July 2002 ECN-C--02-066

FINAL REPORT OF THE PROJECT INPUT – OUTPUT RELATIONSHIPS FOR INTENSIVE MONITORING SITES

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Acknowledgement/Preface

This research is conducted under the EC contract SG(99) D/10844.

Abstract

This report describes the work done within the project "Input – output relationships for Intensive Monitoring sites", EC contract number SG(99) D/10844. The project results are extensively reported in the Technical Report 2000 (De Vries et al., 2001). Input estimates for selected Level II plots are obtained from throughfall measurements corrected for canopy exchange. Output fluxes were obtained using hydrological model output combined with soil concentrations. Leaching fluxes and input estimates provided the balances. Mean yearly interception evaporation ranged from approximately 160 mm for Pine and Oak to approximately 250 mm for Beech and 300 mm for Spruce, reflecting the increasing interception capacity of those tree species. Median transpiration fluxes were rather constant among the tree species and ranged from 325 $mm.yr^{-1}$ for Pine to 385 $mm.yr^{-1}$ for Spruce stands. At most plots, the leaching flux of SO_4 is higher than that of NO_3, despite the generally lower input of S than of N, indicating that SO_4 is still the dominant source of actual soil acidification. The median sulphur budget is close to zero, but at a considerable number of sites, sulphur is released by the soil, indicating that these systems are recovering from previous episodes of high sulphate input.
The leaching of N is generally negligible below throughfall inputs of 10 $kg.ha^{-1}.yr^{-1}$. There is a significant relationship between N leaching and N deposition but no significant relationship was found with the soil C/N ratio. Nitrogen budgets show that at most sites (90%) the N input is higher then the N leaching. Variations in base cations leaching were significantly related to the S input and the pH and base saturation. The median base cation balance is close to zero, implying a net adsorption and a net release of base cations at approximately 50% of the plots. The Al leaching flux was significantly related to the SO_4 input reflected by the fact that sites with a high Al leaching coincide with sites with a high input of SO_4. The geographic patterns of both elements, however, did not coincide very well since soil base saturation was also significantly related to the Al leaching flux.

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SUMMARY

This report describes the work done within the project "Input – output relationships for Intensive Monitoring sites", EC contract number SG(99) D/10844. The project results are extensively reported in the Technical Report 2000 (de Vries et al., 2001), which is summarised here.

Water fluxes through the forest ecosystem
Hydrological fluxes were calculated for 245 monitoring sites with the hydrological model SWATRE, using the Penman-Monteith equation for evapotranspiration, the Gash model to calculate interception and Richards' equation to calculate transport of water within the soil. Calculations were carried out with daily meteorological data on precipitation, temperature, net radiation, relative humidity and wind speed. Measurements were used for the plots where a meteorological survey is carried out, whereas interpolated data from nearby meteorological stations were used for plots where only a deposition survey is carried out. A comparison of measured and interpolated meteorological data showed good agreement for relative humidity, reasonable agreement for temperature and net radiation and poor agreement for wind speed.

Simulated water fluxes through the forest ecosystem were generally plausible in view of available measurements and literature data. The simulated throughfall could be calibrated on measured throughfall figures such that the simulated yearly values were within 5% of the measurements at 85% of the monitoring sites. Biweekly or monthly values were also quite well simulated. Simulated transpiration fluxes and leaching fluxes could not be validated on data for any of the individual sites. However, detailed studies on two sites in Germany and the Netherlands indicated that the model was able to simulate changes in soil water contents and thus in the transpiration and leaching fluxes quite well. The simulated transpiration fluxes were also consistent with literature data, which indicate that transpiration fluxes for European forest are in a very narrow range around 335 mm.yr-1 due to feedback mechanisms with soil and atmosphere.

Mean yearly interception evaporation ranged from approximately 160 mm for Pine and Oak to approximately 250 mm for Beech and 300 mm for Spruce. The interception fluxes for Pine and Oak were relatively low due to the relatively low rainfall on those tree species. Interception fractions increased going from Oak (0,22) < Pine (0.24) < Beech (0.27) < Spruce (0.30), reflecting the increasing interception capacity of those tree species. Median transpiration fluxes were rather constant among the tree species and ranged from 325 mm.yr-1 for Pine to 385 mm.yr-1 for Spruce stands. The range in the sum of soil evaporation and transpiration is also narrow and median values range from approximately 400-450 mm.yr-1 for the various tree species. Leaching fluxes mainly reflected the difference in precipitation on tree species. Median values increased going from 81 mm under Pine stands to 236 mm under Spruce stands. The plots with the lowest leaching fluxes are found in area with relatively low precipitation such as north-eastern Germany parts of Sweden and Finland and locally in southern Europe.

The limited amount of available water in the examined Pine stands was reflected in the calculated mean transpiration reduction which was highest for Pine, with a median value of 15%. For the other tree species, the median value was 10%. In the future reports, more attention will be given to various drought stress parameters, including relative transpiration, that can be used in subsequent analyses relating drought stress to forest growth and forest vitality.

Element fluxes through the forest ecosystem

Input fluxes from the atmosphere were derived from fortnightly or -monthly measurements of the chemical composition of bulk deposition and through fall water, multiplied by the water fluxes while correcting for canopy uptake. An available canopy exchange model was used as a basis and further improved. The resulting canopy exchange was related to available data on bulk deposition, meteorological parameters and foliar chemistry performing multiple regression analysis. Element outputs from the forest ecosystem were derived at intensively monitored plots by multiplying fortnightly or monthly measurements of the soil solution composition at a depth below the rootzone (mostly near 80 cm) with simulated soil water fluxes during those periods (see above). Element retention or release was assessed from the difference between the leaching from the bottom of the root zone and the element input from the atmosphere.

There are considerable uncertainties in the calculated budgets, considering the uncertainties in calculated water fluxes and measured element concentrations in view of spatial variability within a plot. Furthermore, the budgets are based on measurements during a relatively limited number of years. For most sites (58%), budgets were limited to a three-year period (1996-1998) and for 28% of the sites it was even less, while data for a four year period (1995-1998) were available at 14% of the sites. This relatively short time span may lead to over- or underestimation of the budget compared to the long-term situation due to particular hydrological or biological circumstances in specific years. The remarkable high N retention in south-eastern Germany, for example, may be due to the fact that these budgets are mainly based on the year 1996 with a relatively low precipitation, which may lead to unrepresentative budgets.

Element budgets for sulphur, nitrogen, base cations and aluminium clearly reflected the behaviour of those elements in response to atmospheric deposition. Median values for S leaching were nearly equal to the median S deposition, indicating the overall tracer behaviour of S. On a considerable number of sites S leaching was, however, higher than S deposition. Sites with the highest sulphur release are located in central Europe, where the strongest reduction in sulphur deposition has taken place over the last decade. This indicates that these systems are releasing sulphur stored in the soil in previous episodes of higher sulphate input. In accordance with the available literature, N leaching was generally negligible below N inputs of 10 kg.ha-1.yr-1. At higher inputs N leaching increased, but at most sites (90%) the N input was higher then the N leaching, reflecting N retention in the soil. Sites with a net release of nitrogen were found in areas with a high N deposition over a prolonged period of time, such as Belgium and north-western Germany. There was a significant relationship between N leaching and N deposition, but not with the soil C/N ratio, although the C/N ratio appeared to influence the average nitrate concentrations. Due to the different behaviour of S and N, the leaching flux of SO_4 was mostly higher than that of NO_3, indicating that SO_4 is still the dominant source of actual soil acidification despite the generally lower input of S than N.

The median base cation balance was close to zero, implying a net adsorption and a net release of base cation at approximately 50% of the plots. The phenomenon of base cation removal due to man-induced soil acidification is thus limited, specifically since high leaching values were partly due to natural acidification in soils with a high pH and base saturation. The impact of air pollution on base cation removal is, however, clear since the leaching flux of base cations (Ca+Mg+K) increased significantly with an increase in the sulphur (acid) input. The Al leaching flux was also significantly related to the SO_4 input (and leaching) reflected by the fact that sites with a high Al leaching coincide with sites with a high input (leaching) of SO_4. The geographic patterns of both elements did not coincide very well, however, since soil base saturation was also significantly related to the Al leaching flux.

1. INTRODUCTION

A comparison of element inputs from the atmosphere and element outputs leaching from the bottom of the root zone give insight in the fate (accumulation or release) of sulphur, nitrogen, base cations and aluminium in the ecosystem. As such, it is of crucial importance to assess the present and future impacts of atmospheric deposition on the element cycle and nutrient availability. More specifically, budgets of SO_4, NO_3 and NH_4 give insight in (i) the actual rate of acidification due to anthropogenic sources and (ii) the potential rate of acidification by immobilisation of S and N (e.g. Van Breemen et al., 1984; De Vries et al., 1995). Results about the input and output of Al and base cations (BC) give information about the mechanisms buffering the acid input (e.g. Mulder and Stein, 1994; Wesselink, 1995; De Vries et al., 1995). In general, the ratio of Al to BC release is a crucial aspect with respect to soil mediated effects of acid inputs (e.g. Cronan et al., 1989; Sverdrup and Warfvinge, 1993). These insights can therefore be used to derive critical deposition levels for forest soils (ecosystems). Comparison with available data on present loads, leads to insight in the stress of air pollution on the chemical ecosystem condition (e.g. De Vries et al., 2000b). A European wide assessment of element budgets, using all available data on deposition, meteorology and soil solution chemistry at the Intensive Monitoring plots has, however, not yet been carried out. In June 1999 the project Input – output relationships for Intensive Monitoring sites started (EC contract number SG(99) D/10844) aiming to fill the gap in research needs. This project was financed by the EU-DGVI (50%) and by the research institutes. This report gives an overview of the results obtained. The project results are extensively reported in the Technical Report 2000 (De Vries et al., 2001), and will not be repeated here. After this introduction the main findings reported in the Technical Report are summarised in Chapter 2. Chapter 3 provides the main conclusions from the research. In the Appendices of the report Chapter 4 and 5 of the Technical Report 2001 are given, which provide details on methods and results of the project.

2. SUMMARY OF THE PROJECT RESULTS

2.1 Introduction

The focus of this project was on water and element fluxes through the forest ecosystem. The aim of this investigation was the assessment of site specific deposition estimates and input – output balances of sulphur and nitrogen for selected Intensive Monitoring plots based on input and output estimates and to extrapolate such information on a European wide scale. This general aim was sub-divided in following objectives:

- Estimation of the atmospheric input to and canopy uptake of sulphur and nitrogen - species and canopy release of base cations in selected Intensive Monitoring plots, based on measurements of throughfall and bulk deposition.
- Estimation of the retention or release of sulphur and nitrogen species, aluminium and base cations for the selected Intensive Monitoring plots by comparing the input with the soil output, obtained by multiplying soil solution concentration measurements with modelled soil water fluxes, that in turn are based on available meteorological data.

2.2 Water fluxes through the forest ecosystem

Water influences the availability of nutrients by affecting bio/geochemical processes and the loss of nutrients from the rooting zone by leaching. To understand the element cycles in a forest ecosystem and to predict its future development in response to atmospheric inputs, a quantification of the hydrological situation is therefore indispensable. The hydrological budget is mainly determined by the input of water by rainfall and the loss of water from the forest by interception evaporation, soil evaporation, transpiration and leaching. Apart from influencing nutrient availability, and thereby the vitality and growth of forest ecosystems, the availability of water directly influences forest growth by limiting the transpiration. Furthermore, drought stress may have a strong impact on forest condition in terms of defoliation. Water stress is considered very important with respect to forest condition. Innes (1993) mentioned that the most alarming and frequent observations of a decrease in forest condition in Central Europe coincided with the dry years 1982 and 1983. Landmann (1995) mentioned that defoliation appears to be highest in soils poorly supplied with water and/or in stands in which trees, at some stage of development, have suffered from competition for water. The effects of water stress may diverge from yellowing of the foliage, foliage necrosis, to complete defoliation following extreme drought events (Innes, 1993; Landmann, 1995).

Water fluxes due to interception evaporation can be derived at all Intensive Monitoring plots where bulk deposition and throughfall have been measured. Soil evaporation, transpiration and leaching, however, have not been measured at any of the Intensive Monitoring plots and have to be calculated with hydrological simulation models. Information on water stress, such as the ratio between actual and potential transpiration can also be derived from such models. Studies on water fluxes have been carried out for Intensive Monitoring plots in e.g. Ireland (Nunan, 1999), Germany (Hörmann and Meesenburg, 2000) and France (Granier et al., 2000) and also for forested plots in the Integrated Monitoring Network (Starr, 1999), using different model approaches. A comparison of results of various model approaches for Intensive Monitoring plots in Germany is given in Hörmann and Meesenburg (2000). Such a study was now also carried out for the Intensive Monitoring plots on a European scale, and is extensively described in Appendix A. The results are summarised in this section.

2.2.1 Modelling approach

Hydrological fluxes were calculated for 245 monitoring sites with the hydrological model SWATRE, using the Penman-Monteith equation for evapotranspiration, the Gash model to calculate interception and Richards' equation to calculate transport of water within the soil (Van der Salm et al., 2002). Calculations were carried out with daily meteorological data on precipitation, temperature, net radiation, relative humidity and wind speed. Measurements were used for the plots where a meteorological survey is carried out, whereas interpolated data from nearby meteorological stations were used for plots where only a deposition survey is carried out.

2.2.2 Model results

Mean yearly interception evaporation ranged from approximately 160 mm for Pine and Oak to approximately 250 mm for Beech and 300 mm for Spruce. The interception fluxes for Pine and Oak were low due to the relatively low rainfall on those tree species. Interception fractions increased going from Oak (0,22) < Pine (0.24) < Beech (0.27) < Spruce (0.30), reflecting the increasing interception capacity of those tree species. Median transpiration fluxes were rather constant among the tree species and ranged from 325 $mm.yr^{-1}$ for Pine to 385 $mm.yr^{-1}$ for Spruce stands. The range in the sum of soil evaporation and transpiration is also narrow and median values range from approximately 400-450 $mm.yr^{-1}$ for the various tree species. Leaching fluxes mainly reflected the difference in precipitation on tree species. Median values ranged from 81 mm under Pine stands to 236 mm under Spruce stands. The plots with the lowest leaching fluxes are found in area with relatively low precipitation such as northeastern Germany parts of Sweden and Finland and locally in southern Europe, as shown in Fig. 1.

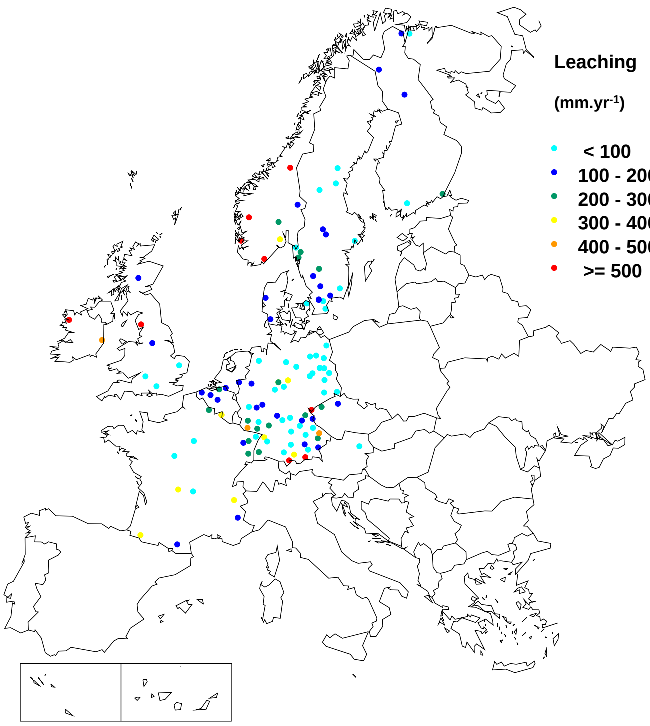


Figure 1 *Average leaching fluxes ($mm.yr^{-1}$) for the 245 monitoring plots for which hydrological budgets have been calculated (top) and the 121 monitoring plots for which chemical budgets have been calculated (bottom)*

2.2.3 Reliability of the model results

Simulated water fluxes through the forest ecosystem were generally within the ranges of available measurements and literature data. The simulated annual throughfall fluxes were calibrated on measured throughfall data such that the simulated yearly values were within 5% of the measurements at 85% of the monitoring sites. Comparison of measured and modelled biweekly or monthly values was also satisfactory. Simulated transpiration fluxes and leaching fluxes could not be validated on data for any of the individual sites. However, detailed studies on two sites in Germany and the Netherlands indicated that the model was able to simulate changes in soil water contents and thus in the transpiration and leaching fluxes (Van der Salm et al., 2002). The simulated transpiration fluxes were consistent with literature data, which indicate that transpiration fluxes for European forest are in a very narrow range around 335 $mm.yr^{-1}$ due to feedback mechanisms with soil and atmosphere (Fig. 2).

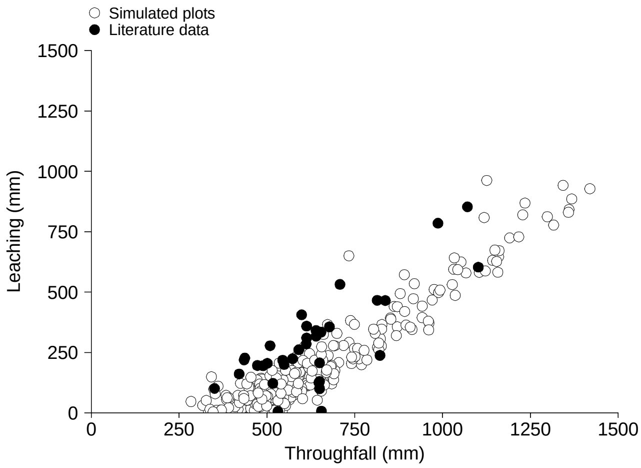


Figure 2 *Simulated and measured yearly leaching fluxes as a function of the yearly throughfall*

A comparison of measured and interpolated meteorological data showed good agreement for relative humidity, reasonable agreement for temperature and net radiation and poor agreement for wind speed. At 80% of the sites average transpiration fluxes were overestimated when interpolated data were used. The median difference in simulated transpiration fluxes was 45 mm. The observed differences in simulated leaching fluxes were comparable to the differences in transpiration fluxes.

2.3 Element fluxes through the forest ecosystem

This section describes the results of the calculated element input by atmospheric deposition, element leaching and element retention and their relation with environmental factors (see Appendix B for details on methods and results). Methods to assess site-specific total atmospheric deposition and total element output for selected Intensive Monitoring plots based on measurements of both throughfall, bulk deposition and soil solution chemistry were developed. Input fluxes were derived from fortnightly or monthly measurements of the chemical composition of bulk deposition and throughfall water, multiplied by the water fluxes while correcting for canopy uptake. A canopy exchange model, developed by Ulrich (1983) and extended by Draaijers and Erisman (1995), was used as a basis and further improved. The resulting canopy exchange was related to available data on bulk deposition, meteorological parameters and foliar chemistry performing multiple regression analysis. Element outputs from the forest ecosystem were derived at intensively monitored plots by multiplying fortnightly or monthly measurements of the soil solution composition at the bottom of the rootzone with simulated unsaturated soil water fluxes. Element retention or release was assessed from the difference between the leaching from the bottom of the root zone and the element input from the atmosphere.

Relationships between canopy uptake, leaching or retention/ release of elements and readily available environmental variables were obtained using a statistical technique. Examples of environmental variables are stand and site characteristics, soil and foliar chemistry, precipitation and bulk deposition. Element leaching for example, is not only influenced by the atmospheric input, but also by the chemical interactions in the soil, which in turn are influenced by stand and site characteristics and soil chemical parameters. Nitrogen retention may e.g. be determined by the soil C/N ratio (e.g. Dise et al., 1998a, b; Gundersen et al., 1998a), whereas the pH and base saturation most likely influence the release of Al and base cations (BC). Reliable relationships can be used for upscaling the results to a larger scale.

2.3.1 Modelling approach

Input fluxes from the atmosphere were derived from fortnightly or monthly measurements of the chemical composition of bulk deposition and throughfall water, multiplied by the water fluxes after correction for canopy uptake. A canopy exchange model (Draaijers and Erisman, 1995) was validated and further improved. The resulting canopy exchange was related to available data on bulk deposition, meteorological parameters and foliar chemistry using multiple regression analysis techniques. Element outputs from the forest ecosystem were derived at intensively monitored plots by multiplying fortnightly or monthly measurements of the soil solution composition at a depth below the rootzone (mostly near 80 cm) with simulated soil water fluxes during those periods (see above). Element retention or release was assessed from the difference between the leaching from the bottom of the root zone and the element input from the atmosphere.

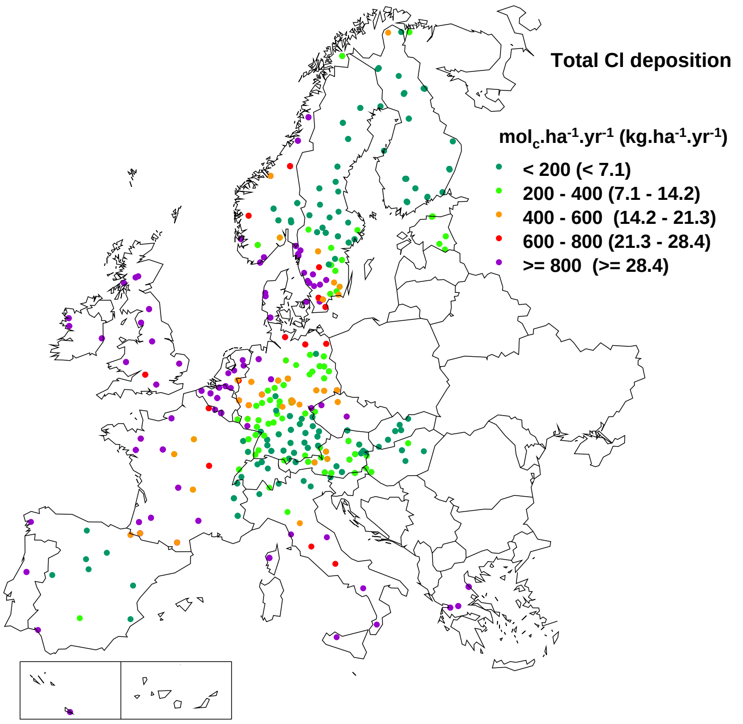
2.3.2 Model results on element deposition

For 309 sites annual throughfall and bulk precipitation fluxes were available for all components for one or more years, leading to 820 plot-year combinations. These sites were distributed over 21 different countries in Europe. Quality checks included a check on the ionic balance and on sodium-to-chloride ratios. Checks on measured and calculated conductivity and on phosphate concentrations could not be applied due to lack of information (data).

Applying the quality checks resulted in about 50% and 37% of the data being lost for bulk precipitation and throughfall, respectively. The quality checks were applied on corrected data. The correction procedure was applied on monthly data available, after which annual fluxes were calculated. These annual fluxes were then used in the multiple regression analysis. Comparisons with uncorrected data showed that an additional 10% of these data could be used for performing the multiple regression analysis.

The geographical distribution of the input fluxes is presented in the Fig. 3 for chloride and sulphate as examples. Chloride input is relatively large (>800 $mol_c.ha^{-1}.yr^{-1}$) in coastal areas throughout Europe. Relatively high sulphate input (>800 $mol_c.ha^{-1}.yr^{-1}$) can be found everywhere in Europe, except for central and northern part of Scandinavia. Many sites with high sulphate input are situated in central Europe (Fig. 3) High N inputs (>1800 $mol_c.ha^{-1}.yr^{-1}$) occur in central Europe. Total nitrogen input is generally much smaller in northern and southern Europe (see Appendix B). Base cation input is relatively high (>800 $mol_c.ha^{-1}.yr^{-1}$) in southern Europe and Lithuania, which is consistent with findings of Draaijers et al. (1997), whereas the input of base cations is low in Scandinavia.

A comparison of modelled depostion estimates, using the EDACS model, with throughfall data at 223 Intensively monitored plots is shown in Fig. 4 (see Appendix D).



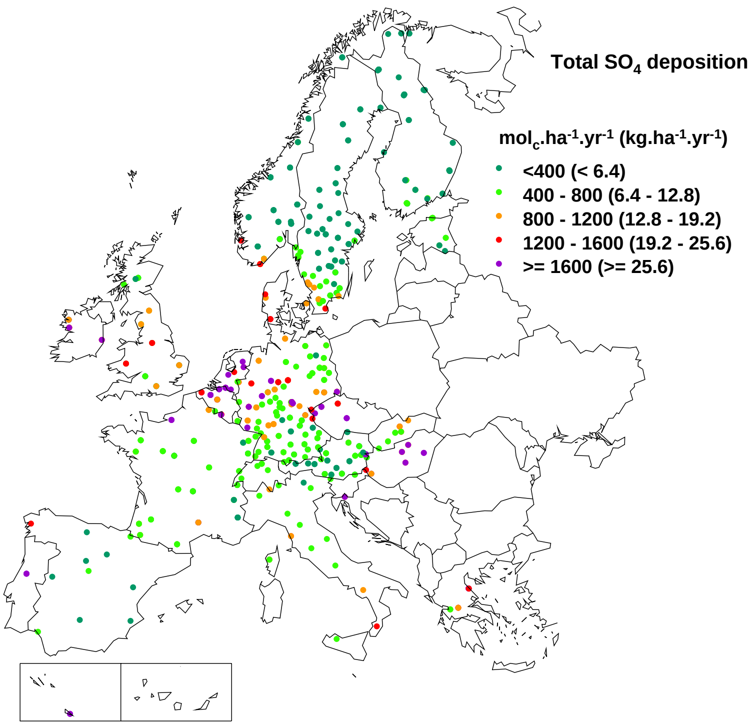


Figure 3 *Geographical variation in input fluxes ($mol_c.ha^{-1}.yr^{-1}$) for chloride (top) and sulphate (bottom) at the Intensive Monitoring plots throughout Europe*

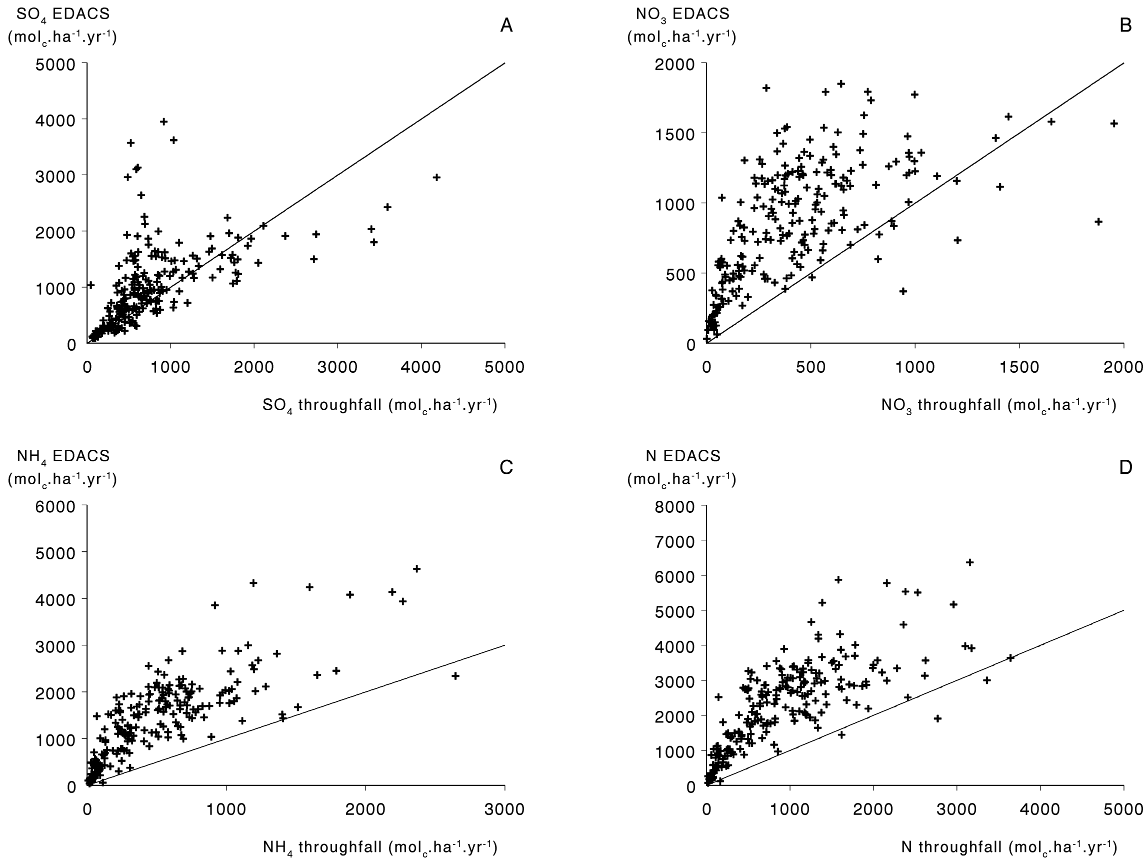


Figure 4 *Comparison of total deposition calculated with EDACS with throughfall measurements of* $(mol_c.ha^{-1}.yr^{-1})$

It appears that the EMEP model overestimates SO_2 concentrations in these areas. On average the modelled S deposition and measured throughfall are comparable, however, indicating the nearly negligible influence of canopy uptake of sulphur. A best regression estimate was

$$SO_{4,model} = 530 + 0.63 \cdot SO_{4,throughfall} \qquad R^2_{adj} = 0.32$$

The N deposition, both of NO_3 and NH_4 are considerably larger than the measured throughfall, although the correlation is larger than for SO_4 (Fig. H4, B, C, D). Specifically the reduced N deposition is higher up to a factor of two, despite the high correlation. Best regression estimate were:

$$NO_{3,model} = 540 + 0.75 \cdot NO_{3,throughfall} \qquad R^2_{adj} = 0.37$$

$$NH_{4,model} = 610 + 1.54 \cdot NH_{4,throughfall} \qquad R^2_{adj} = 0.64$$

2.3.3 Model results on element budgets

Element budgets for sulphur, nitrogen, base cations and aluminium clearly reflected the behaviour of those elements in response to atmospheric deposition. Median values for S leaching were nearly equal to the median S deposition, indicating the overall tracer behaviour of S (Fig. 5). On a considerable number of sites S leaching was, however, higher than S deposition. Sites with the highest sulphur release are located in central Europe, where the strongest reduction in sulphur deposition has taken place over the last decade. This indicates that these systems are releasing sulphur stored in the soil in previous episodes of higher sulphate input. In accordance with the available literature, N leaching was generally negligible below N inputs of 10 kg.ha^{-1}.yr^{-1} (e.g. Dise and Wright, 1995). At higher inputs N leaching increased, but at most sites (90%) the N input was higher then the N leaching, reflecting N retention in the soil. Sites with a net release of nitrogen were found in areas with a high N deposition over a prolonged period of time, such as Belgium and north-western Germany. There was a significant relationship between N leaching and N deposition, but not with the soil C/N ratio, although the C/N ratio appeared to influence the average nitrate concentrations (see also 2.4). Due to the different behaviour of S and N, the leaching flux of SO_4 was mostly higher than that of NO_3, indicating that SO_4 is still the dominant source of actual soil acidification despite the generally lower input of S than N.

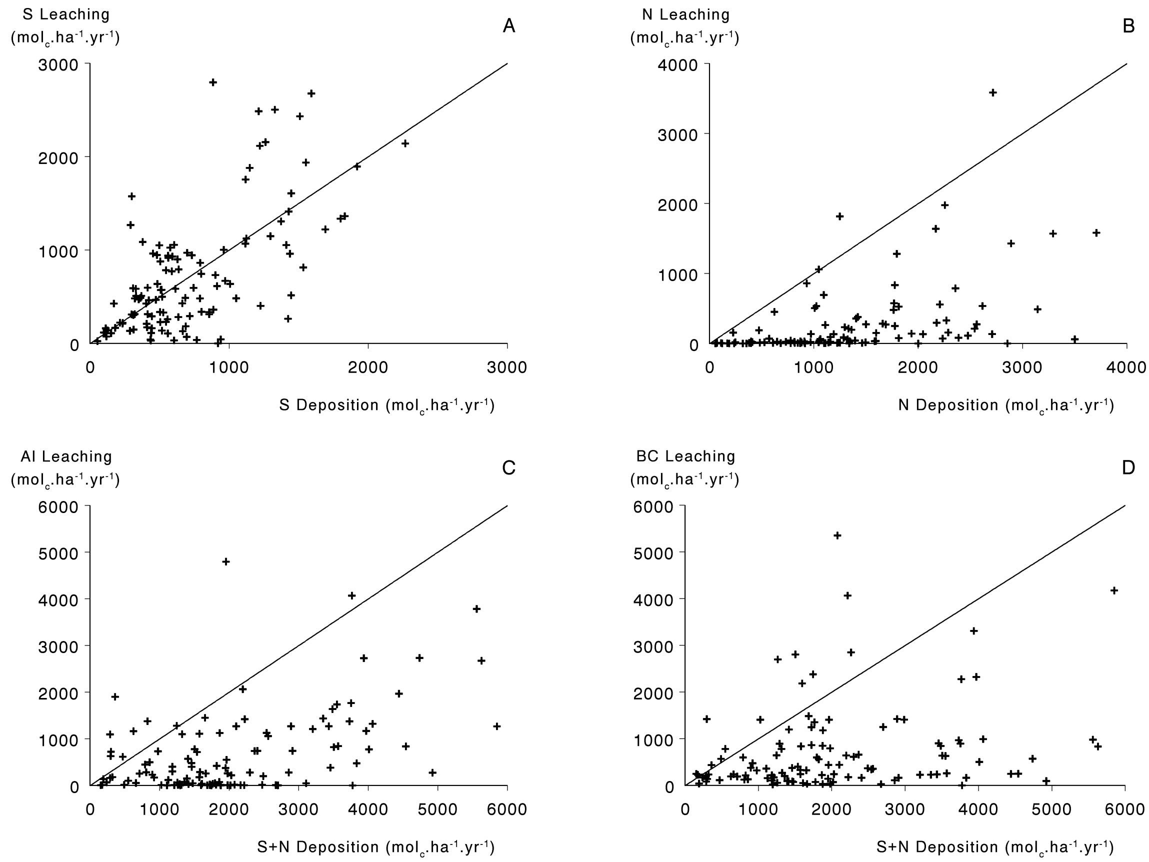


Figure 5 *Relations between total deposition and leaching fluxes of S (A) and N (B) and between the Al leaching fluxes and the total deposition flux (using the deposition model including regression equations to estimate canopy uptake of S+N (C) and BC leaching and S+N deposition (D) at the 121 monitoring sites*

The median base cation balance was close to zero, implying a net adsorption and a net release of base cations at approximately 50% of the plots. The phenomenon of base cation removal due to man-induced soil acidification is thus limited, specifically since high leaching values were partly due to natural acidification in soils with a high pH and base saturation. The impact of air pollution on base cation removal is, however, clear since the leaching flux of base cations (Ca+Mg+K) increased significantly with an increase in the sulphur (acid) input. The Al leaching flux was also significantly related to the SO_4 input (and leaching) reflected by the fact that sites with a high Al leaching coincide with sites with a high input (leaching) of SO_4. The geographic patterns of both elements did not coincide very well, however, since soil base saturation was also significantly related to the Al leaching flux.

2.4 Relationships between element budgets and environmental factors

The results of the study on relationships between element budgets and environmental factors show that S retention from the soil can hardly be explained from environmental variables. N retention increases with an increased stand age and N deposition and a decreased organic C pool and foliar N content. As with N leaching, the N retention fraction was not significantly related to the C/N ratio of the organic or mineral layer. A plot of the N retention fraction against the C/N ratio of the organic and mineral layer, however, shows a tendency of lower N retention fractions at low C/N ratios and high deposition levels but the scatter is large (Fig. 6). As expected, variations in BC release from the soil were positively to the pH (high weathering rates in soils with a high pH).

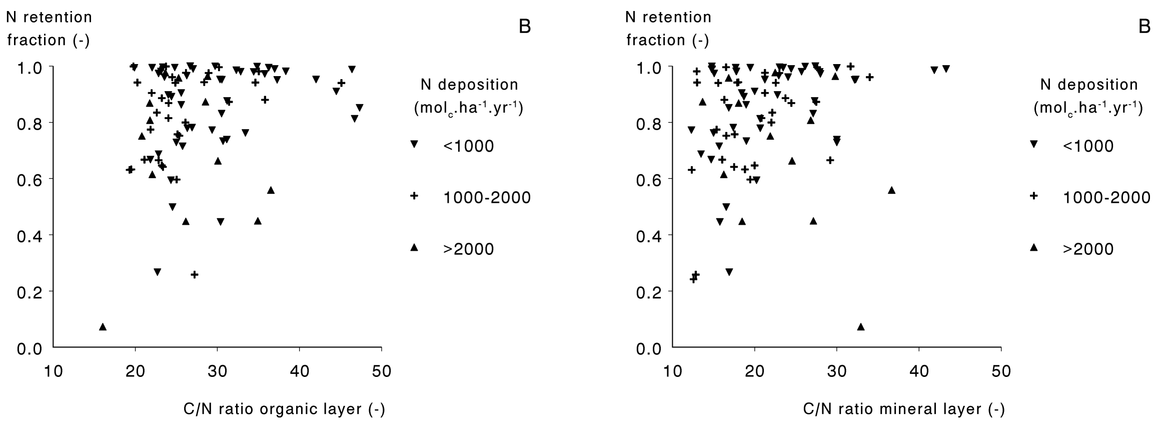


Figure 6 *Relationships between N retention fraction and the C/N ratio of the organic layer (A) and mineral layer (B)*

2.5 Model results on relationships between soil nitrate concentrations and environmental factors

The response of coniferous and broadleaf forest to N deposition is different and the tree-types need to be analysed separately. In coniferous forests N input (throughfall), foliage N concentration, forest floor C/N ratio and nitrate leaching are interrelated variables. Soil nitrate concentrations are best explained by a model with throughfall N and forest floor C/N as main factors, though C/N ratio could be replaced by foliage N. The results confirm conclusions from other datasets (Gundersen et al., 1998a), that the forest floor C/N ratio classes >30, 25-30 and <25 (Fig. 7) as well as the foliage N (mg $N.g^{-1}$) classes <13, 13-17 and >17 (Fig. 8) indicate low, intermediate and high risk of nitrate leaching, respectively.

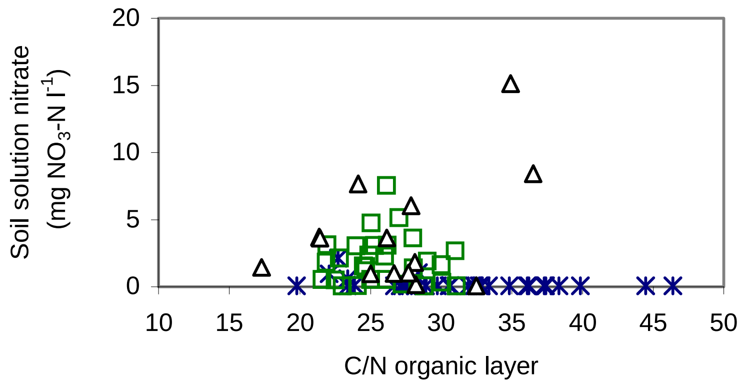


Figure 7 *Average nitrate concentrations in soil solution Jan. 1996 to Jan. 1998 vs. forest floor C/N ratio at low (✷ < 10 kg N.ha^{-1}.yr^{-1}), intermediate (10-30 kg N.ha^{-1}.yr^{-1}) and high (Δ >30 kg N.ha^{-1}.yr^{-1}) throughfall N deposition at Intensive Monitoring plots with conifers only*

In broadleaved forests, correlation's between N input and different factors are less pronounced. A model including throughfall N and soil pH (0-10 cm) as main factors best explained soil nitrate concentrations. The responses of soil nitrate concentration to changes in N deposition will probably be more pronounced in broadleaf than in coniferous forests.

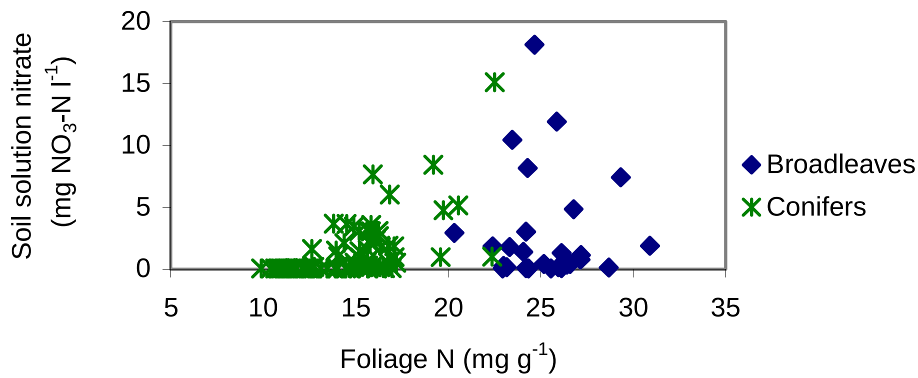


Figure 8 *Average nitrate concentrations in soil solution Jan. 1996 to Jan. 1998 vs. foliage N concentration at Intensive Monitoring plots. For conifers the correlation is significant (r^2=0.34, p<0.0001)*

2.6 Reliability of the model results

There are considerable uncertainties in the calculated budgets, considering the uncertainties in calculated water fluxes and measured element concentrations in view of spatial variability within a plot. Furthermore, the budgets are based on measurements during a relatively limited number of years. For most sites (58%), budgets were limited to a three-year period (1996-1998) and for 28% of the sites it was even less, while data for a four year period (1995-1998) were available at 14% of the sites. This relatively short time span may lead to over- or underestimation of the budget compared to the long-term situation due to particular hydrological or biological circumstances in specific years. The remarkable high N retention in south-eastern Germany, for example, may be due to the fact that these budgets are mainly based on the year 1996 with relatively low precipitation, which may lead to unrepresentative budgets.

The use of interpolated meteorological data instead of local measured data leads to lower element leaching fluxes. The deviation in median leaching fluxes is quite limited and ranges from 15 $mol_c.ha^{-1}.yr^{-1}$ for Al up to 73 $mol_c.ha^{-1}.yr^{-1}$ for base cations (Fig. 9).

