3% for NOy. Even on an annual basis fog input is small compared to dry deposition of gases and aerosols (Vermeulen *et al.*, 1994).

Comparison of throughfall fluxes with atmospheric deposition estimates
Averaged for the whole measurement period, the dry and fog deposition estimate for SO_x derived from micrometeorological measurements and inferential modelling almost equal the measured net throughfall flux of SO_4^{2-}. Dry and fog deposition estimates for NHx and NOy are higher than net throughfall fluxes of NH_4^+ and NO_3^-, respectively. Dry and fog deposition estimates and net throughfall of Na^+ and Cl^- are more or less equal. Dry and fog deposition estimates for Ca^{2+}, K^+ and Mg^{2+} are lower than corresponding net throughfall fluxes. If net throughfall of NH_4^+ and base cations is corrected for canopy exchange by using the canopy exchange model of Ulrich (1983) (Draaijers *et al.*, 1994), good agreement is found with dry and fog deposition estimates (Table 6.3 and Draaijers *et al.*, 1994).

No significant relationships are found when dry and fog deposition estimates are compared to net throughfall fluxes from all the 16 measuring periods between November 1992 and May 1993. This may be explained to a large extent by incomplete wash-off of dry deposition from the canopy by rain, through which no independent samples are obtained. Moreover, in several periods concentration measurements had a relatively small time coverage through which dry deposition estimates were subject to large potential error. Four periods could be distinguished in which complete wash-off of dry deposition was expected (Van Leeuwen *et al.*, 1994). For these four periods, the SOx dry and fog deposition estimate agrees with the net throughfall flux of SO_4^{2-} ($r=0.997$; $p=0.002$). Levels are also about equal. For other components, larger differences are found and relationships are not significant ($p<0.05$). Results are shown in Table 6.4.

TABLE 6.4 Comparison of net throughfall fluxes with atmospheric deposition (% difference calculated as in Table 6.1) for four periods for which complete wash-off of deposited material was expected

Period	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Ca^{2+}	K^+	Mg^{2+}
1	4	-84	18	83	47	78	170	55
2	9	-39	-16	23	0	59	169	86
3	5	-87	-33	8	-16	58	154	6
4	-6	4	-22	47	62	-86	153	0

Canopy exchange processes in the Speulder forest
The results of the comparison between throughfall and atmospheric deposition in Table 6.3 is in line with the expected differences resulting from canopy exchange processes. For sulphur, sodium and chloride no net canopy exchange is observed, whereas nitrogen components are taken up by the canopy and base cations are leached. Ammonium seems to be taken up by the canopy to a larger extent than nitrate. Draaijers *et al.* (1994) tried to assess the influence of canopy exchange processes on the difference between throughfall and atmospheric deposition

using the results of the Speulder forest experiments and the comparison in Table 6.3. Their results are summarised in Table 6.5.

No significant differences were found between the dry and fog deposition estimates of SOx and the net throughfall fluxes of SO_4^{2-}. Moreover, no significant differences were found between the amount of SO_4^{2-} rinsed from Douglas fir and artificial twigs. A S^{35} nutrition experiment performed by ECN at Speulder forest, indicated that leaching of soil-derived sulphur contributes only about 3% (80 mol ha^{-1} a^{-1}) to the throughfall flux of SO_4^{2-} in the Speulder forest (Wyers *et al.*, 1994). 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.*, 1994; Draaijers *et al.*, 1994). It may be concluded that in the Speulder forest sulphur shows a more-or-less conservative behaviour, with SO_2 uptake balancing leaching of soil-derived sulphur.

Differences found between NOy dry and fog deposition estimates and NO_3^- net throughfall fluxes would suggest that approximately 50% (400 mol ha^{-1} a^{-1}) of the total NOy deposition is irreversibly retained within the canopy. Canopy foliage is capable of absorbing and incorporating gaseous NO_2, HNO_2 and HNO_3, as well as NO_3^- in solution. In the Speulder forest, stomatal uptake was estimated to constitute 100%, 11% and 0% of the total NO_2, HNO_2 and HNO_3 dry deposition, respectively (Erisman *et al.*, 1994; Draaijers *et al.*, 1994). The sum of the stomatal uptake of NO_2 and HNO_2 was 130 mol ha^{-1} a^{-1}. Uptake of NO_3^- from the water layer solution is probably of no importance. Subtracting stomatal N uptake from the atmospheric deposition estimate leaves a gap between net throughfall and NOy dry and fog deposition of 30% (270 mol ha^{-1} a^{-1}). This difference is well within the overall uncertainty of the NO_3^- net throughfall fluxes, and NOy dry and fog deposition estimate and fluxes, although the difference is systematic.

Differences found between dry and fog deposition estimates of NHx and net throughfall fluxes of NH_4^+ were not statistically significant. According to the canopy exchange model of Ulrich (1983) and Van der Maas *et al.* (1990) canopy uptake of NH_4^+ in the Speulder forest amounts to 255 mol ha^{-1} a^{-1}. This is considerably larger than the amount of NH_3 estimated to be taken up through stomata (140 mol ha^{-1} a^{-1}) i.e. 10% of the total dry deposition of NH_3. The difference (115 mol ha^{-1} a^{-1}) may be due to uptake of NH_4^+ from the water layer solution. However, results from a rinsing experiments showed no significant differences between NH_4^+ amounts rinsed from Douglas fir and artificial twigs (Römer and te Winkel, 1994). The difference is well within the uncertainty of the two estimates.

Dry and fog deposition estimates of Na^+, Cl^- and Mg^{2+} were not found to be 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 (Römer and te Winkel, 1995). Rinsing experiments indicate some leaching of Mg^{2+} during periods when the canopy is wet but this effect could not be quantified. The

canopy exchange model of Ulrich (1983) and Van der Maas *et al.* (1990) suggests that Mg^{2+} leaching equals 41 mol ha^{-1} a^{-1} but it is assumed that the model slightly overestimates leaching of Mg^{2+}. All in all, it may be concluded that in the Speulder forest, canopy exchange of Na^+ and Cl^- is negligible and canopy leaching of Mg^{2+} is small (<40 mol ha^{-1} a^{-1}).

In the Speulder forest leaching of K^+ is considerable. A comparison with dry and fog deposition estimates reveals 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 exchange model of Ulrich (1983) and Van der Maas *et al.* (1990) (270 mol ha^{-1} a^{-1}) and in reasonable agreement with results obtained by Draaijers *et al.* (1994) using the multiple regression model of Lovett and Lindberg (1984) (190 mol ha^{-1} a^{-1}). Surface wash experiments indicate a K^+ leaching 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 so that results may not be representative for the whole measurement period (Römer and te Winkel, 1994).

TABLE 6.5 Canopy uptake or leaching in Speulder forest estimated using results of different experiments (+ = uptake; - = leaching; 0 = inert or negligible; x = not estimated)

Experiments	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	K^+	H^+
Comparison atm. dep. / throughfall	0	-400	0	0	0	0	-55	-270	-
Stomatal resistance modelling	35[a]	130[b]	140[c]	x	x	x	x	x	x
Model - Ulrich and V_d Maas	0	0	255	0	0	-40	-75	-270	180
Model - Lovett/Lindberg	x	x	x	x	x	x	x	-190	195
Surface wash experiments (twigs)	0	0	0	0	0	0	-30	-105	x
S^{35} nutrition experiment	-80	x	x	x	x	x	x	x	x

[a] stomatal uptake of SO_2
[b] stomatal uptake of NO_2 and HNO_2
[c] stomatal uptake of NH_3

Comparing dry and fog deposition estimates with net throughfall fluxes reveals that 36% (55 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 model of Ulrich (1983) and Van der Maas *et al.* (1990) (73 mol ha^{-1} a^{-1}), especially taking into account that this model probably overestimates leaching of Ca^{2+}. As for K^+, the Ca^{2+} leaching calculated from surface wash experiments (30 mol ha^{-1} a^{-1}) is probably too low. It is estimated that leaching of Ca^{2+} in the Speulder forest is found between 50 and 75 mol ha^{-1} a^{-1} (Draaijers *et al.*, 1994).

Canopy retention of H^+ estimated with the exchange model of Ulrich (1983) and Van der Maas *et al.* (1990) (181 mol ha^{-1} a^{-1}) agrees well with the H^+ canopy uptake calculated with

the Lovett and Lindberg (1984) multiple-regression model (200 mol ha^{-1} a^{-1}). Field experiments were mainly performed in the winter period (November until May) when the vegetation is physiologically less active and frequently wetted. By scaling measurement results to a whole year, 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. Due to the frequent occurrence of water films, uptake and leaching will be relatively intense in the winter period, which may to a certain extent counterbalance 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 are found to intensify canopy exchange processes considerably.

It is relevant to note that canopy exchange rates for the Speulder forest may not automatically be considered representative for other forests in the Netherlands. Canopy exchange is found to depend on tree species and ecological setting (Draaijers *et al.*, 1994).

Synthesis

It has been shown that for canopy exchange most of the Speulder forest experiments point in a similar direction. Although the estimates of the absolute amounts of components retained or leached in the canopy may differ, depending on the experiment (see Table 6.5), the average values give a good picture of the situation in the Speulder forest. The average values are given in Table 6.5. It shows that H^+ is taken up by the canopy; this is accompanied by leaching of Mg^{2+}, Ca^{2+} and especially K. SO_2 taken up by stomata is eventually leached again, whereas NH_3 taken up via stomata is almost completely retained by the canopy. Oxidised nitrogen components, especially NO_2, are taken up by the canopy. Whether NO_3 and NH_4 aerosols are taken up directly or via solution is uncertain. We assume from the results of the experiments that NO_3 uptake is negligible, whereas NH_4 is taken up in exchange with K^+ and Ca^{2+}. Na^+ and Cl^- are considered inert. The highest uncertainty in canopy exchange estimates relates to estimates of the nitrogen components.

Observed differences between dry and fog deposition estimates from micrometeorological measurements and inferential modelling, on the one hand, and net throughfall fluxes on the other cannot be seen as exclusively due to canopy exchange. Dry deposition estimates from micrometeorological measurements and inferential modelling are uncertain due to errors in the air concentration measurements (Arends *et al.*, 1994), their sometimes low time coverage and the uncertainties associated with the parametrisation of the dry deposition velocities (Erisman *et al.*, 1994; Ruijgrok *et al.*, 1994). Fog deposition estimates are uncertain due to uncertainties associated with the estimation of water fluxes and the measurement of the average chemical composition of the fog droplets (Vermeulen *et al.*, 1994). Uncertainties associated with the throughfall method when used for estimating dry and fog deposition include the dry deposition to the forest floor and understorey vegetation, dry deposition directly onto the throughfall gutters, the representativeness of the throughfall sampling, the

wet deposition estimate, and the stemflow contribution and canopy exchange processes (Draaijers and Erisman, 1993). However, with canopy exchange processes being the only exception, the above-mentioned factors probably contributed only to a very small extent to the uncertainty in the throughfall dry and fog deposition estimates in this study.