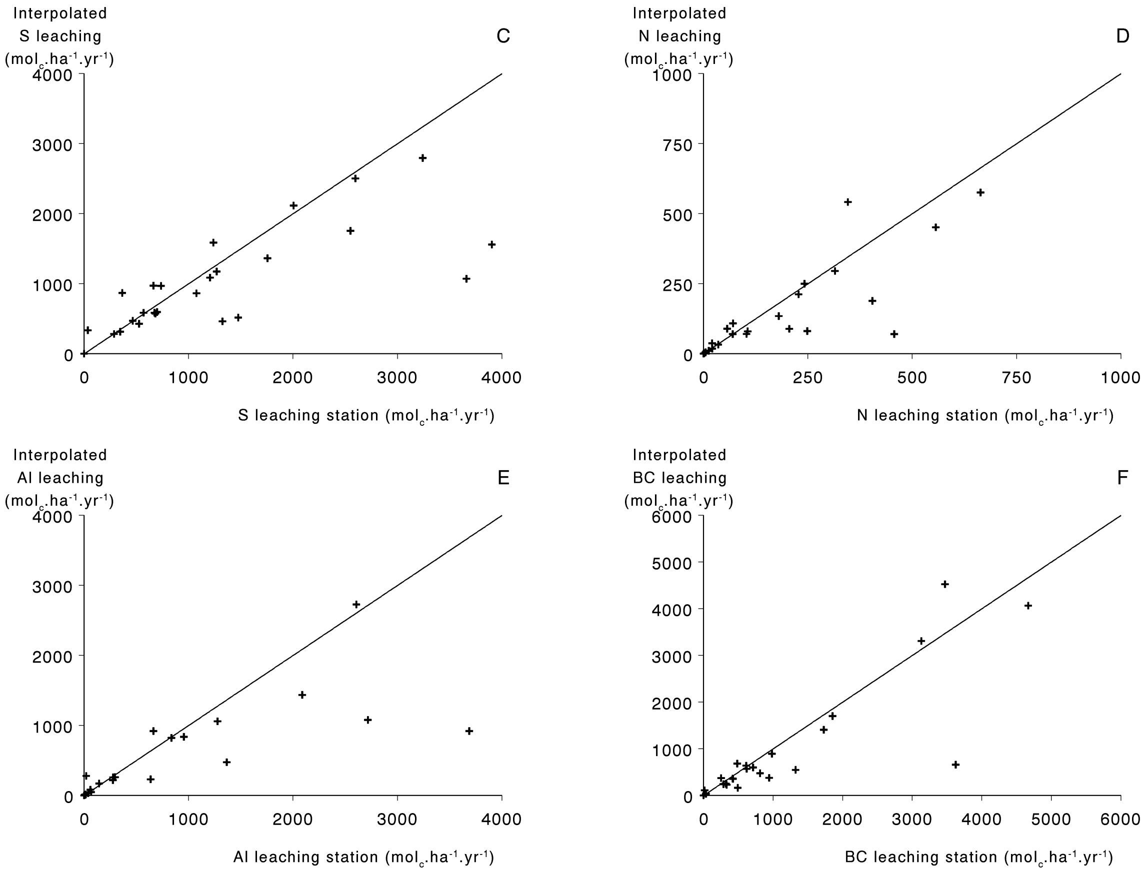


Figure 9 *Leaching fluxes calculated using interpolated meteorological data compared to leaching fluxes calculated using locally measured meteorological data for Cl (A), Na (B), S (C), N (D), Al (E) and BC (F)*

3. MAIN CONCLUSIONS

Major conclusions with respect to the water and element budgets are:

- Mean yearly interception evaporation ranged from approximately 160 mm for Pine and Oak to approximately 250 mm for Beech and 300 mm for Spruce, reflecting the increasing interception capacity of those tree species. Median transpiration fluxes were rather constant among the tree species and ranged from 325 $mm.yr^{-1}$ for Pine to 385 $mm.yr^{-1}$ for Spruce stands. This is consistent with literature data. Leaching fluxes mainly reflected the difference in precipitation on tree species. Median values increased from approximately 80 mm under Pine stands to 240 mm under Spruce stands.
- At most plots, the leaching flux of SO_4 is higher than that of NO_3, despite the generally lower input of S than of N, indicating that SO_4 is still the dominant source of actual soil acidification. The median sulphur budget is close to zero, but at a considerable number of those sites sulphur is released by the soil, indicating that these systems are recovering from previous episodes of high sulphate input.
- The leaching of N is generally negligible below throughfall inputs of 10 $kg.ha^{-1}.yr^{-1}$. There is a significant relationship between N leaching and N deposition but no significant relationship was found with the soil C/N ratio. However, when analysing the directly measure nitrate concentrations in soil water a relation to forest floor C/N was found.
- Nitrogen budgets show that at most sites (90%) are retaining N (the N input is higher than the N leaching).
- Broadleaf forests have higher nitrate concentrations than conifer forest at the same deposition level, probably since they are on the better soils already rich in N.
- Variations in BC leaching were significantly related to the S input and the pH and base saturation. The median base cation balance is close to zero, implying a net adsorption and a net release of base cation at approximately 50% of the plots.
- The Al leaching flux was significantly related to the SO_4 input reflected by the fact that sites with a high Al leaching coincide with sites with a high input of SO_4. The geographic patterns of both elements, however, did not coincide very well since soil base saturation was also significantly related to the Al leaching flux.
- The EDACS model results compare reasonable well with the model results. EDACS can be used for generalisation of deposition to plots where no measurements are available. The advantage is that the relation with emissions is sustained and thus abatement options can be tested.

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APPENDICES A AND B

These appendices contain a reprint from chapter 4 and 5 that were published in the Technical Report 2001 (De Vries et al., 2001).

APPENDIX A ASSESSEMENT OF WATER FLUXES THROUGH THE FOREST ECOSYSTEM

A.1 Introduction

Water influences the availability of nutrients by affecting bio/geochemical processes and the loss of nutrients from the rooting zone by leaching. To understand the element cycles in a forest ecosystem (see also Appendix B) and to predict its future development in response to atmospheric inputs, a quantification of the hydrological situation is therefore indispensable. The hydrological budget is mainly determined by the input of water by rainfall and the loss of water from the forest by interception evaporation, soil evaporation, transpiration and leaching. Apart from influencing nutrient availability, and thereby the vitality and growth of forest ecosystems, the availability of water directly influences forest growth by limiting the transpiration. Furthermore, drought stress may have a strong impact on forest condition in terms of defoliation. Water stress is considered very important with respect to forest condition. Innes (1993) mentioned that the most alarming and frequent observations of a decrease in forest condition in Central Europe coincided with the dry years 1982 and 1983. Landmann (1995) mentioned that defoliation appears to be highest in soils poorly supplied with water and/or in stands in which trees, at some stage of development, have suffered from competition for water. The effects of water stress may diverge from yellowing of the foliage, foliage necrosis, to complete defoliation following extreme drought events (Innes, 1993; Landmann, 1995).

Water fluxes due to interception evaporation can be derived at all Intensive Monitoring plots where bulk deposition and throughfall have been measured. Soil evaporation, transpiration and leaching, however, have not been measured at any of the Intensive Monitoring plots and have to be calculated with hydrological simulation models. Information on water stress, such as the ratio between actual and potential transpiration can also be derived from such models. Studies on water fluxes have been carried out for Intensive Monitoring plots in e.g. Ireland (Nunan, 1999), Germany (Hörmann and Meesenburg, 2000) and France (Granier et al., 2000) and also for forested plots in the Integrated Monitoring Network (Starr, 1999), using different model approaches. A comparison of results of various model approaches for Intensive Monitoring plots in Germany is given in Hörmann and Meesenburg (2000). Such a study was now also carried out for the Intensive Monitoring plots on a European scale, and is described in this chapter. In this chapter, the methods for the derivation of water fluxes due to interception evaporation, soil evaporation, transpiration and leaching are discussed (Section A.2) and results are presented (Section A.3). To derive these fluxes soil hydrological models have been used.

Section A.2 includes a critical review of various hydrological models and gives a description of the particular models used in this study to calculate hydrological fluxes including their parameterisation. Specific emphasis is given to the derivation and use of daily meteorological data, i.e. precipitation, temperature, net radiation, relative humidity and wind speed, which are needed to calculate accurate hydrological fluxes. Those data are only available at the plots where a meteorological survey is carried out. For plots where only a deposition survey is carried out, data availability is, however, limited to monthly or (bi-)weekly rainfall and throughfall data. The missing data have been derived by interpolation using measurements from meteorological stations over Europe (Section A.2). The results in Section A.3 are focused on the hydrological budget as a prerequisite for the element budget (see also Appendix B on element fluxes). The effect of using interpolated data instead of on-site measured data has also been evaluated. In future reports, more attention will be given to various drought stress parameters, including transpiration reduction, that can be used in subsequent analyses relating drought stress to forest growth and forest vitality.

A.2 Methods

A.2.1 Locations

The investigated plots were located in 13 different countries, mostly in Central and Western Europe (Fig. A.1).

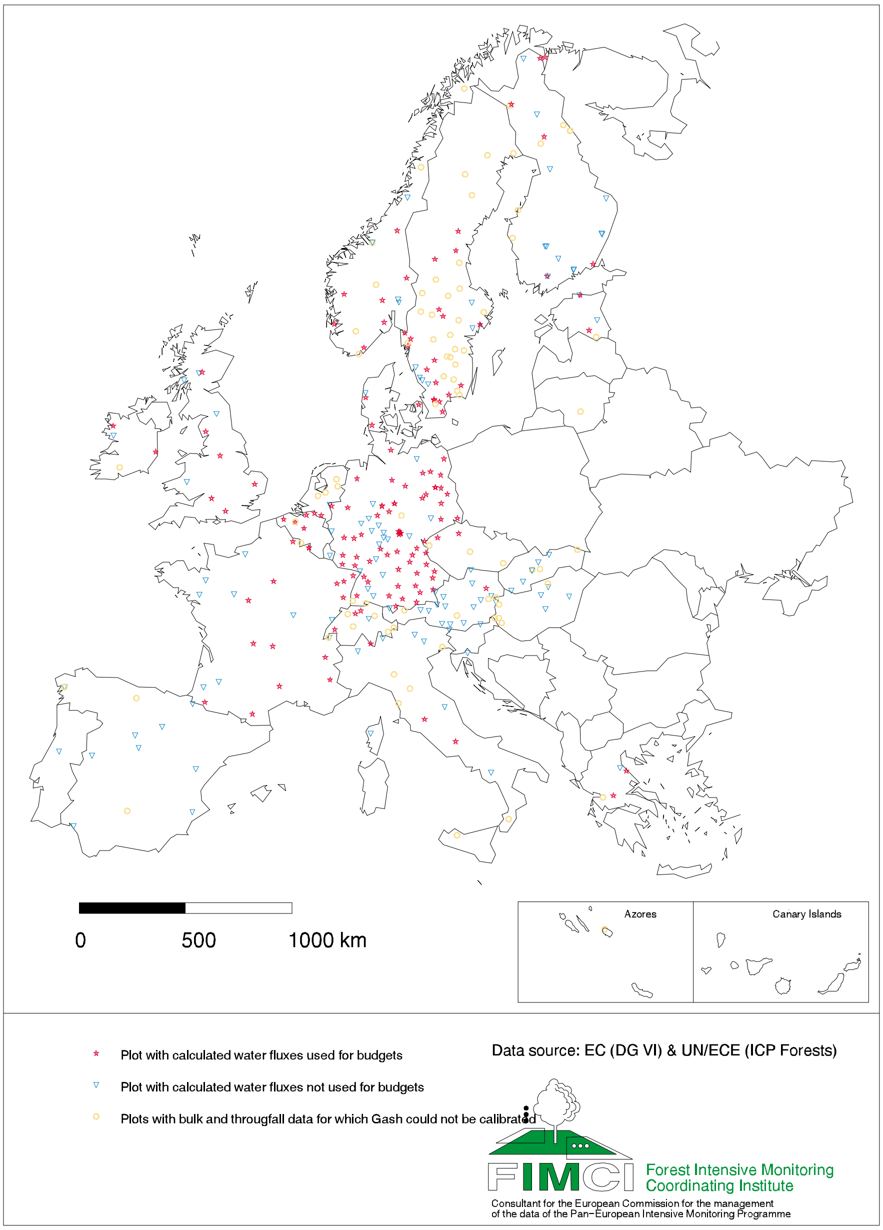


Figure A.1 *Geographical distribution of Intensive Monitoring plots for which water fluxes have been calculated, using data up to 1998.*

Annual water fluxes could in principle be calculated for all Intensive Monitoring sites for which both rainfall and throughfall has been measured at a regular basis for a period of at least 300 days. This included 309 sites for the period up to 1998. The number of sites with both bulk and throughfall data increased from 96 in 1995 to 265 in 1996 and to nearly 300 sites in 1997 and 1998. The sites were located in 13 different countries, mostly in Central and Western Europe

(Fig. A.1). At 64 of the 309 plots, hydrological fluxes could not be successfully calculated due to inconsistencies in the provided data (c.f. Section A.3.1). From the 245 remaining plots for which water fluxes could be calculated, the fluxes of only 121 plots could be used to assess element budgets due to the limited availability of soil solution chemistry data (Appendix B). The geographic distribution of the different types of plots is given in Fig. A.1.

A.2.2 Data assessment methods

To calculate the various water fluxes and the transpiration reduction, a set of daily meteorological data on precipitation, net radiation, temperature, wind speed and relative humidity is required. Daily meteorological measurements were, however, only available for plots where a meteorological survey is carried out. For the remaining plots, data were derived by interpolation from existing meteorological databases. In this section, the measurement methods for meteorological data is first described followed by the derivation of scaled and interpolated meteorological data.

To obtain consistent budgets, we used the interpolated data for all plots throughout this study. The use of interpolated data instead of on-site measured data may lead to errors in the calculated budgets. We therefore also give information on the agreement between measured and interpolated data and on the impact of these discrepancies on the calculated hydrological fluxes at the plots where measurements were available (Section A.3.2.1).

A.2.2.1 Meteorological measurements

At approximately half of the 245 plots at which water fluxes could be calculated, meteorological measurements including methodological information was available. Most equipment, sensors and their placement was in accordance with the Word Meteorological Organisation Standard. For the evaluations carried out in this report, it is assumed that no significant deviations in the measurements have occurred due to measuring errors in the equipment itself. Mandatory data submitted include precipitation (sum), air temperature (mean, min, max), relative humidity (mean, min, max), wind speed (mean, min, max), wind direction (mean) and solar radiation (sum). Available data for the years 1995-1998 used in this evaluation are given in table A.1. The most relevant information on data assessment methods used is given below.

Table A.1 Number of plots with meteorological measurements up to 1998.Numbers in brackets include the available meteorological data at the 121 plots where element budgets could ultimately be carried out

	1995	1996	1997	1998
Precipitation	29 (16)	83 (52)	114 (66)	125 (71)
Net. radiation	7 (3)	56 (37)	89 (53)	103 (61)
Temperature	26 (14)	87 (53)	120 (68)	133 (74)
Relative humidity	24 (12)	85 (51)	118 (66)	131 (72)
Wind speed	7 (3)	64 (39)	92 (51)	103 (57)

Location of measurements

Measurements for almost all mandatory meteorological parameters were mostly carried out on open field stations within the forest area (Table A.2). Sometimes measurements were taken in close proximity (in general not more than 2 km distance) of the monitoring plot or above the forest stand canopy.

Table A.2 Location of meteorological measurements.

Location	Number of plots				
	PR[1)]	AT[1)]	RH[1)]	WS[1)]	SR[1)]
Above the canopy	13	21	21	19	18
Open field in forest area	85	85	83	74	73
Open field outside forest area	9	6	6	6	6
Total	107	112	110	99	97

[1)] PR = precipitation, AT = air temperature, RH = relative humidity, WS = wind speed and SR = solar radiation.

Distance of the meteorological stations to the Intensive Monitoring plots

All meteorological stations for which DAR-Q Information has been received are located at or in the vicinity of the Intensive Monitoring plot. The distance between the meteorological plot and the Intensive Monitoring plot, for meteorological stations that are not on the Intensive Monitoring plot itself, lies within 3200 m (Fig. A.2).

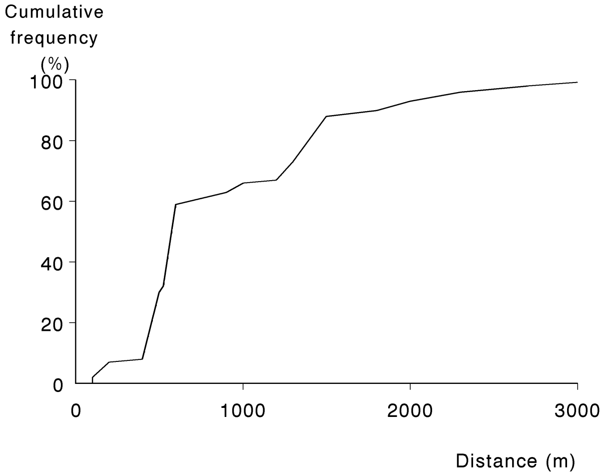


Figure A.2 Distance of meteorological stations to the Intensive Monitoring plots.

A.2.2.2 Rainfall and throughfall data and interpolated meteorological data

Rainfall and throughfall

At all investigated sites, precipitation data are available on a weekly, biweekly or monthly basis from the deposition survey. At 47% of the sites, data were available at a weekly basis, at 27% fortnightly measurements were carried out and at 26% of the sites data were collected monthly. Bulk precipitation is measured using funnels (bulk samplers) situated in the open field near the monitoring plot. Throughfall has been measured at the plots using either gutters or funnels. More detailed information on the number of samplers and the collecting area of the samplers can be found in Chapter B.2.

Interpolated daily precipitation is based on data from the German Weather Service (Deutscher Wetter Dienst, DWD). Precipitation may vary considerably over short distances, leading potentially to large differences in daily precipitation between interpolated site data and the actual (weekly to monthly) measured precipitation at the site. Therefore, interpolated daily precipitation data has been corrected on the measured biweekly or monthly values according to:

$$P_{i,site} = P_{i,int} \cdot \frac{P_{period,site}}{P_{period,int}} \qquad (A.1)$$

where $P_{i,site}$ is the daily precipitation at the site, $P_{i,int}$ is the daily interpolated precipitation for the site, $P_{period,site}$ is the measured precipitation at the site during a given measurement period (two weekly or monthly) and $P_{period,int}$ is the interpolated precipitation during this period.

Other meteorological data

To calculate the (potential) evapotranspiration flux, data on net radiation, temperature, wind speed and humidity have to be provided. Site specific meteorological data were derived by interpolation between data from the main European meteorological stations. Interpolation to each site was performed using an inverse distance weighting procedure for four meteorological stations located in the surroundings of the plot. More information on the interpolation procedure is given in Klap et al. (1997). Data for the meteorological stations were obtained from the NCAR (National Centre for Atmospheric Research), Boulder, USA and ECMWF.

A.2.3 Hydrological model approach

Possible model approaches

To quantify evapotranspiration and leaching fluxes the various terms of the hydrological cycle have to be quantified. Water enters the forest by precipitation. Part of this precipitation is lost by interception evaporation. The remaining part enters the forest as throughfall or stem flow. The water that enters the forest may infiltrate into the forest floor or may be lost by surface runoff. The infiltrated water may be taken up by the roots, leached to a deeper layer or (in case of a saturated zone) be lost by lateral drainage (Fig. A.3). The water balance of a forest stand can thus be described as:

$$P = E + R + D + L \tag{A.2}$$

in which P is the precipitation, E is the evapotranspiration, L is the leaching flux, R is runoff and D is the lateral drainage. Evapotranspiration is divided in interception evaporation (E_i), transpiration (E_t) and soil evaporation (E_s) according to:

$$E = E_i + E_t + E_s \tag{A.3}$$

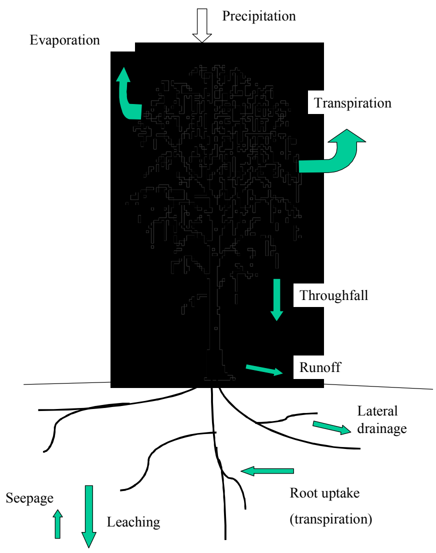


Figure A.3 The hydrological cycle of a forest stand.

To obtain water fluxes for the above mentioned 309 European forest stands a model had to be selected that is able to calculate fluxes for a broad range of forests preferably on the basis of a relatively limited amount of data. Both requirements are difficult to fulfil because simple models require generally less information but their range of application is often more limited, whereas more comprehensive models require more data which are not available. A range of models ranging from simple budget models to comprehensive process oriented soil hydrological models may be used to calculate output fluxes from forests. Although these models differ substantially, they all consist of three separate submodels to calculate:

- Potential evapotranspiration (upper boundary condition)
- Interception evaporation losses
- Water fluxes within the soil compartment

An overview of the most common (sub)models is given in Table A.3.

Table A.3 An overview of some common models used to calculate evapotranspiration, interception and transport of water in forests.

Process	Model complexity			
	Very Simple	Simple	Intermediate	Complex
Evapotranspiration	**Chloride balance**	**Thornwaite (1954)**	**Makkink (1957)**	**Penman-Monteith Monteith (1965)**
Data needs	*E=f(P,L,D) c.f. Eq. 1*	*E= f (Temperature)*	*E=f(radiation, temperature, humidity, crop factor)*	*E=f(radiation, temperature, humidity, wind speed, crop factor)*
Interception	**Measurements**	**Empirical relationship**	**Gash (1979)**	**Rutter et al. (1971)**
Data needs	*Regular measurements of rainfall and throughfall*	$E_i = a + b\ P$	E_i *=f(storage capacity of the crown, soil coverage, rainfall intensity and evaporation rate)*	E_i *=f(storage capacity of the crown, aerodynamic properties of the crown, soil coverage, rainfall intensity and evaporation rate on hourly basis)*
Transport	**Chloride balance**	**One layer capacity model**	**Multi Layer capacity model**	**Richards (Darcy) model**
Data needs	*Long term records of throughfall quantities and Cl concentrations in throughfall and soil solution*	*Soil water retention curve (average for root zone)*	*Soil water retention curves for different horizons*	*Soil water retention curves and hydraulic conductivity for different horizons*

Potential evapotranspiration

The evapotranspiration model calculates the potential loss of water to the atmosphere by evaporation of interception water, by evaporation from the soil surface and by transpiration. Inputs to the model are meteorological data and generally a parameter indicating the resistance of the vegetation to the loss of water from the stomata. The main difference between the various models is the detail of process descriptions and their amount of meteorological data needed to run this (sub)model. Complicated models like Penman-Monteith (Monteith, 1965) need daily data on temperature, radiation, humidity and wind speed. Simple models only require temperature data (e.g. Thornwaite, 1954) or temperature and radiation (e.g. Makkink, 1957). However, these simple models have been developed for specific regions and need to be calibrated when applied over a broader scale of meteorological conditions. This is a major disadvantage when selecting a model for calculating a water balance for all Intensive Monitoring plots. Meteorological data to feed the Penman-Monteith model are, however, measured at part of the Intensive Monitoring plots only. For other plots, data have to be derived from the European network of meteorological stations, as described before (Section A.2.2.2).

Interception evaporation

Interception loss may be calculated using an empirical relation between rainfall and interception, or by simulation models such as the Gash model or the Rutter model. Empirical relationships may be successfully used for coniferous forests where interception losses are almost constant during the year. However, for deciduous forest different relationships have to be used for the winter and the summer period (Granier et al., 2000). The Gash model is a relatively simple model that calculates interception on basis of the interception capacity of a tree and the degree of soil cover. The model has been successfully used for a range of different situations. The Rutter model is much more complicated, requiring information amongst others on the albedo and aerodynamic properties of the crown and meteorological data on a hourly basis (Rutter et al., 1975).

Soil water fluxes

To calculate the soil hydrological fluxes, two types of models are often used: capacity models and models based on the Richards equation. The difference in data requirements for these two types of models is relatively small. Capacity model require only limited information (water content at field capacity and at the wilting point) on the soil physical characteristics of the soil, whereas Richards models require a full water retention curve and data on the (saturated) hydraulic conductivity. However, the use of capacity models is limited to well drained soils with a deep water table.

Soil water fluxes may also be calculated on basis of the chloride balance. This method, which is based on the assumption that chloride is inert in the soil, requires equilibrium between the chloride concentrations in the soil solution and the chloride input. Due to the assumption of equilibrium between the input and output of chloride from the soil, this method can only be successfully applied to long term measurements (5-10 years) where storage of chloride in the soil profile can be neglected. Therefore this method is not very suitable for most of the Intensive Monitoring sites, where the length of the data record is short (on average 3 years).

Model selection

On basis of the model limitations and the available data a selection has been made out of the above model components. Meteorological data can be obtained quite easily either from measured data (limited number of plots) or by interpolation from existing databases. Therefore the relatively complicated Penman Monteith model was used to calculate evapotranspiration. Interception was calculated using the Gash model, because the Rutter model requires too much data whereas empirical rainfall interception relations are less suitable for deciduous forests. The selection of a soil hydrological model was more difficult. Theoretically, Richards models have clear advantages above the capacity models in particular when considering the one-layer models. However, the availability of data is very limited. Soil physical data are not readily available and have to be derived from texture data. In some cases, even texture data have to be estimated using the soil classification. Finally, it is difficult to characterise the different layers because both a profile description and information on root depth and root distribution are lacking for the considered sites. Due to this shortage of data, it is not yet fully clear whether the theoretical advantages of the Richards model will lead to significantly better results than a capacity model.

To select a model, both types of models were compared at a number of long-term Intensive Monitoring sites, using both site-specific soil physical data and estimated data using the same methods for data derivation as for the Intensive Monitoring sites. Results for two sites in Germany and the Netherlands indicate that chloride fluxes simulated with the Richards' model were close to the long-term chloride budget (Van der Salm, in prep). The capacity models both overestimated the long-term Cl output of the soil system by approximately 20%. The use of generic soil physical data instead of on-site measured data affected the hydrological fluxes by 10%, but the difference between the Richards' model and the capacity models remained almost the same. On basis of the theoretical considerations and the above results it was concluded that the Richards' model is most suitable to calculate output fluxes, in particular when focussing on relatively short periods of time.

The selected model components (Gash model, Penman-Monteith model and the Richards' model) form part of the hydrological model SWATRE (Belmans et al., 1983). This model has originally been developed to calculate hydrological fluxes in agricultural systems. Since then the model has been extended to make it more suitable for forests, by including the Gash interception model, a snow module and improving the feed-back mechanism for water uptake during drought conditions (Groenenberg et al., 1995; Tiktak et al., 1995). The model provides a finite difference solution to Richards equation and includes several different options to calculate interception evaporation and transpiration.

A.2.4 Calculation of interception and throughfall

Model description

An important aspect in the calculation of the hydrological fluxes is the loss of water by interception evaporation. Daily interception losses at the 309 Intensive Monitoring sites were calculated using the Gash model (Gash, 1979; Gash et al., 1995). Using this model, first the amount of rainfall necessary to fill the canopy storage capacity (P_s) is calculated, according to:

$$P_s = \frac{R_{avg}}{E_{avg}} \cdot S_{max} \cdot cc \cdot \ln\left(1 - \frac{E_{avg}}{R_{avg}}\right) \qquad (A.4)$$

where R_{avg} is the average rainfall rate ($mm.hr^{-1}$), E_{avg} the average daily evaporation rate during rainfall ($mm.hr^{-1}$), S_{max} the storage capacity of the crown (mm) and cc the canopy closure fraction (-) (mostly erroneously denoted as the soil cover fraction, sc). The total amount of interception (E_i) is then calculated as:

$$E_i = cc \cdot P \qquad \text{when } P < P_s \qquad (A.5)$$

or as

$$E_i = cc \cdot P_s + cc \cdot \frac{E}{R} \cdot (P - P_s) \qquad \text{when } P > P_s \qquad (A.6)$$

where P is the daily precipitation ($mm.d^{-1}$). The maximum interception evaporation is limited by the potential evapotranspiration rate of a wet canopy, e.g. the Penman-Monteith evapotranspiration at a crop resistance of zero (c.f. Eq. A.8 and A.11).

Model parameterisation and calibration

Apart of the meteorological data, the Gash model needs values for the parameters describing the storage and evaporation from the canopy. Normally parameter values for the storage capacity of the crown, S_{max}, and the canopy closure fraction, sc, are derived from analyses of data from single storms using the analysis method described by Leyton (Leyton et al., 1967). Such an analysis could not be made for the Intensive Monitoring plots because the Intensive Monitoring database provides only two-weekly or monthly data for throughfall. Instead the parameters S_{max}, cc and R_{avg}/E_{avg} were calibrated on measured throughfall data for all Intensive Monitoring plots where throughfall has been measured at a regular (weekly to monthly) basis.

To calibrate these parameters an automatic calibration procedure was used based on the Levenberg-Marquardt algorithm (Marquardt, 1963). To guide the optimisation procedure, initial values, upper and lower boundaries for the above parameters had to be provided. Initial parameter estimates for S_{max} were based on Hendriks et al. (1997), as presented in Table 4.10 (initial values). Upper and lower boundaries were set by permitting a 50% deviation from the initial values for S_{max}. The initial value for the R/E ratio was set to 8.0 based on average values reported for a number of studies in Europe (Gash et al., 1980, 1995; Gash and Morton, 1978; Klaassen et al., 1998; Lankreijer et al., 1993; Llorens et al., 1997b; Lousteau et al., 1992b; Pearce et al., 1980; Teklehaimanot and Jarvis, 1991; Valente et al., 1997; Vroom, 1996). For this parameter, wide ranges were used for the upper and lower boundary to account for differences in average rainfall and evaporation rates over Europe.

A problem with the automatic calibration of the Gash model is that the canopy closure and S_{max} are correlated (comparable results may be obtained when lowering the canopy closure while increasing S_{max}). To obtain a good calibration a reasonable initial estimate of the canopy closure is of major importance. The canopy closure of a site is related to stand characteristics such as the number of trees/ha, tree species, LAI and age of trees. To make the best estimate of canopy closure for the Intensive Monitoring sites two different approaches were used and the outcome of both approaches was averaged. The first approach is based on reported data on canopy closure and stand characteristics from interception studies (Carlyle-Moses and Price, 1999; Gash et al., 1980; Granier et al., 2000; Hendriks et al., 1990; Herbst et al., 1999; Hörmann et al., 1996; Lankreijer et al., 1993; Llorens et al., 1997a; Lousteau et al., 1992a; Musters, 1998; Robins, 1974; Teklehaimanot and Jarvis, 1991; Valente et al., 1997). The collected data showed a considerable scatter in canopy closure but regression analyses on the collected data indicated a clear relationship between the (log of) number of trees/ha and the canopy closure fraction (Fig. A.4; Table A.4).

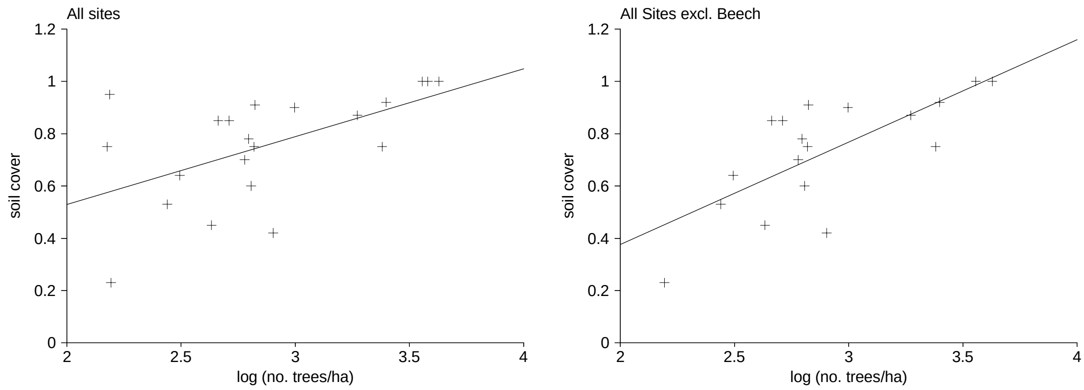


Figure A.4 Relationship between tree density and observed canopy closure in literature data of 21 forest stands incl. Beech forest (left) and excluding Beech forest (right).

The relationship improved significantly when three sites with Beech forest were excluded from the data set. At two of these sites a high canopy closure (0.75 and 0.95) was reported (Hörmann et al., 1996; Herbst et al., 1999) despite the limited number (approx. 150) of trees.

Table A.4 Relationship between tree density and canopy closure in literature data of 21 forest stands.

Data set	Relationship	No sites	$R^2_{adj.}$
All tree species	cc = 0.229 log ($trees.ha^{-1}$) + 0.09	21	0.21
Spruce, Pine, Douglas fir and Oak	cc = 0.396 log ($trees.ha^{-1}$) – 0.42	18	0.47

1) For Beech the relationship derived for all tree species was used

The second approach was based on relationships between the (average) crown dimensions of individual trees and the diameter of the tree (Nagel, 1999). For each plot canopy closure (the area occupied by tree crowns divided by the area of the plot) was calculated from the average crown diameter of the trees and multiplied by the number of trees, according to:

$$cc = \max\left(1, \frac{(a + b \cdot DBH)^2 \cdot 0.25 \cdot \pi \cdot ntrees \cdot 10^{-4}}{plot\ size}\right) \quad (A.7)$$

in which cc is the canopy closure, a (m) and b (m) are constants and DBH is the diameter at breast height (m), ntrees is the tree density (ha^{-1}). Parameters for a and b are listed in table A.5.

Table A.5 Parameters used to calculate the canopy closure (based on Nagel, 1999).

Tree species	a	b
Oak	1.411	0.154
Beech	1.389	0.181
Spruce	0.842	0.110
Pine	0.714	0.133

This relationship is based on a large number of forest measurements in Northwestern Germany. This method leads to quite comparable estimates of the canopy closure for sparse forests. In dense forests, where crowns are overlapping, the method tends to overestimate the canopy closure. To include the uncertainty of both methods in the estimation of the initial value for the canopy closure, initial values were set to the average of the canopy closure derived using both relationships. The lowest calculated value for each site was used as the lower limit and the highest obtained value was used as the upper limit.

A.2.5 Calculation of transpiration and leaching fluxes

Model description

The potential loss of water by evapotranspiration was calculated using the Penman-Monteith equation:

$$E_{pm} = \frac{1}{\lambda} \cdot \frac{s \cdot R_n + \rho \cdot C_p \cdot \delta q / r_a}{s + \gamma \cdot (1 + r_s / r_a)} \cdot f_s \tag{A.8}$$

where E_{pm} is the potential evapotranspiration ($mm.d^{-1}$), λ is the specific heat of evaporation ($J.kg^{-1}$), s is the slope of the saturated water vapour curve ($hPa.°K^{-1}$), R_n is the net radiation ($W.m^{-2}$), ρ is the density of air ($kg.m^{-3}$), C_p is the specific heat capacity of the air ($J.kg^{-1}.°K^{-1}$), δq is the water vapour deficit (hPa), r_a and r_s are the aerodynamic and canopy resistance ($s.m^{-1}$), γ is a psychrometer coefficient ($mbar.°C^{-1}$) and f_s is the number of seconds per day.

For γ, ρ and C_p constant values were applied. Values used equal 0.67 $mbar.°C^{-1}$ for γ, 1.2047 $kg.m^{-3}$ for ρ and 1004 $J.kg^{-1}.°K^{-1}$ for C_p. Net radiation (R_n) was computed from measured global radiation (Beljaars and Holtslag, 1990), the slope of the saturation vapour pressure-temperature curve (s) from the temperature and the water vapour deficit (δq) from measured relative humidity (affecting actual vapour pressure) and temperature (affecting saturated and actual vapour pressure) as presented in Klap et al. (1997). This means that for the use of the Penman/Monteith equation, all mandatory parameters (except for precipitation) are needed.

The aerodynamic resistance was calculated as a function of the wind speed and the roughness of the canopy:

$$r_a(z) = \frac{1}{k^2 \cdot u} \cdot \left(\ln\left(\frac{z-d}{z_0} \right) \right)^2 \tag{A.9}$$

where k is the von Karman constant (-), u the wind speed at height z ($m.s^{-1}$), z is the height of the canopy (m), d is the zero plain displacement (m) and z_0 is the roughness length (m). The wind speed above the canopy was calculated from the wind speed measured at a standard height of 2 m, assuming a logarithmic profile.

The canopy resistance (r_s) is equal to the basic canopy resistance as long as the vapour pressure deficit (δq) is less then 3.0 hPa. At a higher evaporative demand, the canopy resistance was assumed to increase according to:

$$r_s = r_{s,basic} + (25 \cdot (\delta q - 3.0)) \tag{A.10}$$

The potential evapotranspiration is divided over interception evaporation (c.f. 3.2.3), potential soil evaporation and potential transpiration. When the canopy is wet, r_s is zero and the Penman-Monteith equation reduces to:

$$E_{wet} = \frac{\frac{1}{\lambda} \cdot (sR_{net} + \rho C_p / r_a \cdot \delta q)}{(s + \lambda)} \tag{A.11}$$

Using this notation for the evaporation during rainfall, the Penman-Monteith total evapotranspiration can be rewritten to:

$$E_{pm} = \frac{(s + \gamma)}{(s + \gamma \cdot (1 + r_s / r_a))} \cdot E_{wet} \tag{A.12}$$

Interception evaporation equals the minimum of E_{wet} and the potential interception E_i.

Potential soil evaporation was calculated according to Ritchie (1972):

$$E_s^* = \frac{1}{\lambda} \cdot \left(\frac{s}{s + \gamma} \right) \cdot R_{net} \cdot e^{(-0.39 \cdot LAI)} \tag{A.13}$$

where LAI is the leaf area index, which was calculated as a function of canopy closure, cc, according to:

$$LAI = a \cdot cc + b \cdot cc^2 + c \cdot cc^3 \tag{A.14}$$

where a, b and c are constants depending on the tree species.

Actual soil evaporation was calculated from the potential soil evaporation and the time since the last rainfall event according to Black et al. (1969):

$$E_s = \varepsilon \cdot \left(\sqrt{t_d + 1} - \sqrt{t_d} \right) \cdot E_s^* \tag{A.15}$$

where E_s ($m.d^{-1}$) is the actual soil evaporation rate, t_d (d) is the number of days elapsed since the last rainfall and ε ($d^{-0.5}$) is an empirical parameter.

Potential transpiration is calculated from the potential evapotranspiration, given by Eq. (A.8), by reducing the evapotranspiration during rainfall with the calculated interception evaporation according to:

$$E_t^* = \frac{(s + \gamma)}{(s + \gamma \cdot (1 + r_c / r_a))} \cdot (E_{wet} - E_i) \tag{A.16}$$

The actual transpiration depends on the availability of water in the root zone. Reduction of transpiration occurs when the soil water pressure head drops below a certain threshold value.

Water uptake from a soil layer becomes zero when the pressure heads drops below the wilting point. The actual transpiration is obtained by summation of the uptake from the different layers. To calculate the actual evapotranspiration, the potential transpiration was divided over the soil layers on basis of the effective root length. The effective root length (L_{ef}) was calculated from the given root length distribution and the degree of water saturation in the different layers to allow for compensatory uptake from relatively wet layers (Tiktak and Bouten, 1994):

$$L_{ef} = \left(\frac{\theta}{\theta_s}\right) \cdot L \tag{A.17}$$

Surface runoff may occur when the rainfall intensity exceeds the infiltration flux of water into the soil. When this occurs water is stored on the surface until a given storage capacity is exceeded. The surplus of water is then lost by surface runoff. Options to calculate lateral drainage are not used in the present application of SWATRE.

The transport of water through the soil was obtained by a numerical solution of Richards' equation:

$$\frac{\delta\theta}{\delta t} = \frac{\delta}{\delta z} \cdot \left(K(h) \cdot \left(\frac{\delta h}{\delta z} + 1 \right) \right) - S(h) \tag{A.18}$$

where θ ($m^3.m^{-3}$) is the volumetric water content, t (d) is time, z (m) the vertical position in the soil, h (m) soil water pressure head, K ($m.d^{-1}$) hydraulic conductivity and S (d^{-1}) the sink term accounting for root water uptake (actual transpiration).

Model parameterisation

Apart from the meteorological data (c.f. A.2.3), two main groups of input parameters are necessary for the model SWATRE: those related to the abiotic characteristics of the site (such as number and thickness of the soil layers, soil physical characteristics) and the vegetation dependant parameters (e.g. crop factor, evapotranspiration parameters). Part of this information was not available in the Intensive Monitoring database and had to be derived indirectly using literature data and transfer functions (Table A.6).

Table A.6 Derivation of the main input parameters for SWATRE.

Parameter	Obtained from
Depth of the soil profile	Soil type and soil phase
Lower boundary conditions	Soil type
Texture of the layers	Directly from the Intensive Monitoring database, from the parent material or based on the FAO soil code
Soil physical characteristics	Based on texture data using transfer function (Wösten et al., 1999)
Root distribution	Depth of the soil profile and literature data (De Visser and de Vries, 1989)
Basic canopy resistance	Literature values for different tree species (Hendriks et al., 1997)
Tree height	Intensive Monitoring database or estimated (Klap et al., 1997)
Interception parameters	Calibration on measured throughfall

The Intensive Monitoring database does not (yet) contain profile descriptions of the various sites and therefore the depth of the soil profile has been derived on basis of the soil type and soil phase. Soil phase for each plot was derived by overlaying the map with plot locations with the soil map of the Soil Geographical Database of Europe at a 1:1Million scale (Eurosoil, 1999). The depth of the profile was derived from a pedotransfer rule indicating the depth of soil profile (shallow (<40 cm), moderate (40-80cm), deep (80-120cm) and very deep (> 120 cm)) as a function of soil code and phase (Pedotransfer rule 411, European Soil Bureau). A depth of respectively 30, 60, 100 and 230 cm has been allocated to the respective depth classes. The soil profile has been divided into a maximum of 7 horizons (Table A.7). The thickness of the organic layer was calculated from the measured weight of the organic layer (kg m^2) and the bulk density of that layer (kg m^3) calculated with transfer function that relates bulk density to the measured C content of organic soils (Van Wallenburg, 1988).

With respect to the lower boundary conditions, for all soil profiles free drainage of soil water at the bottom of the soil profile was assumed, except when bedrock was found within 30 cm depth (lithic phase). No hydrology was calculated for soils with ground water influence. In the future this will be improved by assigning different lower boundary conditions to soils with ground water influence, which means that we will also define boundary conditions for soils with gleyic and stagnogleyic regimes.

Table A.7 Schematisation of the soil profile.

Horizon	Depth (cm)		Number of soil layers and thickness (cm)	Type of compartment
	From	to		
1	>0		1	Litter layer
2	0	5	2 (2.5 cm)	Topsoil
3	5	10	2 (2.5 cm)	Topsoil
4	10	20	2 (5 cm)	Topsoil
5	20	40	4 (5 cm)	Subsoil
6	40	80	4 (10 cm)	Subsoil
7	80	230	6 (25 cm)	Subsoil

Physical characteristics for each horizon were derived using class transfer functions (Wösten et al., 1999), depending on the texture class and whether the horizon is assumed to be a topsoil (A or E horizon) or a subsoil compartment (B and C horizons). Texture for the different horizons were either obtained directly form the Intensive Monitoring database (voluntary submissions) or derived from the FAO soil code (FAO Composition Rules, 1981). Soil physical characteristics for the litter layer were taken from data for a Douglas fir stand, being the only data we could find in literature for these parameters (Tiktak and Bouten, 1994).

Root distribution was based on estimated soil depth and literature data for deciduous and coniferous forest (Table A.8; c.f. De Visser and de Vries, 1989).

Table A.8 Root distribution (%) as a function of the depth of the soil profile for coniferous and deciduous forest.

Compartment	Depth of the soil profile									
	20		30		60		70		>70	
	Con	Dec	Con	Dec	Con	Dec	Con	Dec	Con	Dec
Litter	5	5	5	5	5	5	5	5	5	5
0-10 cm	60	55	55	40	45	25	40	20	40	20
10-20 cm	35	40	30	35	20	20	20	20	15	20
20-30 cm			10	20	10	20	10	20	10	15
30-40 cm					10	15	10	15	10	15
40-50 cm					5	10	5	10	5	10
50-60 cm					5	5	5	5	5	5
60-70 cm							5	5	5	5
70-80 cm									5	5

The basic canopy resistance (r_s) was derived from a literature overview (Hendriks et al., 1997). Values ranged from 50 $s.m^{-1}$ for Oak species, 85 $s.m^{-1}$ for Beech, 90 $s.m^{-1}$ for Douglas fir to 100 $s.m^{-1}$ for Pine. Tree height was based on the reported measurements in the Intensive Monitoring database. For plots where data for tree height were not reported (26 sites), it was estimated as a function of tree species, tree age, climatic zone and the C/N ratio (Klap et al., 1997). Interception parameters were calibrated on measured throughfall at the plots (c.f. A.2.5 and A.3.1).

A.3 Results and discussion

A.3.1 Interception and throughfall

Model calibration

Throughfall fluxes were calibrated on measured throughfall at 309 sites for which a sufficiently long record of bulk deposition and throughfall measurements was available up to 1998 (c.f. Chapter A.2.1). At 90% of the sites (277) throughfall parameters could be optimised using the above mentioned procedure (Table A.9). At the remaining 32 sites, extreme (combinations of) parameter values had to be used to approach the measured throughfall data. For example on a quite dense spruce stand (704 trees.ha^{-1}; height 22 m) throughfall amounted to 91% of the yearly precipitation. The measured throughfall at this site could only be simulated by assuming low values for both the storage capacity of the crown and the canopy closure and a very high value for the average rainfall intensity, which was considered unlikely. The problems on such sites may be caused by errors in the precipitation and/or throughfall measurements or due to incomplete or incorrect information on site characteristics such as tree height and number of trees/ha. An unsuccessful application of the Gash model may also be due to extreme temporal variation in meteorological conditions (e.g. rainfall intensity or evaporation rate) which are not taken into account in the Gash model.

Simulated throughfall data for the considered sites were close to measured values for 88% (245 sites) of the 277 calibrated sites (Table A.9). At 32 sites the throughfall was not simulated very accurately resulting in a deviation (defined as the absolute value of (measured-modelled)/measured * 100) between simulated and measured total throughfall of more then 10% or leading to a Normalised Root Mean Square Error of more than 10%. Those 32 sites were not used in the budget calculations.

Table A.9 Number of sites for which the Gash model could be successfully applied.

Tree species	Total	Not calibrated	Calibrated		
			Total	Rejected[1]	Accepted[2]
Spruce	136	16	120 (88%)	13	107
Pine	71	6	65 (92%)	10	55
Beech	51	4	47 (92%)	2	45
Oak	38	5	33 (87%)	3	30
Others	13	1	12 (92%)	4	8
Total	309	32	277 (90%)	32	245

[1] Sites with calibrated parameters for which the NRMSE or the deviation between the total measured and modelled throughfall (expressed as (modelled-measured)/measured*100) was more then 10%

[2] Sites with calibrated parameters passing the above mentioned quality criteria

The average calibrated parameter values for the storage capacity of the crown, S_{max}, and the canopy closure, sc, were close to the initial values (Table A.10). Calibrated values for the ratio of the average rainfall rate over the average evaporation rate during rainfall, R/E, where generally lower than initial values, in particular for Beech. The low R/E values for Beech might be due to an underestimation of the canopy closure in Beech stand. The (limited) literature data indicated extremely high values for canopy closure under Beech at relatively low tree densities (c.f. Chapter A.2.4). Moreover, stem flow was neglected in the present application. This may lead to an overestimation of the interception parameters in tree species where stem flow is substantial, such as Beech.

Although the model simulated the measured throughfall quite well and average model parameters were feasible, the range in the optimised parameters was rather high as indicated by the standard deviation (Table A.10).

Table A.10 Initial and calibrated values for the Gash parameters.

Parameter	Tree species	Initial settings[1]			Calibrated values	
		Initial value	Lower boundary	Upper boundary	Average	Standard deviation
S_{max} (mm)	Spruce	2.8	1.5	3.3	2.4	0.8
	Pine	1.0	0.5	1.5	0.9	0.3
	Oak	0.9	0.5	1.5	1.4	0.4
	Beech	1.0	0.7	2.0	1.7	0.5
cc (-)	Spruce	0.71	0.60	0.82	0.78	0.17
	Pine	0.71	0.61	0.81	0.77	0.16
	Oak	0.80	0.64	0.95	0.82	0.16
	Beech	0.76	0.56	0.95	0.79	0.16
R/E (-)	Spruce	8	2	13	5.5	2.7
	Pine	8	2	13	4.6	2.4
	Oak	8	2	13	5.4	2.6
	Beech	8	2	13	3.6	1.9

[1] initial settings for canopy closure (sc) refer to average values because values depend on number of trees/ha and/or DBH (see Table 4.5 and 4.6)

The ratio between average rainfall intensity and evaporation velocity (R/E) was significantly higher in the Boreal and Northern Boreal climate zones (approx. 6.5), whereas significantly lower than average values were found in the south Atlantic zone (R/E = 2.7). These results are partly confirmed when analysing the difference in average R/E between the various countries. For example Finland, where all sites are in the Boreal or northern Boreal zone has a significantly higher R/E ratio (8.0) than countries in central Europe. On the other hand, Sweden has an average R/E of only 4.0, although 30% of the sites have a boreal climate.

The observed variation in the calibrated parameter values for canopy closure and storage capacity of oak, spruce and pine trees were weakly related to the tree density, the altitude and/or the latitude. The observed parameters for Beech were not related to either the geographical characteristics of the site or the tree density (Table A.11).

Table A.11 Relationships between parameter values for canopy closure (cc) and storage capacity (s_{max}) and site characteristics.

Parameter	Tree species	Relationship	$R^2_{adj.}$(%)
cc (-)	Spruce	$0.67 + 1.5\ 10^{-4}$ no trees	22.0
	Pine	$1.41 + 1.6\ 10^{-4}$ no trees - $1.35\ 10^{-2}$ latitude - $1.7\ 10^{-4}$ altitude	45.0
	Beech	$0.77 + 4.9\ 10^{-5}$ no trees	1.0
	Oak	$0.49 + 9.5\ 10^{-5}$ no trees + $1.23\ 10^{-2}$ height	15.4
s_{max} (mm)	Spruce	$2.88 - 2.9\ 10^{-4}$ no trees - $4.8\ 10^{-4}$ altitude	5.7
	Pine	$0.79 + 2.9\ 10^{-4}$ altitude	6.9
	Beech	$1.25 + 1.7\ 10^{-2}$ tree height	4.0
	Oak	$2.30 + 3.7\ 10^{-2}$ tree height - $3.61\ 10^{-2}$ latitude	23.5

The limited physical relationships between the calibrated parameter values and site characteristics indicates that part of the observed variation in calibrated values is probably due to local minima in the optimisation procedure. This means that a good correspondence between measured and simulated throughfall may have been reached by using a combination of incorrect parameters. In extreme situations this may lead to errors in the calculated yearly soil evaporation (strongly influenced by canopy closure) and transpiration fluxes or to deviations in the daily water fluxes due to errors in the daily throughfall fluxes. To avoid such errors, detailed information on either the canopy closure or the storage capacity of the crown is indispensable.

Model results

Yearly but also monthly and two weekly measured data were quite well simulated for the 245 sites passing the calibration procedure and the quality checks (Fig. A.5). However, the deviation for individual measurement periods was sometimes quite large, as indicated by the cumulative frequency distribution of the deviation between measured and simulated throughfall (Fig. A.6).

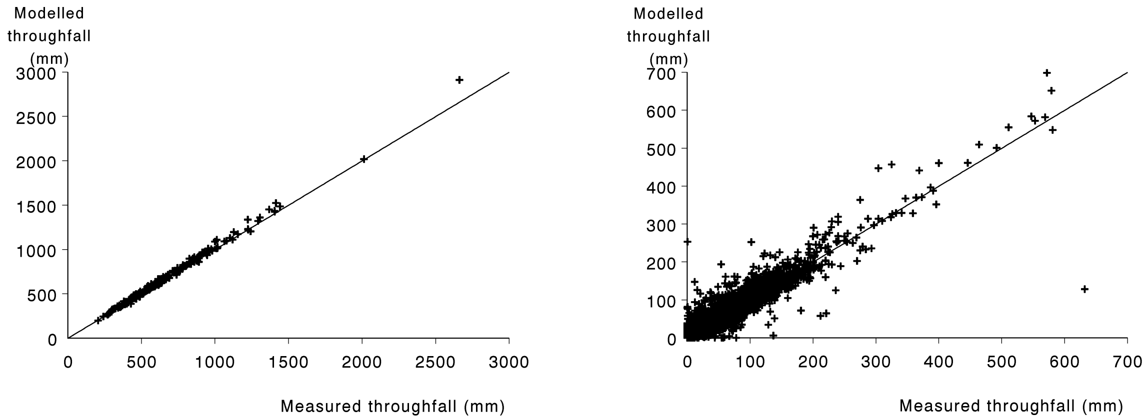


Figure A.5 Measured and modelled yearly (left) and biweekly/monthly (right) throughfall at the Intensive Monitoring sites for the 245 sites that were successfully calibrated.

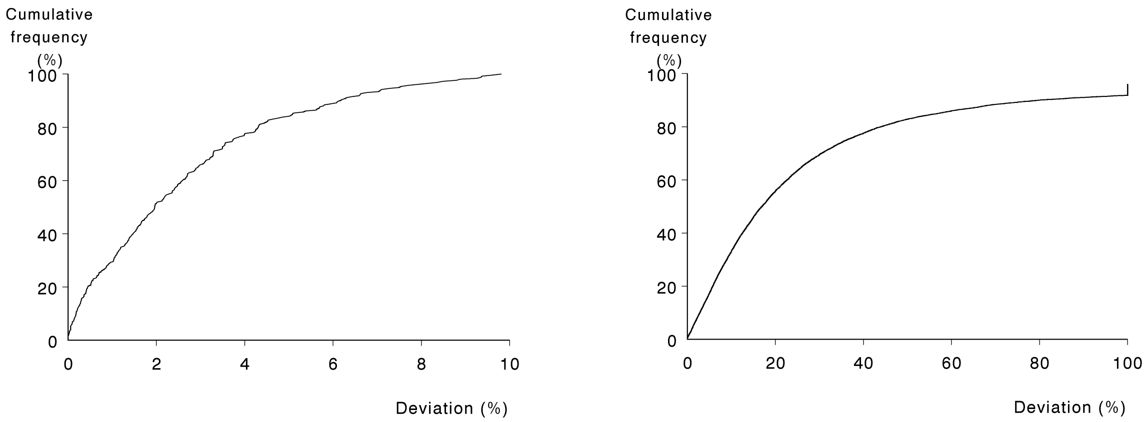


Figure A.6 The cumulative frequency distribution of the deviation between measured and simulated yearly (left) and biweekly/monthly throughfall fluxes (right) for the 245 sites that were successfully calibrated.

Table A.12 Measured precipitation and simulated interception and throughfall fluxes (mm yr^{-1}) at 245 sites at which the Gash model was successfully calibrated.

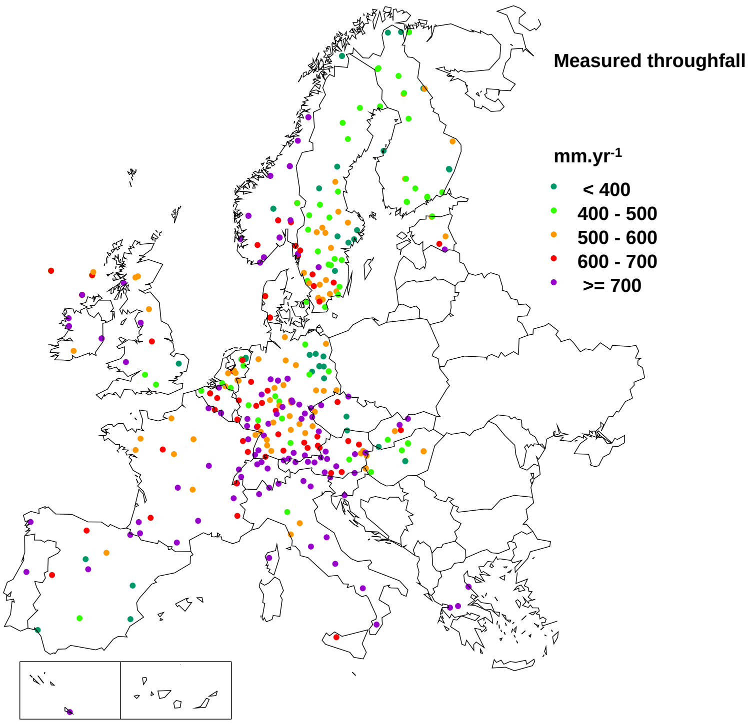
Tree	Precipitation			Interception			Throughfall		
species	5%	50%	95%	5%	50%	95%	5%	50%	95%
Pine	42	64	112	4.5	15	32	35	50	76
Spruce	57	96	172	14.1	29	62	41	66	127
Oak	58	72	131	8.5	18	32	44	57	104
Beech	67	89	163	11.9	24	37	48	64	132
Other	42	112	213	7.7	30	61	34	75	167
All	52	86	162	9.3	24	52	38	60	130

Large differences in rainfall, interception and throughfall fluxes were found within the 245 plots for which fluxes were calculated (Table A.12). Precipitation ranged between 520 and 1620 mm at 90% of the sites. Pine trees received a lower amount of precipitation compared to Beech and Spruce forest. Interception fluxes ranged from 93 to 520 mm (at 90% of the sites). Lowest values were found in Pine forest that received less rainfall compared to the other tree species. Deciduous forests (Oak and Beech) showed relatively lower interception fluxes (median values of 180 and 240 mm respectively) compared to the coniferous tree species. The observed differences in throughfall fluxes correspond to the trends in deposition and interception fluxes. The lowest fluxes are found under Pine trees (median value 500 mm) and higher values are found for Spruce trees and the deciduous tree species (median values 570-660 mm).

An overview of the average measured and modelled throughfall fluxes on the different sites is given in Fig. A.7. Average yearly throughfall is high (> 1200 mm) in mountainous areas in western Norway, central and southern Europe and in Ireland. Low values are found in the eastern part of Sweden and central Europe. The pattern of measured and modelled throughfall was highly comparable (Fig. A.7).

A.3.2 Transpiration and leaching fluxes

In this section we report the modelled soil evaporation and transpiration fluxes and the resulting leaching fluxes from the root zone, that were used in the calculation of element budgets (Appendix B). First the impacts of using interpolated meteorological data on water fluxes is discussed by a comparison of results with measured and interpolated meteorological data (Section A.3.2.1). Then results obtained with interpolated data are presented, while paying attention to model validation on measurements and literature data (Section A.3.2.2).



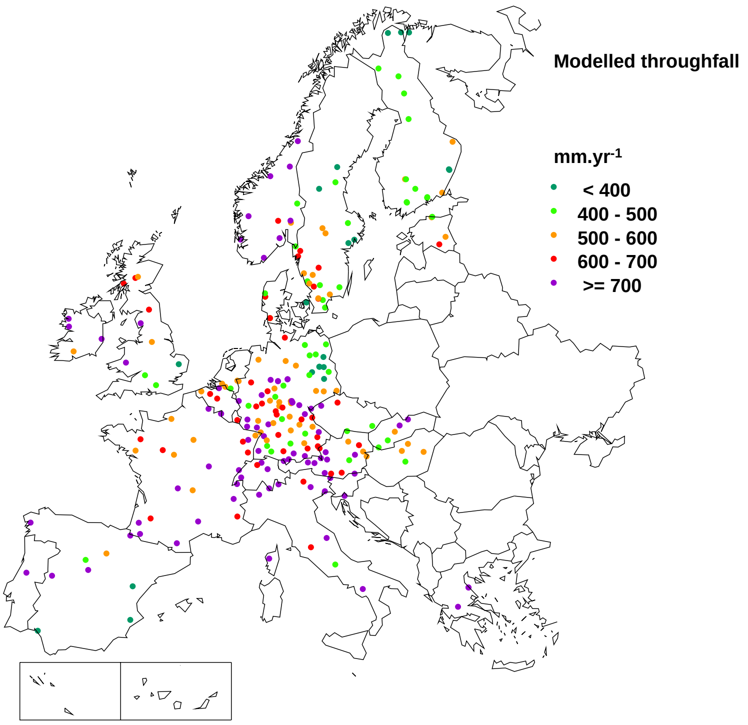


Figure A.7 *Average yearly measured (top) and modelled (bottom) throughfall fluxes (mm.yr^{-1}) at the 245 sites for which both precipitation and throughfall data were available.*

A.3.2.1 Comparison of results with measured and interpolated meteorological data

Comparison of measured and interpolated meteorological data

To obtain an indication of the adequacy of the interpolated daily meteorological data, we compared those data with measured data for the plots where a meteorological survey was carried out in the period 1995-1998. Comparisons were made on a daily, monthly and yearly basis. With respect to precipitation, use was made of the data that were scaled to the biweekly or monthly precipitation measured in the deposition survey. Results thus obtained for net radiation, temperature, wind speed and relative humidity are given in Fig. A.8 for different time intervals. In Fig. A.9, the daily averages over a period of a year are compared.

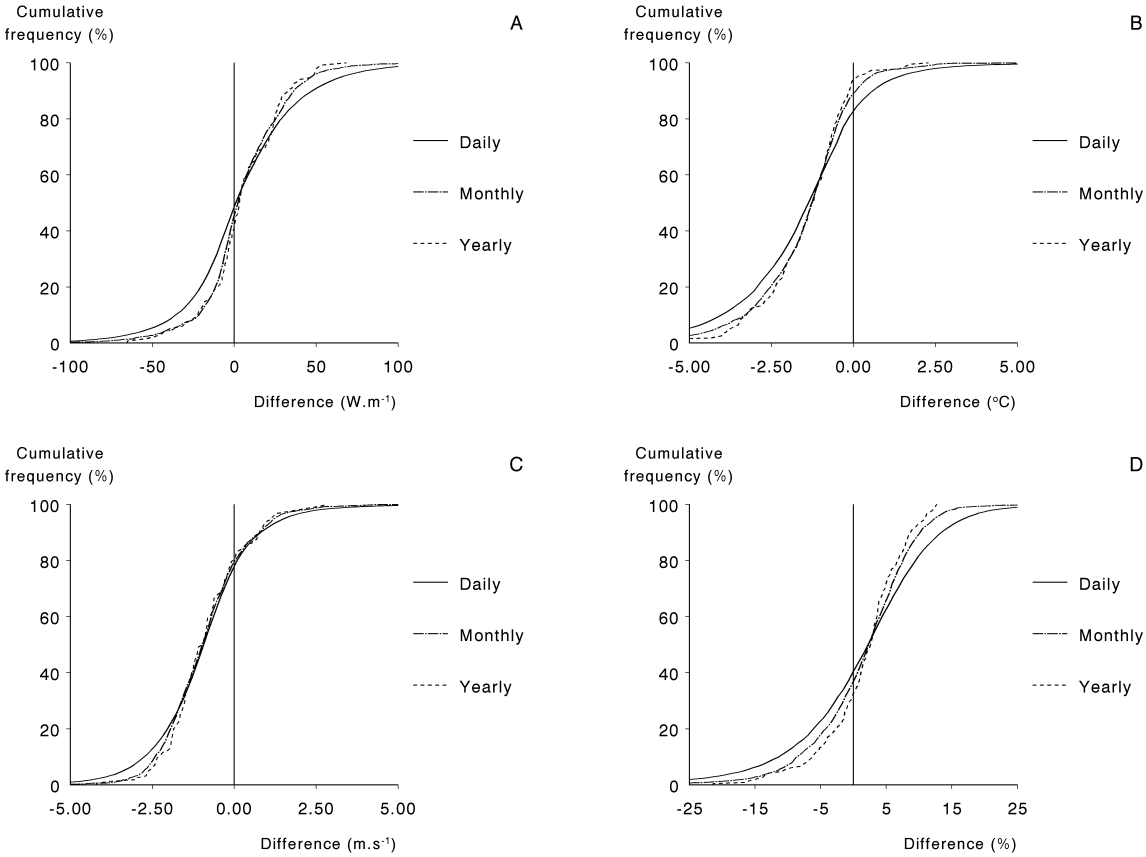


Figure A.8 Difference, expressed as measured-interpolated, between net radiation (A), temperature (B), wind speed (C) and relative humidity (D) on a daily, monthly and yearly basis using interpolated and measured site-specific daily meteorological data at 77-118 plots in the period 1995-1998.

The results show reasonable agreement for relative humidity. Interpolated data were nearly always within 15% of the measured values and at most plots the relative deviations was less then 10%. Interpolated temperatures were also rather close to measured values. At 65% of the sites, daily temperatures were within 2.5 °C of the measured values. This percentage increased to respectively 72 and 85% when comparing average monthly or yearly values. Although the deviation was relatively limited it has to be concluded that measured temperatures are on average lower than the interpolated values. This phenomenon is clearly shown when comparing average measured and interpolated yearly temperatures for the different plots (Fig. A.9). The interpolated temperatures are closely related to the measured temperatures at the plots, but the interpolated temperatures are somewhat higher than the measured values.

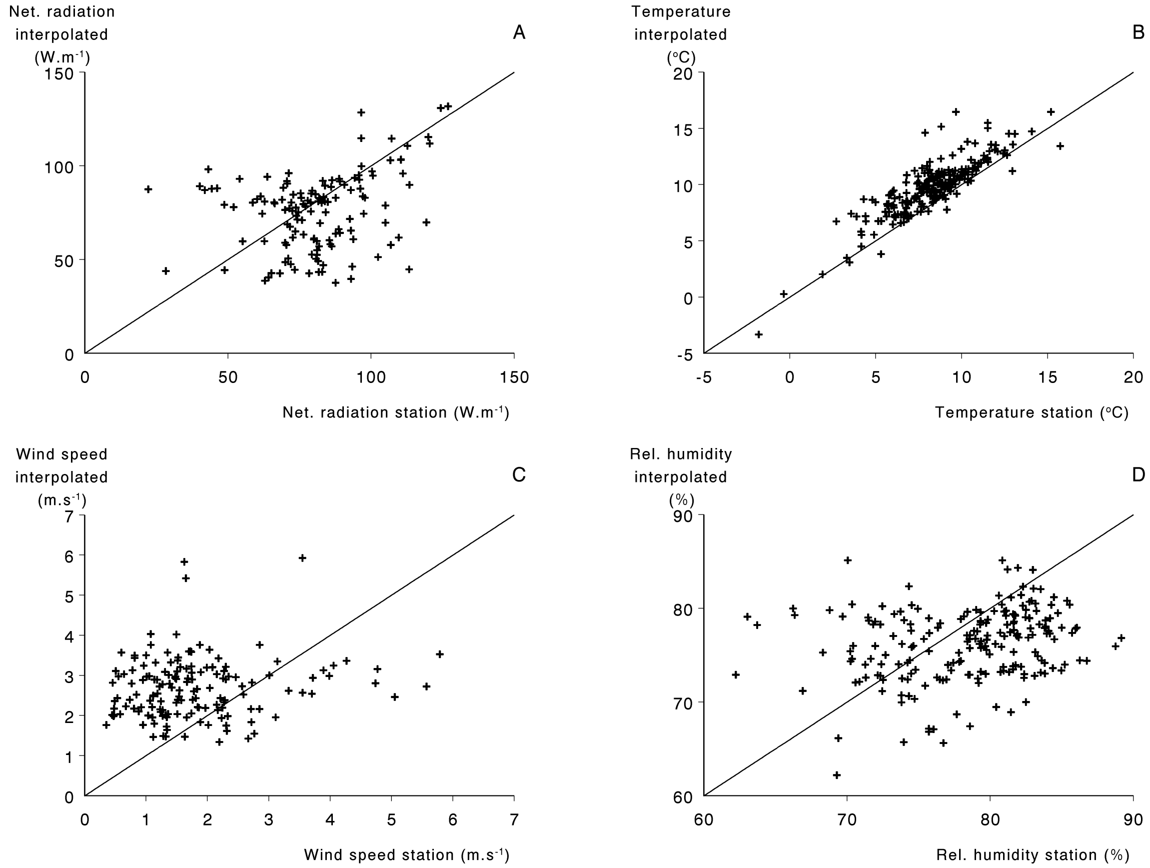


Figure A.9 Comparison between average daily net radiation (A), temperature (B), wind speed (C) and relative humidity (D) on a yearly basis using interpolated and measured site-specific daily meteorological data at 77-118 plots in the period 1995-1998. The 1:1 line is given in the figure.

Net radiation was both underestimated and overestimated by the interpolation procedure. However, at 60 to 90% of the plots the deviation in interpolated and the measured net radiation was within 50%. The correspondence between interpolated wind speed and measured data was rather poor. At only 40% of the plots, the interpolated data was within 50% of the measured data. At 80% of the plots, the interpolated wind speed was higher than measured data, as indicated by the negative relative difference. This discrepancy between interpolated and measured data is prominent at low wind speeds. Measured yearly wind speed may be as low as 0.5 $m.s^{-1}$ whereas interpolated data rarely drop below 2 $m.s^{-1}$. This difference is most probably due to the fact that meteorological stations whose data are used for the interpolation are generally located in large open areas. The wind speeds in or close to the (forested) plots may be expected to be smaller than the wind speed over vast open areas.

A comparison of the precipitation data on a daily, biweekly, monthly and yearly basis is given in Fig. A.10. In those cases where biweekly data were not available in the deposition survey, they were estimated from the monthly values. Since scaled precipitation data were used, the comparison on a biweekly, monthly and yearly basis gives information on the comparability of measured (daily) precipitation in the meteorological survey and in the bulk deposition inventory. It thus provides information on the consistency of both data sets.

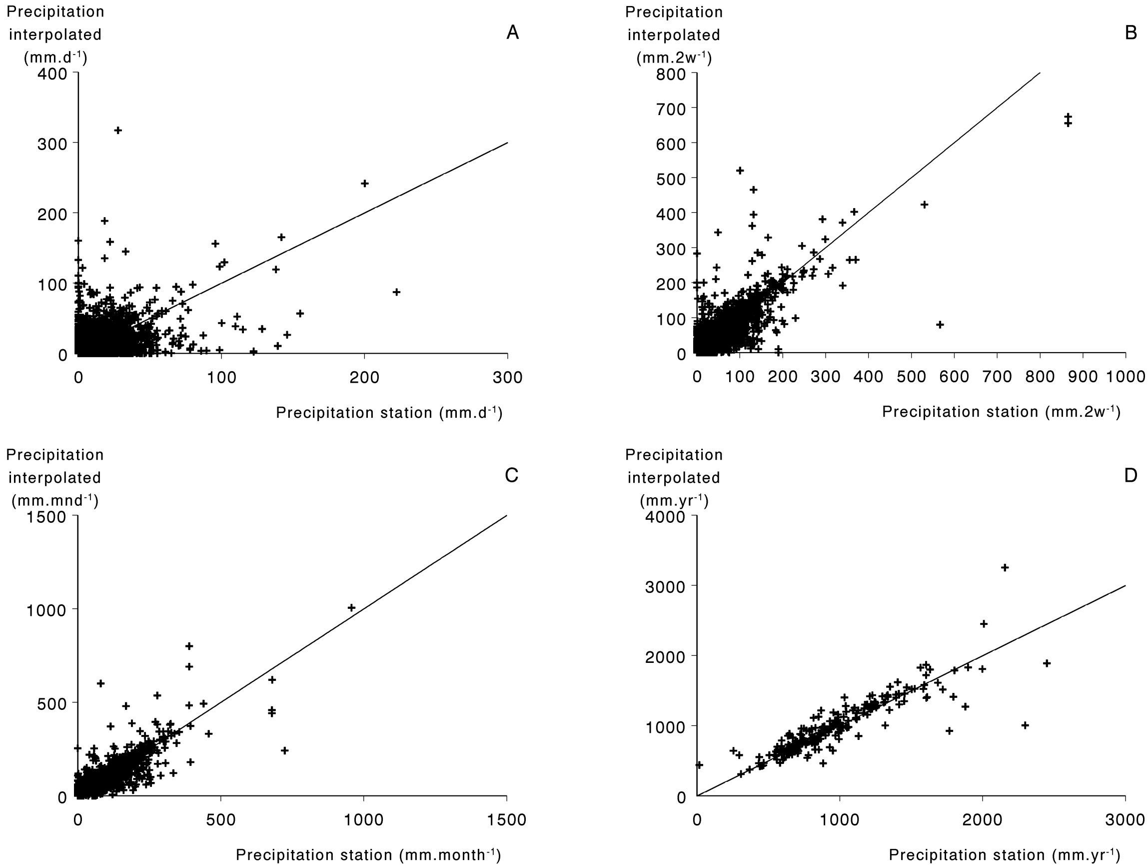


Figure A.10 Comparison between precipitation on a daily basis (A), biweekly basis (B), monthly basis (C) and a yearly basis (D) using measured daily meteorological data and interpolated data scaled on measured biweekly/monthly precipitation data at 118 plots in the period 1995-1998. The 1:1 line is given in the figure.

Results show that the precipitation data have a high comparability on an annual basis. Results of a regression analysis, assuming a negligible intercept, gave a regression coefficient of 1.003. At high precipitation, the bulk measurements at the plot seem to underestimate the precipitation. There are indications that bulk deposition measurements do underestimate precipitation by approximately 15% due to evaporation from the measuring device in the field, but results given in Fig. A.10 do not indicate a systematic difference (measurements at Speuld; Erisman, pers. comm.). On a monthly and biweekly basis, the comparison was reasonable, but on a daily basis the agreement was low. For 70% of the plots, the annual deviation was less that 5%; only occasionally, 10% deviation was found. This means that for plots where no meteorological measurements are carried out, biweekly, monthly and yearly precipitation sums can well be derived from the deposition data sets without introducing large errors. For computations based on daily values, the scaled interpolated data are less well suited, but their ultimate effects on e.g. water fluxes, drought stress indices and element fluxes need to be assessed, as presented below.

Comparison of calculated transpiration and leaching fluxes with measured and interpolated meteorological data

Throughfall fluxes were calibrated on measured throughfall at the 125 sites where meteorological measurements were carried out at a regular basis, using the same calibration procedure as used for the 309 sites for which interpolated meteorological data were used. At 78% of the sites (97) throughfall parameters could be optimised using the above-mentioned procedure. At the remaining 28 sites, extreme (combinations of) parameter values had to be used to approach the measured throughfall data. Simulated throughfall data for the considered sites were close to measured values for 56 of the 97 calibrated sites. At 41 sites the throughfall was not simulated very accurately resulting in a deviation between simulated and measured total throughfall of more then 10% or leading to a Normalised Root Mean Square Error of more than 10%. Those 41 sites were not used in the comparison of fluxes derived using measured and interpolated data.

The number of sites for which the calibrated Gash model could not accurately simulate the measured biweekly or monthly throughfall was relatively large (42% of the sites) compared to the situation when interpolated data were used (12% of the sites). This is probably due to the fact that interpolated precipitation data were corrected on measured (biweekly/monthly) rainfall data at the plots. Although, the meteorological data were collected quite close to the plot (less then 1.5 km for 90% of the plots; c.f. Fig. A.2), differences in measured precipitation between the meteorological station and the biweekly/monthly precipitation collected at the plot were sometimes considerable (Fig. A.10). These discrepancies between measured precipitation at the meteorological station and the actual precipitation at the plot leads to (unrealistic) fluctuations in the throughfall fraction that can not be simulated by the Gash model.

The difference in the median calculated hydrological fluxes obtained with the two data sets was largest for the median transpiration flux and median leaching flux (near 50 mm, Table A.13). The higher (potential) transpiration when interpolated data were used, leading to lower median leaching fluxes is most probably caused by the higher interpolated wind speed compared to the actual measurements.

Table A.13 Simulated median hydrological fluxes (mm yr^{-1}) using local meteorological data and interpolated data.

Flux (mm yr^{-1})	All plots (59)		Budget plots (27)	
	Local data	Interpolated data	Local data	Interpolated data
Precipitation	870	906	849	910
Interception	247	273	255	282
Throughfall	609	622	573	623
Transpiration	337	382	347	399
Soil evaporation	72	72	55	51
Leaching flux	195	148	173	130
Pot. transpiration	381	428	380	439
Pot. soil evaporation	104	98	98	53

An overview of the calculated yearly average hydrological fluxes using the local meteorological data and the interpolated data for the 59 plots is given in Fig. A.11. For most sites differences in precipitation, throughfall and soil evaporation are quite small. At 80% of the sites transpiration fluxes are overestimated when interpolated data are used. This difference in transpiration flux amounts to more than 100 mm at some sites. However, at 50% of the sites the difference in simulated transpiration fluxes in less than 37 mm. The observed differences in simulated leaching fluxes are comparable to the differences in transpiration fluxes. At 85% of the sites simulated leaching fluxes are lower when interpolated data are used. The difference is often quite small (50% of the sites have a difference of less than 27 mm). At some sites the difference in simulated fluxes may increase to nearly 190 mm. However, this are generally sites for which the local meteorological measurements are limited to a 1 year period.

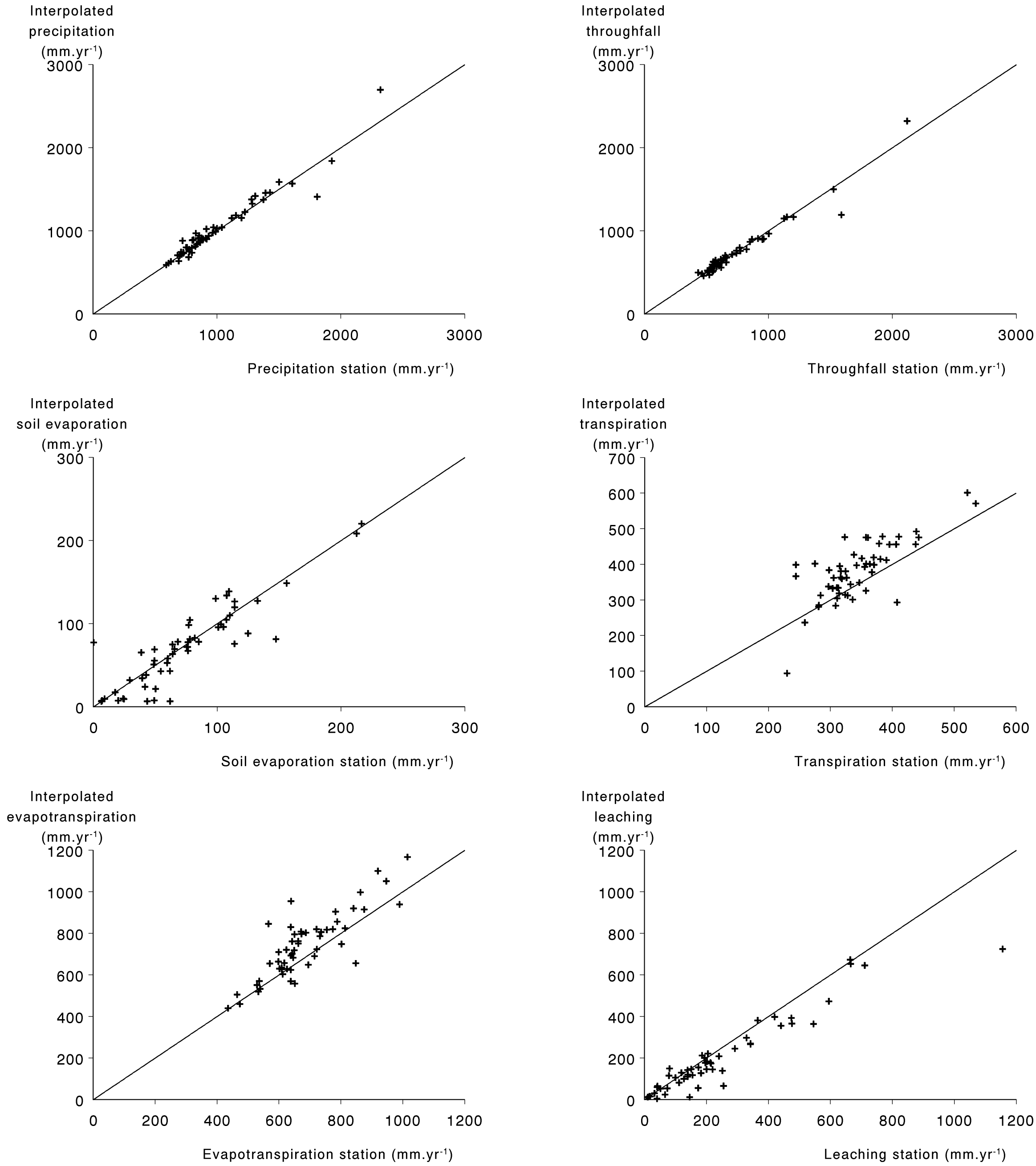


Figure A.11 Comparison between average hydrological fluxes simulated when using local meteorological data and interpolated data.

This strong effect of uncertainty in meteorological data on the calculated transpiration and leaching fluxes for individual years in clearly reflected in the differences in calculated hydrological fluxes for individual plot-year combinations (Fig. A.12). This graph shows that differences in rainfall and simulated throughfall, transpiration and leaching fluxes can be large for certain plot year combinations, although differences are quite limited (less than 50 mm) for more than 50% of the sites.

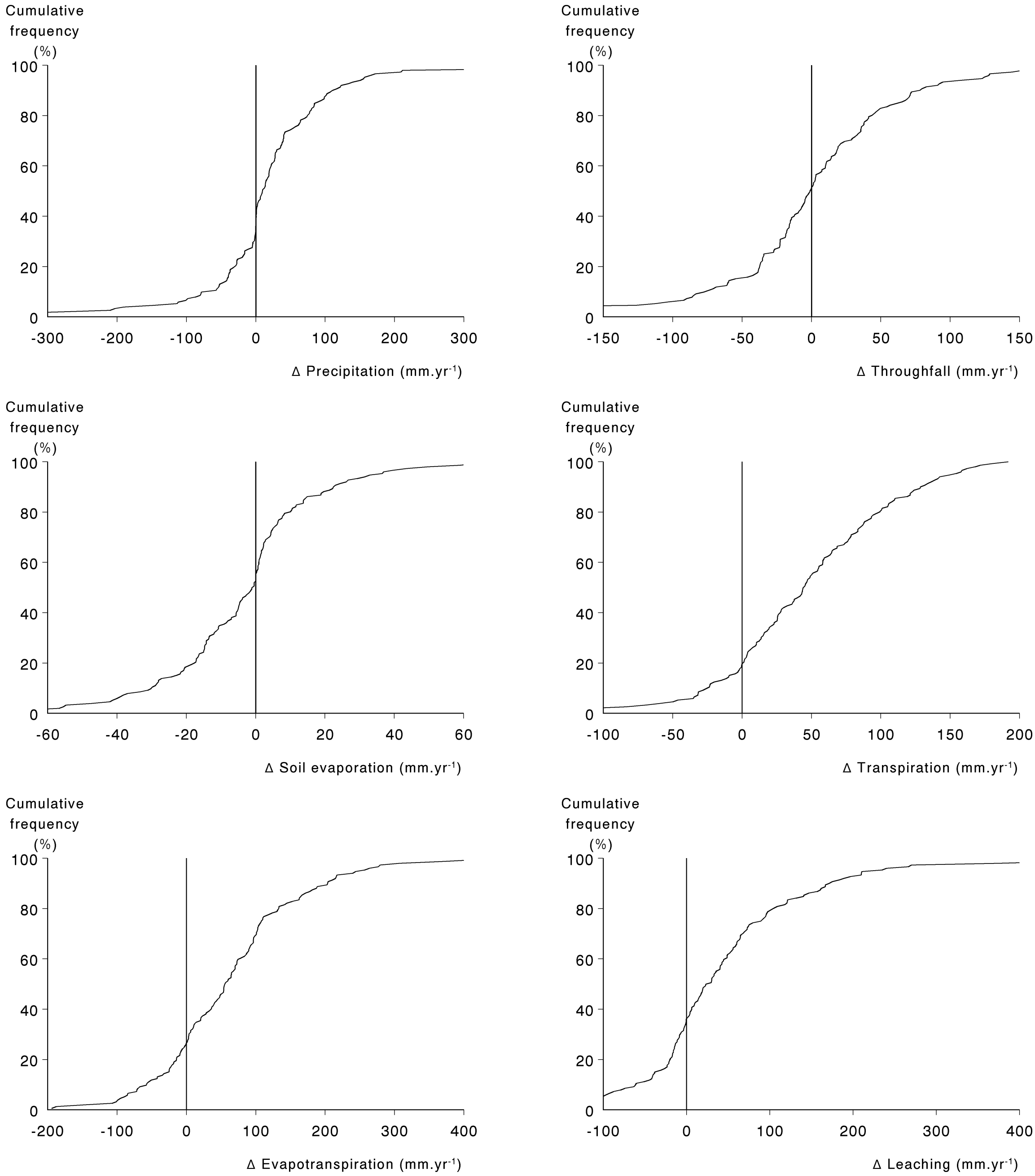


Figure A.12 Cumulative frequency distribution of the difference in simulated water fluxes for individual plot-year combinations when using interpolated meteorological data and local measured data (interpolated - measured).

A.3.2.2 Results with interpolated meteorological data

Model validation

To gain confidence in the model and its parameterisation the model has been validated on two sites in the Netherlands and Germany for which extensive hydrological measurements were available (Van der Salm, in prep). An application to other sites (in Denmark and France) is planned. Preliminary results of the application of the hydrological model on a Douglas fir stand in Speuld and a Norway spruce stand in Solling indicate that the model was able to simulate measured water contents and/or pressure heads quite well when site specific data are used (Fig. A.13). The use of generic data, as used in the application for the Intensive Monitoring sites, led to a larger deviation between measured and simulated data (Fig. A.13). The impact on simulated long-term leaching fluxes varied between 7% for Solling (13 year) and 25% for Speuld for which only a five year period was considered.