6.2.3 THROUGHFALL FLUXES COMPARED TO DEADM DEPOSITION ESTIMATES

Acidifying components

DEADM results were obtained for the locations and time periods in which throughfall was sampled as listed in Erisman (1993a) and Draaijers and Erisman (1993). For each measuring site an inventory of local forest characteristics was made. These data were used in DEADM to calculate the site-specific fluxes. In total, 51 sites were used in the comparison. The first 20 sites, operated in 1987 and 1988 by the University of Nijmegen (*KUN)* (Houdijk and Roelofs, 1991) and the Winand Staring Centre for Integrated Land Soil and Water Research (*SC-DLO*) (De Vries *et al.*, 1990), are scattered over the country (Erisman, 1993b), whereas the other 30 are concentrated in an area of about 3 x 3 km. Table 6.6 gives the average and standard deviations of the throughfall estimates of the different sets of data. Also listed in this table are the average and standard deviations of the total deposition estimates obtained with DEADM. Throughfall fluxes were corrected for canopy exchange by using the Ulrich model, (1983) (Draaijers *et al.*, 1994). Figures 6.4A to D shows throughfall estimates compared to DEADM results for SOx, NOy, NHx and total potential acid, respectively, for the first dataset consisting of 21 sites. Figures 6.5A to D show the same comparison for the dataset consisting of 30 sites. Two different comparisons are made because the throughfall measurements were made in different periods using different methods.

TABLE 6.6 Throughfall estimates and total deposition estimates averaged over different locations (mol ha^{-1} a^{-1})

		KUN/SC-DLO data (Houdijk and Roelofs, 1991; de Vries *et al.*, 1991) (21 sites)				Utrecht Univ. data (Draaijers, 1993) (30 sites)			
		SOx	NOy	NHx	pot. acid	SOx	NOy	NHx	pot. acid
Deposition estimates	average	1792	1262	2853	7700	1265	1209	2892	6710
	sd	599	127	1172	1323	93	63	225	900
Throughfall estimates	average	2090	959	4232	9371	1170	820	2356	5566
	sd	966	316	1889	3921	250	242	722	1409
Correlation coefficient (R^2)		0.04	0.02	0.17	0.10	0.30	0.50	0.01	0.43

On average the estimates are not significantly different, except for NOy fluxes for both datasets and NHx fluxes for the 30 sites. The NHx DEADM estimates are based on 5 x 5 km values. The 30 forests are located in only two 5 x 5 km grid squares, therefore do not show the

same variations as the measurements. The systematic difference between the two estimates for NOy deposition (with atmospheric deposition estimates higher than throughfall estimates), are in line with the results obtained at Speulder forest (section 6.2.2).

In general, the scatter in the graphs displaying the results for the 21 sites is larger than that for the 30 sites. This is the result of the difference in throughfall sampling and handling of samples applied to the two sets. Measurements of throughfall have to meet criteria related to representativeness, contamination, etc. (Draaijers *et al.*, 1994). The measurements made at the 30 sites meet these criteria better than those taken at the 21 sites. The agreement between DEADM and throughfall estimates for the 21 and 30 sites is good, with data scattering around the 1:1 line.

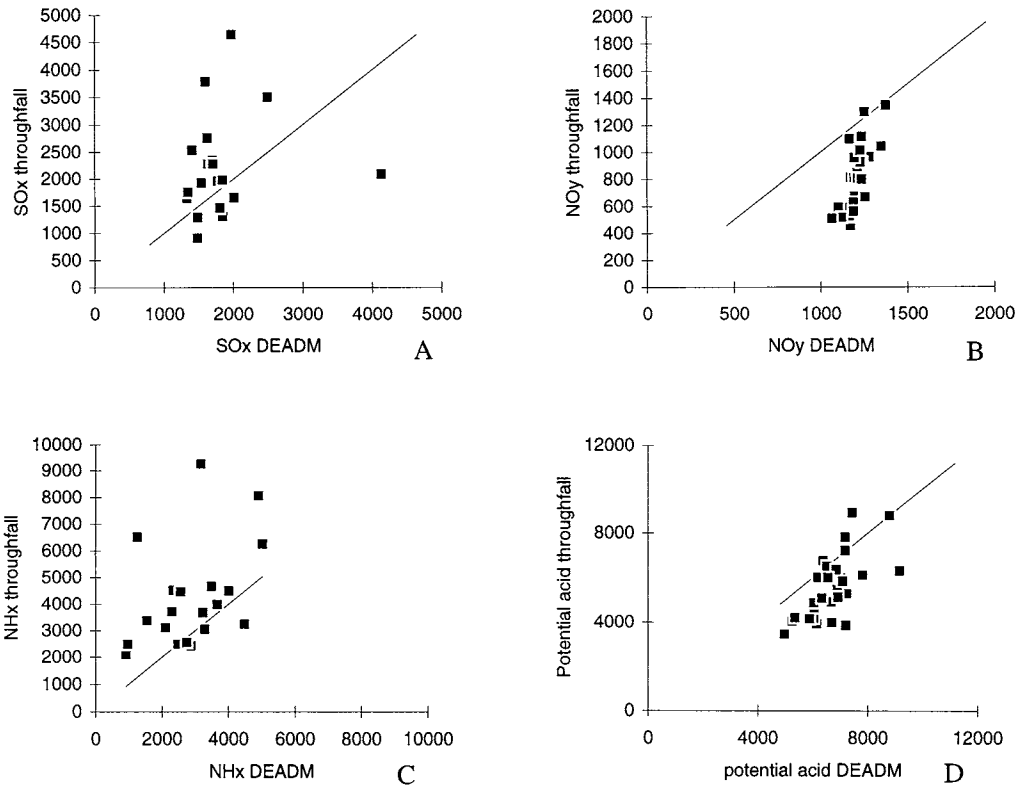

FIGURE 6.4 Throughfall estimates compared to DEADM results for SOx (A), NOy (B), NHx (C) and total potential acid (D) (mol ha^{-1} a^{-1}) for 21 sites. The 1:1 line is also shown.

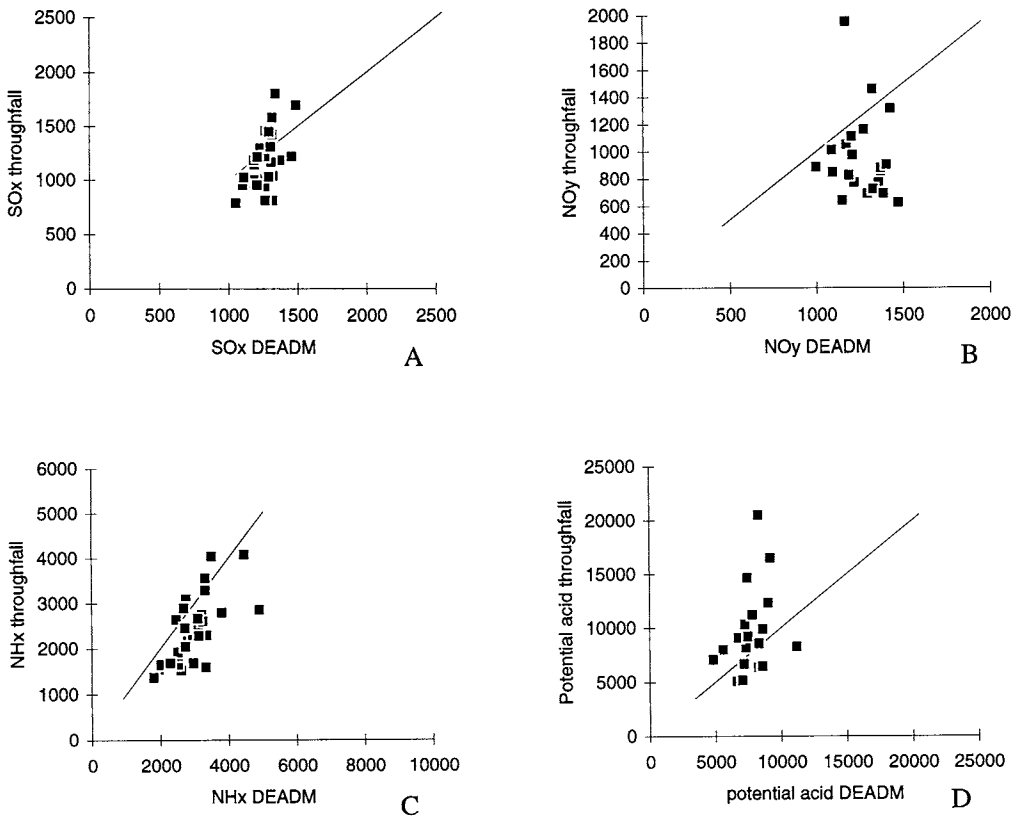

FIGURE 6.5 Throughfall estimates compared to DEADM results for SOx (A), NOy (B), NHx (C) and total potential acid (D) (mol ha^{-1} a^{-1}) for 30 sites. The 1:1 line is also shown.

Considering the sites are situated in one 10 x 10 km grid used in DEADM with constant SO_2, NO_2, wind speed, radiation, temperature, relative humidity and surface wetness data at 50 m high, the agreement for the 30 sites is remarkable. This shows that the blending height method is a good approach for estimating local fluxes (Draaijers and Erisman, 1993; Erisman, 1992).

Base cations

For comparison of base cation deposition estimates using DEADM and throughfall only the dataset containing the 30 sites is used. For the other dataset it was not possible to achieve the

ion balance, either through lack of data or errors in the data. There must be an ion balance made for applying the Ulrich model (Draaijers *et al.*, 1994).

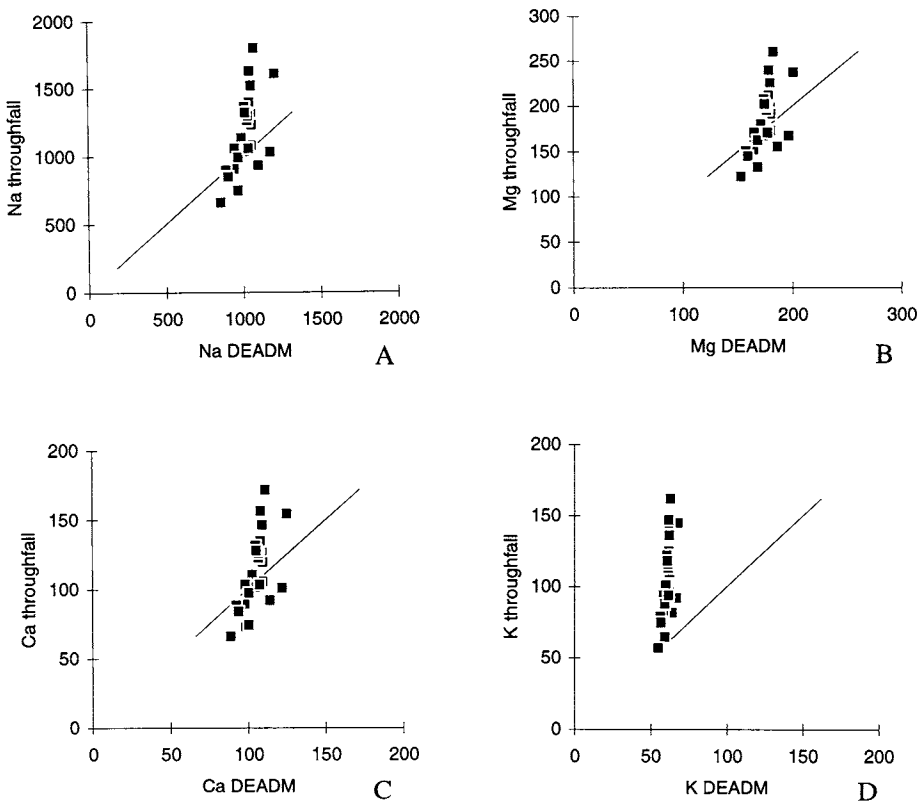

FIGURE 6.6 Net throughfall estimates compared to DEADM dry deposition estimates for 30 sites for Na^+ (A), Mg^{2+} (B), Ca^{2+} (C) and K^+ (D) (mol ha^{-1} a^{-1}). The 1:1 line is also shown.