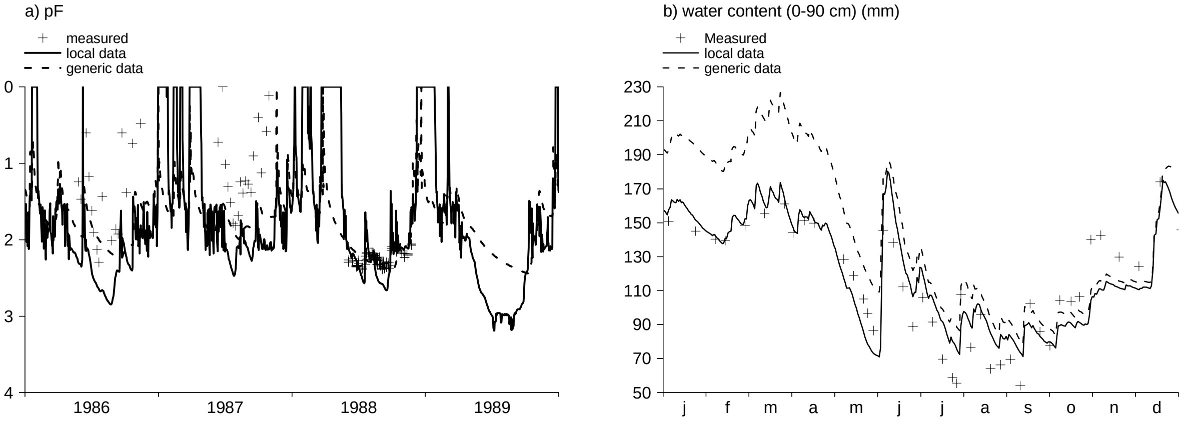


Figure A.13 Measured and simulated pressure heads at 90 cm depth at Solling (left) and measured and simulated water contents in the upper 90 cm of the soil at Speuld (right).

Model evaluation

A possible check of the modelled results can be based on the calculation of chloride budgets for the examined sites. Long-term chloride budgets may be expected to be close to zero. For the Intensive Monitoring sites the measurement period is to short (average 3 year) for such an evaluation. Nevertheless, the calculated Cl budgets do give some indication whether the order of magnitude of the calculated leaching fluxes is feasible (cf. Ch. B.3.3).

Another possibility for a general evaluation of the plausibility of the model results is to compare simulated leaching fluxes with reported fluxes for Intensive Monitoring sites. Literature data were found for 34 sites mainly located in Northwestern Europe (Beier, 1998; Bouten and Jansson, 1995; Bouten et al., 1992; Boyle et al., 2000; Bredemeier et al., 1998; Dolman, 1988; De Visser and de Vries, 1989; Gärdenäs and Jansson, 1995; Granier et al., 2000; Grote and Suckow, 1998; Harding et al., 1992; Hendriks et al., 1990; Herbst et al., 1999; Jaeger and Kessler, 1997; Ladekarl, 1998; Musters, 1998; Tiktak and Bouten, 1990; Tiktak and Bouten, 1994; Van Grinsven et al., 1987). These data indicate that simulated leaching fluxes are within the range of literature data (Fig. A.14), although a considerable part of the measurements is close to the upper site of the range of simulated fluxes. This bias can be partly explained by the fact that the literature data originate from sites in Northwestern Europe, where leaching fluxes are generally higher compared to sites in southern and central Europe. Another reason for this bias might be that leaching fluxes are slightly underestimated when interpolated meteorological data are used (c.f. section A.3.2.1). To obtain more information on the accuracy of simulated fluxes, a closer comparison of the simulated leaching and transpiration fluxes at a site scale is necessary.

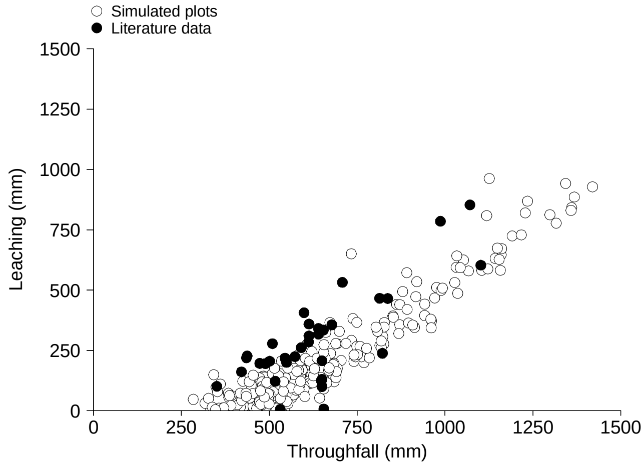


Figure A.14 Simulated and measured yearly leaching fluxes as a function of the yearly throughfall.

Model results

Transpiration and leaching fluxes were calculated for all 245 sites for which throughfall fluxes could be successfully simulated (see also Table A.9). Chemical budgets could only be calculated for sites for which data on both soil solution and deposition where available. Results for this subset of 121 plots are also presented separately in this paragraph. This selection of plots is also used to calculate the element budgets described in Appendix B.

Evapotranspiration and leaching fluxes varied considerably for the investigated sites (Fig. A.15 and A.16). The strongest variation in fluxes was found for the interception evaporation which ranged from less than 100 mm to more than 500 mm, depending on the amount of rainfall and the potential evapotranspiration. Ranges in transpiration and soil evaporation fluxes are much smaller. Transpiration varied between approximately 200 to 400 mm and soil evaporation fluxes ranged between 10 and 100 mm. Leaching fluxes ranged from 0 to more than 1500 mm yr^{-1}. The budget plots showed a much smaller variation in leaching fluxes compared to the total set of plots for which hydrological fluxes were calculated. The median values for both datasets were comparable (approx. 150 mm) whereas the 90 percentile of the leaching fluxes was approximately 500 mm for the budget plots and 900 mm for all hydrological plots.

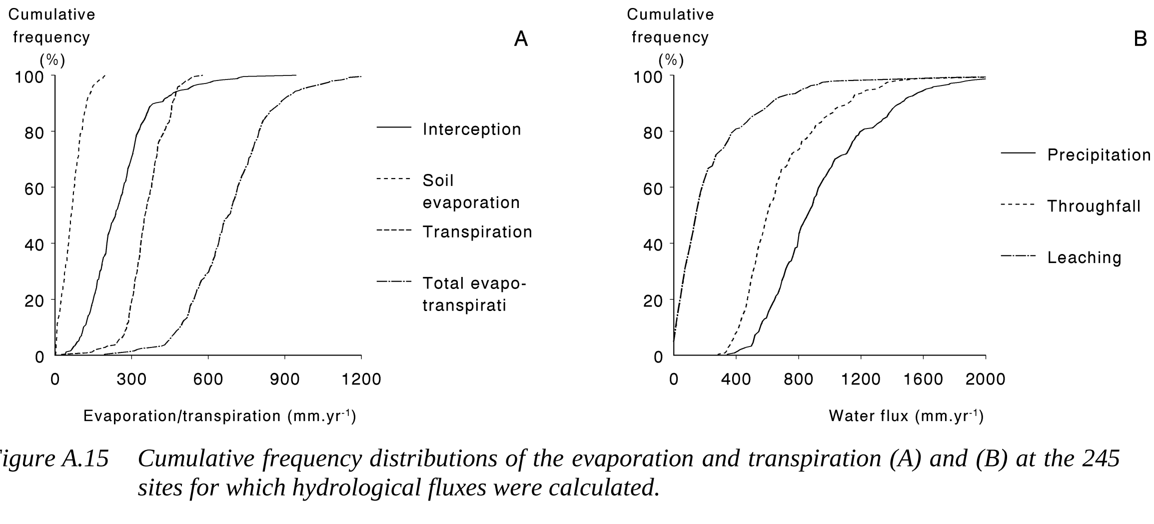


Figure A.15 Cumulative frequency distributions of the evaporation and transpiration (A) and (B) at the 245 sites for which hydrological fluxes were calculated.

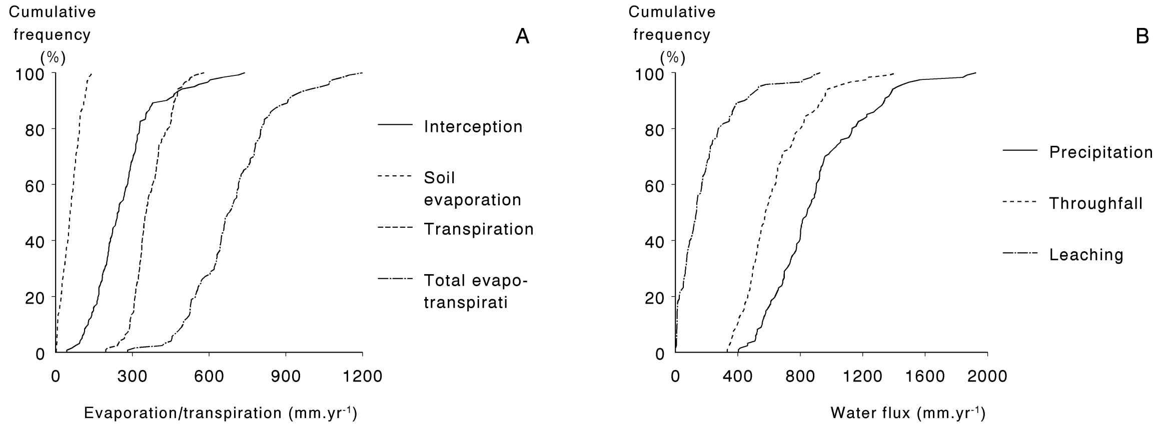


Figure A.16 Cumulative frequency distributions of the evaporation and transpiration (A) and (B) at the 121 sites for which chemical budgets could be calculated.

An overview of the median simulated hydrological fluxes for the different tree species is given in Table A.14. Differences between fluxes calculated for the 245 sites and the subset of 121 sites, used to calculate chemical budgets, are small. Median transpiration fluxes ranged from 314 $mm.yr^{-1}$ at the Pine stands to 385 $mm.yr^{-1}$ for Spruce. The calculated hydrological fluxes are generally in the range of values reported for various European forests. Median transpiration fluxes are close to the mean value of 333 $mm.yr^{-1}$ of Roberts (1983), who found that transpiration fluxes for European forest are in a very narrow range due to feedback mechanisms with soil and atmosphere. Soil evaporation fluxes were highest for the Oak stands, which are generally less dense. The median leaching fluxes ranged from 79 mm on Pine stands compared to 205 mm for Spruce. The leaching fluxes for Pine are quite low because the median precipitation is somewhat lower on Pine compared to Spruce and Beech.

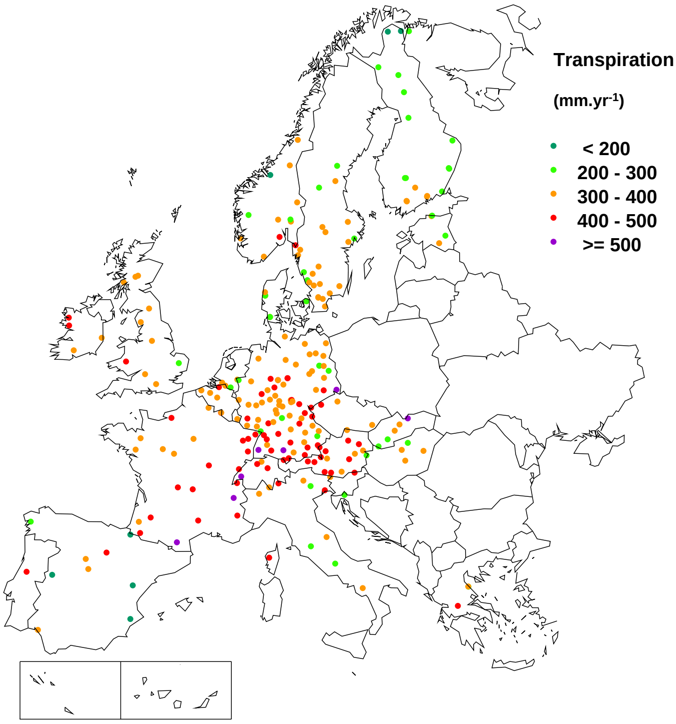
Table A.14 Simulated median hydrological fluxes (mm) for the 245 sites that were successfully calibrated and for the 121 sites for which chemical budgets were calculated (between brackets).

Tree species	Number of sites	Number of years	Calculated fluxes (mm) P	E_i	E_t	E_s	L
Pine	51 (29)	3 (3)	642 (602)	152 (152)	314 (328)	55 (55)	79 (17)
Spruce	98 (51)	3 (3)	963 (943)	290 (303)	385 (365)	32 (27)	205 (192)
Oak	24 (15)	3 (4)	725 (777)	177 (202)	338 (340)	105 (99)	123 (169)
Beech	45 (20)	3 (3)	891 (876)	241 (241)	356 (358)	94 (82)	138 (135)
Others	27 (6)	3 (6)	1122 (1233)	300 (437)	389 (483)	81 (9)	278 (218)
All	245 (121)	3 (3)	860 (846)	240 (247)	356 (356)	64 (57)	152 (136)

The differences in median precipitation fluxes between the tree species are reflected in the calculated average yearly transpiration reduction (Table A.15). The highest transpiration reduction was found in Pine trees (0.84 at the plots for which budgets could be calculated), whereas transpiration reduction for spruce and deciduous trees was much smaller (0.89-0.93).

Table A.15 Mean yearly transpiration reduction at Intensive Monitoring sites.

Tree species	Precipitation (mm) All	budgets	Transpiration reduction (Et_a/Et) all	budgets
Pine	642	602	0.86	0.84
Spruce	963	943	0.93	0.93
Oak	725	777	0.92	0.92
Beech	891	876	0.91	0.93
Others	1122	1233	0.83	0.89
All	860	846	0.91	0.91



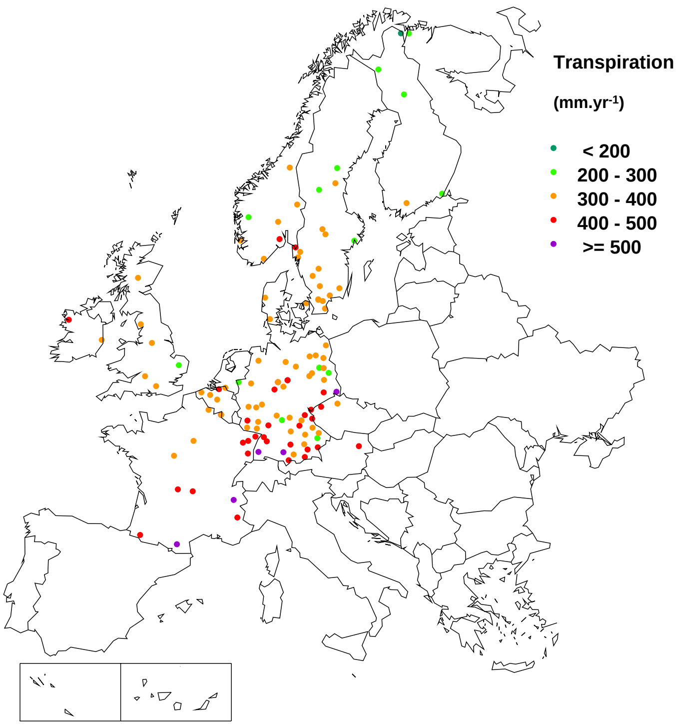
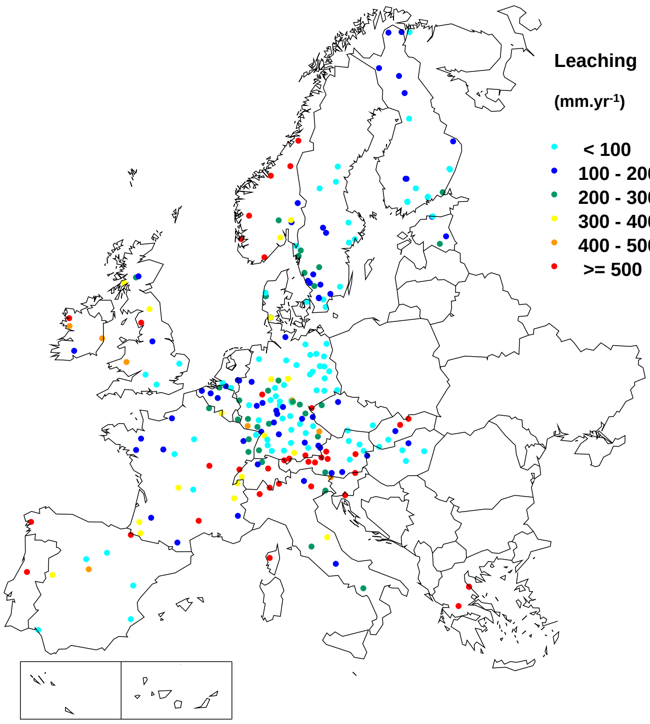


Figure A.17 Average annual transpiration fluxes (mm.yr^{-1}) for the 245 monitoring plots for which hydrological budgets have been calculated (top) and the 121 monitoring plots for which chemical budgets have been calculated (bottom).



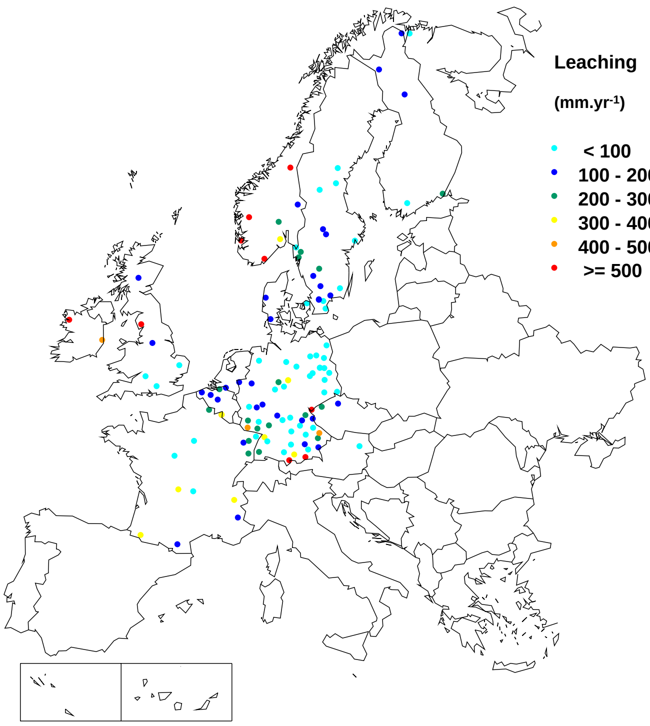


Figure A.18 Average leaching fluxes (mm.yr^{-1}) for the 245 monitoring plots for which hydrological budgets have been calculated (top) and the 121 monitoring plots for which chemical budgets have been calculated (bottom).

Transpiration fluxes are generally highest (> 450 mm) in central Europe where both rainfall and radiation are relatively high (Fig. A.17). At most sites in southern Europe, transpiration is somewhat lower due to the limited rainfall. Exceptions are the sites in mountainous areas, which receive higher amounts of rainfall. In northern Europe transpiration fluxes are lower than in central Europe due to the decrease in radiation with increasing latitude and the relatively low precipitation in part of Sweden and Finland.

The map showing the leaching fluxes for all plots and for the plots for which budgets could be assessed (Fig. A.18) closely resembles the patterns in throughfall maps (Fig. A.7). High leaching fluxes are found in Northwestern Scandinavia, Britain and Ireland and on some plots in mountainous areas in central and southern Europe. Remarkable are the low leaching fluxes (< 100 mm) in parts of Sweden and Northeastern Germany that are caused by the combination of low rainfall and relatively high transpiration fluxes (coniferous forests).

A.4 Conclusions

A comparison of measured and interpolated meteorological data showed good agreement for relative humidity, reasonable agreement for temperature and net radiation and poor agreement for wind speed. The effect of using interpolated data instead of on-site measured data led to an overestimation of the simulated transpiration fluxes and an underestimation of the leaching fluxes. However, on most sites the impact was relatively limited. More specifically, the following conclusions can be drawn with respect to the calculation of the hydrological fluxes:

- The simulated throughfall could be calibrated on measured throughfall data such that the simulated yearly values were within 5% of the measurements at 85% of the monitoring sites. Biweekly or monthly values were also quite well simulated as indicated by the relatively low normalised root mean square error with a mean value of 0.29.
- At 80% of the sites average transpiration fluxes were overestimated when interpolated data are used. The median difference in simulated transpiration fluxes was 45 mm. The observed differences in simulated leaching fluxes were comparable to the differences in transpiration fluxes. At 85% of the sites simulated leaching fluxes were lower when interpolated data are used. The median difference was 47 mm but at some sites the difference in average simulated fluxes increased to nearly 190 mm. However, this were generally sites for which the local meteorological measurements were limited to a 1 year period.
- Mean yearly interception evaporation ranged from approximately 160 mm for Pine and Oak to approximately 250 mm for Beech and 300 mm for Spruce. The interception fluxes for Pine and Oak were relatively low due to the relatively low rainfall on those tree species. Interception fractions increased going from Oak (0.22) < Pine (0.24) < Beech (0.27) < Spruce (0.30), reflecting the increasing interception capacity of those tree species.
- Simulated transpiration fluxes and leaching fluxes could not be validated on data for any of the individual sites. However, detailed studies on two sites in Germany and the Netherlands indicated that the model was able to simulate changes in soil water contents and thus in the transpiration and leaching fluxes quite well. The simulated (evapo)transpiration fluxes for the 245 sites were also in the range of data reported in the literature. However, leaching fluxes tend to be a bit low compared to literature data, which may be partly explained by the fact that measurements are biased to northwestern Europe.
- Median transpiration fluxes were rather constant among the tree species and ranged from 325 $mm.yr^{-1}$ for Pine to 385 $mm.yr^{-1}$ for Spruce stands. This is consistent with literature data, which indicate that transpiration fluxes for European forest are in a very narrow range around 335 $mm.yr^{-1}$ due to feedback mechanisms with soil and atmosphere. The range in the sum of soil evaporation and transpiration is also narrow and median values range from approximately 400-450 $mm.yr^{-1}$ for the various tree species. Leaching fluxes mainly reflected the difference in precipitation on tree species. Median values increased going from 81 mm under Pine stands to 236 mm under Spruce stands. The plots with the lowest leaching fluxes are found in area with relatively low precipitation such as northeastern Germany, parts of Sweden and Finland and locally in southern Europe.

- The limited amount of available water in the examined Pine stands is reflected in the calculated mean transpiration reduction which is highest for Pine, with a median value of 15%. For the other tree species the median value was 10%. In the future reports, more attention will be given to various drought stress parameters, including relative transpiration, that can be used in subsequent analyses relating drought stress to forest growth and forest vitality.

APPENDIX B ASSESSMENT OF ELEMENT FLUXES THROUGH THE FOREST ECOSYSTEM

B.1 Introduction

A comparison of element inputs from the atmosphere and element outputs leaching from the bottom of the root zone give insight in the fate (accumulation or release) of sulphur, nitrogen, base cations and aluminium in the ecosystem. As such, it is of crucial importance to assess the present and future impacts of atmospheric deposition on the element cycle and nutrient availability. More specifically, budgets of SO_4, NO_3 and NH_4 give insight in (i) the actual rate of acidification due to anthropogenic sources and (ii) the potential rate of acidification by immobilisation of S and N (e.g. Van Breemen et al., 1984; De Vries et al., 1995). Results about the input and output of Al and base cations (BC) give information about the mechanisms buffering the acid input (e.g. Mulder and Stein, 1994; Wesselink, 1995; De Vries et al., 1995). In general, the ratio of Al to BC release is a crucial aspect with respect to soil mediated effects of acid inputs (e.g. Cronan et al., 1989; Sverdrup and Warfvinge, 1993). These insights can therefore be used to derive critical deposition levels for forest soils (ecosystems). Comparison with available data on present loads, leads to insight in the stress of air pollution on the chemical ecosystem condition (e.g. De Vries et al., 2000b).

Element budgets have already been carried at Intensive Monitoring plots by several countries including Greece, (FIMCI, 1998), Ireland (FIMCI, 1998; Boyle, 2000; Farrel et al., 2001), Belgium (FIMCI, 1999, 2000), Germany (FIMCI, 1999; Sprangenberg, 1997; Wetzel, 1998; Block et al., 2000) and Slovakia (FIMCI, 2000). Furthermore, there are several literature compilations of element budgets, focusing on the behaviour of nitrogen (e.g. Dise et al., 1998a, b; Gundersen et al., 1998a, b). A European wide assessment of element budgets, using all available data on deposition, meteorology and soil solution chemistry at the IntensiveMonitoring plots has, however, not yet been carried out. This chapter aims to fill this gap.

This chapter first describes the methods used to calculate element input by atmospheric deposition, element leaching and element retention (Section B.2) and then gives results on the range and geographic variation of all these fluxes and their relation with environmental factors (section B.3). In Section B.2, we describe the methods to assess site-specific total atmospheric deposition and total element output for selected Intensive Monitoring plots based on measurements of both throughfall, bulk deposition and soil solution chemistry. Input fluxes were derived from fortnightly or monthly measurements of the chemical composition of bulk deposition and throughfall water, multiplied by the water fluxes while correcting for canopy uptake. A canopy exchange model, developed by Ulrich (1983) and extended by Draaijers and Erisman (1995), was used as a basis and further improved. The resulting canopy exchange was related to available data on bulk deposition, meteorological parameters and foliar chemistry performing multiple regression analysis. Element outputs from the forest ecosystem were derived at intensively monitored plots by multiplying fortnightly or monthly measurements of the soil solution composition at the bottom of the rootzone with simulated unsaturated soil water fluxes. Element retention or release was assessed from the difference between the leaching from the bottom of the root zone and the element input from the atmosphere.

Results on the derived input, output and retention or release of major elements (chloride, sodium, sulphate, nitrogen, base cations and aluminium) are described in Section B.3. Apart from results on ranges and geographic variation, this section focuses on relationships between canopy uptake, leaching or retention/ release of elements and readily available environmental variables using a statistical technique. Examples of environmental variables are stand and site characteristics, soil and foliar chemistry, precipitation and bulk deposition. Element leaching for example, is not only influenced by the atmospheric input, but also by the chemical interactions in the soil, which in turn are influenced by stand and site characteristics and soil chemical parameters. Nitrogen retention may e.g. be determined by the soil C/N ratio (e.g. Dise et al., 1998a, b; Gundersen et al., 1998a), whereas the pH and base saturation most likely influence the release of Al and base cations (BC). Reliable relationships can be used for upscaling the results to a larger scale. Conclusions are given in Section B.4.

B.2 Methods

B.2.1 Locations

Element budgets were calculated for sites where precipitation and throughfall fluxes and element concentrations in soil solution have been measured up to 1998 for a period of more than 300 days. The criterion of 300 days was included because yearly average fluxes may differ substantially from those observed during a short measurement period. Furthermore sites were selected where:

- Soil solution is sampled with tension lysimeters (see section B.2.2);
- Reliable water fluxes could be calculated (i.e. the Gash model could be successfully calibrated);
- The soil type does not indicate the presence of ground water in the soil profile (since the hydrological simulations were made assuming free drainage).

All these criteria were matched at 121 of the 228 sites with soil solution data (Table B.1), located in Belgium, France, Denmark, Germany, Great Britain, Ireland, Norway, Sweden, Finland and Austria (Fig. B.1). The number of selected sites for which budgets could be calculated based on annual input and output fluxes increased from 16 plots in 1995 to 85 plots in 1996, 113 in 1997 and 121 in 1998.

Table B.1 Number of monitoring sites for which sufficiently long records of precipitation, throughfall and soil solution concentration measurements were available to calculate annual element budgets up to 1998.

Quality aspects	Number of sites	
	Bulk deposition[1)] and throughfall	Soil solution chemistry
Total number	309	228
- Input available	309	204
- Calibrated gash parameters	245	138
- Period of at least 300 days	-	164
- Acceptable techniques	-	128
- well drained soils	-	121
Available for budgets	121	121

[1)] Equal to precipitation

The element inputs were not only assessed at the 121 plots for which budgets could be calculated but also at all 309 plots with bulk and throughfall data. Fig. B.1 shows the geographic variation of (i) the 121 plots for which budgets could be calculated, (ii) the 83 plots (204-121; see Table B.1) for which data for bulk deposition, throughfall and soil solution chemistry were available that did not pass the various quality checks and (iii) the remaining 105 plots (309-204; see Table B.1) with only data on bulk deposition and throughfall.

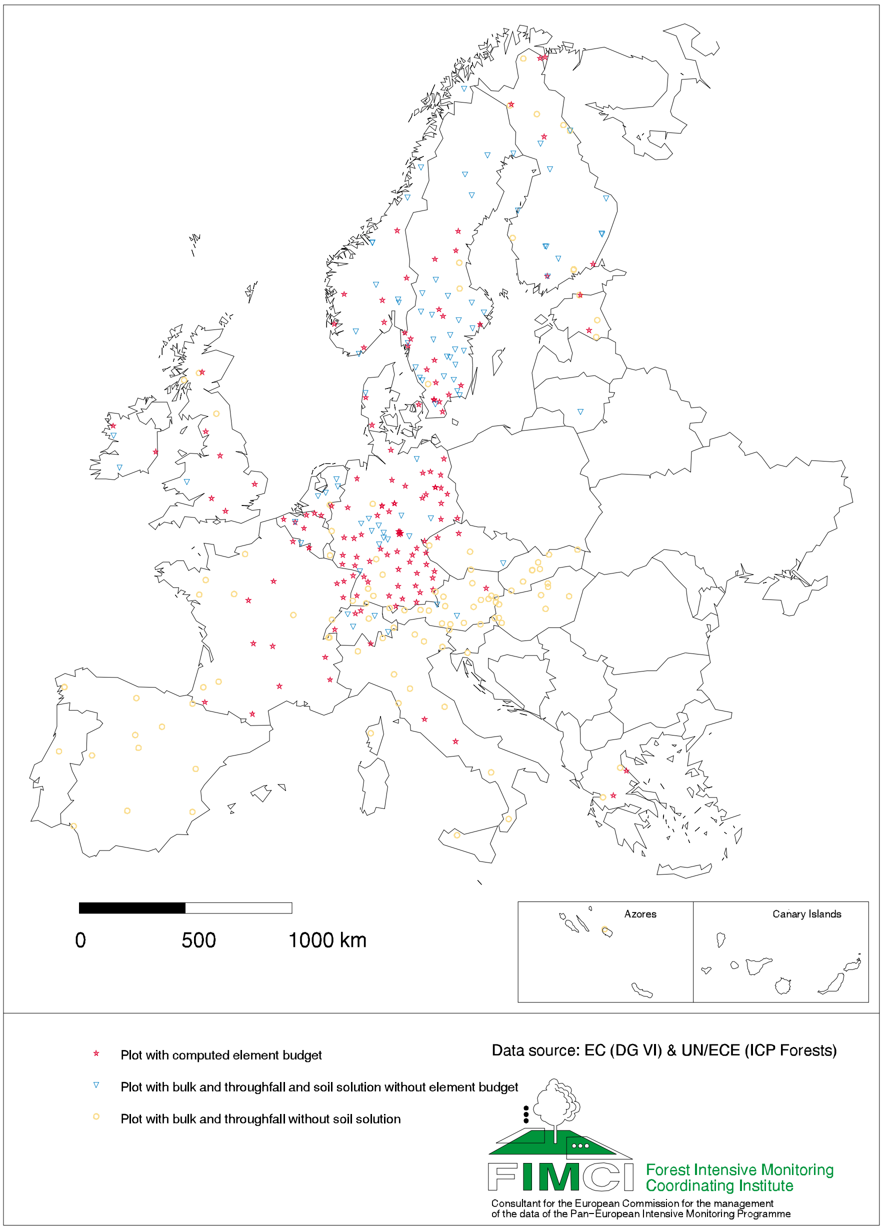


Figure B.1 Geographical distribution of Intensive Monitoring plots for which element inputs and outputs have been calculated up to 1998.

B.2.2 Data assessment methods and data comparability

The relevant EC Regulations and manual of ICP Forests give standard methods for the sampling and analysis of bulk precipitation, throughfall, stemflow and soil solution. Nevertheless, the countries involved in the program sometimes use their own specific sampling equipment, sampling strategy, sample handling and analytical procedures and interpretation methods. This includes methods to interpolate missing values and to calculate annual fluxes. In this context field and laboratory intercomparisons are crucial and enable researchers to identify the most accurate analytical methods, sampling equipment, strategy and handling, thus leading to further harmonisation in methods. Results of such a joint field campaign carried out with respect to deposition monitoring, comparing impacts of different sampler spacing and sampler numbers on throughfall in the Speulder forest and on bulk deposition at the Schagerbrug grassland in the Netherlands, are given in Appendix C.

Through the Data Accompanying Report Questionnaires (DAR-Q's) the participating countries submitted information on the applied methods for most of the plots. Here we report the most relevant aspects with respect to data assessment methods related to atmospheric deposition and soil solution. The presentation of applied methods concerns only those plots for which both atmospheric deposition and soil solution data were available for at least one year. This included 228 plots (Table B.1). More detailed information on sampling techniques, the sampling material, sampling numbers, sampling frequencies and conservation and analyses is given in de Vries et al. (2002).

Deposition data

Data assessment information for deposition monitoring indicates that throughfall and precipitation measurements were obtained mainly by funnels and sometimes gutters (in case of throughfall). The number of funnels was always above 10, being the recommendation in literature (Lövblad, 1994). At 18 of the 228 plots only 3 gutters were used, but those devices had a relatively large collecting area. Nevertheless, the required total collecting area of at least 3140 cm^2 according to the recommendation in the Manual of ICP Forests was not met at 108 sites (47%). From the deposition intercomparison project executed at the Speulder forest (see Appendix C) it was concluded that the accuracy of throughfall measurements will be significantly reduced when the total collecting area is smaller than 2000 cm^2 (Draaijers et al., 2001). Even in this case, 96 plots (42%) did not meet this requirement. We decided to still use the results from those plots but evaluated the results with care in view of plausibility.

The sampling frequencies for both bulk deposition and throughfall measurements were mostly weekly (47%) followed by either biweekly (27%) or 4-weekly periods (26%).

Soil solution data

In the Intensive Forests Monitoring Programme, four different sampling techniques are used for soil solution sampling, i.e. by:
- Placing soil solution collectors in the field: suction cups and zero tension lysimeters.
- Taking soil samples and extraction of soil solution: centrifugation or extraction methods.

In order to ensure that results are as comparable as possible, assessment of the input-output budgets was limited to the results obtained with tension lysimetry, being used at 210 of the 228 plots. In selecting those plots we focused on the sampler within a depth of 40 –100cm, that was used to calculate the outflow from the forested ecosystem. We also skipped 7 plots in which perched water or ground water occurred within the soil-solution sampling layer as this causes problems in (i) assessing the effects of acidifying deposition on soil water quality (ii) deriving water fluxes. Since no information was available about the occurrence of ground water or perched water, we have only omitted results obtained from soils with gleyic features that indicate the sporadic presence of ground water within the root zone.

The equipment used in sampling soil solution (lysimeters, tubing, collection bottles etc.) should be made of materials that neither contaminate the samples nor decrease (e.g. through sorption) the concentrations of ions in the samples. A review of the materials used (Derome et al., 2001) showed that ions whose concentrations may be biased due to the sampling equipment are not used in our budget studies (see also de Vries et al., 2001). Consequently, we used the data from all the types of lysimeter in our calculations. As with deposition data, the recommended number of samplers for monitoring soil solution is at least 10 and this requirement was not met at 90 plots. At 21 plots, only three lysimeters were used. As with deposition, we have not removed those plots from the assessment of input-output budgets but used the information in evaluating the plausibility of the results.

B.2.3 Data quality assurance

B.2.3.1 Quality checks

Procedures for quality assurance and quality control (QA/QC) included a check on all individual measurements with respect to:
- the balance between cations and anions
- the difference between measured and calculated electric conductivity
- the ratio between Na and Cl concentrations

This is the standard procedure introduced by FIMCI in the Technical reports and will be summarised here. However in order to increase the number of data used in the evaluation, a correction procedure was developed which is described in Section B.2.3.2.

Ionic balance

On an equivalent basis, the sum of all major cations should equal the sum of all major anions. The percentage difference was therefore calculated according to:

$$PD = 100 * \frac{(\sum cat - \sum an)}{0.5 * (\sum cat + \sum an)} \tag{B.1}$$

$$\sum cat = [Ca^{2+}] + [Mg^{2+}] + [Na^{+}] + [K^{+}] + [H^{+}] + [NH_4^{+}] \tag{B.2}$$

$$\sum an = Alk + [SO_4^{2-}] + [NO_3^{-}] + [Cl^{-}] + [RCOO^{-}] \tag{B.3}$$

where:
PD = percentage difference (%)
Alk = alkalinity ($mmol_c.m^{-3}$)

In principle, H should be neglected when alkalinity is positive. The basic assumption is that the charge of the other cations and anions present in solution can be neglected. The concentration of organic acids in bulk deposition and throughfall was calculated from measured concentrations of DOC (when available), according to Oliver et al. (1983). More information is given in Appendix D.

When DOC was not measured, the charge balance check was still made assuming that the influence was small. This is specifically true in bulk deposition, where concentrations of low molecular organic acids, such as formic and acetic acid, only have a minor role in the ionic balance.

The difference between the sum of all major cations and anions in soil solution was calculated similarly. However, unlike atmospheric deposition, Al was included in the calculation of cations. Checks on the ionic balance were only made when all cations and anions were measured. The only allowances made were situations where (i) Al was missing at a pH > 5, (ii) alkalinity was missing at a pH < 5 and (iii) DOC was missing (separate calculation). In general, it is required that PD is less than 10% for bulk deposition and less than 20% for throughfall when the sum of cations and anions is larger that 500 $mmol_c.m^{-3}$ (WMO, 1992; Ulrich and Mosello, 1998). Larger relative differences are acceptable at low concentrations of the sum of cations and anions (Table B.2).

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

Cations+anions ($mmol_c.m^{-3}$)	Acceptable difference (%)
≤ 50	≤ 60
50 – 100	≤ 30
100 – 500	≤ 15
> 500	≤ 10

Electric conductivity

Another quality check is the difference between measured and calculated electric conductivity, when available. Electric conductivity (EC) is a measurement of the ability of an aqueous solution to carry an electric current. Apart from temperature, this ability depends on the type and concentration (activity) of ions in solution according to:

$$EC = \sum_i \lambda_i \cdot f_i \cdot c_i \tag{B.4}$$

where:

EC = electric conductivity ($\mu S.cm^{-1}$)

λ_i = equivalent ionic conductance, being the capacity of a single ion to carry an electric current in ideal conditions of infinite solution at 20 °C ($kS.cm^2.eq^{-1}$)

c_i = concentration of ion i with i = H, Ca, Mg, K, Na, Al, NH_4, NO_3, SO_4, Cl, Alk ($mmol_c.m^{-3}$)

f_i = activity coefficient of ion i.

Values used for λ_i for the various ions, are given in De Vries et al. (2000a). Activity coefficients were calculated as a function of the ionic strength (I), using the Davies equation (Stumm and Morgan, 1981). The percentage difference between calculated and measured conductivity was calculated as:

$$PD = 100 \cdot \frac{(EC_{calc} - EC_{meas})}{EC_{calc}} \tag{B.5}$$

According to WMO (1992), the discrepancy between measured and calculated conductivity should therefore be no more than 20% at a measured conductivity above 30 $\mu S.cm^{-1}$ (Ulrich and Mosello, 1998). At lower ionic strength, the acceptable difference was set at 30%.

Sodium to chloride ratios

The correlation between ions in solution and the covariance between ion concentration ratios is a third possibility to check the quality of the data. An important check is the ratio between Na and Cl. Assuming that seasalt is a dominant source of both ions, the Na to Cl ratio should resemble the ion ratio in seawater being equal to 0.858 $mol_c.mol_c^{-1}$. Ivens (1990) found a Na to Cl ion ratio mostly varying between 0.7 and 1.0 in annual bulk deposition and throughfall fluxes with a median value resembling the ratio in seawater (0.84 in bulk deposition and 0.88 in throughfall). Draaijers (pers. comm.) stated that on an annual basis, the Na to Cl ratio should vary between 0.5 and 1.0.

B.2.3.2 Correcting outliers

Throughfall, stemflow and bulk precipitation concentration data in the Intensive Monitoring database regularly did not pass the quality checks described in chapter B.2.3.1. For this reason a ‘correction’ procedure was implemented resulting in more data available for further analysis. First, concentration data were log-transformed because they have log-normal distributions. Then for each plot the following sequential procedure was applied:

- The average log transformed concentration of each ion X (X = H, NO_3, NH_4, SO_4, Mg, Ca, K, Na and Cl) and its standard deviation was determined as well as the average ratio of ion X to each other ion Y (8 ratio's) and the associated standard deviations, using all available measurements (mostly bi-weekly or monthly values).
- Approved log-transformed concentration data were then selected by removing concentration data outside 95% confidence interval (average + 2 * standard deviation). With this approved data set, linear regression analysis (assuming that there is no trend in concentrations) was carried out to find the relationship for each combination of ions X and Y.
- For each measurement (sample) with an error in the charge balance exceeding the maximum allowable error, all ratio's of X to Y were determined. If more than 4 out of the possible 8 ratio's of ion X to the other ions were outside the 95% confidence interval, the concentration of ion X was considered to be an outlier. A 'corrected' concentration for ion X was then computed from the ion Y that has the highest correlation coefficient using the regression equation derived in step 2, with the restriction that the concentration-value of ion Y itself was not considered to be an outlier.

This procedure did correct a number of outliers in the data set that probably originate from analysis errors or errors in transferring the data, but was not always successful. To avoid the 'correction' of sound measurement data, finally a comparison was made for each period between the original and corrected data. Only if either the error in the charge balance or the error in the computed versus measured conductivity decreased when using the 'corrected' data, these corrected values were used, otherwise the original data were maintained.

B.2.4 Calculation of canopy exchange and element input

Model description and parameterisation

Total deposition was calculated according to a slightly adapted canopy budget model developed by Ulrich (1983) and extended by Bredemeier (1988), Van der Maas et al. (1991) and by Draaijers and Erisman (1995). In the canopy budget model, annual total deposition is derived by correcting the input by both throughfall and stemflow for exchange processes, occurring within the forest canopy. At plots where stemflow data were missing, the annual stemflow was estimated from the annual throughfall according to Ivens (1990):

$$X_{sf} = X_{tf} \cdot \alpha/(1-\alpha) \qquad \text{(B.6)}$$

where:

X	=	a given ion (H, Ca, Mg, K, Na, NH_4, NO_3, SO_4, Cl)
sf	=	stemflow ($mol_c.ha^{-1}.yr^{-1}$)
tf	=	throughfall ($mol_c.ha^{-1}.yr^{-1}$)
α	=	an empirical value

For coniferous forests, the value of α was calculated as a function of stand age according to (Ivens, 1990):

$$\begin{aligned} &\alpha = 0.24 && \text{age} < 20 \\ &\alpha = 0.31 - 0.0034 \cdot \text{age} && 20 < \text{age} < 90 \\ &\alpha = 0.0 && \text{age} > 90 \end{aligned} \qquad \text{(B.7)}$$

For deciduous forests, α was set at 0.12 independent of age. The same values were used for coniferous forests with an unknown age (Ivens, 1990). More information is given in De Vries et al. (1999).

Total deposition fluxes of base cations were calculated according to (Ulrich, 1983):

$$BC_{td} = \frac{Na_{tf} + Na_{sf}}{Na_{bd}} \cdot BC_{bd} \tag{B.8}$$

where:
BC = Ca, Mg, K
td = total deposition ($mol_c.ha^{-1}.yr^{-1}$)
bd = bulk deposition ($mol_c.ha^{-1}.yr^{-1}$)

Eq. (B.8) is based on the assumption that (i) Na does not interact with the forest canopy (inert tracer) and (ii) the ratios of total deposition over bulk deposition are similar for Ca, Mg, K and Na. Specifically in coastal areas, this assumption is not always valid (Baloutes. Greece, pers. comm.) Canopy leaching induced by the internal cycle of these nutrients, was thus computed by the difference between the sum of BC in throughfall and stemflow minus total deposition according to:

$$BC_{ce} = BC_{tf} + BC_{sf} - BC_{td} \tag{B.9}$$

where:
ce = canopy exchange ($mol_c.ha^{-1}.yr^{-1}$)

Canopy exchange of SO_4^{2-} is assumed negligible. The total deposition of this ion was thus calculated as:

$$SO_{4,td} = SO_{4,tf} + SO_{4,sf} \tag{B.10}$$

NH_4 and H interact with the forest canopy by exchange with base cations (Roelofs et al., 1985). We assumed that the total canopy uptake of H^+ and NH_4^+ is equal to the total canopy leaching of Ca^{2+}, Mg^{2+} and K^+ taking place through ion exchange, corrected for the leaching of weak acids. The NH_4 throughfall and stemflow flux was thus corrected for canopy uptake to calculate the total deposition of NH_4 according to (After Van der Maas et al., 1991; Draaijers and Erisman, 1995):

$$NH_{4,td} = NH_{4,tf} + NH_{4,sf} + NH_{4,ce} \tag{B.11}$$

with:

$$NH_{4,ce} = BC_{ce} - WA_{ce} - H_{ce} \tag{B.12}$$

and:

$$H_{ce} = \left(\frac{H_{tf} \cdot xH}{NH_{4,tf} + H_{tf} \cdot xH} \right) \cdot \left(BC_{ce} - WA_{ce} \right) \tag{B.13}$$

where:
xH = an efficiency factor of H in comparison to NH_4
WA = weak acids

Based on experiments in the laboratory (Van der Maas et al., 1991), it was assumed that H^+ has per mol an exchange capacity six times larger than NH_4^+ (xH = 6). The estimation of the weak acid concentration was based on the sum of HCO_3^-, derived from the pH and an assumed atmospheric CO_2 pressure, and $RCOO^-$ derived from DOC or the difference in concentration of cations minus strong acid anions (see Appendix D). The weak acid canopy exchange was calculated as:

$$WA_{ce} = WA_{tf} + WA_{sf} - 2WA_{bd} \tag{B.14}$$

The total deposition of protons was calculated as:

$$H_{td} = H_{tf} + H_{sf} + H_{ce} \tag{B.15}$$

Total deposition of NO_3^- was calculated according to:

$$NO_{3,td} = NO_{3,tf} + NO_{3,sf} + NO_{3,ce} \tag{5.1}$$

where the canopy exchange of NO_3^- equals the canopy exchange of nitrogen minus the canopy exchange of NH_4^+. The canopy exchange of nitrogen was calculated according to:

$$N_{ce} = NH_{4,ce} \cdot \left(\frac{NH_{4,tf} \cdot xNH_4 + NO_{3,tf}}{NH_{4,tf} \cdot xNH_4} \right) \tag{B.16}$$

where $NH_{4,ce}$ is calculated according to Eq. (B.12) and the xNH_4 is an efficiency factor of NH_4^+ in comparison to NO_3^- (we assumed that $xNH_4 = 6$). Actually, Draaijers and Erisman (1995), assumed canopy uptake of NO_3^- to be negligible. There is, however, ample evidence that this is not true, specifically since NO_3 in throughfall is often less than NO_3 in bulk deposition in low deposition areas. Up to now, several basic assumptions in the model (e.g. the ratio in exchange capacity between H^+ and NH_4^+) are not properly evaluated for different environmental conditions (tree species, ecological setting, pollution climate) which limits its application (Draaijers et al., 1994; Draaijers and Erisman, 1995). Furthermore, the model has only been validated in relatively polluted areas, such as the Netherlands and Denmark. An independent estimate of the canopy exchange can be made by subtracting throughfall and stemflow data from estimated total deposition values obtained by an atmospheric deposition model such as EDACS (Erisman and Draaijers, 1995). Such an estimate is, however, completely dependant on the validity of EDACS model results. A comparison of EDACS model estimates and measurements at 223 Intensive Monitoring plots is given in Appendix E.

Assessment of relationships with stand and site characteristics

To gain insight in the impact of various environmental factors on the calculated canopy exchange, multiple regression analysis was carried out. The canopy exchange of base cations (BC_{ce}) for coniferous and deciduous tree species, was related to the deposition of base cations (BC_{dep}), base cations content of the leaves/needles (BC_{fol}), acid deposition (H_{dep}), ammonium deposition ($NH_{4,dep}$), total annual precipitation amount (P_{tot}), surface wetness duration (SW) and vitality/defoliation (Def) according to:

$$BC_{ce} = f(BC_{dep}, H_{dep}, NH_{4,dep}, BC_{fol}, P_{tot}, SW, Def) \tag{B.17}$$

Surface wetness duration was approximated by taking the fraction of days in the year with (any amount of) rainfall. Defoliation was estimated according to the method presented by Klap et al. (1997). Biotic stress factors were not taken into account but used to explain possible outliers.

The canopy exchange of reduced nitrogen components ($NH_{4,ce}$) was related to:

$$NH_{4,ce} = f\left(H_{dep}, NH_{4,dep}, N_{fol}, P_{tot}, SW, Def, R_{stom}\right) \tag{B.18}$$

where $NH_{4,dep}$ is the deposition of reduced nitrogen, N_{fol} the nitrogen content in leaves/needles and R_{stom} the stomatal resistance. By using the model of Baldocchi et al. (1987), it was assumed that R_{stom} only depends on surface temperature and global radiation (Q):

$$R_{stom} = R_i \cdot \left(1 + \left[\frac{200}{Q + 0.1}\right]^2\right) \cdot \left(\frac{400}{T_s(40 - T_s)}\right) \tag{B.19}$$

Values for the internal resistance (R_i) were obtained from a look-up table for different land-use categories and seasons, as described by Wesely (1989).

The canopy exchange of oxidised nitrogen components ($NO_{3,ce}$) was related to:

$$NO_{3,ce} = f\left(NO_{3,dep}, N_{fol}, Def, R_{stom}\right) \tag{B.20}$$

where $NO_{3,dep}$ is the deposition of oxidised nitrogen. Finally, the canopy exchange of total nitrogen (N_{ce}) was related to the following environmental factors:

$$N_{ce} = f\left(N_{dep}, H_{dep}, N_{fol}, P_{tot}, SW, Def, R_{stom}\right) \tag{B.21}$$

in which N_{dep} is equal to the sum of oxidised and reduced nitrogen deposition. As for base cations, biotic stress factors were not taken into account but used to explain outliers.

B.2.5 Calculation of leaching fluxes and element retention

Model description

Leaching fluxes of the considered elements were calculated by multiplying the measured soil solution concentrations with the water leaching fluxes at the corresponding depth. For sites with a thick soil profile (> 1 m), element leaching fluxes were calculated at a depth of approx. 80 cm. This is often the deepest lysimeter cup and may be assumed to represent the leaching fluxes at the bottom of the root zone. At sites with more shallow soils the deepest available lysimeter cup was used.

Concentrations in lysimeter cups were generally measured with weekly to monthly intervals, whereas water fluxes were calculated on a daily basis (Appendix A). To calculate leaching fluxes, concentrations either have to be interpolated or water fluxes have to be accumulated over the measuring period. Both methods were applied in calculating leaching fluxes by multiplying:

1. The (average) measured concentration during the period between two subsequent measurements with the accumulated water flux during that period.
2. The daily interpolated concentrations with daily water fluxes.

Multiplication of yearly average concentrations with yearly average leaching fluxes is also possible, but the reliability of this approach is relatively small (De Vries and Janssen, 1994). Application of this method may only be preferred when large errors occur in the measured concentrations, when measurement are infrequent or when daily calculated leaching fluxes are assumed to be very uncertain. Since we only used data from sites where concentrations are measured at regular intervals, we only used the two methods described above.

The choice between the first and second method described above depends somewhat on the method and the measurement frequency used to sample the soil solution. In most cases samples are obtained by putting suction on lysimeter cups and collecting the water samples after a period of 1 to 4 weeks. During the sampling periods the suction of the cups gradually reduces and accordingly more soil water is collected at the start of the sampling period compared to the end of the period. When the sampling frequency is high, the collected samples will be representative for the average concentration during the sampling period and method 2 may be preferred. When longer sampling intervals are used, interpolation of the measured concentrations between two subsequent measurements may be preferred. In that case the measured concentrations are assumed to represent the concentration at the day of the start of the sampling period. Concentrations at the following days are calculated by interpolation between these concentrations and the concentrations measured during the next sampling period (method 2). In this study both method 1 and 2 have been used to indicate the uncertainty of the calculated leaching fluxes.

Element budgets were calculated by subtracting the leaching flux from the total deposition flux, in which total deposition fluxes were derived by both the canopy exchange model and by regression models (c.f. B.2.4). For each site four estimates of the element budgets were thus obtained based on (i) the standard canopy uptake and average soil solution concentrations, (ii) the standard canopy uptake model and interpolated soil solution concentrations, (iii) the regression canopy uptake and standard soil solution concentrations and (iv) the regression canopy uptake model and interpolated soil solution concentrations. Positive budgets indicate that a certain element is retained in the soil, whereas negative budgets indicate a net release of this element from the soil.

Assessment of relationships with stand and site characteristics

To investigate relationships between element leaching and element input, use was made of multiple regression models relating element leaching to the input and all predictor variables affecting element retention. Regression analysis relates a given response variable to (environmental) predictor variables. The term response variable stems from the idea that it responds to the environmental variables in a causal way, but causality cannot be inferred from regression analysis. Supposed relationships were of the form:

$$\log y = \alpha_0 + \alpha_1 x_1 + \alpha_2 x_2 + \cdots\cdots + \alpha_n x_n \qquad \text{(B.23)}$$

where log y is the expectation value of the response variable (atmospheric deposition, soil solution chemistry), x_1 to x_n are predictor variables (stand and site characteristics, meteorological parameters etc.) and α_1 to α_n are the regression coefficients.

The regression analyses was applied by using a so-called Select procedure. This procedure combines predictor variables that were qualitative (indicator variables), such as tree species and/or soil type with quantitative variables. This approach combines forward selection, starting with a model including one predictor variable, and backward elimination, starting with a model including all predictor variables. The 'best' model was based on a combination of the percentage of variance accounted for ($R^2_{adj.}$), that should be high and the number of predictor variables, that should be low. In order to meet the requirement of regression analyses that the response variable is normally distributed with a constant variance at fixed values of the predictor values, the considered responses (the leaching data) were log-transformed. This also causes interaction to be less significant. Normality was checked by a scatter plot of the residuals against the fitted values.

An overview of the predictor variables included in the various regression models is given in Table B.3. Site characteristics included as predictor variables were soil type and humus type. Stand characteristics included tree species and stand age, being all variables that appear to influence element retention or uptake (e.g. Dise et al., 1998a, b; Gundersen et al., 1998a). All stand and site characteristics were included as qualitative variables. Regarding soil type, 3 main groups were distinguished i.e.: Podzols and Arenosols, being acidic sandy soils, Cambisols and Luvisols being slightly acidic sandy soils or clayey soils and remaining non-calcareous soils. The humus types were distinguished in mor, moder, moder/mull and mull. For tree species 5 major groups were distinguished: pine, spruce, other coniferous, oak, and beech (see also De Vries et al., 1998). Regarding stand age, a distinction was made in young (< 30 years) and mature (> 30 years) stands. The limitation of the various characteristics to the distinguished groups was based on the expected differences, considering the limited number of data (only 121 plots at maximum). As a rule of thumb, the number of observations should exceed 4 times the degrees of freedom (Oude Voshaar, 1994).

Table B.3 Overview of the predictor variables used to explain element leaching and element budgets at the 121 Intensive Monitoring plots where both deposition data and leaching fluxes were available.

Predictor variables	S	N	BC	Al
Site/Stand characteristics				
Tree species	X	X	X	X
Soil type group	X	X	X	X
Humus type group	X	X	X	X
Stand age	X	X	X	X
Deposition				
S	X		X	X
N		X	X	X
$FrNH_4$		X	X	X
BC			X	X
Foliage				
N-content		X		
Soil chemistry				
Organic C pool		X		
C/N ratio litter		X		
C/N ratio mineral layer		X		
pH topsoil	X	X		
pH subsoil	X		X	X
Base saturation			X	X
Interactions				
N deposition.C/N ratio		X		

With respect to atmospheric inputs, use was made of the calculated total deposition using the original canopy exchange model. Results obtained from the regression equations were considered less adequate, specifically for base cations (Section B.3.1). Soil chemical variables included were those that were assumed to influence either N retention processes (C/N ratio in the organic layer and mineral topsoil and soil pH) and BC or Al release (base saturation and pH).

B.3 Results and discussion

B.3.1 Element input by deposition

In Table B.4 results are presented of the quality checks applied on annual throughfall and bulk precipitation fluxes for the period 1995-1998 stored in the Intensive Monitoring database.

Table B.4 Overview of the results of the quality checks performed on available annual throughfall and bulk precipitation data for the period 1995-1998 as stored in the FIMCI database.

	Bulk precipitation	Throughfall
Total number before quality checks	820	820
Missing data	86	97
Data failing the ionic balance check	301	169
Data failing the sodium-to-chloride check	75	71
Total number passing quality checks	411	515

For 309 sites annual throughfall and bulk precipitation fluxes were available for all components for one or more years, leading to 820 plot-year combinations. These sites were distributed over

21 different countries in Europe. Quality checks included a check on the ionic balance and on sodium-to-chloride ratios. Checks on measured and calculated conductivity and on phosphate concentrations could not be applied due to lack of information (data).

Applying the quality checks resulted in about 50% and 37% of the data being lost for bulk precipitation and throughfall, respectively. The quality checks were applied on corrected data as described in Section B.2.3.2). The correction procedure was applied on monthly data available, after which annual fluxes were calculated. These annual fluxes were then used in the multiple regression analysis. Comparisons with uncorrected data showed that an additional 10% of these data could be used for performing the multiple regression analysis.

B.3.1.1 Relationships between canopy exchange and environmental factors

Annual throughfall and bulk deposition data for the years in the period 1995-1998 that successfully passed the applied quality checks were subsequently used for multiple regression analysis using the functions presented before. Sites passing the quality checks were located in northwestern Europe (France, Norway, Sweden, Finland, Germany and Ireland). By far most sites were coniferous forest stands. The relationships described below were derived for both coniferous and deciduous forests. For this study the tree species *Picea abies* and *Pinus silvestris* were selected to represent the coniferous forests, while for deciduous forest the selected tree species were: *Fagus sylvatica*, *Quercus petraea* and *Quercus robur*. For all deposition parameters in the regression functions up to now bulk precipitation fluxes are used. Instead of bulk precipitation fluxes, total deposition estimates will be used when modelled dry deposition fluxes are available from the EDACS model (Erisman and Draaijers, 1995). The relationships described below were derived according to the functions shown in Section B.2.4. Parameters not significantly contributing to the regression were excluded.

For total base cations the following relationships were derived for coniferous forests (n=180) and deciduous forests (n=68), respectively:

$$BC_{ce} = -0.353 + 0.850 \cdot BC_{fol} + 0.828 \cdot NH_{4,dep} + 0.002 \cdot P_{tot} \qquad R^2_{adj} = 0.53 \qquad (B.24)$$

$$BC_{ce} = 0.085 + 0.911 \cdot BC_{fol} \qquad R^2_{adj} = 0.10 \qquad (B.25)$$

in which BC_{ce} and $NH_{4,dep}$ are in $kmol_c.ha^{-1}$, BC_{fol} in $mmol_c.kg^{-1}$ and P_{tot} in $mm.yr^{-1}$. Instead of calculating the total canopy exchange of base cations, also the canopy exchange of the separate components was calculated leading to the following relationships for coniferous forests (n=180) and deciduous forests (n=68), respectively:

$$Mg_{le} = -0.079 + 0.142 \cdot BC_{fol} + 0.098 \cdot NH_{4,dep} + 0.0005 \cdot P_{tot} \qquad R^2_{adj} = 0.22 \qquad (B.26)$$

$$Mg_{le} = -0.022 + 0.158 \cdot BC_{fol} \qquad R^2_{adj} = 0.10 \qquad (B.27)$$

$$\begin{aligned} Ca_{le} = & -0.112 + 0.270 \cdot BC_{fol} + 0.298 \cdot NH_{4,dep} - 0.0005 \cdot P_{tot} \\ & + 2.787 \cdot H_{dep} + 0.010 \cdot Def \end{aligned} \qquad R^2_{adj} = 0.41 \qquad (B.28)$$

$$Ca_{le} = -0.061 + 0.480 \cdot BC_{fol} - 0.569 \cdot Ca_{dep} \qquad R^2_{adj} = 0.31 \qquad (B.29)$$

$$\begin{aligned} K_{le} = & \ 0.052 + 0.349 \cdot BC_{fol} + 0.408 \cdot NH_{4,dep} + 0.002 \cdot P_{tot} \\ & - 0.976 \cdot K_{dep} - 0.013 \cdot Def - 0.298 \cdot SW \end{aligned} \qquad R^2_{adj} = 0.48 \qquad (B.30)$$

$$K_{le} = 0.228 + 0.347 \cdot BC_{fol} + 0.001 \cdot P_{tot} - 1.640 \cdot K_{dep} \qquad R^2_{adj} = 0.21 \qquad (B.31)$$

in which Mg_{le}, Ca_{le}, K_{le}, $NH_{4,dep}$, H_{dep}, Ca_{dep} and K_{dep} are in $kmol_c.ha^{-1}$, BC_{fol} in $mmol_c.kg^{-1}$, P_{tot} in $mm.yr^{-1}$, SW in % and Def is the logit transformation of the defoliation (in %/100).

Surface wetness can be a difficult parameter to determine, due to lacking information on the precipitation data on a day by day basis. When leaving surface wetness out of the function for K_{le}, the relationship is very similar to the function mentioned above and becomes (coniferous forests; n=180):

$$K_{le} = -0.169 + 0.440 \cdot BC_{fol} + 0.434 \cdot NH_{4,dep} + 0.002 \cdot P_{tot} - 0.843 \cdot K_{dep} - 0.015 \cdot Def \qquad R^2_{adj} = 0.46 \qquad (B.32)$$

Relationships were quite strong for coniferous forests but relatively weak for deciduous forests. Results clearly show that base cation leaching increases with increasing base cation foliar content and increasing NH_4 deposition. Leaching of calcium positively relates to H deposition as well. Leaching of Ca and K is significantly smaller with increasing deposition of the mentioned cations. Leaching of base cations generally increases with increasing annual precipitation amount, Ca leaching being the exception showing significant larger leaching in less wet regions. K leaching increases with smaller vitality and smaller surface wetness duration. Ca leaching increases with less defoliation. For reduced nitrogen the following equations were derived:

$$NH_{4,up} = 0.106 - 0.278 \cdot N_{fol} + 1.171 \cdot NH_{4,dep} - 0.020 \cdot Def + 0.0004 \cdot R_{stom} \qquad R^2_{adj} = 0.62 \qquad (B.33)$$

$$NH_{4,up} = 0.449 + 0.404 \cdot NH_{4,dep} - 0.001 \cdot P_{tot} \qquad R^2_{adj} = 0.22 \qquad (B.34)$$

in which $NH_{4,up}$ and $NH_{4,dep}$ are in $kmol_c.ha^{-1}$, N_{fol} in $mmol_c.kg^{-1}$, P_{tot} in $mm.yr^{-1}$, R_{stom} in $s.m^{-1}$ and DEF is the logit transformation of the defoliation (in %/100).

As with surface wetness, stomatal resistance (R_{stom}) can be a difficult parameter to determine. Leaving R_{stom} out of the function for NH_4, up for deciduous trees shows the following result, for which the relationship is less strong than the function mentioned above:

$$NH_{4,up} = 0.233 + 0.355 \cdot NH_{4,dep} - 0.001 \cdot P_{tot} \qquad R^2_{adj} = 0.08 \qquad (B.35)$$

For oxidised nitrogen the following equations were derived. Because for deciduous trees no significant relationship could be found, the equation derived for all tree species taken together can be used instead.

$$NO_{3,up} = -0.031 + 0.218 \cdot NO_{3,dep} - 0.008 \cdot Def \qquad R^2_{adj} = 0.30 \qquad (B.36)$$

$$NO_{3,up} = -0.017 + 0.179 \cdot NO_{3,dep} - 0.007 \cdot Def \qquad R^2_{adj} = 0.23 \qquad (B.37)$$

in which $NO_{3,up}$ and $NO_{3,dep}$ are in $kmol_c.ha^{-1}$ and Def is the log transformation of the defoliation (in %/100). As for base cations, relationships were (much) stronger for coniferous forests compared to deciduous forests. Nitrogen uptake positively relates to nitrogen deposition. Ammonium uptake is found to be larger at lower nitrogen foliar content, small stomatal resistance (indicating NH_3 uptake) and low vitality.

B.3.1.2 Ranges in total deposition

Results of a comparison of total element deposition for the 309 sites, using the canopy uptake model and regression equations derived from it, are shown in Fig. B.2.

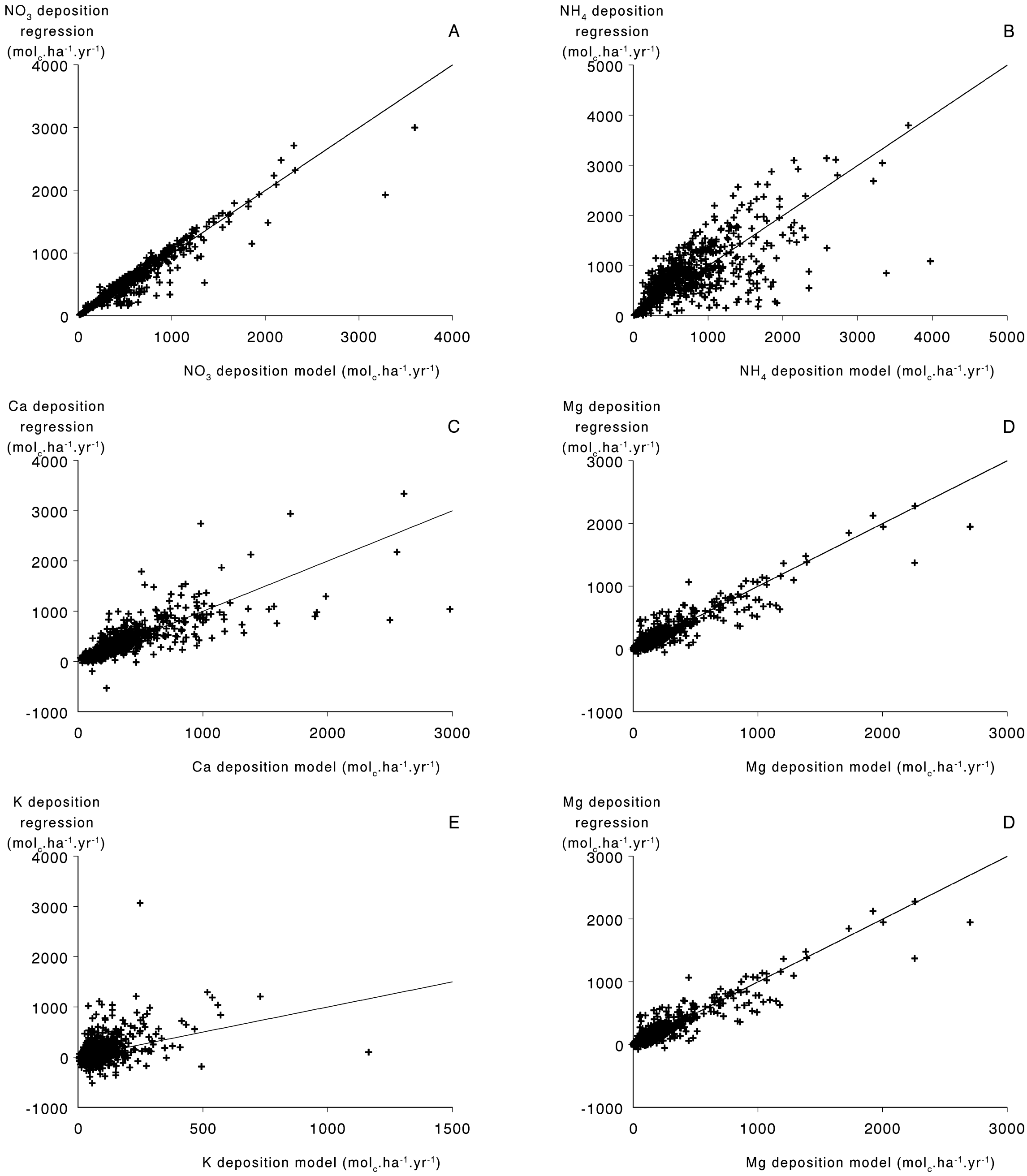


Figure B.2 *Comparison of total deposition fluxes of NO_3 (A), NH_4 (B), Ca (C), Mg (D), K (E) and BC (Ca+Mg+K) (F) for 309 sites using the canopy uptake model and regression equations derived from it.*

For NO_3 and Mg the comparison is reasonable, but for NH_4, Ca and specifically K it is weak. Note that the regression equations were only derived on a high quality subset of the data (Section B.3.1). The results obtained by the regression model may cause negative deposition values in case of base cations, indicating that it is better to use the original canopy exchange model for those elements. Another reason for this choice is that the assumption of comparable dry to bulk deposition ratio for Na and the other base cations, applied in the canopy exchange model seems reasonable. The range in total deposition of the major elements is illustrated in Fig. B.3.

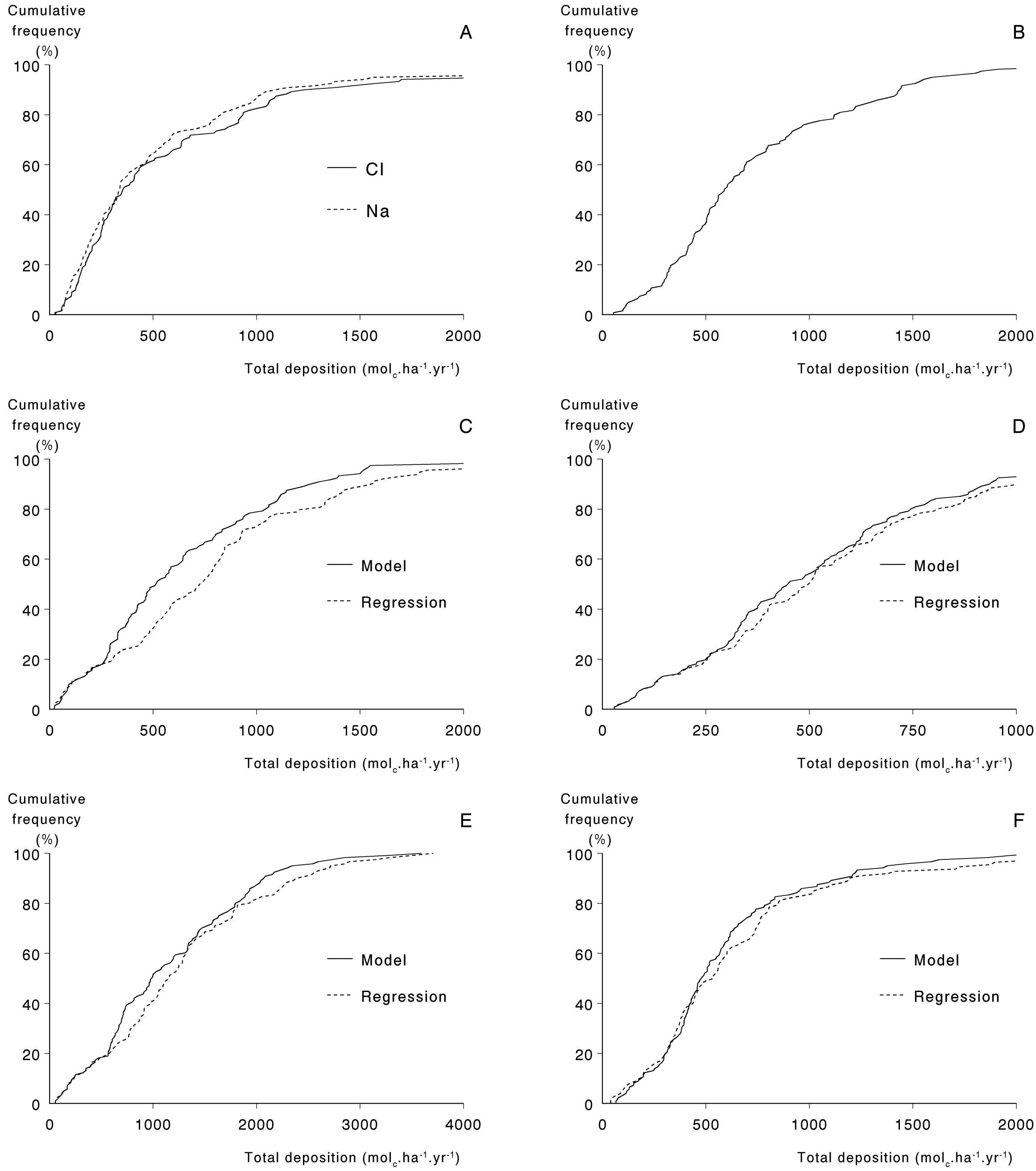


Figure B.3 Cumulative frequency distributions of the total deposition of Cl and Na (A), SO_4 (B), NH_4 (C), NO_3 (D), N (E) and BC (F).

Results show a comparable range in Cl and Na input (Fig. B.3A). Total S deposition generally stays below 2000 mol$_c$.ha^{-1}.yr^{-1} (Fig. B.3B) but the N deposition does exceed 3000 mol$_c$.ha^{-1}.yr^{-1} at several plots (Fig. B.3E). The figure illustrates that for both nitrogen and base cations, the regression equations generally lead to higher deposition estimates than the canopy exchange model (Fig. B.3C- B.3F).

The ratio in annual Na to Cl deposition ranged between 0.5 and 1.5 with most of the values near 0.86 being the Na/Cl ratio in seawater (Fig. B.4A). The N/S ratio was mostly above 1.0, the percentage varying between approximately 65 and 85% depending on the canopy model used (Fig. B.4B). Despite this uncertainty, the results show the dominating influence of nitrogen in the atmospheric input. The results for the NH_4/NO_3 ratio (Fig. B.4C) clearly illustrate the dominance of ammonium over nitrate in the deposition. This was already clear from the results presented in Figure 5.3, showing that the NH_4 input can be as high as 2000 mol$_c$.ha^{-1}.yr^{-1} (Fig.

B.3C), whereas the NO_3 input stays nearly always below 1000 $mol_c.ha^{-1}.yr^{-1}$ (Fig. B.3D). The results for the ratio of base cations to the sum of sulphur and nitrogen (Fig. B.4D) illustrate that at approximately 30-50% of the plots (depending on the model used to calculate canopy exchange), the acid input by S and N is buffered by base cation input.

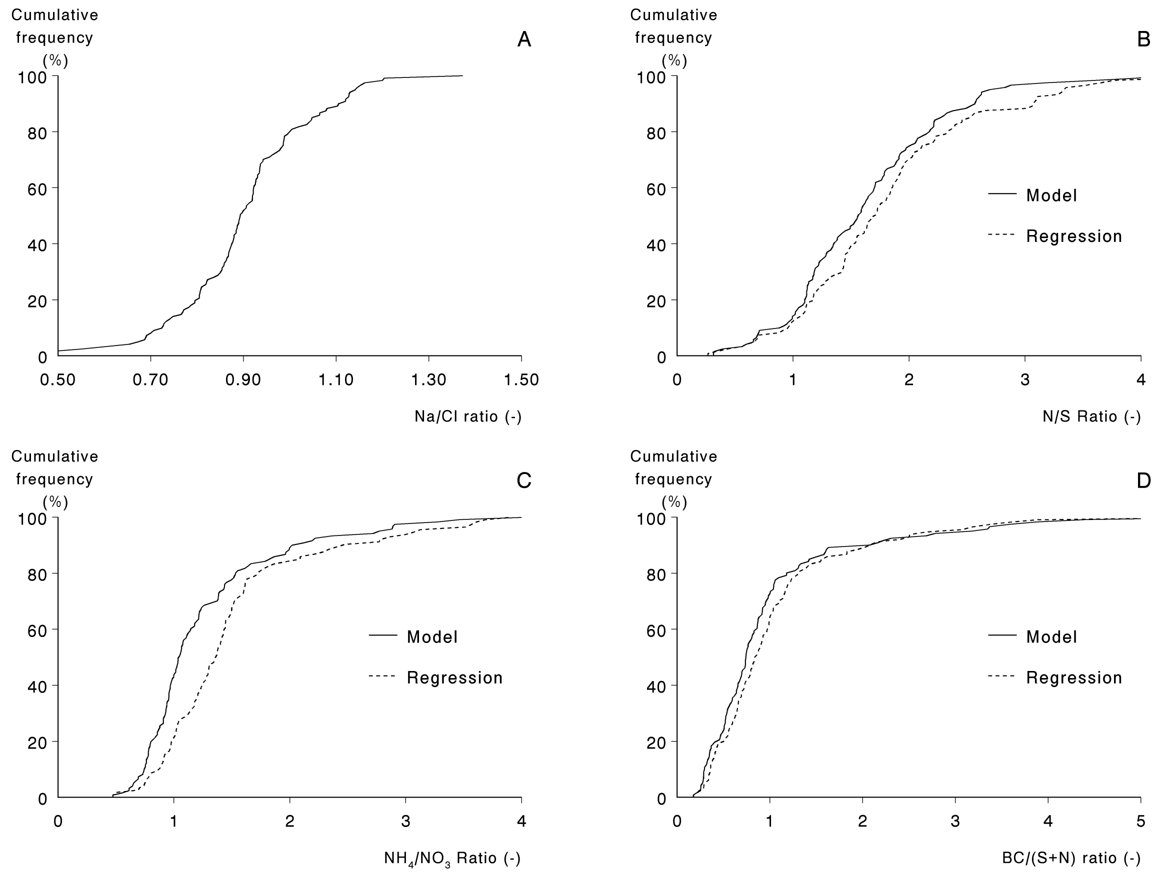


Figure B.4 Cumulative frequency distributions of the ratio's in the total deposition of Na/Cl (A), N/S (B), NH_4/NO_3 (C) and BC/(N+S) (D).

Results of the variation in element input fluxes for the 309 and 121 sites are shown in Table B.5 and B.6, respectively. As with Figure B.3, both tables illustrate that for nitrogen compounds input fluxes are generally somewhat higher when calculated with the multiple regression models compared to the canopy budget model. Median nitrogen inputs in oak stands calculated from the multiple regression model were even twice as large when compared to the original canopy budget calculations. For base cations a mixed picture arises, with smaller median total base cation input calculated using the multiple regression models for pine, beech and 'other' stands and higher median total base cation input calculated for spruce and especially oak stands.

Table B.5 Median input fluxes (in $mol_c.ha^{-1}.yr^{-1}$) of sodium, chloride, sulphate, nitrate, ammonium and total base cations at 309 investigated sites using canopy exchange model to calculate canopy exchange. Values in brackets are the median input fluxes using the regression equations.

Tree species	Number of sites	Total deposition ($mol_c.ha^{-1}.yr^{-1}$) Cl	Na	SO_4	N		BC	
Pine	67	236	210	408	621	(611)	394	(357)
Spruce	125	316	305	505	900	(844)	485	(544)
Oak	31	481	412	646	910	(1188)	562	(835)
Beech	51	346	334	663	1330	(1550)	629	(616)
Other	35	770	643	578	1047	(1078)	770	(723)
All	309	315	305	560	939	(1033)	534	(557)

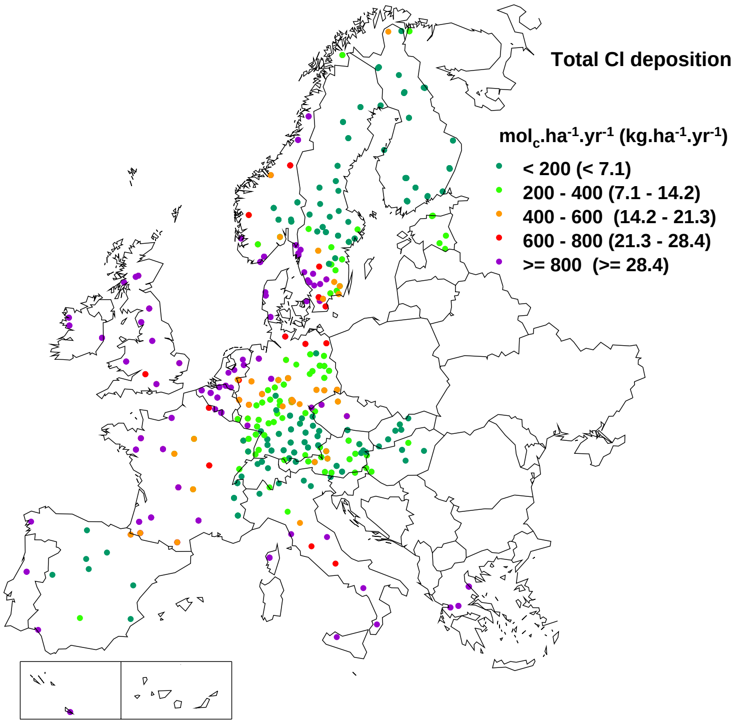
Table B.6 Median input fluxes (in $mol_c.ha^{-1}.yr^{-1}$) of sodium, chloride, sulphate, nitrate, ammonium and total base cations at 121 sites for which budgets were calculated using canopy exchange model to calculate canopy exchange. Values in brackets are the median input fluxes using the regression equations.

Tree species	Number of sites	Total deposition ($mol_c.ha^{-1}.yr^{-1}$)						
		Cl	Na	SO_4	N		BC	
Pine	29	280	241	517	714	(846)	491	(377)
Spruce	51	462	403	685	1198	(1312)	469	(559)
Oak	15	640	475	637	962	(1249)	519	(805)
Beech	20	398	389	634	1340	(1497)	489	(440)
Other	6	287	246	509	826	(796)	751	(653)
All	121	356	340	592	995	(1158)	482	(536)

Nitrogen (nitrate and ammonium) input fluxes are found highest in beech stands, that may possibly be explained by the location of these sites close to polluting sources. Relatively high inputs of nitrogen are also found for oak stands. Pine stands show much smaller input fluxes of acidifying compounds whereas spruce stands take up an intermediate position. The differences between tree species only partly reflect differences in surface roughness, influencing dry deposition. Part of the variation is explained by the location with e.g. pine stands being more dominant in Northern Europe where the N input is lower. For sulphate, the differences are much less distinct. Sodium and chloride input fluxes generally strongly depend on the input of sea salt and is generally found largest near sea areas. Largest inputs of sodium and chloride are found in oak stands and smallest inputs in pine stands. Base cation input is largest in beech and oak stands and smallest in pine stands.

B.3.1.3 Geographic variation in total deposition

The geographical distribution of the input fluxes is presented in the Figs B.5-B.7. Chloride input is relatively large (>800 $mol_c.ha^{-1}.yr^{-1}$) in coastal areas throughout Europe. Relatively high sulphate input (>800 $mol_c.ha^{-1}.yr^{-1}$) can be found everywhere in Europe, except for central and northern part of Scandinavia. Many sites with high sulphate input are situated in central Europe (Fig. B.5) High N inputs (>1800 $mol_c.ha^{-1}.yr^{-1}$) occur in central Europe. Total nitrogen input is generally much smaller in northern and southern Europe (Fig. B.6). Base cation input is relatively high (>800 $mol_c.ha^{-1}.yr^{-1}$) in southern Europe and Lithuania, which is consistent with findings of Draaijers et al. (1997), whereas the input of base cations is low in Scandinavia (Fig. B.7).