Figure 6.6 displays the comparison between net throughfall estimates, corrected for canopy exchange using the Ulrich model, and dry deposition estimates using DEADM. Average fluxes and standard deviations are given in Table 6.7. The concentrations of base cations used to estimate dry deposition are derived from wet deposition measurements and scavenging coefficients (see Chapter 5). The agreement between the two estimates is very good, given the uncertainty in the two methods. The throughfall estimates are somewhat higher than deposition estimates; this may be due to the uncertainty in the Ulrich model (Draaijers *et al.*,

1994) or uncertainty in *Vd* estimates (Erisman *et al.*, 1994). However, the strong correlation (see Table 6.7) suggests that the modelled deposition of base cations leads to accurate values and/or that the throughfall method might be used for estimating atmospheric deposition for base cations, provided the Ulrich model is applied to estimate canopy exchange.

TABLE 6.7 Net throughfall estimates and dry deposition estimates averaged over 30 different locations (mol ha^{-1} a^{-1})

		Na^+	Mg^{2+}	Ca^{2+}	K^+
Dry deposition estimates	average	534	74	55	20
	sd	75	10	8	3
Net throughfall estimates	average	683	82	63	63
	sd	292	35	27	27
	R^2	0.381	0.382	0.381	0.383

6.3 UNCERTAINTY IN DEADM RESULTS

The objective of the uncertainty analysis is to define confidence intervals for the results obtained and to identify gaps in the applied methods or procedures. A comparison of results obtained from a preliminary version of the DEADM model with measurements at a heathland site (Asselse heide) showed good agreement, especially for the deposition parameters u_* and V_d (Duyzer *et al.*, 1989; Erisman (1993a; 1993b). Although the model concept has been changed since then at several points, these results supported confidence in the approach. In this section the uncertainty analysis comprises the comparison of DEADM results with results from other estimates for the Netherlands and an error propagation analysis. Results are compared with flux measurements on a local scale made in the Netherlands and with fluxes calculated with another regional scale model.

6.3.1 DRY DEPOSITION MEASUREMENTS

The two main problems in comparing model results with flux measurements are, first of all, the local character of the measurements and, secondly, the large uncertainty in the measurements. The flux measurements available for different types of vegetation and gases are listed in Table 6.8, along with the year and measuring height. The latter can be taken as a measure of the surface area covered by the measurements (roughly a radius of 100 times the height). The same table presents the estimated fluxes for the 1 x 1 km and 5 x 5 km (NH_3) grids, where the locations are situated, being obtained from calculations from the model for the same year. The uncertainty in flux measurements is not given in the table. The uncertainty in yearly average fluxes is about 50-100% (Erisman *et al.*, 1992; Erisman 1993a).

From Table 6.8 it is obvious that the inference estimates of the NH_3 dry deposition flux over heathland are higher than fluxes obtained from the measurements. At the Speulder forest site, NH_3 fluxes as estimated by the model are lower than measured fluxes. However, the uncertainty in the measurements is large and the values presented here are median values (Van Aalst and Erisman, 1991; Duyzer *et al.*, 1991). It must be emphasised that the model resolution for NH_3 fluxes is 5 x 5 km. Variations of the flux within such a grid can be large, about a factor of 4 (Asman *et al.*, 1989; Asman and Van Jaarsveld, 1992). The location of the area where measurements are made relative to the NH_3 sources in the grid determines whether the depositions will be higher or lower than the average over the grid. The table probably gives an indication of this variation rather than a real comparison. Therefore no conclusions can be drawn on uncertainty in modelled NH_3 fluxes from this comparison.

The estimated HNO_3 and SO_2 dry deposition fluxes to low vegetation are slightly lower than those measured. However, agreement is reasonable. Estimates of dry deposition to the Douglas fir forest located near Speuld show a systematic overestimate for NOx. SO_2 fluxes

are underestimated by the model. Generally, it can be concluded that fluxes obtained using the model and those derived from measurements show differences of 20 % or more.

TABLE 6.8 Flux measurements and estimates for different locations in the Netherlands in mol ha^{-1} a^{-1} using different methods

Location	Component	Height (m)	Year	Reference	Measured flux	Estimate (this study)
Speuld	SO_2	30	1988	Duyzer *et al.* (1994)	590	530
	NOx	30		Duyzer *et al.* (1994)	360	400
Speuld	SO_2	30	1989	Duyzer *et al.* (1994)	540	584
	NOx	30		Duyzer *et al.* (1994)	270	440
	NH_3	30		Duyzer *et al.* (1994)	1860	1645
Elspeet	SO_2	4	1989	Erisman *et al.* (1993a)	350	510
	NH_3	4		Erisman *et al.* (1993a)	810	980
Assel	NH_3	1.5	1987	Duyzer *et al.* (1989)	550	975
Cabauw	HNO_3	200	1986	Erisman *et al.* (1988)	220	180
Zegveld	SO_2	4	1988	Erisman *et al.* (1993a)	590	484

The estimates have been presented in more significant figures than those consistent with their accuracy for intercomparison.

Monthly mean concentrations obtained by measurements at a height of 30 m at Speuld (Vermetten *et al.* 1990), and concentrations obtained by extrapolation to 50 m from the LML measuring sites and interpolation over the 10 x 10 km grid, agree reasonably well, as can be seen in Figure 6.7. The most extreme outlier is a month with only a limited set of measurements (Vermetten *et al.*, 1990). These results suggest that the procedure to calculate concentrations at 50 m height from monitoring network observations can be used to estimate concentrations over the Netherlands accurately enough on a monthly basis and that the differences for SO_2 fluxes are the result of uncertainty in deposition parameters.

Figure 6.8 shows a comparison between monthly average dry deposition velocities of SO_2, NH_3, NO_2 and SO_4 aerosol measured at Speuld (36 m above ground level) in 1993 and calculated with DEADM (50 m above ground level). The agreement is reasonable, with an average deviation of about ±25%. Calculated SO_4 aerosol *Vd* values are somewhat higher than those derived from measurements. This is the result of a combination of a difference in height (36 m compared to 50 m) and a difference in roughness length estimates used locally (z_0 = 2 m) and from land-use data and forest statistical information in DEADM (z_0 = 1.3 m). The parametrisation of aerosol dry deposition velocities appears to be sensitive to the roughness length because the wind speed at canopy height used in the parametrisation is sensitive to z_0 values (Ruigrok *et al.*, 1994; Erisman *et al.*, 1994a). This influence is larger for V_d of coarse particle than that of fine particles, DEADM average V_d for coarse particles in Speulder forest amounts to 3.3 cm s^{-1}, whereas V_d based on measurements equals 5.0 cm s^{-1} (Erisman *et al.*, 1994a; section 7.3).

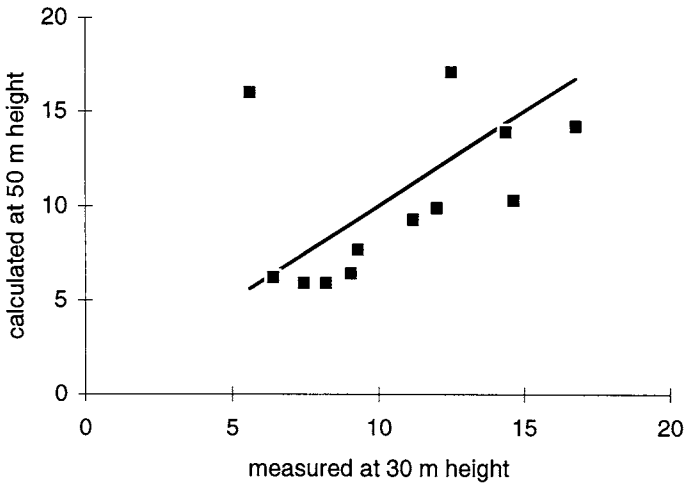

FIGURE 6.7 Comparison of measured concentrations in Speulder forest (30 m) and those obtained from the model's calculations (50 m).

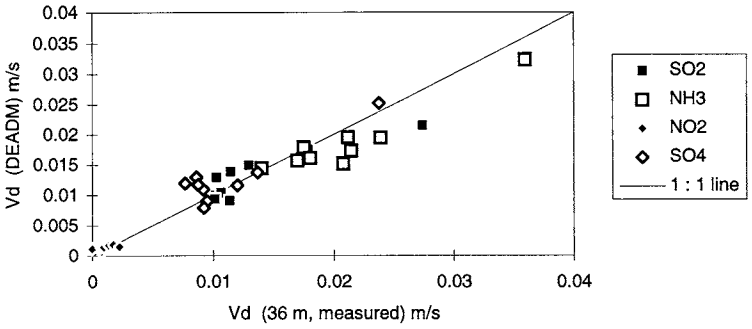

FIGURE 6.8 Comparison of monthly V_d values calculated with DEADM (50-m height) and measured in Speulder forest (36-m height) (m s^{-1}).

Monthly average modelled *Vd* values of SO_2 and NO_2 are in good agreement with those based on measurements with no systematic differences. NH_3 dry deposition velocities calculated with DEADM are smaller than those derived from measurements at the Speulder forest. DEADM calculations are representative for the 5 x 5 km area surrounding the Speulder forest, whereas measurements are representative for local surface characteristics. It must be noted that the comparison of modelled *Vd* with those derived from measurements in Speulder forest is not independent because parametrisations of *Vd* used in DEADM are partly based on data

from Speulder forest. Annual average fluxes derived from measurements and calculated using DEADM for the Speulder forest are listed in Table 6.9 (Erisman *et al.*, 1994a).

Agreement is reasonable, keeping in mind that DEADM results are 1 x 1 km grid averages, calculated with parameters such as land use, forestry statistics, etc. derived from long-term statistics. Furthermore, DEADM results for NH_3, NH_4 and base cations are estimated on a 5 x 5 km, whereas fluxes derived from the measurements/model are representative for more local conditions.