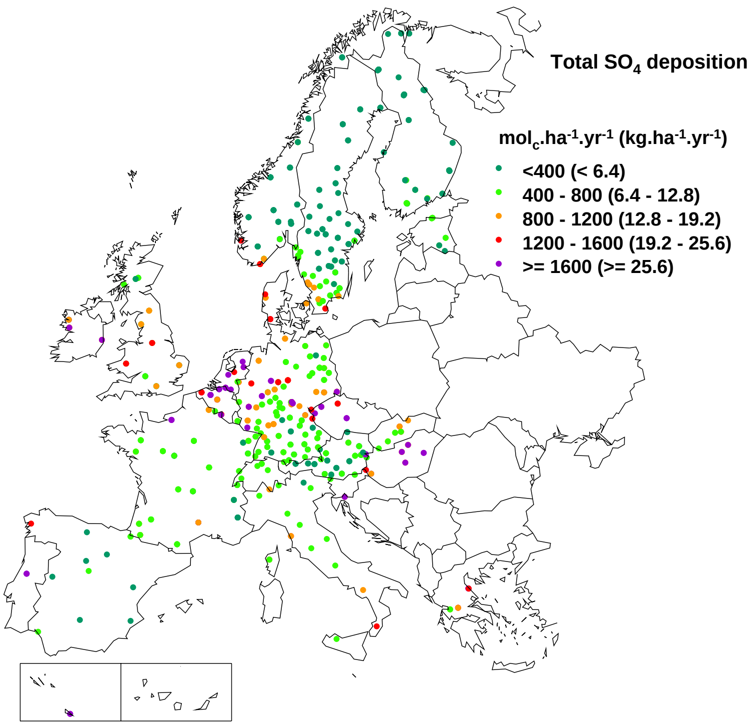
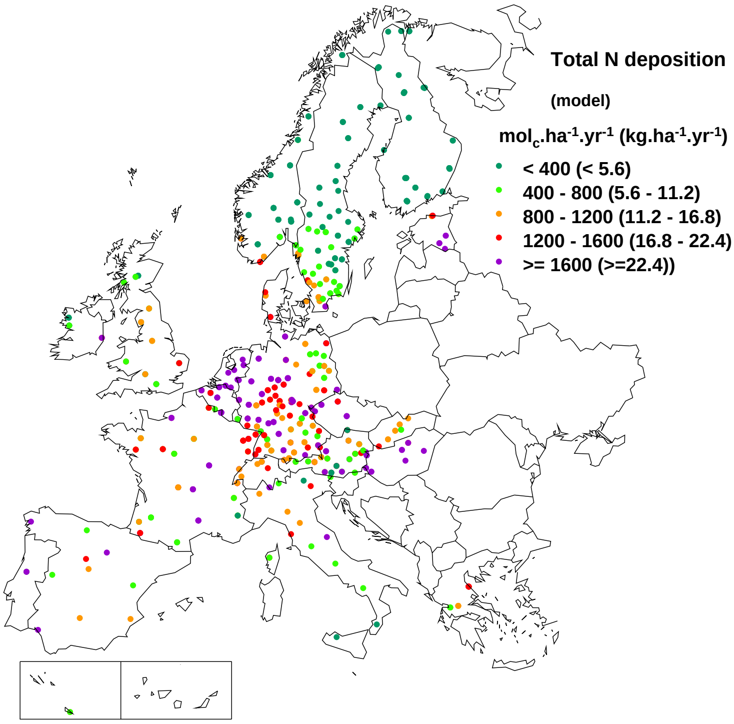


Figure B.5 *Geographical variation in input fluxes ($mol_c.ha^{-1}.yr^{-1}$) for chloride (top) and sulphate (bottom) at the Intensive Monitoring plots throughout Europe.*



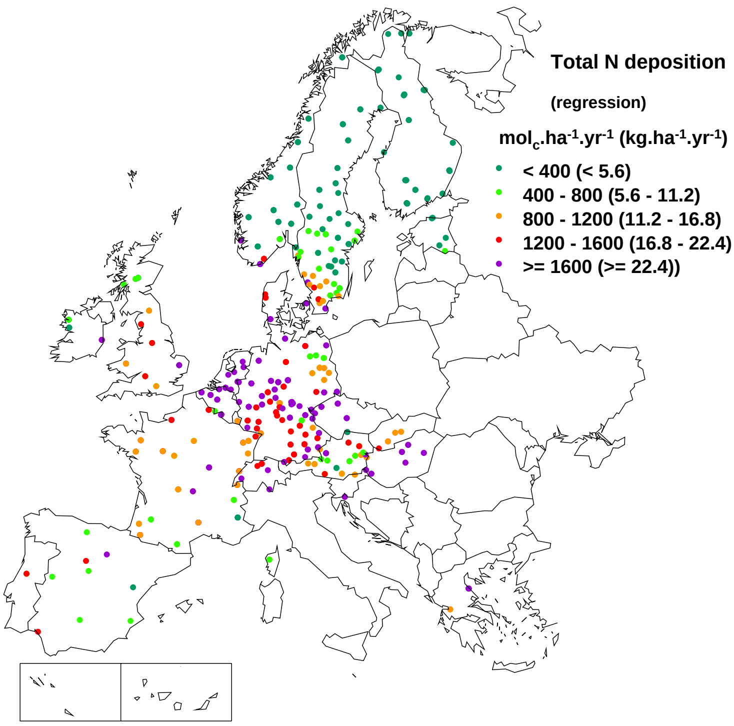
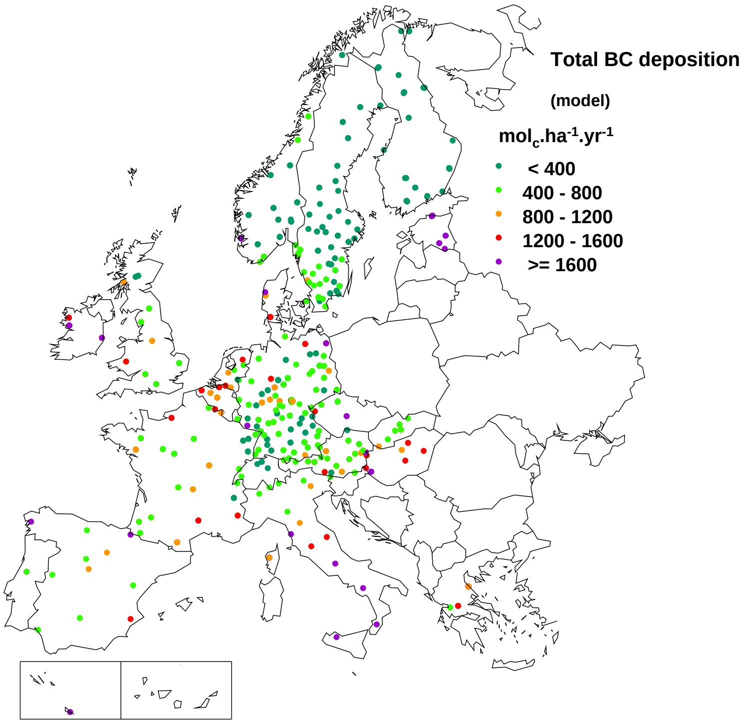


Figure B.6 *Geographical variation in total deposition ($mol_c.ha^{-1}.yr^{-1}$) at the Intensive Monitoring plots for nitrogen based on the canopy exchange model (top) and regression equations (bottom) to calculate canopy exchange (Fig. 5.5) throughout Europe.*



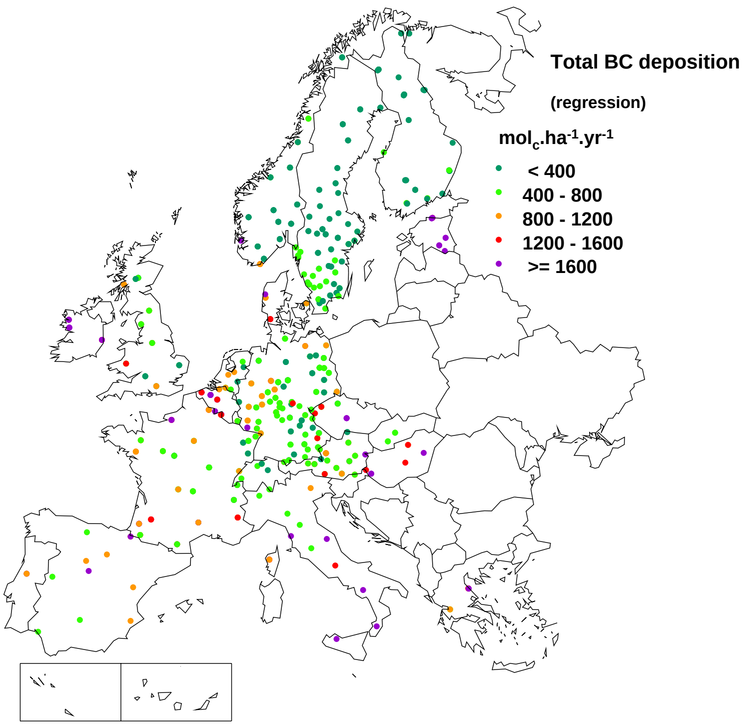


Figure B.7 *Geographical variation in total deposition ($mol_c.ha^{-1}.yr^{-1}$) at the Intensive Monitoring plots for base cations (Ca+Mg+K) based on the canopy exchange model (top) and regression equations (bottom) to calculate canopy exchange (Fig. 5.5) throughout Europe.*

B.3.2 Element output by leaching

B.3.2.1 Comparison of results with measured and interpolated meteorological data

Fig. 5.8 shows the leaching fluxes based on interpolated data against the fluxes based on local data for 26 sites where both calculations could be made.

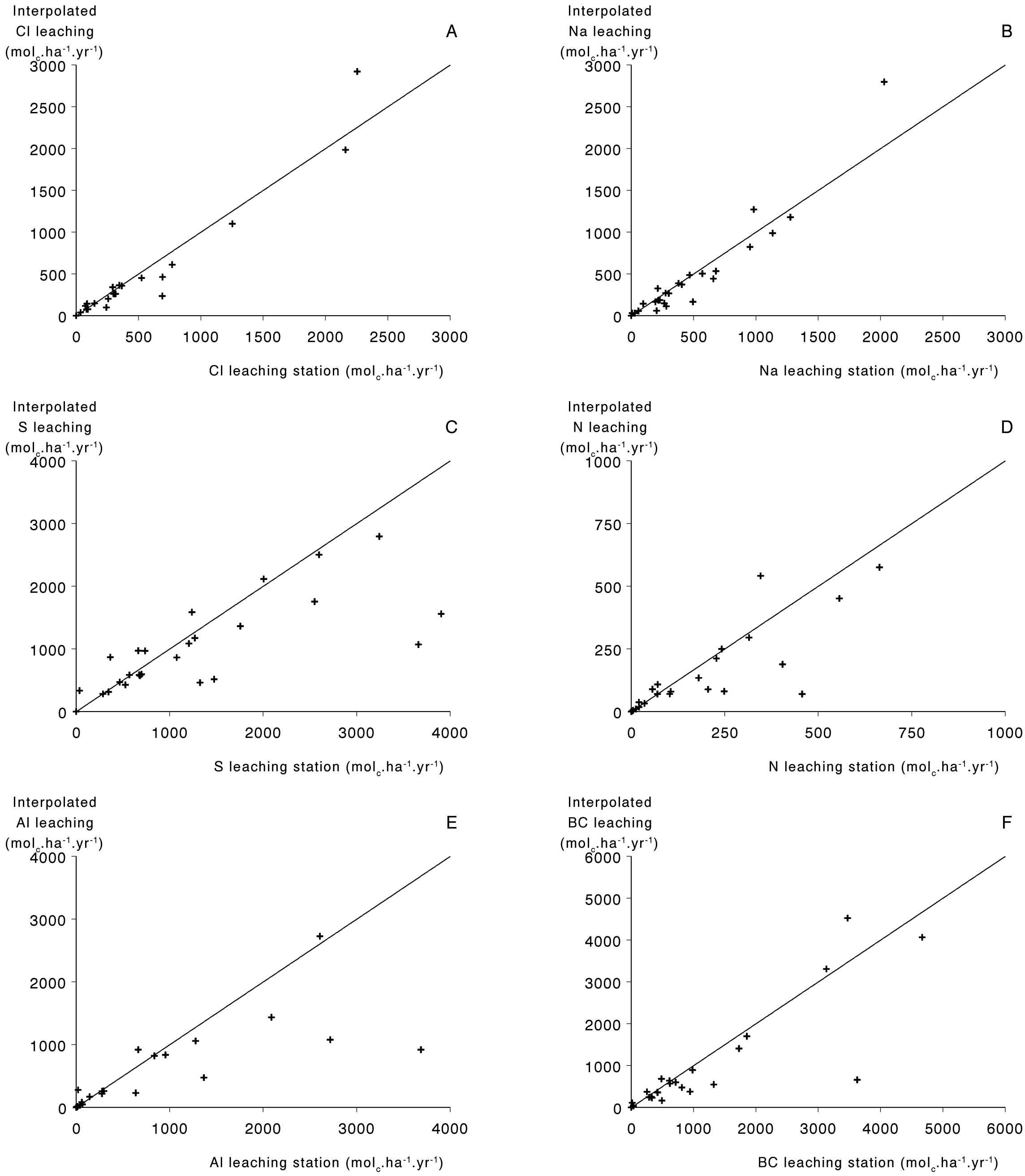


Figure B.8 Leaching fluxes calculated using interpolated meteorological data compared to leaching fluxes calculated using locally measured meteorological data for Cl (A), Na (B), S (C), N (D), Al (E) and BC (F).

Due to differences in meteorological data (in particular with respect to wind speed), transpiration fluxes were overestimated when interpolated meteorological data were used, resulting in lower leaching fluxes (cf. section A.3.2.1). These lower hydrological fluxes lead to slightly lower element leaching fluxes when interpolated data are used compared to the use of local meteorological data. The difference in median leaching fluxes for the 26 sites is quite limited and ranges from 15 $mol_c.ha^{-1}.yr^{-1}$ for Al up to 73 $mol_c.ha^{-1}.yr^{-1}$ for base cations (Table B.7). The difference in leaching fluxes are negligible (less < 4%) at 10% of the sites. At 50% of the sites the error is larger than 16 to 21%, and at 10% of the sites it is even larger than 60%.

Table B.7 Leaching fluxes calculated using local and interpolated meteorological data and median, 10% and 90% differences in calculated leaching fluxes.

Element	Leaching fluxes ($mol_c.ha^{-1}.yr^{-1}$)						Deviation		
	local meteorological data			interpolated meteorological data			(interpolated-local)/local (%)		
	10%	50%	90%	10%	50%	90%	10%	50%	90%
Cl	50	312	2217	61	260	2390	3	17	65
Na	46	301	1192	47	270	1215	2	20	67
S	317	907	2920	324	866	1935	2	18	68
N	5	106	517	5	80	497	0	21	64
BC	35	620	4008	80	547	4248	2	16	62
Al	5	210	2348	4	225	1069	4	21	66

B.3.2.2 Ranges in leaching fluxes

Differences in calculated element leaching fluxes using average or interpolated concentrations were small (Fig. B.9). Leaching fluxes and budgets were calculated using the measured (average) concentrations, because this method is more straightforward. Results of element leaching fluxes obtained for the 121 investigated sites show a considerable variation as indicated in Figure B.10.

The median water flux (not shown) was 144 $mm.yr^{-1}$, but the 10 percentile was nearly 7 times as low, whereas the 90 percentile was approximately 4 times as high. For the major ions, the range is even higher. The 10 percentile leaching flux is lower than 100 $mol_c.ha^{-1}.yr^{-1}$ for most elements, except for sulphur which has a 10 percentile leaching flux of 130 $mol_c.ha^{-1}.yr^{-1}$. The 90 percentile leaching flux ranges from approximately 1000 $mol_c.ha^{-1}.yr^{-1}$ for Cl, Na and N up to almost 3000 $mol_c.ha^{-1}.yr^{-1}$ for base cations. Remarkably are the strong differences for N which is almost negligible in 50% of the soils, whereas the 90 percentile leaching flux is 1000 $mol_c.ha^{-1}.yr^{-1}$ (Fig. B.10). This indicates that nitrogen is strongly retained or denitrified in the soil until a certain threshold in deposition levels is exceeded (cf. B.3.2.2). Unlike the deposition, the leaching of ammonium is lower than that of nitrate.

Median leaching fluxes for Cl, Na, S, N, BC and Al concentrations for the various tree species are presented in Table B.8. The highest leaching fluxes are found for sulphate corresponding to a relative high median input of sulphate. Median sulphate leaching fluxes for Oak are significantly higher than for pine which are relatively low compared to the median input of sulphur which is almost equal for the considered tree species. The high leaching fluxes for sulphate compared to nitrogen indicates that SO_4 is still the dominant source of actual soil acidification, although the total N deposition is generally larger than the total S deposition. This in turn indicates a clear difference between S and N retention in the forest ecosystem (see Section B.3.3).

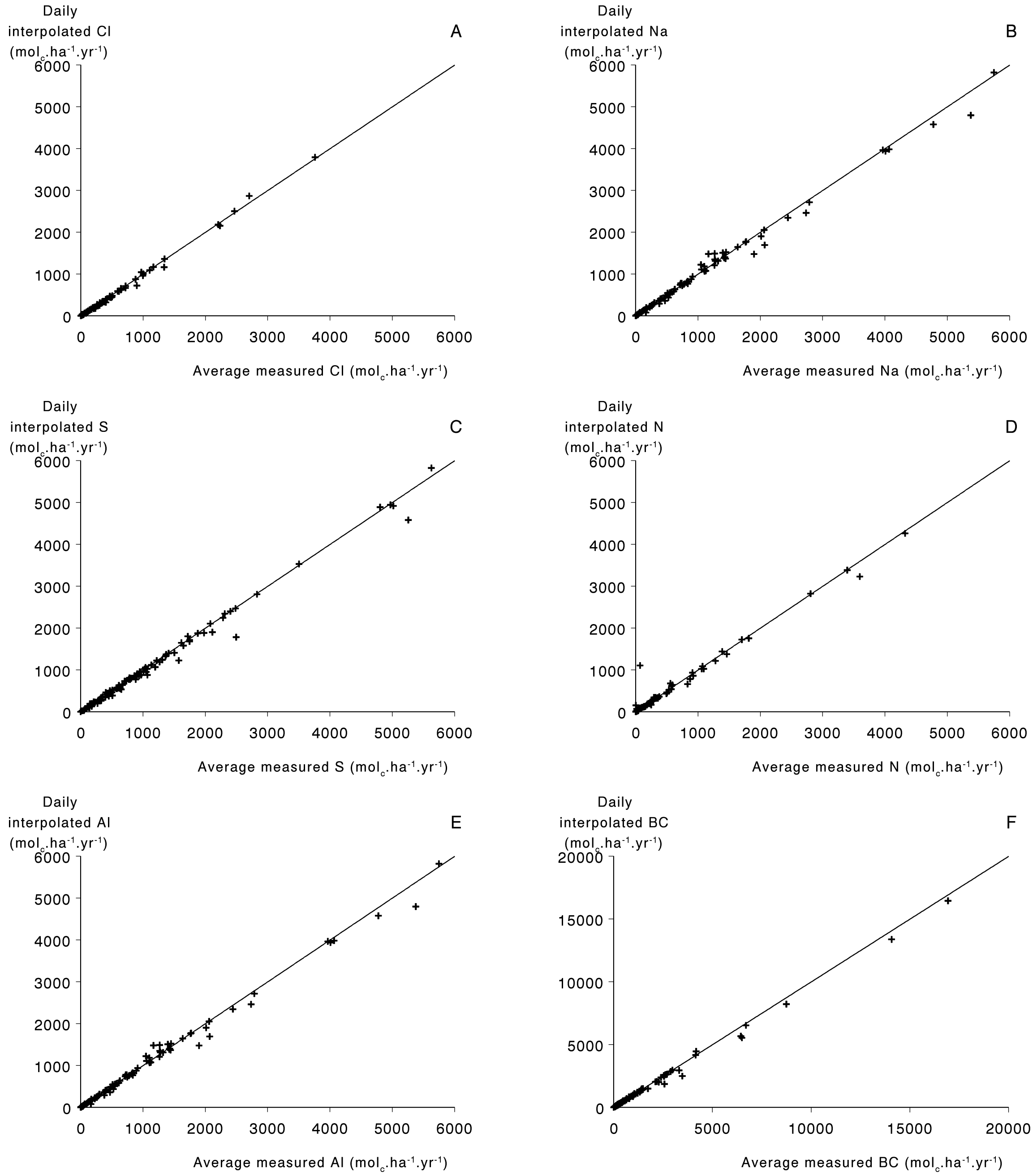


Figure B.9 Comparison of calculated the Cl (A), Na (B), S (C), N (D), Al (E) and BC (Ca+Mg+K) (F) leaching fluxes using (average) measured concentrations and daily interpolated concentrations.

Table B.8 Median element leaching fluxes ($mol_c.ha^{-1}.yr^{-1}$) for chloride, sodium, sulphate, nitrogen, base cations (Ca+Mg+K) and aluminium at 121 investigated sites.

Tree species	Number of sites	Leaching fluxes ($mol_c.ha^{-1}.yr^{-1}$)					
		Cl	Na	S	N	BC	Al
Pine	29	49	54	197	7	156	138
Spruce	51	203	233	590	112	331	774
Oak	15	427	548	1025	212	2184	30
Beech	20	272	269	604	135	717	326
Other	6	147	185	590	54	1149	31
All	121	200	211	509	60	377	294

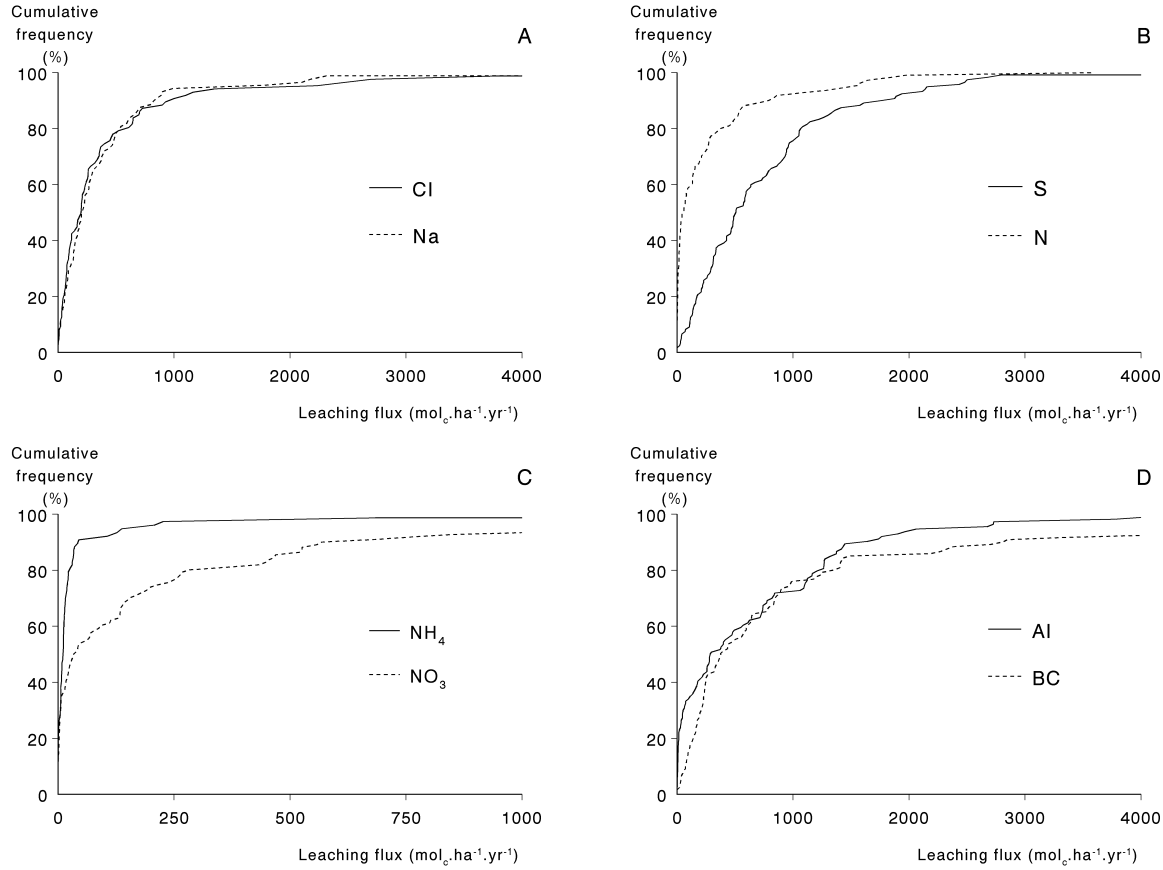


Figure B.10 Cumulative frequency distribution (% plots) for the Cl and Na (A), S and N (B), NH_4 and NO_3 (C) and Al and BC (Ca+Mg+K) (D) leaching fluxes calculated using average concentrations.

Median leaching fluxes are lowest for nitrogen indicating that nitrogen is strongly retained in the soil or denitrified. A considerable difference in nitrogen fluxes is found between the different tree species. The lowest median N leaching flux is found under pine trees which is partly caused by the low hydrological leaching fluxes (Table A.15) which also leads to low median leaching fluxes for Cl and Na under Pine. Nitrogen leaching fluxes under Spruce are also lower compared to the fluxes under the deciduous tree species.

The median leaching flux of base cations is generally higher than for aluminium, indicating that the annual average Al/BC ratio is generally less than 1.0, being considered as an average critical value with respect to impacts on roots (e.g. Sverdrup and Warfvinge, 1993). An exception is formed for Spruce where the median leaching flux of Al is almost twice as high as for base cations. The ratio between Al and BC in the leaching water does not directly give information on the ratio of Al and BC release by weathering and cation exchange buffering the soil system against acid atmospheric inputs. The reason is that Al input from the atmosphere is negligible, whereas this is not the case for base cations. More information on the latter aspect can be derived from the element budgets (Section B.3.3).

B.3.2.3 Geographical variation in leaching fluxes

The geographic variation of the leaching fluxes is presented in Fig. B.11 and B.12.

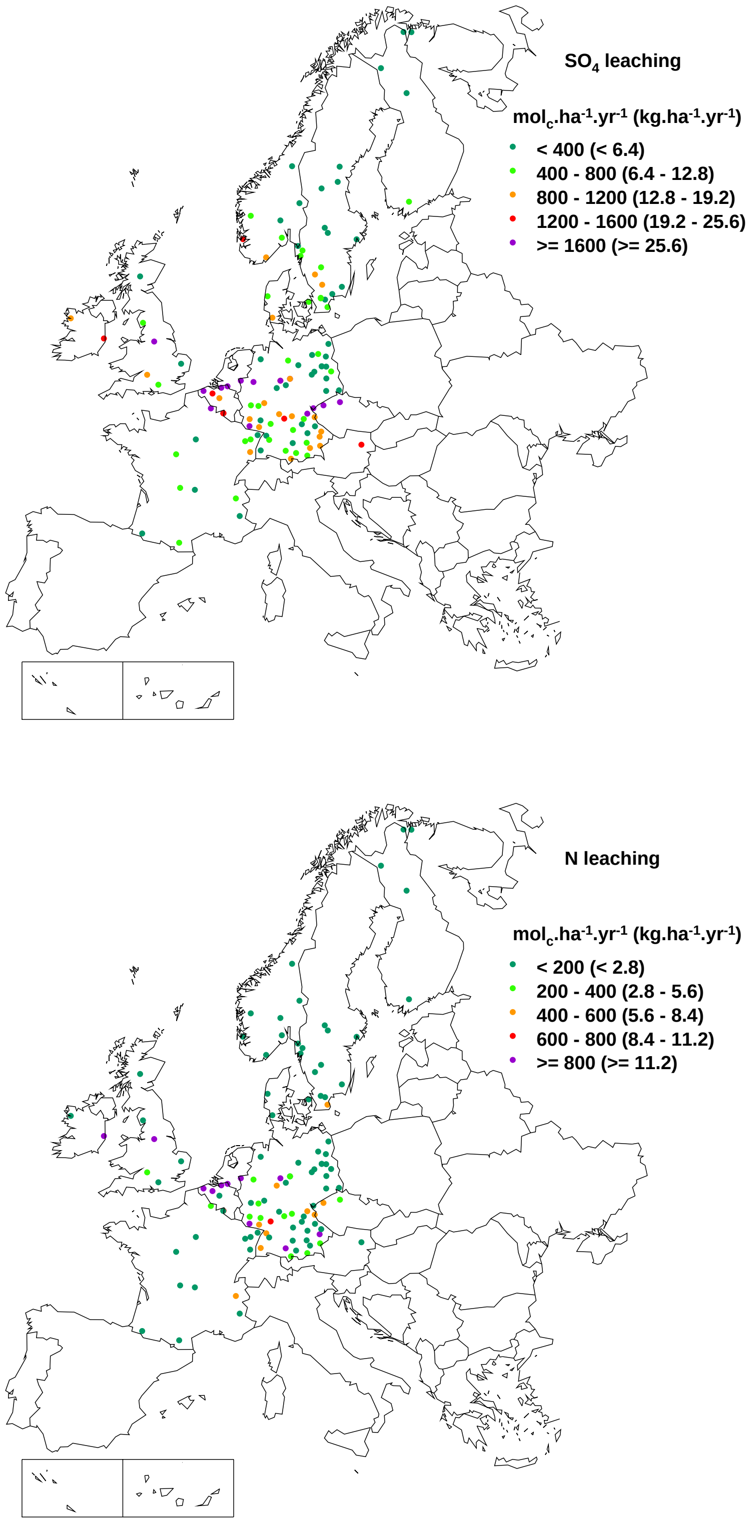
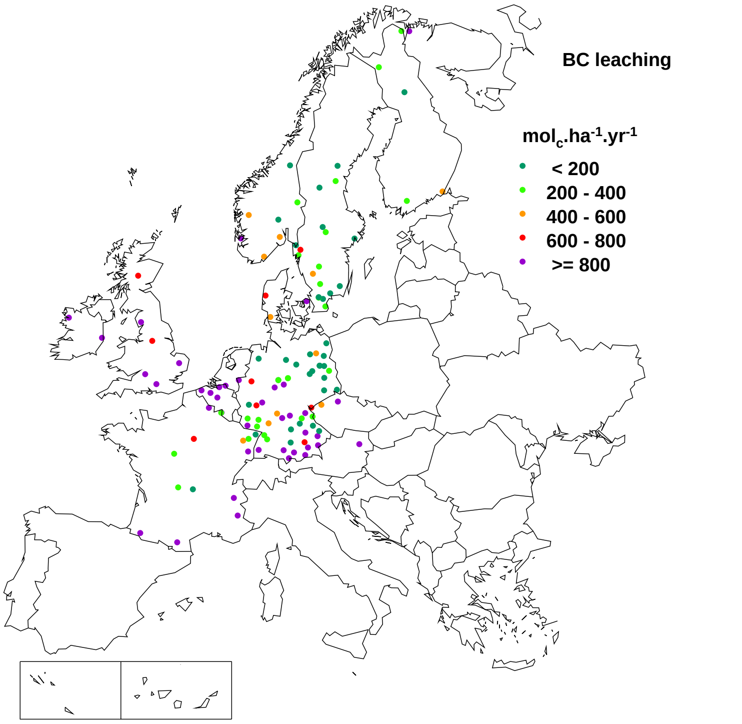


Figure B.11 Geographical variation in leaching fluxes (mol$_c$.ha^{-1}.yr^{-1}) of sulphate (top) and nitrogen (bottom) at the Intensive Monitoring plots throughout Europe.



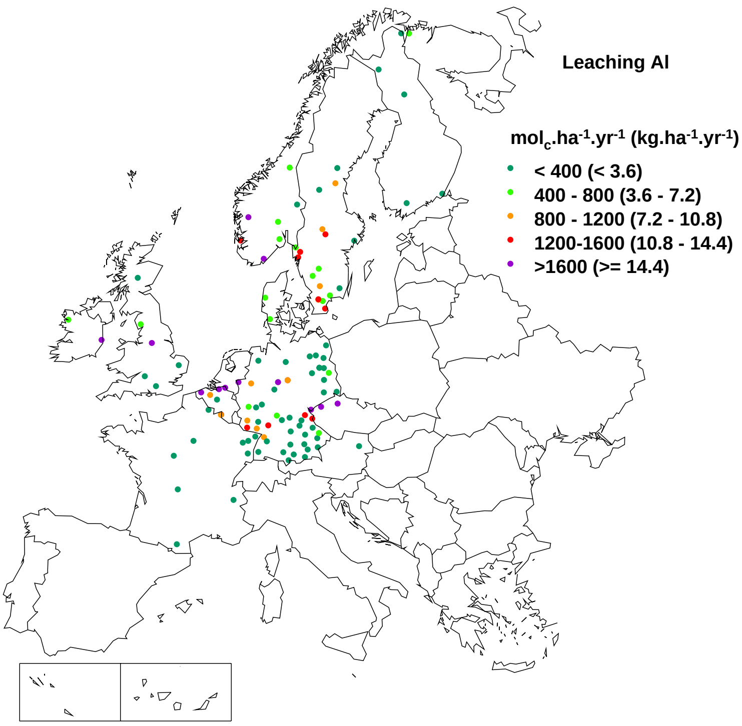


Figure B.12 Geographical variation in leaching fluxes ($mol_c.ha^{-1}.yr^{-1}$) of base cations Ca+Mg+K (top) and aluminium (bottom) at the Intensive Monitoring plots throughout Europe.

Extremely high Cl leaching fluxes (above 2000-3000 $mol_c.ha^{-1}.yr^{-1}$) mainly occur near the coast in Ireland and Denmark, where the input of Cl is very high. At more continental sites the Cl leaching fluxes are generally less than 500 $mol_c.ha^{-1}.yr^{-1}$. Very high leaching fluxes of SO_4 mainly occur in Western and Central Europe (Belgium and parts of Germany and the Czech Republic), reflecting the high deposition at those sites. At part of those sites, the leaching flux of

Al is also high indicating the occurrence of an acid soil releasing mainly Al in response to the high input (leaching) of SO_4. High N leaching fluxes (> 1000 $mol_c.ha^{-1}.yr^{-1}$) do occur in Belgium and central Germany where the input of N (specifically of NH_4) is also high. Data for the Netherlands are not available due to the use of the centrifugation method and only one measurement per year, excluding the assessment of a reliable leaching flux. In northern Europe and in France N leaching fluxes are low (< 200 $mol_c.ha^{-1}.yr^{-1}$). However, the geographic variation of N leaching is large (specifically in Germany), indicating that both N deposition and soil characteristics influence N leaching. The extremely high leaching fluxes for BC (above 7000-8000 $mol_c.ha^{-1}.yr^{-1}$) all occur at near neutral or even calcareous sites in Central Europe, where the leaching of Ca is high due to natural decalcification. At these sites the leaching of bicarbonate (not shown) is also high.

B.3.2.4 Relationships between element leaching and environmental factors

The range in S and N leaching is generally comparable to the range in S and N deposition as illustrated in Figure B.13.

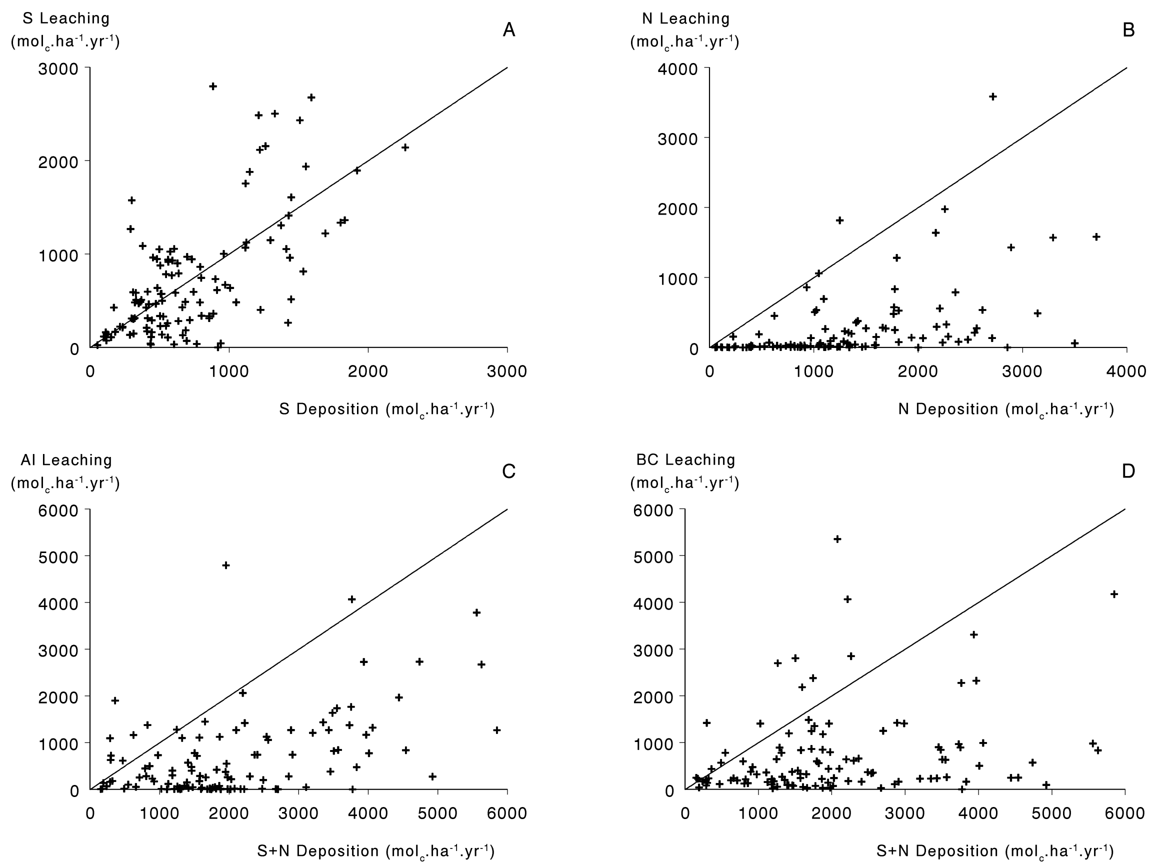


Figure B.13 Relations between total deposition and leaching fluxes of S (A) and N (B) and between the Al leaching fluxes and the total deposition flux (using the deposition model including regression equations to estimate canopy uptake) of S+N (C) and BC leaching and S+N deposition(D) at the 121 monitoring sites.

On average S leaching is close to S deposition, but there is a large variation that can partly be attributed to errors in both the input and output assessment (Fig. B.13A). At five sites the leaching of SO_4 is considerably higher (approximately 3000-5000 $mol_c.ha^{-1}.yr^{-1}$) than the deposition (approximately 1500 $mol_c.ha^{-1}.yr^{-1}$), indicating a strong release of SO_4. Most of these sites are located in areas that received a high sulphur deposition over the past decades (Czech-German border). The present high leaching fluxes at these sites are probably due to the release of sulphur, which has been adsorbed during previous decades.

In accordance with results found by e.g. Dise et al. (1998a, b) and Gundersen et al. (1998a), the leaching of N is generally negligible below a throughfall input of 10 $kg.ha^{-1}.yr^{-1}$. At N throughfall inputs above 10 $kg.ha^{-1}.yr^{-1}$, leaching of N is generally elevated, although lower than the input indicating N retention at most of the plots. At 2 sites, however, N leaching is larger than the N input (Fig. B.13B), indicating the occurrence of a disturbance in the N cycle. The range in Al leaching fluxes is quite comparable to the range in throughfall S and N fluxes (Fig. B.13C). At several sites, Al leaching fluxes are even higher than the acid deposition, indicating that the leaching of sulphate is higher than the input (S release from the soil causing acidification) and this acid input is almost completely buffered by the release of Al. At all other sites the Al leaching flux is lower, indicating that part of the potential acid input is buffered by N retention and/or base cation release. In soils with a pH above 5.0, the release of Al is generally negligible, independent of the S and N input, since BC release by weathering and cation exchange buffers the incoming net acidity in those soils. This is illustrated by a site with a high input of S and N by throughfall (near 8000 $mol_c.ha^{-1}.yr^{-1}$) and hardly Al leaching. The range in BC leaching fluxes is quite comparable to the range in Al leaching fluxes (Fig. B.13D). As with Al, at several sites BC leaching fluxes are higher than the acid deposition. Apart from the possibility of S release from the soil, this is mostly due to natural acidification by bicarbonate leaching.

To gain insight in the various factors affecting element leaching, a multiple regression analyses was carried out (see Section B.2.5). Results are presented in Table B.9.

Table B.9 Overview of the predictor variables explaining element leaching at 97-112 Intensive Monitoring plots with the number of plots and the percentage variance accounted for.

Predictor variables	S	N	BC	Al
Site/Stand characteristics				
Tree species	+			
Humus type group				+
Stand age	+			
Deposition				
S	++			++
N		++	+	
$FrNH_4$				
Foliage				
N-content		+		
Soil chemistry				
pH subsoil			++	
N[1)]	112	97	109	106
R^2_{adj} (%)[2)]	46	24	30	35

++ significant at the p 0.01 level and t>3 and positive correlated with response variable
+ significant at the p 0.05 level and t>2 and positive correlated with response variable
-- significant at the p 0.01 level and t>3 and negative correlated with response variable
- significant at the p 0.05 level and t>2 and negative correlated with response variable
[1)] N = number of plots.
[2)] R^2_{adj} = percentage variance accounted for.

The results show that variations in the element leaching fluxes are often related to the atmospheric deposition (the S input in case of Al being the major source of acidification). SO_4 leaching was related to the deposition and was higher in mature stands (> 30 year old) compared to young stands. The relation with stand age may be explained by the fact that the cumulative sulphur accumulation in the soils of the young stands is less compared to the mature stands. Sulphur deposition was also (weakly) related to the tree species, being lowest under Pine trees, somewhat higher under Spruce and highest under deciduous forest. The reason for this relationship with tree species is unclear and may be an artefact of regional differences in S leaching.

N leaching is positively related to the N content in the foliage and the total N deposition. There was no significant correlation between the calculated NO_3 and NH_4 (and total N) leaching flux and the C/N ratio of the organic or mineral layer, which is contradictory to the results presented by Dise et al. (1998a, b) and Gundersen et al. (1998a).

A visual inspection of the relationship between N leaching and N deposition against C/N ratio of the organic layer and mineral soil, however, showed that soils with very high C/N ratios (> 30) in the organic layer tend to have lower leaching fluxes in particular when N deposition is low (Fig. B.14). An exeption are two plots with C/N ratios near 35 and an N leaching flux near 1500 $mol_c.ha^{-1}.yr^{-1}$ (Fig. B.14A). Below C/N ratios of 30, however, the scatter is quite large. For example, the N leaching ranges between 150 and 1500 $mol_c.ha^{-1}.yr^{-1}$ at a C/N ratio of the organic layer of approximately 25 and a N deposition of more than 2000 $mol_c.ha^{-1}.yr^{-1}$. We did find, however, a statistically significant impact of the C/N ratio on soil NO_3 concentrations for approximately 240 Intensive Monitoring plots (see Appendix F). A more in-depth analysis, based on (much) more input-output budgets of N is thus necessary to further investigate the possible role of the C/N ratio of the soil on the N dynamics.

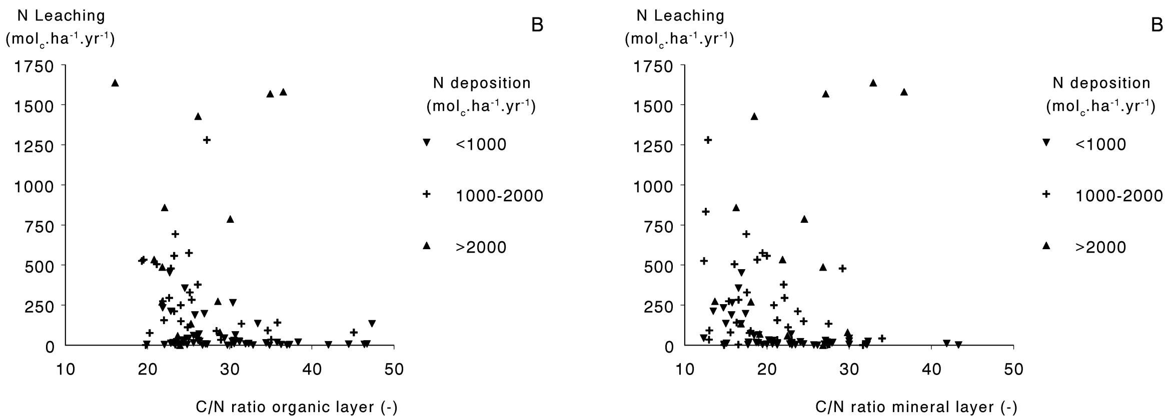


Figure B.14 Relationships between N leaching and the C/N ratio of the organic layer (A) and mineral layer (B).

Variations in BC leaching were significantly related to the N input, but also the pH of the subsoil. Al leaching shows a positive relation with sulphur deposition and was higher in mull type humus compared to mor and moder type humus. This indicates that the solubility of Al is probably lower in soils with a mor type humus compared to more strongly decomposed humus types.

B.3.3 Element budgets

B.3.3.1 The effect of the use of interpolated meteorological data on the calculated element budgets

The use of interpolated data instead of local measured meteorological data leads to a underestimation of the calculated leaching fluxes (cf. section A.3.2.1 and section B.3.2.1). This affects the calculated budgets in particular for elements where the output flux is comparable or higher than the input. This is shown in Fig. B.15 where the budgets based on interpolated data are plotted against the budgets based on local data.