TABLE 6.9 Average dry deposition fluxes) for the Speulder forest (mol ha^{-1} a^{-1}) based on measurements (November 1992 - September 1993) and calculated using DEADM (January 1993 - September 1993

Component	Measurements	DEADM results
SO_2	488	509
SO_4^{2-} aerosol	189	146
Dry SOx	677	655
NH_3	1409	816[a]
NH_4^+ aerosol	563	685[a]
Dry NHx	1972	140[a]
NO_2	136	190
HNO_2	96	109
HNO_3	144	126
NO_3^- aerosol	388	216
Dry NO_3	764	614
K^+	30	47[a]
Na^+	574	759[a]
Ca^{2+}	94	135[a]
Mg^{2+}	113	122[a]

[a] 5 x 5 km estimates

6.3.2 COMPARISON WITH OTHER MODEL RESULTS

The DEADM results have been compared to results calculated with the TREND model. The TREND model calculates yearly average dry and wet deposition of SOx, NOy and NHx based on yearly meteorology statistics and detailed emission inventories for Europe (Van Jaarsveld, 1990; Van Jaarsveld and Onderdelinden, 1992; Asman and Van Jaarsveld, 1992). The most accurate emission inventory is that of 1980. Calculations using TREND for the 1980 emissions are compared to results obtained in this study for the year 1980. The Netherlands has been divided into 20 so-called acidification areas (Figure 5.2). In Figure 6.9, the estimates

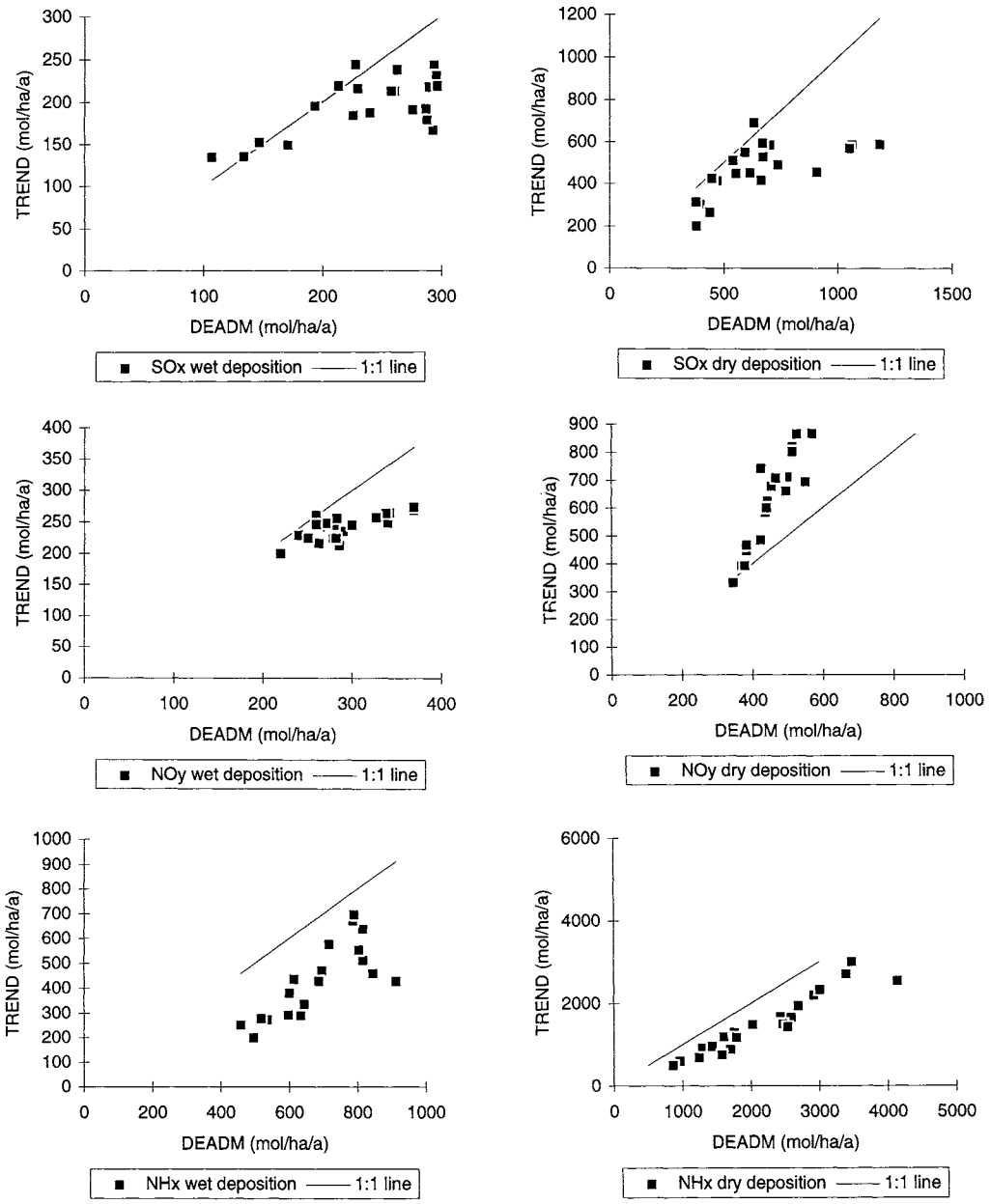

FIGURE 6.9 Comparison of TREND model results with estimates from this study (mol ha^{-1} a^{-1}). The 1:1 line is shown for comparison.

from TREND calculations per acidification region for dry and wet SOx, NOy and NHx deposition are compared to results from this study. From these figures it can be concluded that estimates from both models agree well on this scale. Differences in SOx and NHx dry deposition estimates are mainly a consequence of different assumptions for the roughness length. The TREND model uses a uniform z_0 field. The average z_0 value in the Netherlands used in TREND (0.15 m) is lower than that obtained in this study (0.22 m).

6.3.3 ESTIMATION OF UNCERTAINTY RANGES

Uncertainties in the deposition flux estimates are the result of random and systematic errors. Random errors could be the result of a certain variability in measured quantities and parameters used, as a result of e.g. measuring errors, correction procedures or parametrisations. Random errors in the total deposition will be a function of number of measurements and of averaging time intervals and the spatial scales under consideration. Systematic errors result from neglecting processes or variables on which knowledge is insufficient. Examples of systematic errors might be neglecting: 1) the difference in R_c values for different receptor surfaces, 2) neglecting the spatial variability in concentrations of HNO_3, HNO_2, HCl and aerosols, 3) neglecting occult deposition, errors in NH_3 emission factors (and resulting errors in NH_3 and NH_4^+ concentrations), and 4) neglecting roughness transition zones and correlations which are not taken into account (e.g. the influence of NH_3 concentrations on the SO_2 dry deposition rate and vice versa). Systematic errors can be reduced only partly as a result of averaging in time and space. The difference between random and systematic errors is not always very clear. Certain corrections or assumptions can lead to both types of errors.

The propagation of errors in the process of estimating fluxes on different scales can be determined by error propagation methods. The most difficult part in the uncertainty analysis is the definition of the uncertainty ranges in the basic measured or theoretically derived parameters. Lack of reference or validation measurements necessitates assumptions on error or uncertainty ranges. Furthermore, poor understanding of physical, biological or chemical processes lead to the introduction of extra uncertainty, next to the mathematical uncertainty. This is of special importance in extrapolation and interpolation procedures. For some parameters the uncertainty can be determined directly from intercomparison studies (section 6.3.1).

The mathematical procedure followed for the error propagation can be so summarised:
- the individual absolute errors (random or systematic) for variables are squared and added;
- the square root of the result is the resulting absolute error (S_a) in the result when the variables are added or subtracted.

This is only valid if one assumes no correlation between the variables. When the variables are multiplied or divided the same procedure is followed, however, relative (Q_a) rather than absolute errors are considered. Again no correlation between the variables is assumed. If the variables are correlated an extra term must be added: R times the product of individual errors, where R is the correlation coefficient between the variables:

$$\begin{aligned} a &= b + c \qquad S_a = \sqrt{S_b^2 + S_c^2 + 2\,R\,S_b\,S_c} \\ a &= b * c \qquad Q_a = \sqrt{Q_b^2 + Q_c^2 + 2\,R\,Q_b\,Q_c} \end{aligned} \qquad [6.1]$$

For many cases the correlation coefficient is unknown. Therefore two cases were considered: first, a propagation of errors without correlation (conservative), and second, a propagation with full positive correlation (worst case). In the following sections the random and systematic errors in the basic parameters will be discussed. Then the propagation of errors and the associated uncertainty in the final results will be described and summarised in a table for the conservative and the worst-case estimates. Numbers are presented as percentages reflecting the relative deviation from the estimated value for an average grid cell in terms of one standard deviation (σ), implying that the probability is 68% that the real value is the estimated value $\pm\, x\%$.

Wet deposition

Random errors

Random errors in wet deposition are determined by the uncertainty in the determination of the concentration in the precipitation samples and the determination of the precipitation amount. Random errors in individual samples have been investigated by comparison studies with more than one sampler at a location (Slanina *et al.*, 1988; Buijsman, 1990). Furthermore, analytical errors have been determined by reproducibility tests. The accuracy by which yearly average wet deposition can be estimated (reproduced) for an individual LML station is 1% for SO_4^{2-}, 5% for NO_3^- and 11% for NH_4^+ (Van Egmond and Onderdelinden, 1981; van Egmond *et al.*, 1985). By interpolating the wet deposition fluxes over a 10 x 10 km grid, an extra uncertainty is introduced. The random errors on this scale can be obtained through theoretical considerations. This was done by Van Egmond and Onderdelinden (1981). They estimated the uncertainty in the spatial distribution of concentrations (and depositions) obtained from interpolation of monitoring network data and theoretical considerations. They concluded that the relative interpolation error for monthly mean SO_4^{2-}, NO_3^- and NH_4^+ deposition is 17, 14 and 20%, respectively, in a monitoring network of 12 stations. Combined with the uncertainty in the fluxes due to measuring errors, this will lead to total random errors in the yearly wet deposition flux of 5% for SO_4^{2-}, 6% for NO_3^- and 13% for NH_4^+. The results for the different

components on a local scale (10 x 10 km) and for the Netherlands as a whole are listed in Table 6.10. The uncertainty due to random errors in wet deposition flux is relatively low.

Systematic errors

Systematic errors in the wet deposition flux are introduced by dry deposition of gases and aerosols onto the funnels of the measuring devices, by the influence of local sources through below-cloud scavenging processes, terrain irregularities or differences in shower patterns and by measuring artefacts (e.g. the efficiency of collecting the amount of precipitation and small drops and fog, systematic sampling and analytical errors). Collectors often show systematic differences in the collection of the amount of water (e.g. Stedman *et al.*, 1990; Sevruk *et al.*, 1991). In this study the amount of water is obtained from the official rain gauges of the meteorological institute KNMI and not from the chemical collectors themselves.

Before 1988 open samplers were used in the monitoring network. Corrections had to be applied to the dry deposition in these samplers. For these data systematic errors may have been introduced through the application of correction factors. Application of dry deposition correction factors for fluxes before 1988 introduces an extra 10-20% uncertainty, depending on the location of the station (see, for example, Buijsman, 1990). The uncertainty introduced by the Ca^{2+} correction is negligible for these errors and will be small for wet-only samples (< 5%) on a yearly basis. For the calculation of wet deposition, amounts of rain measured by KNMI using official rain gauges are used. It was found that the amount of rain collected by the (chemical) samplers could be either more-or-less that found in the official KNMI samplers (Buijsman, personal communication). A systematic error of about 20% was found in this comparison.

Systematic errors can be estimated by comparing results of measurements in a local network to those obtained by interpolation. This method was applied using data from a local precipitation network (six stations) in the province of Limburg in the southeast of the country (RIVM, 1990). From the comparison it was concluded that the agreement between SO_4^{2-} and NO_3^- fluxes is reasonable, usually within 20%. Agreement between NH_4^+ fluxes, however, is poor. The difference can be the result of different analytical procedures used by the two measuring institutes, scavenging through a strong variability in NH_3 concentrations and/or local disturbance at the measuring sites. Interpolation results heavily rely on the only LML station in the region. This one LML station is situated about 10 m from a station in the local network. The wet deposition fluxes at this location differ by about 15% for NH_4^+ and SO_4^{2-} and 5% for NO_3^-, which can be taken as a measure of the uncertainty introduced by a difference in sampling and analytical procedures.

It was assumed that systematic errors are 25% for SO_4^{2-} and NO_3^-, and 40% for NH_4^+. This assumption is based on the comparison study and on the systematic errors which result from dry deposition to open samplers and differences in the collecting efficiency of amounts of

rain. For the Netherlands as a whole, local influences are assumed to be of less importance. Systematic errors on this scale have been estimated at 20% for SO_4^{2-} and NO_3^-, and 30% for NH_4^+. The overall systematic errors for 10 x 10 km grids and the Netherlands as a whole are presented in Table 6.10.