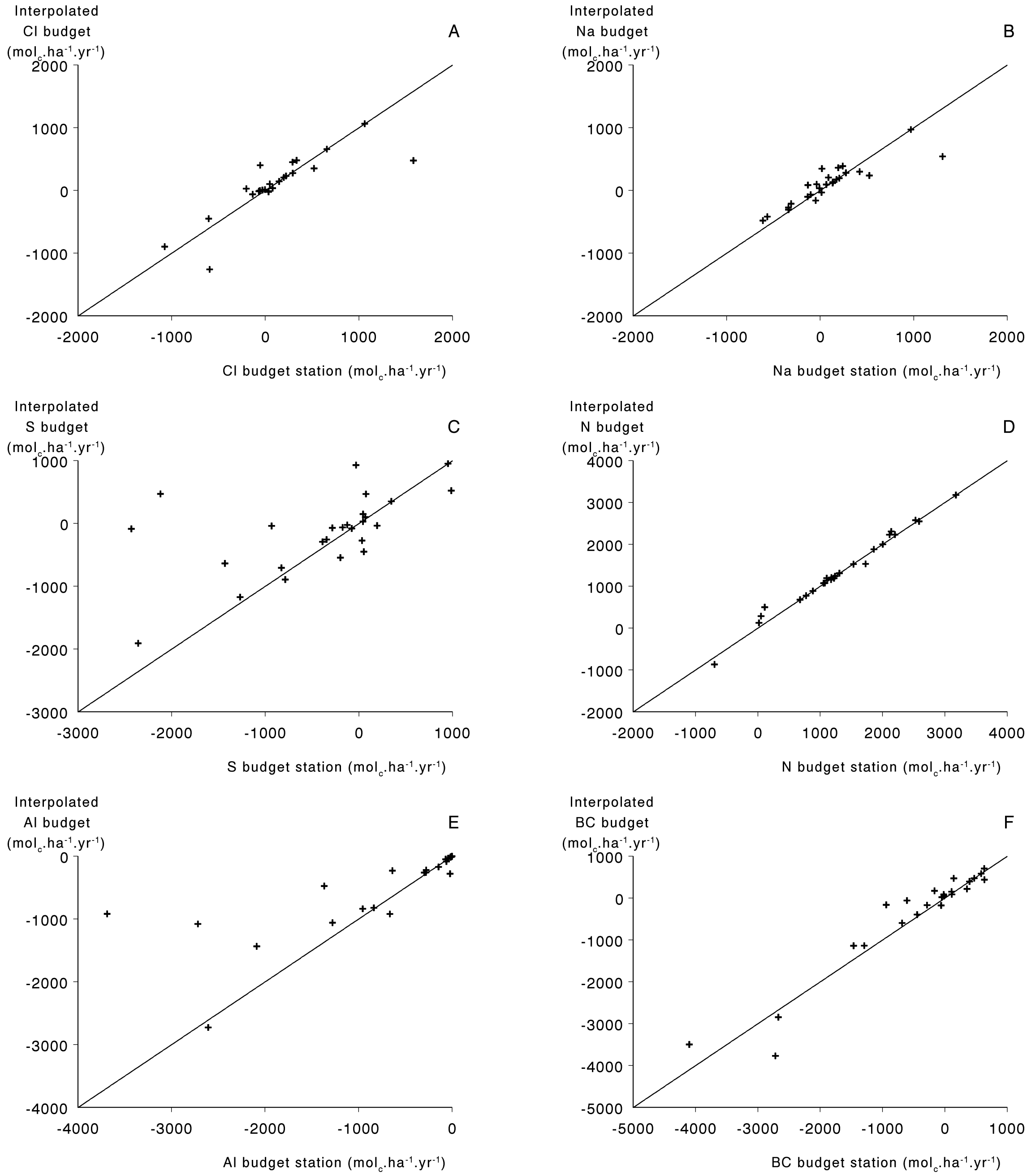


Figure B.15 Element budgets based on interpolated meteorological data compared to local meteorological data for Cl, Na, S, N, Al and BC.

Differences in nitrogen budgets (an element that is strongly retained in the soil) are rather small, whereas differences in sulphur, aluminium or base cation budgets are much larger. The difference in median element budgets ranges from 12 $mol_c.ha^{-1}.yr^{-1}$ for N to 188 $mol_c.ha^{-1}.yr^{-1}$ for base cations (Table B.10). The difference in impact of the deviation in leaching fluxes on the calculated budgets is clearly reflected in the relative deviation of the budgets for the various elements. Nitrogen budgets are hardly affected at more than 50% of the sites, whereas S, Cl, Na and BC budgets are more strongly affected (deviation of more than 20% at 50% of the sites).

Table B.10 Element budgets calculated using local and interpolated meteorological data and median, 10% and 90% differences in calculated budgets.

Element	Element budget ($mol_c.ha^{-1}.yr^{-1}$)						Deviation		
	local meteorological data			interpolated meteorological data			(interpolated-local)/local (%)		
	10%	50%	90%	10%	50%	90%	10%	50%	90%
Cl	-600	36	603	-256	93	568	3	55	150
Na	-430	19	464	-285	117	450	2	33	330
S	-1776	-149	271	-800	-67	500	6	60	710
N (model)	115	973	2021	127	950	2067	0	2	120
N (regr.)	75	1222	2397	234	1200	2428	0	2	220
BC (model)	-3270	-166	516	-3605	22	517	0	38	213
BC (regr.)	-2991	-113	638	-3231	10	666	0	23	135
Al	-2347	-210	-5	-1068	-225	-4	4	21	66

B.3.3.2 Ranges in element budgets

Ranges in element budgets for chloride, sulphate, nitrate, base cations (Ca+Mg+K) and aluminium for the 121 monitoring sites are presented in Figure B.16 and Table B.11.

For most sites the Cl budget is close to zero: 80% of the sites have a Cl budget between -60 and 600 $mol_c.ha^{-1}.yr^{-1}$. This is quite close to values for the Cl budget at the Solling spruce stand for which long term measurements are available, At this site Cl budgets ranged from -560 to 830 $mol_c.ha^{-1}.yr^{-1}$ for a one year period (Van der Salm, in prep). For a four year period this range was somewhat smaller (-280 to 101 $mol_c.ha^{-1}.yr^{-1}$).

The median sulphur budget is also close to zero. However, the range in sulphur budgets is much broader compared to chloride. Budgets for 80% of the sites range from -700 to 550 $mol_c.ha^{-1}.yr^{-1}$. At a considerable number of sites sulphur is released from the soil, indicating that these system are recovering from previous episodes of high sulphate input. This is affirmed by the geographical differences in sulphur budgets (Section B.3.3.2).

Nitrogen budgets (NH_4 + NO_3) range from 60 to 1800 $mol_c.ha^{-1}.yr^{-1}$ when the canopy exchange model is used to calculate canopy exchange and total deposition. A slightly broader range is found when the regression model is used, due to the fact that the regression model yields a somewhat higher canopy uptake of N in areas with a relatively low N deposition, whereas differences are negligible in areas with a high N deposition. At most sites (85%) the N input is higher then the N leaching.

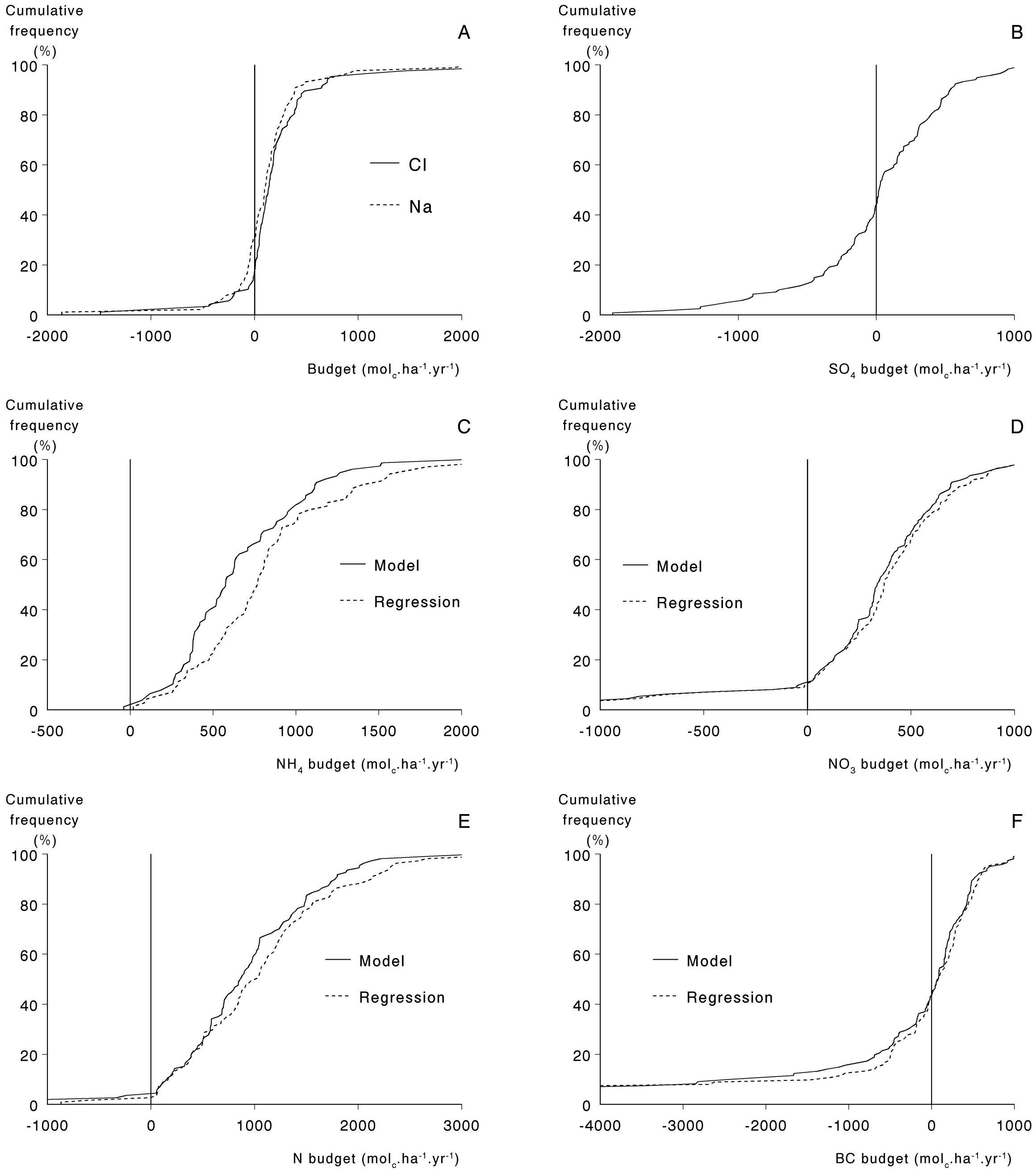


Figure B.16 Cumulative frequency distribution (% plots) for the Cl and Na (A), S (B), NH_4 (C), NO_3 (D), N (E) and BC (Ca+Mg+K) (F) budgets calculated using (average) measured concentrations.

Table B.11 Element budgets for chloride, sodium, sulphate, nitrogen, base cations (Ca+Mg+K) and Aluminium.

Element	Number of sites	Element budget (mol$_c$.ha^{-1}.yr^{-1})			Behaviour	
		10%	50%	90%	Retention	Release
Cl	87	-60	135	614	83	17
Na	89	-141	99	391	70	30
S	120	-672	21	540	57	43
N (regression)	111	169	1028	2129	97	3
N (model)	111	159	871	1787	96	4
BC (regression)	112	-1307	86	576	57	43
BC (model)	121	-2240	86	517	57	43
Al	114	-1648	-294	-7	1	99

At 45% of the sites the BC balance is positive (retention) indicating that the input of base cations by throughfall, weathering, mineralisation and ion-exchange is higher than the uptake by the plant. Some sites on highly weatherable parent material (chalk, gypsum etc.) have a strong negative BC balance (up to -15000 $mol_c.ha^{-1}.yr^{-1}$).

The Al balance is always negative (Al is leached) because the input of Al is negligible. The median Al balance is -300 $mol_c.ha^{-1}.yr^{-1}$. This corresponds to a median leaching concentration of 0.25 $mol_c.m^{-3}$, which is above a critical limit of 0.2 $mol_c.m^{-3}$, indicated in the literature with respect to impacts on roots for the most sensitive tree species (Cronan et al., 1989).

Median element budgets for chloride, sulphate, nitrate, base cations (Ca+Mg+K) and aluminium for the different tree species at the 121 monitoring sites are presented in Table 5.12. The median budget for Cl and Na is slightly positive, deposition exceeds leaching except for oak. The sulphur budgets is close to zero in coniferous forests, in deciduous forest the median sulphur budget is slightly negative. Nitrogen is strongly retained in a large part of the sites and accordingly the median nitrogen budget is positive for all tree species. The median nitrogen budget is approximately 300 $mol_c.ha^{-1}.yr^{-1}$ higher when canopy exchange is calculated by the regression model due to a lower canopy uptake estimated by the canopy exchange model (cf. B.3.12). The median base cation budget is zero to slightly positive for the coniferous tree species and negative for the deciduous species. The high values for base cations budgets for soil under deciduous forest are partly due to the occurrence of calcareous soils.

Table B.12 Median element budgets for chloride, sodium, sulphate, nitrogen, base cations (Ca+Mg+K) and Aluminium using the canopy exchange model. Values in brackets are the median input fluxes using the regression equations to calculate the input.

Tree species	Number of sites	Element budget ($mol_c.ha^{-1}.yr^{-1}$)							
		Cl	Na	S	N		BC		Al
Pine	29	211	204	216	703	(861)	253	(210)	-138
Spruce	51	167	121	16	1040	(1094)	94	(216)	-774
Oak	15	-37	-86	-256	686	(846)	-911	(-445)	-30
Beech	20	113	37	-22	984	(1225)	30	(53)	-326
Other	6	102	19	28	772	(782)	-862	(-864)	-31
All	121	135	99	21	871	(1028)	86	(86)	-294

In general, the range in element release is comparable to element leaching. This broad range in budgets is partly due to the wide geographic range in locations leading to very diverse circumstances with respect to deposition, hydrology and bio-geochemical processes. However, it has to be stated that the budgets are based on measurements during a relatively limited number of years. For 14% of the sites data for a four year period (1995-1998) where available. For most sites (58%) budgets were limited to the period 1996-1998. For 20% of the sites two years of measurements were available, whereas for 8% of the sites budgets are based only on data from 1999. This relatively short time span may lead to over- or underestimation of the budget compared to the long-term situation due to particular hydrological or biological circumstances in specific years. For example, the extraordinary high leaching of sulphur and nitrogen at two sites is caused by extreme leaching in 1998, whereas the other years have a much lower release of sulphur and nitrogen.

B.3.3.3 Geographic variation in element budgets

Extreme values for the Cl budget are mainly found in coastal areas (e.g. Ireland, western France) where the input of Cl is extremely high (Fig. B.17). Rather high values for the Cl budget (> 600 $mol_c.ha^{-1}.yr^{-1}$) are also found for a number of sites at the Czech-German border. At these sites the input of chloride was up to three times higher compared to other sites in Germany. Sites with the highest sulphur release are located in central Europe, where the strongest reduction in sulphur deposition has taken place over the last decade.

Sites with a net release of nitrogen are found in Belgium and Northwestern Germany (Fig. B.18). This corresponds to the area which have received a high N deposition over a prolonged period of time. Remarkable is the high N retention in Southeastern Germany. According to the present calculations these sites still retain a lot of nitrogen despite relatively high depositions of N. This discrepancy may be explained by a very long period (centuries) of intensive use of litter on these poor soils until the 1950th and a therefore still existing deficit in the N budget. High BC release values are generally found in areas with a high N or S deposition such as Belgium, Northwestern Germany and the area around the German-Czech border. The Al budget is equal to Al leaching (Fig. B.12) and no map is therefore given here.

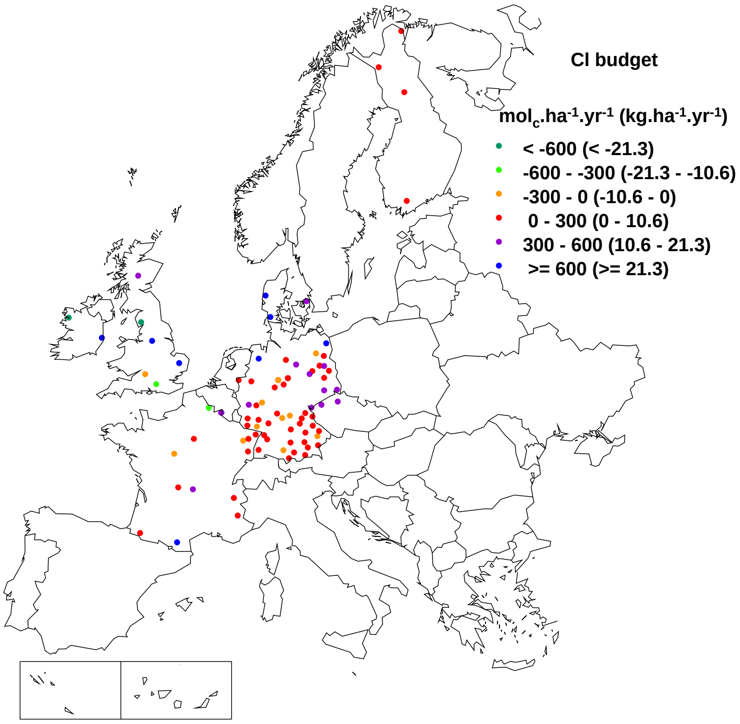
B.3.3.4 Relationships between element budgets and environmental factors

Results of the multiple regression analyses relating element budgets to environmental factors are presented in Table B.13.

Table B.13 Overview of the predictor variables explaining element budgets at 73-112 Intensive Monitoring plots with the number of plots and the percentage variance accounted for.

Predictor variables	S	N	BC
Site/Stand characteristics			
Tree species	-		
Stand age	-	+	
Deposition			
N		++	-
Foliage			
N-content		- -	
Soil chemistry			
Organic C pool		-	
pH subsoil			- -
N[1]	112	73	109
R^2_{adj} (%)[2]	9	61	29

++ significant at the p 0.01 level and t>3 and positive correlated with response variable
+ significant at the p 0.05 level and t>2 and positive correlated with response variable
-- significant at the p 0.01 level and t>3 and negative correlated with response variable
- significant at the p 0.05 level and t>2 and negative correlated with response variable
[1] N = number of plots.
[2] R^2_{adj} = percentage variance accounted for.



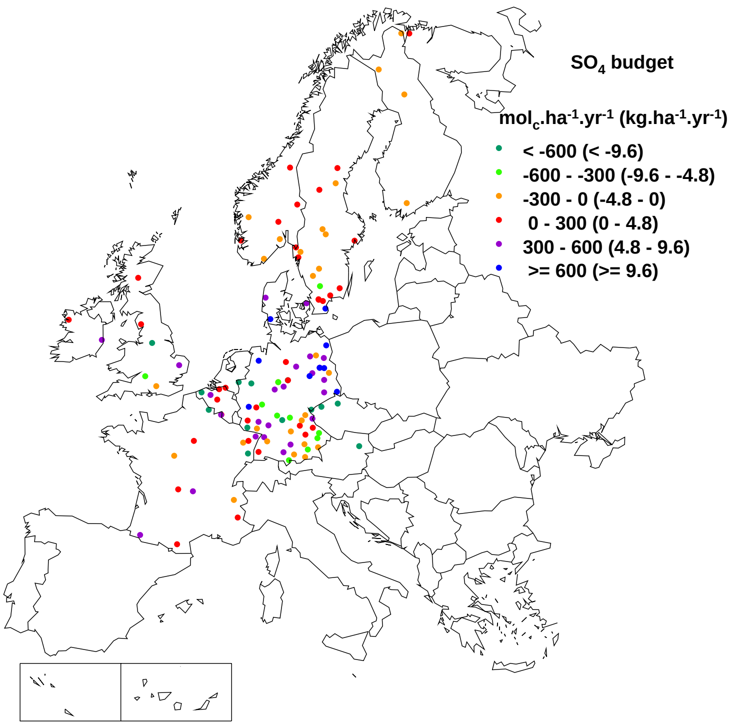
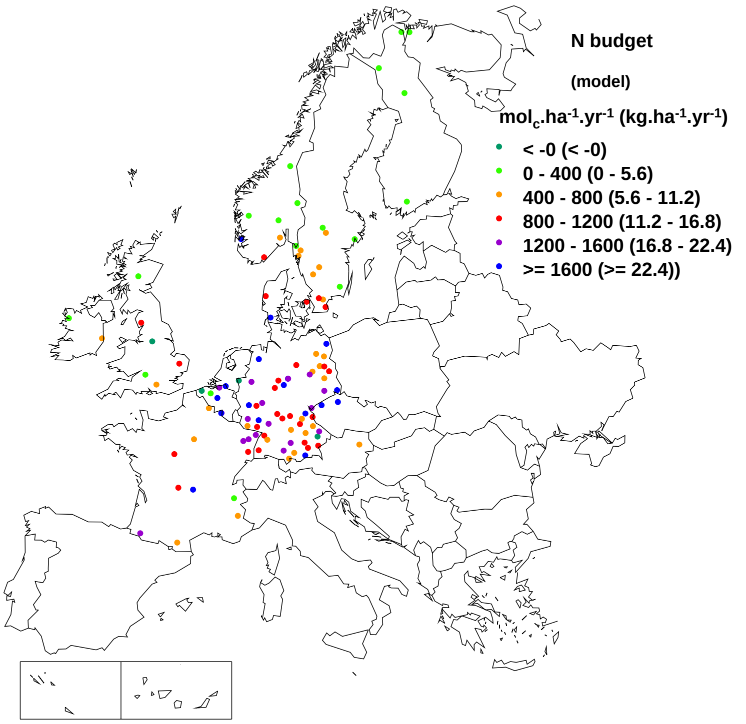


Figure B.17 Geographical variation in budgets ($mol_c.ha^{-1}.yr^{-1}$) for chloride (top) and sulphate (bottom) at the Intensive Monitoring plots throughout Europe.



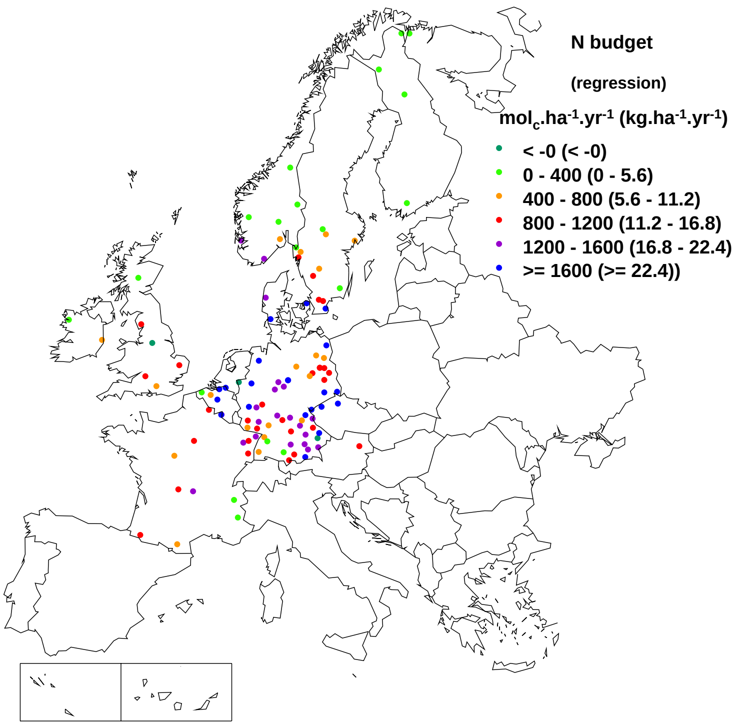
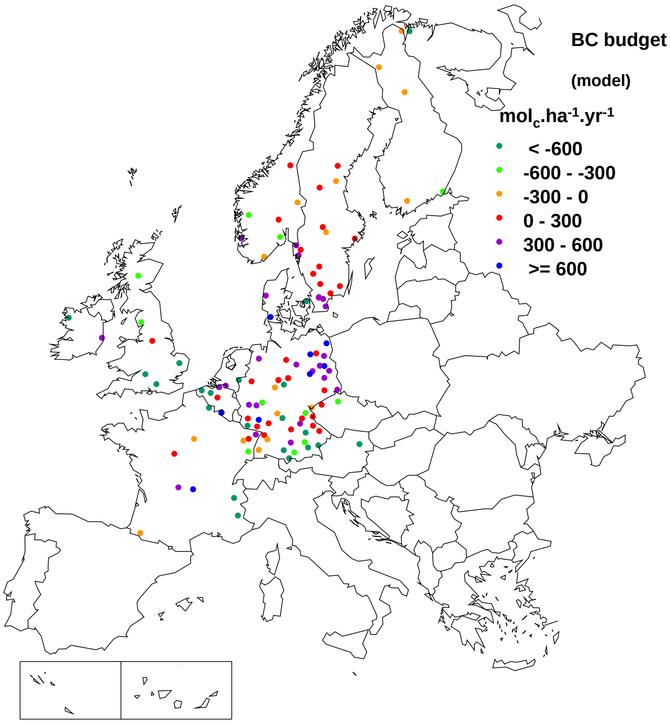


Figure B.18 Geographical variation in budgets ($mol_c.ha^{-1}.yr^{-1}$) for nitrogen using total deposition based on the canopy exchange model (top) and regression equations to calculate canopy exchange (bottom) at the Intensive Monitoring plots throughout Europe.



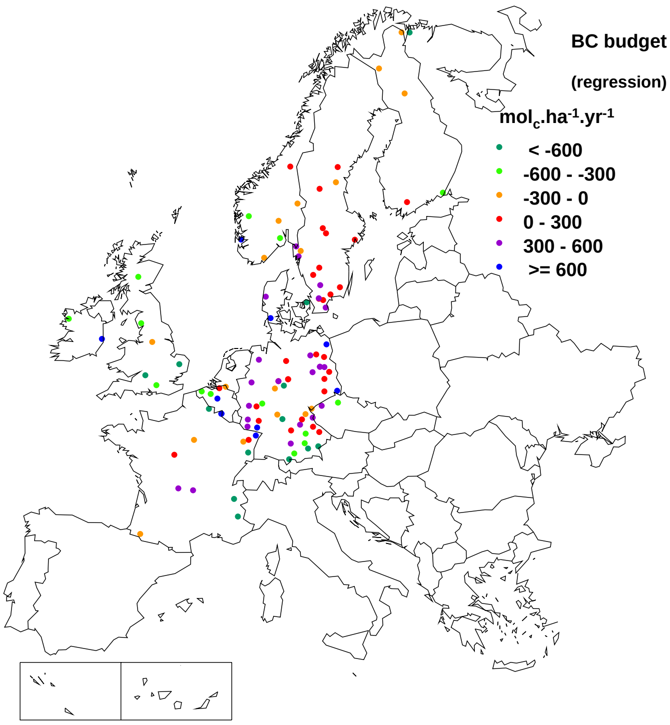


Figure B.19 *Geographical variation in budgets ($mol_c.ha^{-1}.yr^{-1}$) for base cations (Ca+Mg+K) using total deposition based on the canopy exchange model top) and regression equations to calculate canopy exchange (bottom) at the Intensive Monitoring plots throughout Europe.*

The results show that S retention from the soil can hardly be explained from environmental variables. N retention increases with an increased stand age and N deposition and a decreased organic C pool and foliar N content. As with N leaching, the N retention fraction was not significantly related to the C/N ratio of the organic or mineral layer. A plot of the N retention fraction against the C/N ratio of the organic and mineral layer, however, shows a tendency of lower N retention fractions at low C/N ratios and high deposition levels but the scatter is large (Fig. B.20). As expected, variations in BC release from the soil were positively to the pH (high weathering rates in soils with a high pH). Al release is equal to Al leaching and consequently, we refer to Table B.10 for the effects of environmental variables on the Al budget.

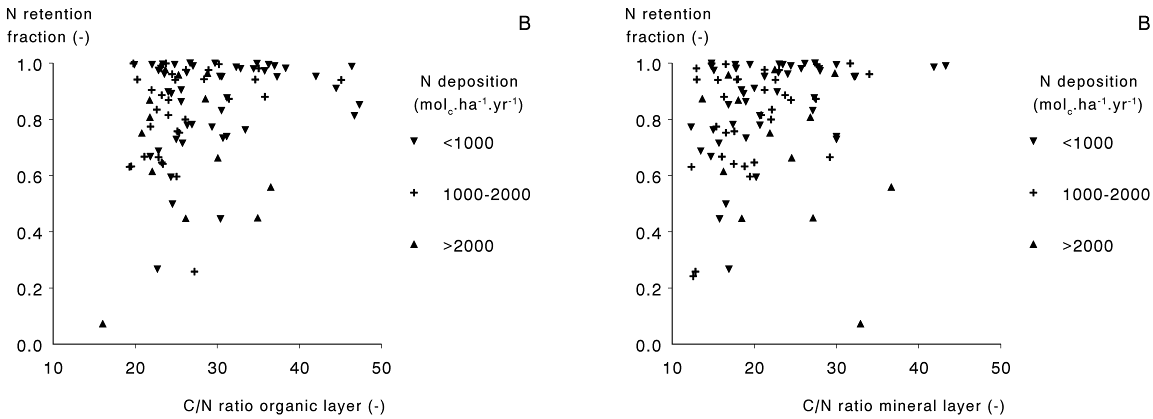


Figure B.20 Relationships between N retention fraction and the C/N ratio of the organic layer (A) and mineral layer (B).

B.4 Conclusions

The following conclusions can be drawn with respect to the leaching and retention of the different elements:

- The use of interpolated meteorological data instead of local measured data leads to lower leaching fluxes. The deviation in median leaching fluxes is quite limited and ranges from 15 mol$_c$.ha^{-1}.yr^{-1} for Al up to 73 mol$_c$.ha^{-1}.yr^{-1} for base cations. However, the (absolute) deviation in leaching fluxes at the individual sites is somewhat larger and ranges from 20 mol$_c$.ha^{-1}.yr^{-1} for (a median) N leaching flux up to 180 mol$_c$.ha^{-1}.yr^{-1} at a medium S leaching flux. The lower leaching fluxes lead to a difference in median element budgets between 12 mol$_c$.ha^{-1}.yr^{-1} for N and 188 mol$_c$.ha^{-1}.yr^{-1} for base cations.
- At nearly all plots, the leaching flux of SO_4 is much higher than that of NO_3 indicating that SO_4 is still the dominant source of actual soil acidification. The median sulphur budget is close to zero, but on average, S leaching is higher than S deposition. The median budget of zero does not imply tracer behaviour of S, since there is a large variation. Very high leaching fluxes of SO_4 mainly occur in Western and Central Europe (Belgium and parts of Germany and the Czech Republic), reflecting the high deposition at those sites. At a considerable number of those sites, sulphur is released by the soil, indicating that these systems are recovering from previous episodes of high sulphate input.
- The leaching of N is generally negligible below throughfall inputs of 10 kg.ha^{-1}.yr^{-1}. At sites with throughfall inputs above this level, leaching of N is generally elevated, although lower than the input indicating N retention at most of the plots. The significant relationship of N leaching with throughfall is reflected by the fact that highest N leaching fluxes do occur in areas where the input of N (specifically of NH_4) is also high. Nitrogen budgets show that at most sites (90%) the N input is higher then the N leaching. Despite the large variation in N leaching at comparable N inputs no significant relationships were found with either stand and site characteristics or with the soil C/N ratio. We did find, however, a statistically significant impact of the C/N ratio on soil NO_3 concentrations. A more in-depth analysis, based on (much) more input-output budgets of N is thus necessary to further investigate the possible role of the C/N ratio of the soil on the N dynamics.
- At most of the plots, the leaching flux of base cations (Ca+Mg+K) is higher than that of Al. Extremely high leaching fluxes for BC (above 7000-8000 mol$_c$.ha^{-1}.yr^{-1}) all occur at

near neutral or even calcareous sites in Central Europe, where the leaching of Ca is high due to natural decalcification. Variations in BC leaching were significantly related to the S input and also to the pH and base saturation. The median base cation balance is close to zero, implying a net adsorption and a net release of base cation at approximately 50% of the plots.

- With the exception of some strongly acidified sites, the Al leaching flux was generally lower than the atmospheric input of S and N, indicating that part of the potential acid input is buffered by N retention and/or base cation release. The Al leaching flux was significantly related to the SO_4 input (and leaching) reflected by the fact that sites with a high Al leaching coincide with sites with a high input (leaching) of SO_4. The geographic patterns of both elements, however, did not coincide very well since soil base saturation was also significantly related to the Al leaching flux. The median Al balance is 370 $mol_c.ha^{-1}.yr^{-1}$. High values are generally found in areas with a high N or S deposition.

B.5 Discussion and conclusions

Conclusions on the evaluations were presented in the last sections of each chapter. Here we summarise those conclusions, focusing on the validity of the presented results, related to the species composition of the ground vegetation and water and element fluxes through the forest ecosystem.

Water fluxes through the forest ecosystem

Leaching fluxes mainly reflected the difference in throughfall on forest stands. Median values increased going from approximately 80 mm under Pine stands to approximately 210 mm under Spruce stands. The strong relationship between annual throughfall and leaching is due to the calculated narrow range in the sum of soil evaporation and transpiration, with median values ranging from approximately 400-450 $mm.yr^{-1}$ for the various tree species. Plots with the lowest leaching fluxes are thus located in areas with relatively low precipitation such as north-eastern Germany, parts of Sweden and Finland and locally in southern Europe.

Simulated water fluxes through the forest ecosystem were generally plausible in view of available measurements and literature data. Simulated yearly throughfall values were within 5% of the measurements at 85% of the monitoring sites. Simulated transpiration fluxes and leaching fluxes could not be validated but detailed studies on two sites in Germany and the Netherlands indicated that the model was able to simulate changes in soil water contents quite well. Simulated yearly interception evaporation was well within the range observed in literature. The increase in average interception fractions going from Oak < Pine < Beech < Spruce from approximately 0.2 to 0.3 is well in line with the reported increasing interception capacity of those tree species (e.g. a literature compilation by Hiege, 1985). The simulated relatively constant transpiration fluxes among the tree species, with median values ranging from 314 $mm.yr^{-1}$ for Pine to 385 $mm.yr^{-1}$ for Spruce stands, is also consistent with literature data. A literature compilation by Roberts (1983) indicates that transpiration fluxes for European forest are in a very narrow range around 335 $mm.yr^{-1}$ due to feedback mechanisms with soil and atmosphere. The simulated evapotranspiration fluxes for the 245 sites were also in the range of data reported in the literature.

The above mentioned results were obtained using interpolated daily data for precipitation, relative humidity, temperature, net radiation and wind speed. A comparison of measured and interpolated meteorological data showed good agreement for relative humidity, reasonable agreement for temperature and net radiation and poor agreement for wind speed. The effect of using interpolated data instead of on-site measured data led to an overestimation of the simulated transpiration fluxes at 80% of the sites. However, at 50% of the sites, the effect is quite limited (deviation < 37 mm). Due to the overestimation of the transpiration fluxes, leaching fluxes tend to be underestimated at 85% of the sites when interpolated meteorological data are used. At 80% of the sites average transpiration fluxes were overestimated when interpolated data were used. The median difference in simulated transpiration fluxes was 45 mm. The observed differences in simulated leaching fluxes were comparable to the differences in transpiration fluxes. The use of interpolated meteorological data instead of local measured data leads to lower element leaching fluxes. The deviation in median leaching fluxes is quite limited and ranges from 15 $mol_c.ha^{-1}.yr^{-1}$ for Al up to 73 $mol_c.ha^{-1}.yr^{-1}$ for base cations.

Element fluxes through the forest ecosystem

Element budgets for sulphur, nitrogen, base cations and aluminium clearly reflected the behaviour of those elements in response of atmospheric deposition. Median values for S leaching were close to the median S deposition. On a considerable number of sites S leaching was, however, higher than S deposition leading to a higher average S leaching than S deposition. Sites with the highest sulphur release are located in central Europe, where the strongest reduction in sulphur deposition has taken place over the last decade. This indicates that these systems are releasing sulphur stored in the soil in previous episodes of higher sulphate input.

In accordance with the available literature, N leaching was generally negligible below throughfall N inputs of 10 $kg.ha^{-1}.yr^{-1}$. At higher inputs N leaching increased, but at most sites (85%) the N input was higher then the N leaching, reflecting N retention in the soil. Sites with a net release of nitrogen were found in areas with a high N deposition over a prolonged period of time such as Belgium and north-western Germany. There was a significant relationship between N leaching and N deposition, but not with the soil C/N ratio, although the C/N ratio appeared to influence the average nitrate concentrations. Furthermore, N leaching was limited at high C/N ratios (>30) in the organic layer. Due to the different behaviour of S and N, the leaching flux of SO_4 was mostly higher than that of NO_3. This indicates that SO_4 is still the dominant source of actual soil acidification despite the generally lower input of S than N.

The median base cation balance was close to zero, implying a net adsorption and a net release of base cation at approximately 50% of the plots. The phenomenon of base cation removal due to man-induced soil acidification is thus limited, specifically since high leaching values were partly due to natural acidification in soils with a high pH and base saturation. The impact of air pollution on base cation removal is, however, clear since the leaching flux of base cations (Ca+Mg+K) increased significantly with an increase in the sulphur (acid) input. The Al leaching flux was also significantly related to the SO_4 input (and leaching) reflected by the fact that sites with a high Al leaching coincide with sites with a high input (leaching) of SO_4. The geographic patterns of both elements did not coincide very well, however, since soil base saturation was also significantly related to the Al leaching flux.

The large ranges in budgets for all the considered elements was to be expected considering the wide geographic range in locations with diverse circumstances with respect to deposition, hydrology and bio-geochemistry. However, there are also considerable uncertainties in the calculated budgets, considering the uncertainties in calculated water fluxes and measured element concentrations in view of spatial variability within a plot. Furthermore, the budgets are based on measurements during a relatively limited number of years. For most sites (58%), budgets were limited to a three-year period (1996-1998) and for 28% of the sites it was even less, while data for a four year period (1995-1998) were available at 14% of the sites. This relatively short time span may lead to over- or underestimation of the budget compared to the long-term situation due to particular hydrological or biological circumstances in specific years. Further improvements of the budgets can be expected when the time period increases. Furthermore, the regression relationships that were found between canopy exchange and environmental factors may be used to improve the existing canopy exchange model. Independent validation of the canopy model can be performed by using dry deposition estimates from the EDACS inferential deposition model (Appendix E). This validated model may subsequently be used for estimating atmospheric deposition on all Intensive Monitoring plots.

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APPENDIX C FIELD INTERCOMPARISON OF BULK DEPOSITION AND THROUGHFALL DATA AT SPEULD AND SCHAGERBRUG

C.1 Aim

Efforts to improve quality assurance and keep it at a high level are necessary to yield credibility in the data sets obtained. In this context, both field and laboratory intercomparisons are crucial (compare Lövblad, 1997; Mosello et al., 1999). Recently, in the Joint Research Centre of the EC (JRC) an important step forward was made, in view of the QA/QC of the laboratories involved. Those comparisons enable researchers to assess the relative importance of the different error sources (sampling methods versus chemical analysis) when measuring atmospheric inputs and soil outputs. It also enables them to select the most accurate analytical methods, sampling equipment, sampling strategy and sample handling, thus leading to further harmonisation in methods. At the same time knowledge transfer among participants is promoted and an assessment can be made on the quality and comparability of the results from the different monitoring sites. Here we report the first results of a field intercomparison related to the assessment of precipitation, throughfall, stemflow fluxes within the framework of the Intensive Monitoring Program (Draaijers et al., 2001).

A field intercomparison of sampling equipment, sampling strategy and sample handling has been set up aiming amongst others at:

- Assessing the quality and comparability of the results of the throughfall, stemflow and precipitation measurements performed within the framework of the Intensive Monitoring Program.
- Identifying throughfall, stemflow and precipitation measurements methods not fulfilling minimal requirements given the needs of and the accuracy needed in the Intensive Monitoring Program.
- Coming up with recommendations for optimal sampling equipment, sampling strategy and sample handling and on quality assurance and quality control procedures necessary concerning throughfall, stemflow and precipitation measurements performed within the framework of the Intensive Monitoring Program.

C.2 Methods

The field intercomparison was conducted at the Speulder forest (throughfall and stemflow) and Schagerbrug (bulk precipitation) research sites, both situated in the Netherlands. The Speulder forest consists of a 2.5 ha homogeneous monoculture of Douglas fir (*Pseudotsuga menziessii*), 40 years old, with a stem density between 785 and 1250 trees.ha^{-1} and a mean tree height of about 25 m. The experiment at Schagerbrug was hosted by the National Institute of Public Health and the Environment (RIVM, Bilthoven) and carried out by TNO Institute of Environmental Sciences, Energy Research and Process Innovation in cooperation with the ECN Netherlands Energy Research Foundation. Members of a Review Group act as external referees to control the quality of the set-up, interpretation and reporting of this study. The countries participating in the Intensive Monitoring Program were invited to install throughfall, stemflow and precipitation equipment at both research sites according to their own experimental protocol regarding sampling strategy (number and siting of the collectors) and sampling equipment. Sampling and chemical analysis were conducted for half a year on basis of the countries own experimental protocol with respect to e.g. sample handling, sampling frequency and frequency of analysis. Experimental protocols were in part described in the so-called Data Accompanying

Report Questionnaires (DAR-Q's), which the participating countries submitted to FIMCI. Additional information was obtained from the participating countries.

Data gathered during the field experiments are evaluated with respect to throughfall, stemflow and precipitation volumes, volume weighted average concentrations and fluxes. The evaluation concentrates on the mandatory parameters Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, alkalinity, N_{total} en pH. Deviations from the mean volume, volume weighted average concentration and flux are investigated in relation to the different technical aspects of the measurements, e.g. (i) sampling equipment (type, material, shape, size), (ii) sampling strategy (number and siting of samplers) and (iii) sample handling (e.g. sample frequencies, sample filtering, sample preservation, cleaning procedures and intervals, frequencies of analysis). To investigate the impact of the sampling frequency, a throughfall sample has been stored in the field and chemically analysed on a weekly basis for one month period. By digital processing of photographs taken of the canopy above each individual throughfall sampler, the crown coverage was assessed to investigate the impact of differences in canopy closure.

C.3 Results

The number of countries that participated in the field intercomparison were 20 for throughfall, 6 for stemflow and 20 for bulk precipitation. The quality and comparability of the results of the different countries was assessed from statistical analysis. In Table C.1, summary statistics for the deviation from the best estimate is presented for 6-month total fluxes of throughfall, stemflow and bulk precipitation, respectively. The best estimate was calculated as the mean flux of countries whose results were within the range of 2 times the standard deviation.

Table C.1 Summary statistics for the deviation from the best estimate for 6-month total fluxes of throughfall, stemflow and bulk precipitation, respectively (in %). are presented as well (after Draaijers et al., 2001).