TABLE 6.10 Total systematic uncertainty (%) in yearly average total deposition flux on different spatial scales for all individual components (1993)

Component	F (mol ha^{-1} a^{-1})	5 x 5 km			Country average		
		c/c	*Vd/Vd*	F/F	c/c	*Vd/Vd*	F/F
Dry SO_2	530	20	30	36	15	20	25
Dry SO_4^{2-}	45	20	40	45	15	30	34
Wet SO_4^{2-} [a]	195			25			20
Total SOx	770			25			15
Dry NO	0	30	200	200	20	100	102
Dry NO_2	210	30	50	58	20	50	54
Dry HNO_2	50	50	60	78	40	40	57
Dry HNO_3	100	50	60	78	40	30	50
Dry NO_3^- [a]	65	40	40	57	25	30	39
Wet NO_3	320			25			20
Total NOy	745			40			25
Dry NH_3	1250	40	30	58	30	20	36
Dry NH_4^+	60	40	40	71	40	30	50
Wet NH_4^+ [a]	680			40			30
Total NHx	1990			50			30
Total acid	4270			35			15

[a] Wet deposition is calculated on a 10 x 10 km scale.

Dry deposition

The uncertainty ranges in dry deposition fluxes were determined on different scales by applying the error propagation method and the inferential framework. The random and systematic errors in the dry deposition fluxes of the components considered were calculated by defining uncertainty ranges in hourly concentrations, in R_c values and in meteorological parameters. Via these ranges uncertainty ranges in the concentration field and wind field were calculated and accordingly in u_*, R_a, R_b, V_d and F. In the cases where uncertainty ranges are not known, these are based on expert judgement.

Random errors

The random error in R_a is mainly determined by the uncertainty in the wind speed values and accordingly in u_*. The hourly measured u values usually exhibit an error of about 10% (Beljaars, 1988; Erisman and Duyzer, 1991). The wind field at 50 m height can be estimated

relatively accurately in situations where the assumption of the constant flux layer is valid, under near neutral conditions. In times of non-neutrality, stability corrections have to be made. This is the case more than 50% of the time during the year in the Netherlands. Especially when stability corrections are large, the extrapolated wind field will be very uncertain. The largest errors will be made at night when ground temperature inversions occur, and a decoupling between the layers separated through these inversions occurs. In these situations, however, fluxes will be low because of the low surface-exchange rates (stable conditions). These uncertainties can be considered systematic. However, because the uncertainty in the final results due to these uncertainties will be a function of averaging time intervals, they are processed as random errors. They will, however, not decrease due to spatial averaging. The uncertainty in the stability corrections $\psi(z/L)$ is assumed to be 100%.

The z_0 maps are used for deposition calculations. The uncertainty is hard to describe because of lack of any references or measurements. Furthermore, the uncertainty in the roughness length concept itself is hard to quantify; see the discussion in Beljaars (1988). It is assumed that the uncertainty in the z_0 maps is about 40-60% (Erisman, 1990; 1993a). Locally, however, the uncertainty can be more than 100%.

Under neutral conditions uncertainty of 60% in z_0 leads to a maximum error of 15% in u_* values. The overall error in u_* due to z_0, u and stability corrections is estimated to be 20% in near-neutral conditions, and 50% in very stable or unstable conditions. If averaging the stability classes for one year, the average uncertainty in u_* would lie somewhere between 20% and 50%. This value is assumed to be 30%. This leads to a random error of about 70% in R_a, calculated from Eqn.(6.1).The R_b concept is generally used, but uncertainties are found to be large (Hicks *et al.*, 1989). The uncertainty in the R_b concept can be considered systematic. However, it is assumed that the uncertainty can act both ways, i.e. it can lead to an overestimation or an underestimation. This uncertainty is therefore processed as random errors. The random error in u_*, combined with an overall error due to the uncertainty in the concept, leads to an uncertainty range of 50% in R_b.

The uncertainty in R_c is much larger than in either R_a or R_b. This, however, is due to systematic errors (see Section 6.3.3, Dry deposition). The random error in R_c values was arbitrarily taken as 100% for the 1 x 1 km grids for forests, heathland and agricultural areas in the Netherlands.

The random errors in concentrations on a 1 x 1 km scale are assumed to range from 40% for SO_2 to 120% for HNO_2 , HNO_3, and HCl, and the random error on the 5 x 5 km scale is 120% for NH_3. These values are related only to the quantity of available measurements for each component (in time and space), and to the expected local variation due to, for example, the difference in source height, source strength and amount of sources. The random error in F for each component per 1 x 1 km grid can be calculated from the random errors in R_a, R_b and R_c

and in c by the error propagation chain. These random errors are very large for 1 x 1 km grids, ranging from about 70% for the SO_2 flux to 225% for aerosols. For NH_3, random errors in the flux on 5 x 5 km are calculated at 130%. Random errors can be neglected for most components when considered for the flux in the Netherlands as a whole. Random errors for 5 x 5 km grids and as country averages are listed in Table 6.10.

Systematic errors

Systematic errors in the dry deposition fluxes are much harder to quantify. Systematic errors have been estimated for the fluxes on a 5 x 5 km scale and for the Netherlands as a whole. The difference between systematic errors for the two scales considered is due only to the contribution of processes influencing the dry deposition flux on a local scale. This can be, for example, many roughness transition zones and/or forest edges within one grid, or a grid mainly composed of arable land where several crops are grown during one year, local sources within a grid, etc. The influence of transition in roughness in forests to the deposition is assessed using throughfall measurements. This study is summarised in section 7.2. Apart from these local contributions, errors will be independent of the scale considered.

An uncertainty in R_c is introduced through differences in R_a and R_b calculation schemes. From parallel measurements of u_* in the Netherlands at the Elspeetsche Veld (Erisman and Duyzer, 1991) and in Scotland at Halvergate (Duyzer *et al.*, 1990) using different methods, up to a 20% difference in averages of u_* has been observed. This leads to differences in R_a of 30-40% and in R_b of about 20%. This difference is directly reflected in the R_c values obtained from these measurements, leading to different estimates by different methods for the same location (receptor surface). The systematic error in R_c was estimated separately for forest, heather and agricultural land-use categories. These estimates are based on results obtained from measurements of HNO_3, SO_2 and NH_3 over grassland and moorland, reported in Erisman (1993A), and on literature values, as listed in Table 6.11

TABLE 6.11 Range in annual average R_c values (s m^{-1}) for forests, heathland and agricultural areas

Component	Forests		Heathland		Agricultural areas	
	min	max.	min	max.	min	max.
SO_2	40	200	40	200	20	100
NH_3	10	100	10	60	10	100
NO	1000	4000	1000	4000	1000	4000
NO_2	150	700	150	700	150	700
HNO_2	40	200	40	200	20	100
HNO_3 and HCl	-20[a]	20	-20[a]	20	-20[a]	20

[a] Formally, negative surface resistance has no meaning. The data here reflect a range of uncertainty in total deposition velocity.

The systematic errors in V_d can be calculated from the ranges of R_c in Table 6.11 and the uncertainty in R_a and R_b based on the results of the intercomparison experiment on u_* (Erisman and Duyzer, 1991).

Over very rough areas, the interpolated wind speed at 50-m height might be overestimated because of the increased surface drag relative to the smoother areas where wind speeds are routinely monitored. In areas with the highest z_0 values this may lead to overestimations of u_* values of about 30%.

The systematic error in concentration values is rather different for different components. Overall, the systematic error in local concentration is determined by: systematic measuring artefacts, extrapolation and interpolation errors. The systematic errors in concentrations on different spatial resolutions are listed in Table 6.10. The possible measuring artefacts are greatest for aerosols and NH_3 (the latter used for testing model results). The systematic error in SO_2 concentrations is mostly determined by the interpolation procedure, whereas the error in NO and NO_2 concentrations is largely determined by the extrapolation procedure. This is due to the emissions of NOx from low-level sources (traffic) and the photostationary equilibrium, both of which can have a large impact on the vertical gradient (Duyzer *et al.*, 1990). The systematic errors in concentration as listed in Table 6.10 have been estimated following discussions with experts in the field of monitoring and modelling air pollution.

From the yearly average absolute values in concentration and deposition parameters, and corresponding systematic errors, the systematic error in F was calculated using the inference method and the error propagation method. The estimated errors in c and the calculated errors in V_d and F, averaged over the Netherlands and 5 x 5 km grids are listed in Table 6.10.

Total deposition
The random and systematic errors in the total deposition are calculated from the errors in the wet and dry deposition fluxes for the different components by the error propagation theory. The random and systematic errors in the total depositions for different spatial scales have been listed in Table 6.10. From this table it is obvious that both for the Netherlands and for 5 x 5 km scale, random errors, compared to systematic errors, can be neglected, except for the random error in the total NH_x deposition on a 5 x 5 km basis.

The uncertainty in the total potential acid deposition can be estimated from the errors in the individual fluxes for SOx, NOy and NHx. The estimated uncertainty in the yearly average total potential acid deposition flux is 35% for the 5 x 5 km grids (random errors taken for NHx) and 30% for the Netherlands as a whole.

Most processes in the atmosphere are correlated to some extent, e.g. the dry deposition of gases is linked by surface exchange processes, stomatal behaviour, etc.. Furthermore, co-

deposition can occur, for instance, between acid-forming and base-forming gases (SO_2 and NH_3). Also some correlation is expected between dry and wet deposition, and total deposition of SOx, NOy and NHx. All these correlations are implicitly accounted for in the uncertainty analysis. However, by assuming 100% correlation in all these processes a worst-case uncertainty estimate can be obtained. If 100% correlation is assumed between systematic errors, the resulting uncertainty is much larger, leading to 70% for total potential acid deposition for each 5 x 5 km grid and 30% for the Netherlands on the whole (Erisman, 1995). The best estimate for the errors in total fluxes will probably be found somewhere between the non-correlated and fully correlated estimates.

For SOx the main uncertainties are in the deposition velocities of SO_2 and sulphate. For grassland and heathland, deposition studies have provided much information on SO_2 deposition velocity, resulting in rather small error ranges (Erisman *et al.*, 1992). Budget calculations also support present estimates of deposition fluxes (Van Jaarsveld, 1990). In the case of SO_x, emissions, export, wet deposition and total air concentration are sufficiently accurate to estimate dry deposition as the only remaining unknown with reasonable accuracy. Unfortunately, this is not possible for NOy and NHx. For NOy, the uncertainty in concentrations of reaction products (e.g. organic nitrates, HNO_2) and their fate is large. For NHx the emission uncertainty is at least 40% (Erisman, 1989). Moreover, due to high spatial variability in the concentration, it is hard to obtain an experimental estimate of total content of NHx in air. These two factors preclude a budget estimate of NHx dry deposition.

The uncertainty in the total potential acid deposition is dominated by the uncertainty in NHx and NOy fluxes on a 5 x 5 km scale. For the country average the uncertainty in the total potential acid flux is dominated by the uncertainty in NHx.

6.4 UNCERTAINTY IN THE EDACS RESULTS

For the EDACS model (European deposition estimates), no uncertainty study has been more extensive than the one performed for the Netherlands (section 6.3). The method described here will be applied both to the model and its results in the near future. It can be hypothysed that, as a result of the data available for The Netherlands are much more accurate and numerous than for Europe, that the uncertainty ranges presented here for The Netherlands can be assumed to be equal to or the lower boundary of the uncertainty in European estimates. The aim of the deposition maps is to show the variations of the deposition of acidifying components on a small scale in Europe and to demonstrate the possibilities of the method used. The maps presented here are considered as preliminary and of limited accuracy (van Pul *et al.*, 1995). Several uncertainties and shortcomings will be discussed here.

6.4.2 WET DEPOSITION

The wet deposition maps are subject to several sources of uncertainty. This section contains an estimation of these uncertainties. The uncertainties are divided into three main categories: *(1)* uncertainty associated with the measurements, *(2)* uncertainty associated with assumptions and simplifications in the methods used, and *(3)* uncertainty caused by the interpolation procedure.

The first source of uncertainty consists of measurement errors and other uncertainties associated with the original data. This can be caused by errors in the field when the samples are collected and in the laboratory when the chemical composition of the samples is analysed. Furthermore, different chemical analytical methods were used by the laboratories in different countries to analyse the chemical composition of the samples, hampering intercomparison of data. De Ridder *et al.*, (1984) reported systematic differences of approximately 10% between the same samples analysed at three different laboratories in the Netherlands. Mosello *et al.* (1994) report an experiment in which 98 laboratories from 18 different countries participated in a study to reveal the magnitude of systematic differences between results analysed in different laboratories. They found differences of about 10% for SO_4^{2-}, NH_4^+ and Ca^{2+}, 15% for NO_3^-, Na^+ and K^+, 25% for Cl^- and even up to 50% for Mg^{2+}.

Besides, data at about 500 locations originated from 1989, while at other locations data from other years or an average of several years were used. For the acidifying components Kovar and Puxbaum (1992) showed that in the Alps the yearly variability in concentration only adds an uncertainty of approximately 10% to the overall uncertainty.. In the United Kingdom the annual mean of the acidifying components at individual sites varied by ± 10-20% over the years (UK Review Group on Acid Rain, 1990). The variability in the average European concentrations is smaller than that for individual sites because the variability is smoothed by

the averaging over Europe in the interpolation procedure. Concentrations of the base cations, however, appear to be more variable than acidifying components. In 1987 the network mean concentration in the United Kingdom was approximately 40% lower than in 1986, probably due to meteorological conditions (particularly wind speed) (UK Review Group on Acid Rain, 1990). The uncertainty introduced by these factors collectively for an average 50 x 50 km grid cell is assumed to be 40%.

The second source of uncertainty consists of errors caused by simplifications and assumptions in the methods used. Major error sources might be *(a)* the representativeness of the sites and *(b)* the use of long-term mean precipitation amounts instead of year-specific data. Besides, *(c)* the seeder-feeder mechanism and *(d)* problems in high rainfall areas were not taken into account, because there is a lack of relevant information on a European scale. Furthermore, the influence of *(e)* topography (altitude), as well as the uncertainty introduced by *(f)* not capturing snow in the precipitation samplers and *(g)* the derivation of correction factors for the contribution of dry deposition to bulk precipitation samplers are considered. And at last, *(h)* uncertainty in sulphate concentration introduced by correction for the influence of sea salt through the use of interpolated sodium concentrations is taken into account.

a) The representativeness of the sites is determined by two components. First, it is questionable whether results obtained at a particular measurement site are representative for the area surrounding that point. This might lead to uncertainties, e.g. when a sample is taken near sources, whereas it should represent a large area where sources are sparse. Second, although the rainfall measurement technique is not a very complex one, the collection of representative rainfall measurements for a specific area can have an uncertainty factor, because nearby objects like trees, houses and hills can change rainfall amounts systematically through their influence on turbulent transport of rain drops. For this reason it is recommended to position rainfall samplers at a distance of at least four times the height of the nearest porous obstacle and at a distance of at least eight times the height of the nearest stationary obstacle. Furthermore, it is recommended to measure precipitation amounts using a standard meteorological device situated 40 cm above the ground (WMO, 1971). The uncertainty in representativeness for an average 50 x 50 km grid cell is assumed to approximate 50%.

b) The usage of long-term mean precipitation amounts instead of year-specific data introduces an uncertainty of 45% on average. However, locally large deviations can occur. Of all 867 stations, 19 ODS stations deviate from EPA more than ±200% and 90 stations deviate to more than ±100%. Over the whole of Europe the precipitation amount balance is fairly correct as the summed total of all positive deviations almost equals the summed total of all negative deviations (the average deviation is 3%). However, strictly these values can not be regarded as average relative uncertainties, as ODS is not a correct standard for average precipitation amounts in 1989. Deviations between ODS and EPA are therefore caused by uncertainty in ODS as well as uncertainty in EPA. The values can thus be considered as 'maximum average

uncertainties' introduced by the usage of long-term mean data instead of year specific data. The uncertainty introduced in the interpolation procedure performed by EPA is thought to be of minor importance.

c) In upland areas in north-west Europe a substantial proportion of rainfall originates from scavenging of cap cloud by the seeder-feeder process (Browning *et al.,* 1974). The effect of orography on rainfall composition has been investigated experimentally in the Great Dun Fell in the United Kingdom. The work showed that concentrations of major ions in rain increased with altitude by between a factor of 2 to 3 over the range of 200 to 850 m above sea level (UK Review Group on Acid Rain, 1990). The four major ions SO_4^{2-}, NO_3^-, NH_4^+ and H^+ behaved in approximately the same way. Over this height range the amount of rain roughly doubled due to orographic effects, so that wet deposition increased by a factor of 4 to 6 (Dollard *et al.,* 1983; Fowler *et al.,* 1988 and Mourne *et al.,* 1990). The increase in concentration of major ions at high altitude occurs when the cap cloud (feeder) droplets contain larger concentrations than rain from higher levels (seeder). In this process, aerosols containing elements mentioned above (and all other ions) are lifted by hills and activated into orographic clouds. Cloud droplets in the orographic (feeder) cloud are efficiently scavenged by precipitation falling from a higher level. For upland areas where orographic enhancement of rainfall is an important contributor to wet deposition, the additional scavenging of pollutant from orographic cloud is therefore expected to increase wet deposition above the values that would be predicted when chemical composition is assumed to be constant with altitude. Large uncertainties remain, and the values mentioned should be regarded as providing an initial estimate and applicable only to regions with a similar climate, precipitation and topography to the United Kingdom. Dore *et al.* (1992) mapped wet deposition in the United Kingdom, incorporating the seeder-feeder effect over mountainous terrain. Over high ground they found an increase in wet deposition of 41 to 76% compared to the situation when ion concentrations are considered to be constant with height. The areas with large enhancements represent a relatively small fraction of the land area and have therefore only a small impact on the total pollutant budget. The uncertainty introduced by ignorance of the seeder-feeder process in the concentration mapping in this study is smaller than the values reported by Dore *et al.* (1992), as local wet deposition enhancements will be smoothed out when data are interpolated to a grid with 50 x 50 km blocks. If in areas where wet deposition is enhanced by the seeder-feeder process measurement sites are located at high altitudes then, of course, there is no problem at all. However, in practice sites are mostly located in lowland areas.

d) In high rainfall areas (e.g. in mountainous areas and near coasts) dilution of precipitation by condensation is likely to occur. To obtain wet deposition fluxes, interpolated concentration fields were multiplied by rainfall amounts from EPA. In this way there is no physical coupling between concentration and precipitation amount. As a result, precipitation amounts are multiplied by a constant concentration, leading to an overestimation in high rainfall areas. This is the case when (high) concentrations from areas with low precipitation amounts are

interpolated to areas with large precipitation amounts. The opposite, i.e. underestimation in low rainfall areas, is possible as well. However, the former is more likely to occur, as most high rainfall areas are located at large distances from major anthropogenic pollution sources (background areas). In areas where sampler density is low, underestimation is expected to be largest. In the areas concerned this uncertainty is assumed to be about 20%.

e) Unlike the uplands of north west Europe, concentrations in precipitation in the Alps generally decrease with increasing altitude. In regions with large mountains, snow and rain chemistry reveal marked vertical gradients in composition (Ronseaux and Delmas, 1988; Delmas *et al.*, 1988; Puxbaum *et al.*, 1988). For these regions the very high elevation snows (>2000 m) are, in general, less polluted than those on lower slopes because the majority of the pollutant burden is restricted to the boundary layer. This effect might lead to an overestimation, which is assumed to approximate 20%. Besides, because of the differentiated topography in mountainous areas, the spatial variability of annual precipitation amounts is rather large. To calculate accurate wet deposition fluxes in these areas it is therefore necessary to use precipitation amount maps based on a large number of measurements (Kovar *et al.*, 1991). However, at high altitudes sampler density is, in general low due to large maintenance costs. A better result might be obtained by using a digital terrain model (DTM) in combination with an empirically obtained relationship between altitude and annual rainfall (Behr, 1990). In the Alps, the highest rainfall is observed in the pre- and high Alpine areas along the northern and southern Alps, whereas in the valleys in the centre of the Alps the smallest rainfall amounts are measured (Kovar *et al.*, 1991). Generally, concentrations in the Alps are lower than outside the Alps. Concentrations increase to the north, south and especially the south-east (Kovar *et al.*, 1991).

f) High wind velocities prevent snowfall being captured by the funnels of samplers. Especially in the winter season, this leads to an underestimation of rainfall amounts in mountainous areas. Depending on altitude and wind conditions of the sites, the underestimation will vary between 0 and 30% (Kovar *et al.*, 1991). For snow, good data can be obtained by using specially designed snow collectors situated at ground level (Lövblad *et al.*, 1994).

g) The uncertainty introduced by the method to derive correction factors for the contribution of dry deposition to bulk precipitation samplers is a combination of *(1)* uncertainty in the measurements and *(2)* uncertainty in the derivation method itself. Buijsman (1990) reports that application of dry deposition correction factors introduces 10-20% uncertainty in the Netherlands, depending on the location of the station. Together with uncertainty introduced by *(2)*, total uncertainty is estimated to be 30%.

h) For sulphate, additional uncertainty is added in the non-marine sulphate calculation procedure, as for about 200 locations interpolated sodium values were used to correct for the contribution of sea salt. This uncertainty is assumed to be of minor importance as *(1)* only 200

sites are concerned, and *(2)* the correction causes a decrease in sulphate concentration of 25% at a maximum. Only at high sodium concentration levels will the interpolation error caused by the interpolation procedure have some impact. Besides, the 200 locations are distributed over Europe randomly, hampering quantification of the introduced uncertainty.

The third source of uncertainty is a result of uncertainties inherent to the interpolation procedure, because derived values are nothing more than an estimation of the expected value at locations where no measurements were made. This uncertainty is expressed as Kriging variances. As the original values were transformed to their common logarithms, all subsequent analyses were performed on the transformed values. Retransformation of the data (from log to original values) was performed by taking the exponent. In this way the median value of the block is obtained (Journel and Huijbregts, 1978). Because the original data were distributed skewly, with some large outliers of high concentrations, the median gives a more representative block value than the mean does. Interpolation errors can be quantified in kriging standard deviation maps or can be used to map confidence intervals to give an idea about the reliability of the interpolation. The smallest errors occur where data are numerous and the largest where data are sparse. Because interpolation was performed on concentration data, kriging variances were only available for interpolated concentrations and not for fluxes. Kriging variances cannot be transformed back to the original values by just taking the exponent. A cumbersome procedure is needed and interpretation of the results will be difficult (Journel and Huijbregts, 1978). Therefore, to investigate the error information, 68% confidence intervals (the estimation ±1 standard deviation) were calculated and mapped (i.e. upper and lower boundary maps) for non-marine sulphate, nitrate and ammonium concentrations. When upper and lower boundary maps of a particular element are compared, the probability is 68% that at a particular location the actual value will fall within the range between the values on the lower- and upper boundary maps at that location. For non-marine sulphate the average relative error for an average 50 x 50 km grid cell varied from 15% in Western Europe to 40% in the largest part of the southwest and southeast of Europe. (only very locally in the former Soviet Union). For nitrate, interpolation errors varied from 10 to 30%, and for ammonium between 15 and 40%. For all elements, only very locally in the former Soviet Union did uncertainties exceed 50%. A wide interval (i.e. large uncertainties) may be caused by *(1)* small-scale differences in the concentration field (so that even in areas with a large number of measurement sites the estimation of the average block value is more variable), *(2)* a lack of measurement sites (so that even in areas with only large-scale differences the average block value is based on too few measurements to derive a confident result) or *(3)* a combination of these factors. For all components, confidence intervals are rather large in (south)east Europe and the former Soviet Union, because of a lack of data. In these areas the interpolation error is by far the largest source of uncertainty. For ammonium, large intervals might also be caused by characteristics of emission sources of NH_3, i.e. many local sources showing strong variation.

Total uncertainty in the wet deposition maps

To assess the total uncertainty in the wet deposition maps obtained in this study is very difficult and therefore the estimates themselves are uncertain as well. The numbers presented here should therefore be regarded as a best guess based on expert judgement. To assess the total uncertainty a division into three categories is made, i.e. *(a)* West, northwest and Central Europe as 'good quality areas' where data quality is assumed to be good and sufficient (representative) data is present, *(b)* areas on edges of the maps, i.e. East, southeast and southwest Europe as 'poor quality areas', where less data is available of which the representativeness and quality can be questionable and *(c)* mountainous areas (e.g. the Alps) and upland areas (e.g. United Kingdom and Scandinavia), even though located in areas with many data, as 'complex terrain areas with additional uncertainties'. Total uncertainty in concentrations and in rainfall amounts have been estimated separately. For both variables the most dominating uncertainty (which could be quantified either in this study or by literature) was taken to represent total uncertainty, as all uncertainties are distributed around the same mean. The mathematical procedure followed for the error propagation is that of Eqn (6.1). In the case of calculation of the wet deposition fluxes the correlation coefficient is unknown. Therefore, two cases are considered: first a propagation of errors without correlation (conservative), and second, a propagation with full positive correlation (worst case). The numbers of total uncertainty are also presented as percentages, which show the total relative deviation from the estimated value in terms of 1 standard deviation, i.e. the probability is 68% that the real value is the estimated value $\pm$ x%. As the estimates are rather crude, no distinction between different components was made. In the conservative case *(1)*, the overall uncertainty for an average 50 x 50 km grid cell is estimated to be 50% in West, north-west and Central Europe, whereas in the worst case *(2)* the overall uncertainty is estimated to be 70% here. In areas on the edges of the maps, i.e. East, southeast and southwest Europe, *(1)* is estimated to be 65% and *(2)* 90%, whereas in complex terrain areas *(1)* is estimated to be 85% and *(2)* 120% (Table 6.12).

TABLE 6.12 Summary of total uncertainty in wet deposition per average grid cell of 50 x 50 km for different areas in the conservative and the worst cases.

Area	Conservative case	Worst case
West, northwest and Central Europe	50%	70%
East, southeast and southwest Europe	65%	90%
Mountainous and upland areas	85%	120%

6.4.2 DRY DEPOSITION

Probably the highest uncertainty contribution is the result of the using the simple resistance formulation for such a complex process as dry deposition, and, more specifically, the surface resistance parametrisations used to determine the surface exchange of gases and particles. The resistance model represents a simple approach to a highly variable process. It assumes a constant flux layer, i.e. there are no surface inhomogeneities, edge effects or chemical reactions. How much these simplifications contribute to the total uncertainty in the annual average deposition fluxes has not been quantified. The uncertainty in the surface resistance parametrisation is the largest uncertainty in this simplified scheme. Therefore more and more accurate parametrisations are needed for various vegetation species and surface types. Moreover, there is a lack of measurements which can be used to test these parametrisations, especially for southern and eastern European climates and surfaces. The vegetation and land use classes used in EDACS should be expanded when more parametrisations become available. Surface wetness is found to be one of the major factors influencing the deposition process of soluble gases. In the present version of EDACS only rain and indication of dew are used. Because of the great influence of surface wetness, processes leading to surface wetness should be taken into account in greater detail. The overall uncertainty in the surface resistance due to these factors is different for each component and surface type. This uncertainty varies on an annual basis, between 20 percent or more to more than 100%.

In the current version of EDACS, the EMEP-LTRAP modelled concentrations on a 150 x 150 km grid are used. The uncertainty in the concentrations are estimated to amount 40 - 70% using a statistical analysis with the EMEP measurements (Krüger, 1993). These concentrations represent the background situation in Europe. In source areas the uncertainty can be even higher. It is assumed that the concentration distribution within a grid is homogeneous. This is not the case in a grid which contains industrialised areas or many scattered sources such as with NH_3 and NOx. For such conditions, sub-grid concentration variations are present and will lead to underestimates of the deposition in that grid. To obtain an indication of the errors, a small-scale, short range model can be useful here to resolve sub-grid concentration gradients for dense source areas. The uncertainty in the deposition in an EDACS grid cell due to these gradients is estimated at 25% (Berg and Schaug, 1994).

The deposition in EDACS is based on the EMEP-LTRAP concentrations which in turn are dependent on EMEP deposition parametrisations. The deposition in the EMEP model and in EDACS are parametrised in different ways. By using other dry deposition velocities in EDACS, a mass inconsistency between EMEP-calculated deposition and the small-scale maps of EDACS might be introduced. However, if the differences in the deposition descriptions used between the two models are not very large and non-systematic over a larger region, this will not lead to large mass inconsistencies. Figure 6.10 shows a comparison between the sulphur dry deposition per country estimated by EMEP and EDACS. It can be seen that on the

average there is a good agreement, indicating that for the model area the mass inconsistency is not violated to a large extent. However, for some countries the deviations can be as large as 50%. To avoid the mass inconsistency, implementation of the deposition module used in EDACS in the EMEP-LTRAP model it is planned. In this way, the calculated concentration fields are consistent with the EDACS deposition description.

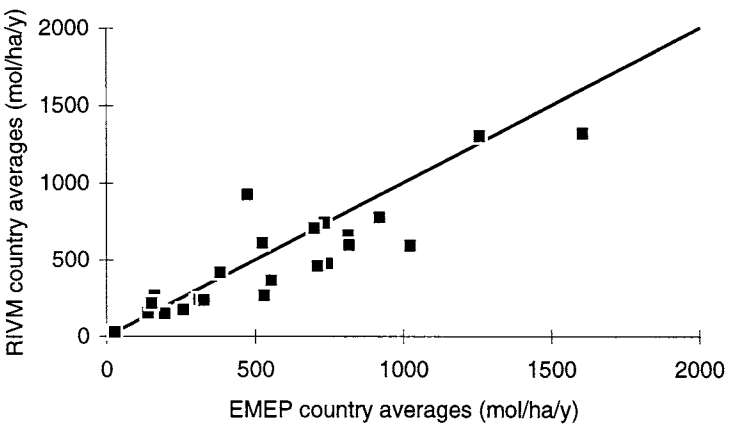

FIGURE 6.10 Comparison of the country average calculated dry deposition of sulphur using EMEP and EDACS (mol ha^{-1} a^{-1}).

The accuracy of the presented results depends on the availability and quality of the input data, such as the land-use map and the meteorological observations. In the gridded version of the RIVM land-use database, forest is not subdivided into deciduous and coniferous forest. All forest is classified as coniferous forest. This will probably lead to overestimates of the deposition velocity to deciduous forests for all components during winter. However, the stomatal resistance in winter will generally be large due to the low temperatures. This overestimate will therefore not be very large.

The dry deposition is calculated on a daily basis. However, due to the daily averaging of the concentration and deposition velocity, a loss in temporal interpolation is introduced. This error is component-specific and estimated to be smaller than 20% (van Pul *et al*, 1993).

6.4.3 TOTAL DEPOSITION

The uncertainty in regional scale deposition estimates strongly depends on the pollution climate and on landscape complexity of the area under study. The uncertainty is determined by the uncertainty in wet, dry or cloud and fog deposition. Furthermore, deposition estimates

yield higher uncertainty in areas built up by complex terrain and with strong horizontal concentration gradients. In section 7.3 the influence of roughness transition zones and forest edges to the deposition in the Netherlands is quantified. It shows that there is a systematic underestimation of the dry deposition in the order of 5 - 10% as the result of these factors. Estimates for other types of complex terrain, such as mountainous regions, are not available.

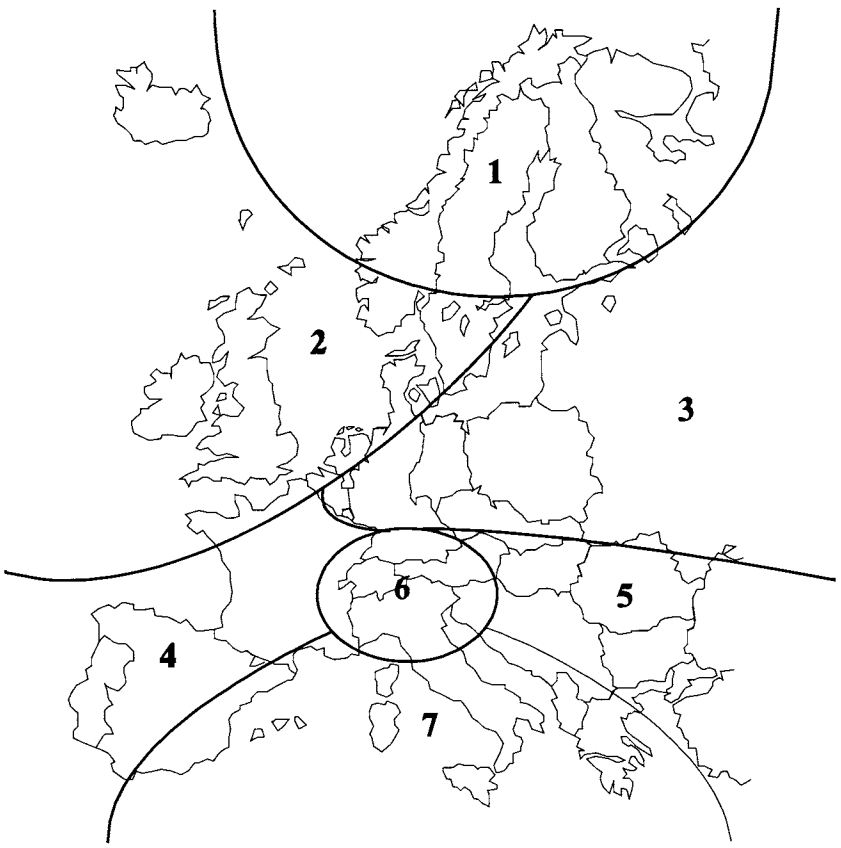

FIGURE 6.11 Distribution of the pollution regions in Europe in Table 6.13 (see text for explanation).

Table 6.13 shows the uncertainties associated with major key factors in deposition for seven (pollution) regions in Europe. The seven regions are shown on a European map in Figure 6.11. These regions are chosen because there is a marked difference in dominating deposition process: region 1: main input is wet deposition: region 6: main input is fog or cloud

deposition; or there is a marked difference in climate: region 2 exhibits a sea climate, whereas region 7 exhibits a Mediterranean sea climate and region 4 mainly an inland climate; or there is a marked difference in industrial activity: region 1 is remote, region 3 is mainly dominated by large old industrial complexes and region 2 exhibits high reduced nitrogen emission densities. This is only a crude classification. Furthermore, Table 6.13 shows only a crude estimate of uncertainty. Because of the strong local variations in dry deposition and the associated uncertainty, as discussed in section 6.4.1, local scales should be considered.

TABLE 6.13 Uncertainty of key factors influencing deposition estimates of S and oxidised and reduced N in different pollution regions in Europe

Key Factors	NOy							NHx							SOx						
Regions[a]:	1	2	3	4	5	6	7	1	2	3	4	5	6	7	1	2	3	4	5	6	7
emission/type of	-	++	++	+	++	+	+	-	++	+	+	+	+	-	-	+	++	+	+	+	-
source	2	2	2	2	2	2	2	2	3	3	3	3	3	2	1	1	3	1	3	1	1
concentration	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++
	2	2	3	3	3	3	2	1	3	3	3	3	3	2	1	2	3	3	3	2	2
wind speed	-	+	+	-	-	+	-	+	++	++	+	++	++	-	+	++	++	+	++	++	-
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
roughness length	-	+	+	+	+	+	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	1	1	2	2	2	2	2	1	1	2	2	2	2	2	1	1	2	2	2	2	2
surface wetness	-	-	-	-	-	-	-	+	++	++	+	++	+	+	+	++	++	+	++	++	+
	1	1	1	1	1	1	1	3	2	3	2	3	3	3	3	2	3	2	3	3	3
orography	-	-	-	-	-	++	-	++	-	-	+	+	++	-	+	-	+	+	+	++	-
	1	1	1	1	1	1	1	2	1	1	2	2	2	1	2	2	2	2	2	2	1
co-deposition	-	-	-	-	-	-	-	-	++	++	+	+	+	-	-	++	++	+	+	+	+
	1	1	1	1	1	1	1	3	2	3	3	3	3	3	3	2	3	3	3	3	3
surface	++	++	++	++	++	++	++	++	++	++	+	++	+	+	++	++	++	+	++	+	-
resistance	2	2	2	2	2	2	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3
dry deposition	-	+	+	+	+	+	-	-	++	++	+	++	+	-	-	++	++	+	++	+	-
	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
wet deposition	++	+	+	+	+	++	+	++	+	+	+	+	++	+	++	+	+	+	+	++	+
	1	1	1	1	2	2	2	1	1	1	1	2	2	2	1	1	1	1	2	2	2
cloud and fog	+	++	-	-	+	++	-	+	++	-	-	+	++	-	+	++	-	-	+	++	-
	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3

legend:
importance of key factors:
++ dominating
+ important
- neutral
-- unimportant

uncertainty:
1 low <30%
2 median 30-70%
3 high > 70%

[a]the distribution of these regions is given in Figure 6.11

6.5 GENERAL SYNTHESIS

In this section the work described in this book will be evaluated. This book describes the current state of knowledge on atmospheric deposition of acidifying components to ecosystems. Methods and their limitations are described in Chapter 1 to 6 to come to a generalised description of deposition in the Netherlands and Europe. Chapter 7 gives an extensive summary of three case studies on deposition which have been executed in a multidisciplinary cooperation during recent years in the Netherlands. The results of these studies have been used in the methods and results described in Chapter 1 to 6.

The historical overview in section 1.3 has shown that the need for receptor or ecosystem specific deposition estimates is fairly new. Up to now deposition was treated as a loss term from the atmosphere and not as a highly variable spatial input parameter to sensitive systems. In this book we tried to quantitatively assess the actual atmospheric input of acidifying compounds to ecosystems in Europe. The emphasis is on the methodology development and on the application and evaluation of resulting current loads. The results can be used to estimate critical load exceedances and to determine where ecosystems are at risk. The method can be used with long-range transport models which are used in assessments. Such models are used for the determination of critical loads exceedances in scenario studies and to optimise abatement strategies in order to protect the most sensitive ecosystems by implementing the most effective measures on emission reduction. The inferential method is a good alternative for the combination of large-scale deposition estimates and filtering factors and percentile values of critical loads which are currently used for policy development. The method applied here for acidifying components which play a role in the issue of acidification can easily be used for other components related to other issues, such as heavy metals, persistent organic components, etc.

The methodology which is used to assess the loads is based on the coupling of measurements and models. Measurements are used to explore and understand processes and to derive parameters which are used in models for generalisation. Measurements are also used to evaluate model results and to determine long-term trends. Models are used for generalising experimental results and to extrapolate them in space and time. For this, the parameters derived from experiments are used. For the Netherlands this methodology has proved its value already. Also in other countries as the UK (RGAR, 1990), Sweden (Lövblad *et al.*, 1994) and the USA (Hicks *et al.*, 1991) similar methods have been applied. In this book, the method is applied here for the first time for Europe as a whole.

In this chapter (no. 6) the uncertainty in the estimates in the Netherlands and Europe are assessed. Especially the uncertainty in small scale European estimates are large. This has to do with the concentration estimates, which are calculated on a coarse grid (150 x 150), and with the surface resistance estimates. Although surface resistance parametrisations are based on

measurements, the number and accuracy of most of these measurements is not enough to be representative for all receptor types and pollution climates in Europe. Measurements of dry deposition fluxes of different components are therefore needed for different areas of Europe. Currently a pilot project is executed in Europe, which aims at developing and implementing deposition monitoring sites in three different areas at three different receptors, i.e. over moorland near Edinburgh (UK), over semi-natural grassland near Leipzig (Germany) and over Douglas fir forest, the Speulder forest (the Netherlands). The project is financed by the EC Life programme. Three deposition monitoring stations are equipped with methods to continually determine vertical gradients of SO_2, NH_3 and NOx, together with meteorological instruments and equipment to monitor particle concentrations in two size classes and concentrations of acid gases such as HNO_3, HNO_2 and HCl. The gradient measurements are used to determine the fluxes of the three gases and to determine receptor specific surface resistances. The three gases are chosen because they represent three different types of surface uptake. From the surface resistance parametrisations derived for the three gases, parametrisations for other gases might be derived. In this way, dry deposition of all gases and particles can be determined using the inferential technique. Wet deposition is measured using wet-only samplers and cloud and fog deposition is determined by the inferential technique: concentrations are determined from fog and cloud droplets sampled with a string collector and fog and cloud occurrence is registered with optical instruments. The project is running for one year now, and continuous measurements are available for three months. It appears that the methods are suitable for determining the deposition and continuos application is possible. More of such sites should be established at several other locations in Europe. These so-called intensive monitoring sites can serve as reference stations for deposition. Trends in deposition can be determined at these sites to evaluate abatement strategies. Furthermore, the stations can serve as reference stations for testing more simple low cost deposition monitoring methods, which can be implemented at a large number of sites in Europe to determine the spatial variability of deposition and to test parametrisations and models at different receptors in different pollution climates. In combination with the methodology to determine deposition, as outlined in Chapter 5, such monitoring activities can serve as the measuring/modelling strategy which is suggested at the end of Chapter 3 (section 3.4.4). In this way, process oriented studies, evaluation of models and detection of trends can be established.

Regarding the cheap and low cost deposition monitoring methods for forests, the throughfall method is often suggested (e.g. Johnson and Lindberg, 1992, Ivens, 1990, Lövblad *et al.*, 1994, Draaijers *et al* 1995). Throughfall measurements have been used in several places in this book and it has proven to be of great value. An important achievement regarding the application of throughfall measurements for estimating deposition has been the simultaneous measurements of deposition and throughfall, and the testing of the canopy exchange model by Ulrich and Van der Maas at the Speulder forest. These comparisons show that at Speulder forest, throughfall estimates are as accurate as inferred deposition estimates, except for nitrogen components. When using the critical load concept, it is inevitable to consider soil

loads and establish the relation between soil loads (throughfall) and atmospheric deposition. Furthermore, throughfall can be helpful in understanding the canopy uptake and/or exposure. Finally, as demonstrated in section 7.2, throughfall measurements can serve to study the influence of deposition processes which cannot easily be studied by micrometeorological techniques, i.e. the influence of complex terrain. For sulphur, atmospheric deposition to forests may usually be considered more-or-less equal to the forest soil load. For inorganic nitrogen, however, atmospheric deposition will always be larger than the forest soil load as a result of canopy retention. Canopy uptake of inorganic nitrogen may be partly compensated by canopy leaching of organic nitrogen. Forest soil loads may also be estimated from simple regression models with canopy structure characteristics obtained (see section 7.2). Information on the situation of the forest stand within the landscape will make it possible to also account for edge effects. The throughfall method has to be further tested and parameters for the canopy exchange model have to be derived for other tree species and pollution climates, before general application can be advised.

A relatively large chapter in this book is about uncertainties, and in several subsections uncertainties are addressed also. We feel that uncertainty is an essential part of assessments. Especially in this kind of research where the resulting numbers can have large economic and political impact. The uncertainty analysis is in first instance used to check the results: how do they compare with other, independent estimates: modelled or measured. Moreover, it can help to trace errors in procedures. Furthermore, it is useful to determine what uncertainty of subparts contribute most to the total uncertainty, in order to focus future research on. Finally, it is a good way of showing the value of the research results and the chance that newest insights will produce data that are far from or close to your estimate.

Summary of gaps in knowledge
Based on information presented in this synthesis several gaps in our knowledge regarding deposition monitoring and estimation of deposition can be identified. The most important ones leading to uncertainty in deposition estimates in the Netherlands and Europe can be summarised as follows:

There is a great need to increase our understanding of the factors of importance for the spatial and temporal variability in deposition in order to take such factors into account in the design of monitoring programmes, in modelling, and in the assessment and evaluation of deposition measurements.

There is a great need for further knowledge about canopy processes, especially for nitrogen components, in order to distinguish the deposition and the in-canopy contribution to the throughfall flux. This may involve further use of radioactive tracers, more detailed canopy sampling in both time and space, and comparisons of surface sampling techniques with micrometeorological methods. In general, there is a need for direct method intercomparisons.

There is a general need for further development of sensors (especially for NH_3 and particles) and micrometeorological methods to be used for process studies. Furthermore, micrometeorological methods should be developed for routine application. Process-oriented studies need to be extended to obtain parametrisations of parameters such as size specific V_d for particles and R_c for gases for different land uses, meteorological circumstances and pollution climates. These parametrisations have to be incorporated in deposition estimates using inference to improve accuracy.

Cloud and fog deposition measuring methods need further development and testing.

Existing monitoring programs (EMEP, NADP) should be extended with dry, and cloud and fog deposition measurements or with measurements needed for the application of inferential techniques. Furthermore, monitoring programmes should be extended with several extensive monitoring locations and with many simple and cheap routine monitoring sites (e.g. throughfall sampling). Network design and representativeness of sites with regard to homogeneity, type of vegetation, and pollution climate need special attention.

Emissions, concentrations and atmospheric behaviour of base cations and other components relevant in the issue of acidification, such as HF, HCl, organic acids, PAN, etc. need to be quantified.

Extrapolating these fluxes or derived deposition parameters to larger areas is still a great problem, because of varying surface properties and roughness characteristics and accordingly non-homogeneous turbulent behaviour. There is a need to develop methods to extrapolate point measurements to regions, especially in complex terrain.

Deposition may vary within grids as the result of differences in land use, but also as the result of roughness transitions within a specific land use class, or because of edge. It should be realised that if measures to reduce atmospheric deposition are based on average deposition values within grids, deposition reductions will not be enough for preventing adverse effects. Therefore, it is recommended to determine a subgrid frequency distribution of deposition values for each land-use category, and take this frequency distribution into account when assessing the emission reduction required.