Statistic	Deviation (%) for throughfall										
	Na	Mg	K	Ca	NH_4^+	Alk.	NO_3^-	SO_4^{2-}	Cl^-	Kj N.	H^+
Mean	11.5	12.9	10.4	13.2	11.4	15.5	10.4	11.1	11.1	10.2	27.4
s.d.	9.1	9.0	6.2	8.9	9.8	13.8	9.2	10.2	8.3	8.4	17.8
Min	0.4	1.8	1.0	0.5	0.5	0.9	1.4	0.3	1.6	0.4	0.7
Max	33.3	35.5	21.2	29.9	36.0	45.8	35.0	36.7	30.8	31.5	73.2

Statistic	Deviation (%) for stemflow										
	Na	Mg	K	Ca	NH_4^+	Alk.	NO_3^-	SO_4^{2-}	Cl^-	Kj N.	H^+
Mean	24.8	31.5	25.5	25.7	21.2	41.5	19.3	25.6	22.3	19.4	30.8
s.d.	12.9	18.6	7.5	15.0	13.0	19.1	15.0	12.9	15.0	13.7	22.8
Min	8.0	1.1	15.9	1.6	7.7	12.8	0.4	4.8	8.2	5.7	2.5
Max	43.7	62.8	37.7	41.8	44.6	64.7	41.0	40.8	44.0	44.5	63.6

Statistic	Deviation (%) for bulk precipitation										
	Na	Mg	K	Ca	NH_4^+	Alk.	NO_3^-	SO_4^{2-}	Cl^-	Kj N.	H^+
mean	25.9	27.9	33.6	25.8	19.5	22.4	16.5	24.0	25.8	19.5	147.7
s.d.	16.2	18.9	26.1	16.4	19.3	17.0	10.0	16.7	14.0	19.2	305.3
min	0.3	0.5	1.0	3.9	0.7	1.9	3.4	2.5	1.5	2.6	42.3
max	66.3	74.6	112.2	80.8	90.6	64.9	36.4	78.7	56.7	80.9	1477.2

For throughfall fluxes, deviations from the best estimate up to 35% occurred, with the exceptions of H^+ and alkalinity with deviations up to 75% and 45%, respectively. The average deviation from the best estimate for the 20 participating countries was between 10 and 15%, depending on component, with the exception of the throughfall flux of H^+ with an average deviation of 25%.

For stemflow fluxes deviations from the best estimate up to 45% occurred, Mg^{2+}, alkalinity and H^+ stemflow fluxes being the exceptions with deviations up to 65%. The average deviation from the best estimate for the 6 participating countries was between 20 and 30%, depending on component and alkalinity being the exception (average deviation of 40%).

For bulk precipitation fluxes deviations from the best estimate up to 90% occurred, K^+ and H^+ bulk precipitation fluxes being the exceptions with deviations up to 110% and 1500%, respectively. The extremely large deviations found for H^+ are caused by very small fluxes. As a consequence, small absolute deviations result in large relative deviations. The average deviation from the best estimate for the 20 participating countries was between 15 and 35%, depending on component and H^+ being the exception (average deviation of 150%).

More information on the results of the field inter-comparison project executed at the Speulder forest and Schagerbrug can be found in Draaijers et al. (2001).

C.4 Evaluation

Throughfall

Representativity of measurements
From the Field intercomparison project at the Speulder forest it became clear that the number of collectors (funnels) recommended in the Manual of ICP Forest (10-15) is generally too small to reach an accuracy of 10%. To reach the required accuracy forest for all components a minimum number of about 25 funnels would have been necessary at the Speulder forest. Performing a pre-study to determine the number of funnels (or gutters) necessary is recommended. The number of collectors necessary will depend on the homogeneity of the forest stand.

The Manual of ICP Forests (UN/ECE, 1998) recommends using at least 10-15 funnels with a diameter of 20 cm for collecting throughfall. This means that the total collecting area should exceed 3140cm^2. For only 35% of countries participating in the field inter-comparison the total collecting area was found to exceed this value. For 20% of the countries the total collecting area not even exceeded half of the recommended value. From the field inter-comparison it was concluded that a total collecting area less than 2000 cm^2 significantly reduces the accuracy of the throughfall measurements

Throughfall collectors should be placed in such a way that a large number of canopies are covered and results are representative for the forest plot. 75% of the countries fulfilled this requirement. When gutters are used instead of funnels, these gutters generally only cover a limited number of tree canopies.

Determination of volumes
It has been found relatively difficult to estimate throughfall volumes accurately. When averaging the deviations from all countries, the mean deviation from the best throughfall volume estimate equalled 8%, the largest deviation 23%. 35% of the countries were able to estimate throughfall volumes within 5% of the best estimate. Apart from the representativity of the measurements, deviations could be explained by a number of other parameters. Important parameters included the collecting area of the funnels deviating from those reported and used in the flux calculations, and the collector height above the ground surface, influencing wind flow around the funnels. Sometimes there was a relatively loose connection between the funnel and storage container, allowing water to run down on the outside of the collector directly into the storage container. Reduced filter drainage and long tubes containing dips sometimes postponed and/or prevented through-flow and/or induced wetting loss.

Determination of concentrations
It also has been found quit difficult to estimate throughfall concentrations accurately. Deviations from the best estimate for volume-weighted mean throughfall concentrations were found dependent on component and country. When averaging the deviations from all countries, the mean deviation ranged between 8% (K^+) and 21% (H^+). Maximum deviations ranged between 21% (Cl^-) and 61% (H^+). When averaging the deviations from all components, the mean

deviation ranged between 6% and 22%. Apart by non-representative sampling, deviations could be explained by the efficiency of the collectors to collect dry deposition (dependent on their height above the ground surface and the aerodynamic properties of the funnel), by algae present in tubes or litter present in the samples causing biochemical transformation, by restricted cleaning frequencies and/or by the chemical interactions with the collector material.

Stemflow

Representativity of measurements
From the field inter-comparison project it was concluded that the number of stemflow collectors recommended in the Manual of ICP Forest (5-10) is too small to reach the required accuracy of 10%, even at a homogeneous forest stand like the Speulder forest. Most countries measure stemflow at less than 5 trees. Trees should be carefully selected to assure representative stemflow sampling within the forest plot. In a single species forest stand it is recommended to select trees on basis of information on diameter at breast height or tree height. A limited number of countries do not select their trees on these selection criteria.

Determination of volumes
It has been found relatively difficult to estimate stemflow volumes accurately. When averaging the deviations from all countries participating in the stemflow field inter-comparison, the mean deviation from the best stemflow volume estimate equalled 23%, with a maximum deviation of 50%. Apart from non-representative sampling, inaccurate stemflow volume determination results from leakage as a result of inadequate attachment of the spoiral cord to the bark. Other explanations include the small capacity of the spiral cords and/or storage containers inducing overflow.

Determination of concentrations
It also has been found quit difficult to estimate stemflow concentrations accurately. Deviations from the best estimate for volume-weighted mean stemflow concentrations were found dependent on component and country. When averaging the deviations from all countries, the mean deviation ranged between 13% (NO_3^-) and 52% (H^+). Maximum deviations ranged between 19% (Kjehldall-N) and 136% (H^+). When averaging the deviations from all components, the mean deviation ranged between 15% and 44%. Deviations could usually be explained by a number of parameters. Apart from non-representative sampling, important parameters explaining deviations from the best estimate included planing of the bark surface (inducing bark leaching), the restricted cleaning frequency, the absence of a filter system, and chemical interactions with the sampler material.

Bulk precipitation

Representativity of measurements
From the field inter-comparison project it was concluded that the minimum number of bulk precipitation collectors (funnels) recommended in the Manual of ICP Forests (2) is to small to reach the required accuracy of 10% at Schagerbrug for all components. The number of bulk collectors required will be site-specific and will mainly depend on the relative amount of dry deposition onto the collectors.

The Manual of ICP Forests recommends using at least 2 funnels with a diameter of 20cm. This means that the total collecting area should exceed 680cm^2. For 70% of the countries participating in the field inter-comparison, the total collecting area was found not to exceed this minimum value. For 30% of the countries the total collecting area not even exceeded half of the recommended value. Several studies have indicated that the collecting area had actually only a minor influence on the precision of rainfall quantification (Thimonier et al., 1998). In the field-intercomparison, however, samplers with lower collection areas tended to collect higher precipitation amounts. This might be related to the specific weather situation during the field inter-comparison. Regularly showers with high winds frequently occurred. With such conditions a vacuum is formed in funnels. This vacuum is expected to be lower for small collectors, leading to better collection than larger samplers.

Determination of volumes
It has been found relatively difficult to estimate precipitation volumes accurately. The deviation for precipitation volumes compared to the best estimate ranges from +103% to -27%. Deviations result from rainwater flowing directly into the storage container, aerodynamic blockage related to the height of the collector and its aerodynamic properties of the collector, and/or differences between actual and reported collecting areas.

Determination of concentrations
It has been found difficult to estimate precipitation concentrations accurately because of the relatively large impact of dry deposition onto the collectors, strongly varying with funnel characteristics. Nitrogen components, alkalinity, K^+ and H^+ were found sensitive to biological conversion, which may happen when no conservatives are added and the sample stays in the field long than 2 weeks. In general deviations from the best estimate were found largest for alkalinity, Kjehldall-N, H^+ and K^+, followed by Ca^{2+}, Mg^{2+}, Na^+ and Cl^-. Deviations were found lowest for SO_4^{2-}, NH_4^+ and NO_3^-.

A more extensive evaluation of the results of the field inter-comparison performed at the Speulder forest and Schagerbrug can be found in Draaijers et al. (2001).

APPENDIX D THE USE OF CANOPY EXCHANGE OF WEAK ACIDS IN THE CALCULATION OF TOTAL DEPOSITION OF AMMONIUM AND ACIDITY

D.1 Introduction

One of the aims of the Bal-N-s project is to assess site-specific atmospheric deposition for selected Intensive Monitoring plots (level II) based on measurements of throughfall and bulk deposition. To estimate atmospheric deposition, the canopy exchange model developed by Ulrich (1983), improved and extended by Bredemeier (1988), Van der Maas et al. (1991) and by Draaijers and Erisman (1995). In the canopy budget model, annual total deposition is estimated by correcting the input by both throughfall and stemflow for exchange processes, occurring at the forest canopy. At plots where stemflow data are missing, the annual stemflow is estimated from the annual throughfall according to Ivens (1990).

The major assumptions of the extended canopy budget model are as follows:
- Canopy exchange of SO_4^{2-} and NO_3^- is assumed negligible.
- Total deposition of the base cations Ca, Mg and K is calculated by multiplying the bulk deposition of those cations with the ratio of the sodium input by both throughfall and stemflow to the sodium input in bulk deposition. Canopy exchange (leaching) is then computed by the difference between the sum of BC in throughfall and stemflow minus total deposition. This approach is based on the assumption that (i) Na does not interact with the forest canopy (tracer) and (ii) the ratios of total deposition over bulk deposition are similar for Ca, Mg, K and Na.
- Total canopy uptake of NH_4^+ and H^+ is assumed to be equal to the total canopy leaching of Ca^{2+}, Mg^{2+} and K^+ taking place through ion exchange, while subtracting the leaching of weak acids. In allocating the uptake of H^+ and NH_4^+, it is assumed that H^+ has per mol an exchange capacity six times larger than NH_4^+ (Van der Maas et al., 1991) (xH = 6).
- The dry total deposition of weak acids is assumed to equal the bulk deposition (total deposition equals twice the bulk deposition). The leaching of weak acids is calculated by subtracting the total deposition from the measured throughfall and stemflow.

The inclusion of weak acid leaching also requires an estimate of the concentration of weak acids (WA) in both bulk deposition and throughfall, since the concentration of bicarbonate and organic acids is not measured directly. The estimation of the weak acid concentration can be based on either (i) alkalinity, (ii) the sum of HCO_3, derived from the pH and an assumed atmospheric CO_2 pressure, and $RCOO^-$ derived from DOC or (iii) the difference in concentration of cations minus strong acid anions. A comparison of those estimates is needed to get an impression of the accuracy of the estimated WA concentration. If such estimates differ widely, it is not likely that the inclusion of weak acid leaching improves the assessment of the uptake of NH_4^+ and H^+, also considering the uncertain assumption that bulk and dry deposition of weak acids are equal. The aim of this paper is to critically review the assumption that weak acid leaching needs to be included to adequately assess the uptake of NH_4^+ and H^+.

Mathematical formulation of the canopy budget model including and excluding weak acid leaching

Model including weak acid leaching

In mathematical terms the exchange (leaching) of base cations and weak acids and the related uptake of NH_4^+ and H^+ is formulated as:

$$BC_{td} = \frac{Na_{tf} + Na_{sf}}{Na_{bd}} \cdot BC_{bd} \tag{D.1}$$

$$NH_{4,td} = NH_{4,tf} + NH_{4,sf} + NH_{4,ce} \tag{D.2}$$

with:

$$NH_{4,ce} = \left(\frac{NH_{4,bd}}{NH_{4,bd} + H_{bd} \cdot xH} \right) \cdot (BC_{ce} - WA_{ce}) \tag{D.3}$$

$$BC_{ce} = BC_{tf} + BC_{sf} - BC_{td} \tag{D.4}$$

$$WA_{ce} = WA_{sf} + WA_{sf} - 2WA_{bd} \tag{D.5}$$

$$H_{td} = H_{tf} + H_{sf} + H_{ce} \tag{D.6}$$

with:

$$H_{ce} = BC_{ce} - WA_{ce} - NH_{4,ce} \tag{D.7}$$

where:

WA = weak acids
BC = Ca, Mg, K
td = total deposition ($mol_c.ha^{-1}.yr^{-1}$)
bd = bulk deposition ($mol_c.ha^{-1}.yr^{-1}$)
ce = canopy exchange ($mol_c.ha^{-1}.yr^{-1}$)
xH = an efficiency factor of H in comparison to NH_4 (xH = 6)

Model excluding weak acid leaching

In the model excluding weak acid leaching, Wa_{ce} is set to 0 (Eq A4.3 is not included) and the Eqs. D.3 and D.7 related to the uptake of NH_4^+ and H^+ thus change to

$$NH_{4,ce} = \left(\frac{NH_{4,tf}}{NH_{4,tf} + H_{tf} \cdot xH} \right) \cdot BC_{ce} \tag{D.8}$$

$$H_{ce} = BC_{ce} - NH_{4,ce} \tag{D.9}$$

In the situation where weak acid exchange is negative (leaching is positive, so the throughfall and stemflow is larger than the estimated total deposition), the estimated uptake of NH_4^+ and H^+ decreases when neglecting this process (compare Eq. D.3 and D.8). The reverse is true when weak acid exchange is positive, implying that weak acids are taken up by the forest canopy, together with e.g. protons (a situation that is unlikely to occur)

D.2 Estimation of the weak acid concentration

The estimation of the weak acid concentration was derived with three independent estimates. In the first approach, the WA concentration is estimated from the sum of HCO_3, derived from the pH and an assumed atmospheric CO_2 pressure, and RCOO- derived from DOC according to (Oliver et al., 1983):

$$WA = HCO_3 + RCOO \tag{D.10}$$

with:

$$HCO_3 = \frac{K_{CO_2} \cdot pCO_2}{H} \tag{D.11}$$

$$RCOO = m \cdot DOC \cdot \frac{K_a}{K_a + H} \tag{D.12}$$

The constant K_a was estimated according to (Oliver et al., 1983):

$$pK_a = a + b \cdot pH - c \cdot pH^2 \tag{D.13}$$

where:

K_{CO2}	= Dissociation constant of CO_2, being the product of Henry's law constant for the equilibrium between CO_2 in soil and air and the first dissociation constant of H_2CO_3 ($mol^2.l^{-2}.bar^{-1}$)
pCO_2	= Partial CO_2 pressure in the soil (bar)
DOC	= Dissolved organic carbon concentration ($mg.l^{-1}$)
m	= Concentration of acidic functional groups on dissolved organic carbon ($mol_c.kg^{-1}$)
K_a	= Dissociation constant for organic acid ($mol.l^{-1}$)
H	= Proton concentration ($mol.l^{-1}$)

For pK_{CO2}, a value of 7.8 was used, the partial CO_2 pressure was set at 0.3 mbar (0.0003 bar) and the value of m was set at 5.5 $mol_c.kg^{-1}$ or 0.0055 $mmol_c.mg^{-1}$. Values of a, b and c have been derived by calibrating the pKa value on soil chemistry data (e.g. Van Wesemael and Verstaten, 1993) and surface water chemistry data (e.g. Oliver et al., 1983; Driscoll et al., 1989). In this calculation, we used the values by Oliver et al. (1983) for both deposition and soil solution data (a = 0.96, b = 0.90 and c = 0.039). A comparison of results using values derived by Van Wesemael and Verstaten (1993) or Driscoll et al. (1989) shows a deviation of 5-25%, depending upon the pH (De Vries and Bakker, 1998).

In the second approach, the WA concentration was calculated from the measured alkalinity, while correcting for the pH according to:

$$WA = Alk + H - OH \tag{D.14}$$

since alkalinity can be defined as:

$$Alk = HCO_3 + RCOO + OH - H \tag{D.15}$$

In the third approach, the WA concentration was calculated from the difference in concentration of cations minus strong acid anions according to:

$$WA = \sum cat - \sum an \quad (D.16)$$

with:

$$\sum cat = [Ca^{++}] + [Mg^{++}] + [Na^{+}] + [K^{+}] + [H^{+}] + [NH_4^{+}] \quad (D.17)$$

$$\sum an = [SO_4^{--}] + [NO_3^{-}] + [Cl^{-}] \quad (D.18)$$

The comparison between the three estimates was made for the plots where data on major cations and anions (needed in the third approach), alkalinity (second approach) and DOC (first approach) were all available. Those plots were located in Finland, Germany and the Czech Republic only. The problem with the last approach (which is generally used to estimate weak acids) is that it requires a good quality of the assessment of all major cations and anions. This approach may even lead to negative WA concentrations in case of either an overestimate of the major anions and/or an underestimate of the major cations. The estimates rely on the accuracy of the concentrations of all major and cations and anions, thus giving easily rise to large uncertainties. We thus also made a comparison in which we required that the difference between the sum of all the major cations and anions was less than 20% (limited to plots in Finland and Germany). Furthermore, in both cases we put negative concentrations to zero.

D.3 Results

Estimated concentrations of weak acids according to the three methods

Results of the estimated WA concentration in bulk deposition and throughfall according to the three methods show that the estimate based on the alkalinity measurement generally strongly deviates from the two other assessments (Figure D.1).

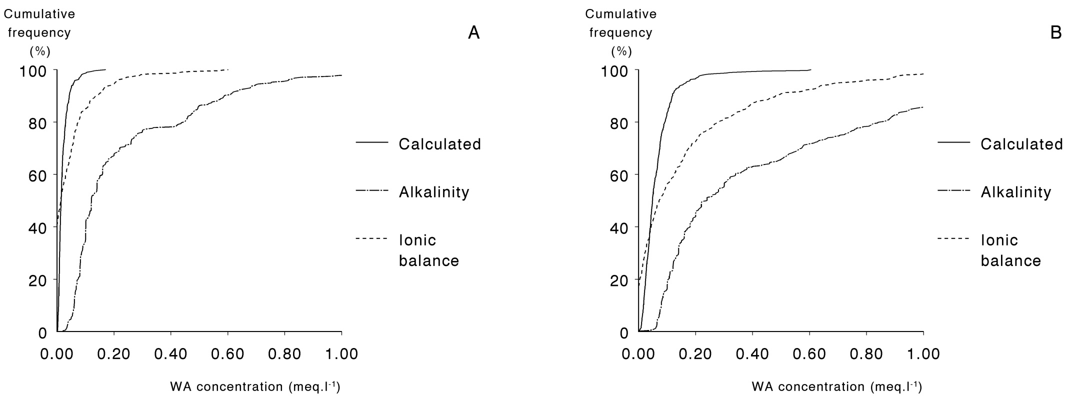

Figure D.1 Estimated weak acid concentrations in bulk deposition (A) and throughfall (B) with three independent methods using all available data.

Without a quality check on the ionic balance data, the calculated alkalinity from pH and DOC is usually lower than the estimate based on the charge balance, both in bulk deposition and in throughfall. The difference is, however, small when allowing a relative difference of 20% in the charge balance only (Fig. D.2). This requirement, however, hardly affected the percentage of plots where the estimated WA concentration is negative, being approximately 45% in case of bulk deposition and 20% in case of throughfall (Compare Fig. D.1 and Fig. D.2).

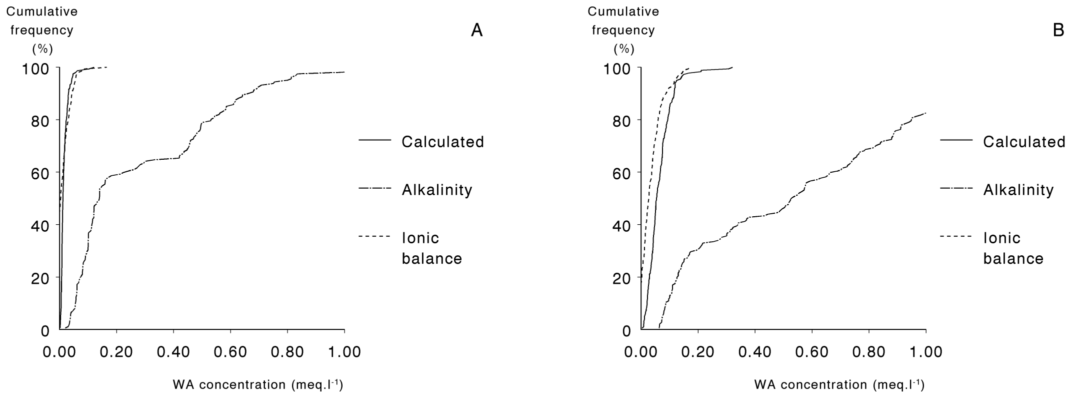

Figure D.2 Estimated weak acid concentrations in bulk deposition (A) and throughfall (B) with three independent methods using only those data where the relative difference between the sum of cations and the sum of anions is less than 20%.

Considering the large deviation between the alkalinity assessment and the other two estimates, we considered the alkalinity measurement unreliable for the calculation of the weak acid exchange fluxes. A direct application of the ionic charge balance approach was also considered inadequate, due to the large percentage of plots with calculated negative (and thus zero) weak acid concentrations. Therefore, we further used a mixed approach in which the weak acid concentration was the maximum of a bicarbonate estimate based on the pH (according to Eq. D.11) and the ionic balance (according to Eq. D.16- D.18). Using this mixed approach, weak acid concentrations are never zero, although it can be low at sites where the pH is high (low HCO_3 concentration) and the charge balance is negative, since the RCOO concentration is assumed negligible in those situations. In the further comparison we thus focus on the calculation approach, which seems most adequate considering data quality and the mixed approach, which can also be applied when no DOC data are available, being the case at many plots.

Concentrations and fluxes of weak acids in bulk deposition and throughfall using the calculation method and the charge balance method

The parameters determining the estimated weak acid concentration according to the first assessment are the pH and the DOC concentration. Insight in the values of those parameters and the HCO_3 and RCOO concentration thus derived is given in Figure D.3. Results show that the pH and DOC concentration generally increases in throughfall compared to bulk deposition (Fig. D.3A,B), thus leading to higher concentrations of bicarbonate and HCO_3 and RCOO (Fig. D.3C,D). The higher pH indicates the occurrence of acid buffering in the forest canopy, that might be due to uptake of H in exchange to base cations (or by release of CO_2 causing a decrease of the bicarbonate flux). The higher DOC and RCOO concentrations might indicate the release of organic anions from the canopy, but this may also be due to dry deposition of those compounds.

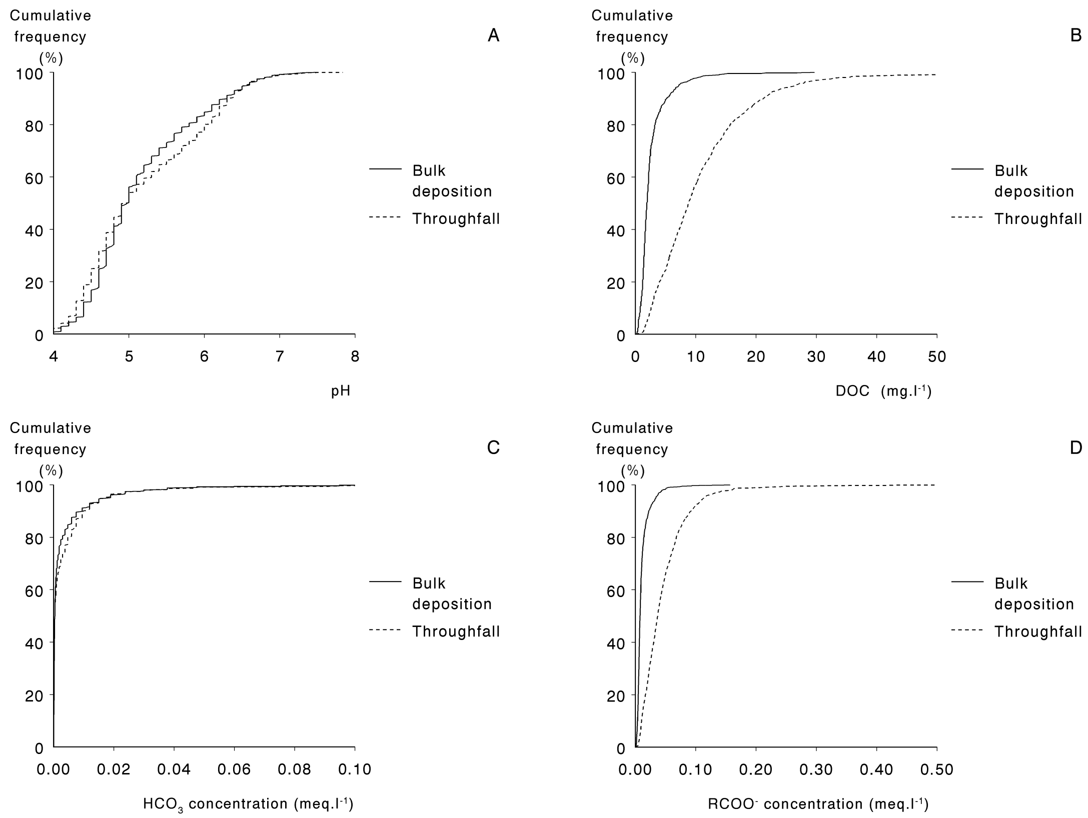

Figure D.3 *Values for the pH (A) and concentrations of DOC (B), HCO_3 (C) and RCOO (D) in bulk deposition and throughfall.*

The estimated WA concentration is also higher in throughfall than in bulk deposition, when using the calculation approach, as it reflects the concentration behaviour of bicarbonate and organic anions (Fig. D.4A). Concentrations above 0.05 $mmol_c.l^{-1}$ are mainly due to high DOC values, specifically in throughfall, since HCO_3 concentrations hardly exceed this value considering the low CO_2 pressure of the atmosphere. Using the mixed (calculation and charge balance) approach, the concentrations in throughfall are also consistently higher in throughfall than in bulk deposition (Fig. D.4B).

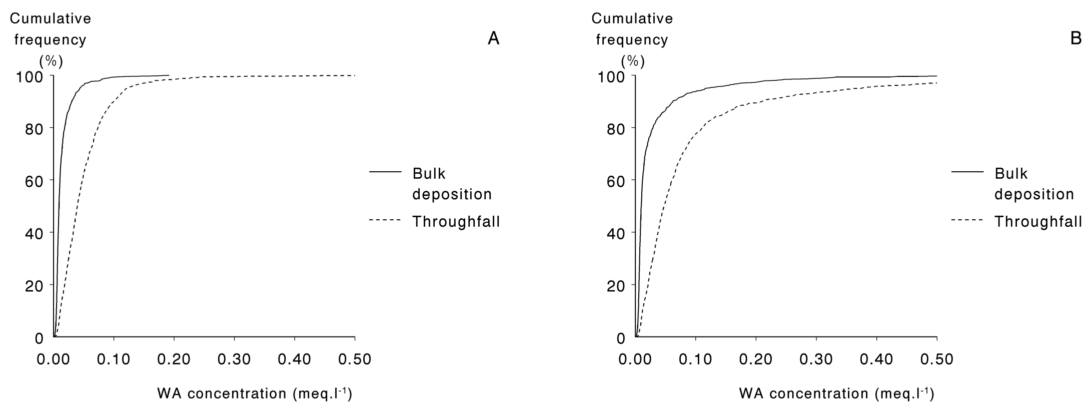

Figure D.4 *Estimated WA concentrations using the calculation approach (A) and the mixed approach (B) in bulk deposition and throughfall.*

The difference in the two estimates is further illustrated in Fig. D.5, where the annual weak acid flux in throughfall is plotted against the annual weak acid flux in bulk deposition.

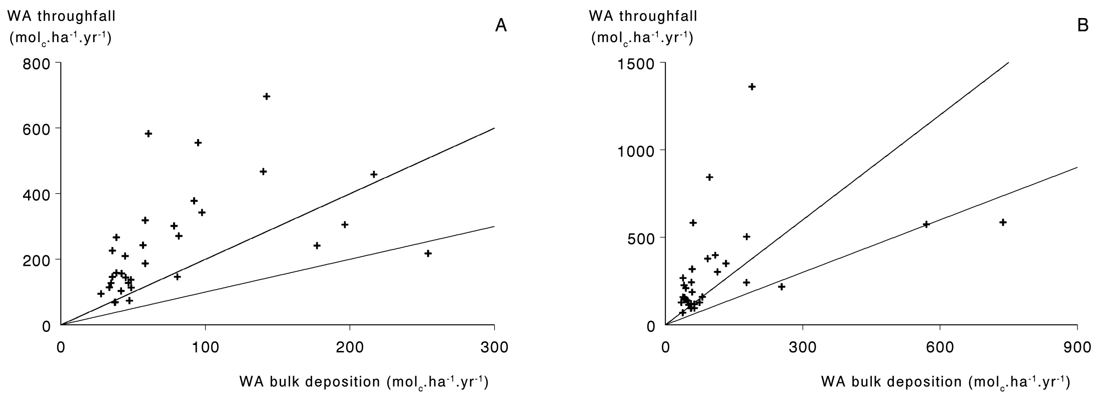

Figure D.5 Relationships between estimated annual WA fluxes in bulk deposition and throughfall using the calculation approach (A) and the mixed approach (B).

Using the calculation approach, in nearly all cases (one exception) the throughfall flux is larger than the bulk deposition flux. At most plots, it is even larger than twice the bulk deposition flux, indicating weak acid leaching, since we assume that bulk and dry deposition of weak acids are comparable (Fig. D.5A). Using the mixed approach, a similar conclusion holds (Fig. D.5B). The plots do show directly the sensitivity of the assumption that bulk and dry deposition are equal with respect to the estimation of weak acid leaching or weak acid " uptake".

Calculated canopy exchange fluxes using the calculation method and the charge balance method

The ranges in weak acid exchange fluxes based on the calculation approach and the mixed method are shown in Fig. D.6. The figure also includes information about the range in calculated fluxes in throughfall plus stemflow below the forest canopy and the total deposition above the forest canopy (estimated as twice the bulk deposition).

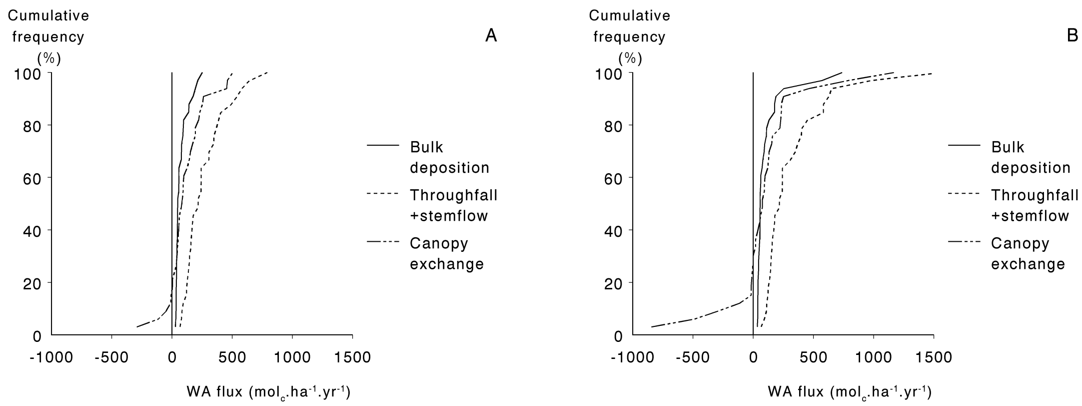

Figure D.6 Estimated annual WA fluxes in total deposition, throughfall and stemflow and canopy exchange, using the calculation approach (A) and the mixed approach (B).

Results show a large range in exchange fluxes, ranging from highly positive values (indicating canopy leaching of weak acids, what is expected) to negative values indicating weak acid adsorption/uptake, which is unlikely to occur. In the latter case the calculated uptake of NH_4^+ and H^+ will increase compared to a calculation excluding the weak acid exchange. Negative weak acid leaching (uptake) fluxes occur in less than 20% of the plots in both procedures, but the negative values become higher in the mixed approach compared to the calculation approach.

Results illustrating the difference in calculated uptake of NH_4^+ and H^+ for the different methods are illustrated in Table D.1. It also includes results of the charge balance approach only putting negative values to zero. The results show that on average both the NH_4^+ and H^+ uptake will decrease when including canopy exchange (in line with the average positive value for canopy leaching), but effects are largest for protons. Differences are small between the calculation approach and the mixed method indicating that this approach is a reasonable alternative when no DOC data are available. Even when neglecting the weak acid exchange, negative uptake fluxes for ammonium and protons are calculated, being due to estimated negative base cation leaching fluxes (Table D.1). On average the proton adsorption is higher than the ammonium uptake, due to the preference factor of H compared to NH_4 of 6.

Table D.1 Ranges in calculated exchange fluxes of base cations, weak acids, ammonium and protons using various approaches.

Type of exchange Flux	Method	Exchange flux ($mol_c.ha^{-1}.yr^{-1}$) mean	Min	5%	50%	95%	max
Base cation leaching	Sodium	256	-524	-87	131	996	1164
Weak acid leaching	Calculated	114	-290	-103	86	461	506
	Charge balance	6	-1071	-423	-2	519	1168
	Mixed approach	95	-844	-458	78	738	1168
Ammonium uptake	Calculated	51	-526	-107	2	363	576
	Charge balance	89	-14	-3	20	453	491
	Mixed approach	65	-90	-35	7	366	487
	Without WA	90	-471	-14	20	465	1019
Proton uptake	Calculated	91	-89	-83	21	445	590
	Charge balance	161	-72	1	94	459	760
	Mixed approach	95	-85	-68	40	423	590
	Without WA	166	-79	-51	76	585	760

D.4 Conclusions

This analyses leads to the following conclusions:
- Considering the large deviation between the alkalinity assessment and independent estimates based on pH and DOC measurements and a charge balance, the alkalinity measurement seems unreliable for the calculation of the weak acid exchange fluxes.
- Considering the calculation of negative weak acid concentrations in both bulk deposition and throughfall, the charge balance approach seems also unreliable for the calculation of the weak acid exchange fluxes, unless a severe quality control is carried out.
- The calculation approach based on pH and DOC measurements seems most reliable. When no DOC data are available, a mixed approach including the calculation of bicarbonate based on pH and of DOC based on the charge balance seems quite comparable to the calculation approach.
- The assumption that total deposition equals twice the bulk deposition may be questioned considering the occurrence of positive weak acid exchange fluxes at approximately 20% of the plots. This fact can only be explained by CO_2 release from the forest canopy, but the impact of this process is likely to be low.

Considering the results given above, it is suggested to:
- Further evaluate the assumption that total deposition equals twice the bulk deposition and that the preference factor of H compared to NH_4 of 6.
- Compare ammonium and proton adsorption while including and neglecting weak acid exchange and put attention to sites where weak acid adsorption is calculated.

APPENDIX E COMPARISON OF MODELLED DEPOSITION ESTIMATES WITH THROUGHFALL DATA AT 223 INTENSIVE MONITORING PLOTS

E.1 Introduction

Currently throughfall measurements are made at about 300 Intensive Monitoring plots to estimate the site specific inputs of nutrients. Deposition is site specific, determined by factors such as tree species, crown density, homogeneity of the stand, stand density, distance to the nearest edge, climate, environmental factors and vitality of the stand. Measurements are expensive and do not provide a direct link to emissions, which is necessary to develop and evaluate policies to abate pollution and forest damage. Therefore, there is a need for a tool to upscale results to sites where no measurements are available. The first tool to calculate site specific deposition fluxes, EDACS (European Deposition of Acidifying Components on a small Scale) was developed at RIVM (Erisman and Draaijers, 1995). The results of this model were used in the 10 years overview report to estimate deposition for Level I plots as described in Van Leeuwen et al. (2000). This model is now re-programmed and improved by ECN and meteorological input is updated, based on data from the European Centre for Meteorology and Weather Forecast (ECMWF). Concentrations of gases and aerosols are derived from the EMEP model. In this Appendix a short model description will be given and model results are compared with throughfall measurements at the Intensive Monitoring plots. Model results can also be used to estimate canopy exchange, assuming that the total deposition values are correct. The plausibility of the results are thus reviewed in the last section.

E.2 Description of the EDACS model

The basics of the EDACS model can be found in Erisman and Draaijers (1995), Van Pul et al. (1994) and Van Leeuwen et al. (2000). The basis for the total deposition estimates is formed by results of the EMEP long-range transport model. With this model dry, wet and total deposition is estimated on a 150x150 km grid over Europe using emission maps for SO_2, NO_x and NH_3. The model results are used for estimating country-to-country budgets, as a basis of sulphur and nitrogen protocols, and for assessments. Calculated ambient concentrations of the acidifying components in 150x150 km grids by EMEP are multiplied with dry deposition velocity fields over Europe that are constructed with EDACS using a detailed land use map and meteorological observations to estimate small-scale dry deposition fluxes (Figure E.1). The model input and output is flexible and depends on the land use information that is used. Currently land use maps for Europe (1/6 x 1/6^o), for Germany on a 1 x 1 km^2 scale are available. This allows total deposition estimates on the European scale for 10 x 20km cells. In this approach we made a site specific calculation using site specific information available for the Intensive Monitoring plots. Every 6 hours the ECMWF meteorological data is used to calculate a deposition velocity for each grid or each plot. The deposition velocity is combined with a concentration obtained from calculations with the EMEP model to estimate the flux. An annual flux is the summation of all 6 hour values. The dry deposition flux is calculated as the product of the dry deposition velocity and air concentration at a reference height above the surface. In the inferential technique, the choice for a reference height (50 m) is a compromise between the height where the concentration is not severely affected by local deposition or emission and is still within the constant flux layer (Erisman, 1993). The parameterisation of the dry deposition velocity for particles was based on Erisman et al. (1994).

By using calculated concentration maps, the relationship between emissions and deposition is maintained and scenario studies, budget studies and assessments can be carried out on different scales. Wet deposition is added to the dry deposition to estimate total local scale deposition in

Europe. Wet deposition can either be obtained directly from the EMEP model, or from measurements made in Europe.

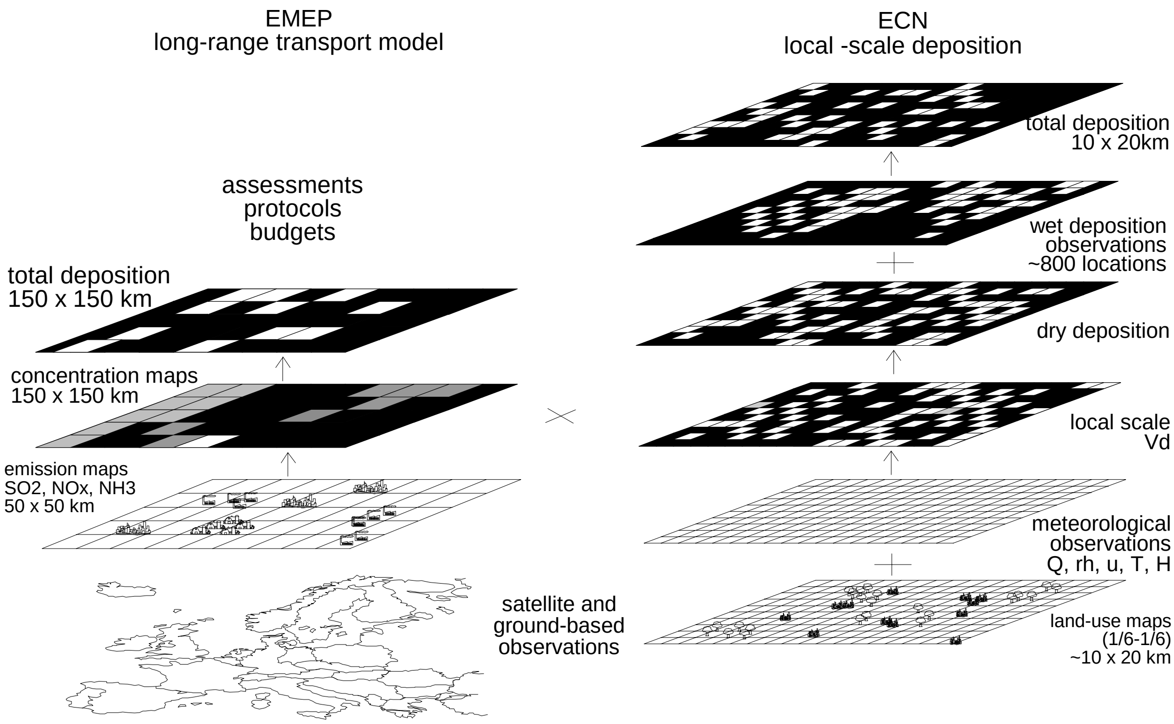

Figure E.1. Outline of method to estimate local scale deposition fluxes.

E.3 Comparison of model results with throughfall measurements

The EMEP model results are only available until 1996. Since then, a new model was developed and is still not operational. The comparison of model results with throughfall data has therefore been made for 1996 (223 plots). Figure E.2 shows the model comparison with throughfall measurements at the plots. The correlation for sulphur is small (Fig. E.2A). This is especially due to an overestimation of sulphur deposition at a few sites. These sites are all located close to or in the Black triangle. It appears that the EMEP model overestimates SO_2 concentrations in these areas. On average the modelled S deposition and measured throughfall are comparable, however, indicating the nearly negligible influence of canopy uptake of sulphur. A best regression estimate was

$$SO_{4,model} = 530 + 0.63 \cdot SO_{4,throughfall} \qquad R^2_{adj} = 0.32 \qquad (E.1)$$

The N deposition, both of NO_3 and NH_4 are considerably larger than the measured throughfall, although the correlation is larger than for SO_4 (Fig. A5.2B, C, D). Specifically the reduced N deposition is higher up to a factor of two, despite the high correlation. Best regression estimate were:

$$NO_{3,model} = 540 + 0.75 \cdot NO_{3,throughfall} \qquad R^2_{adj} = 0.37 \qquad (E.2)$$

$$NH_{4,model} = 610 + 1.54 \cdot NH_{4,throughfall} \qquad R^2_{adj} = 0.64 \qquad (E.3)$$

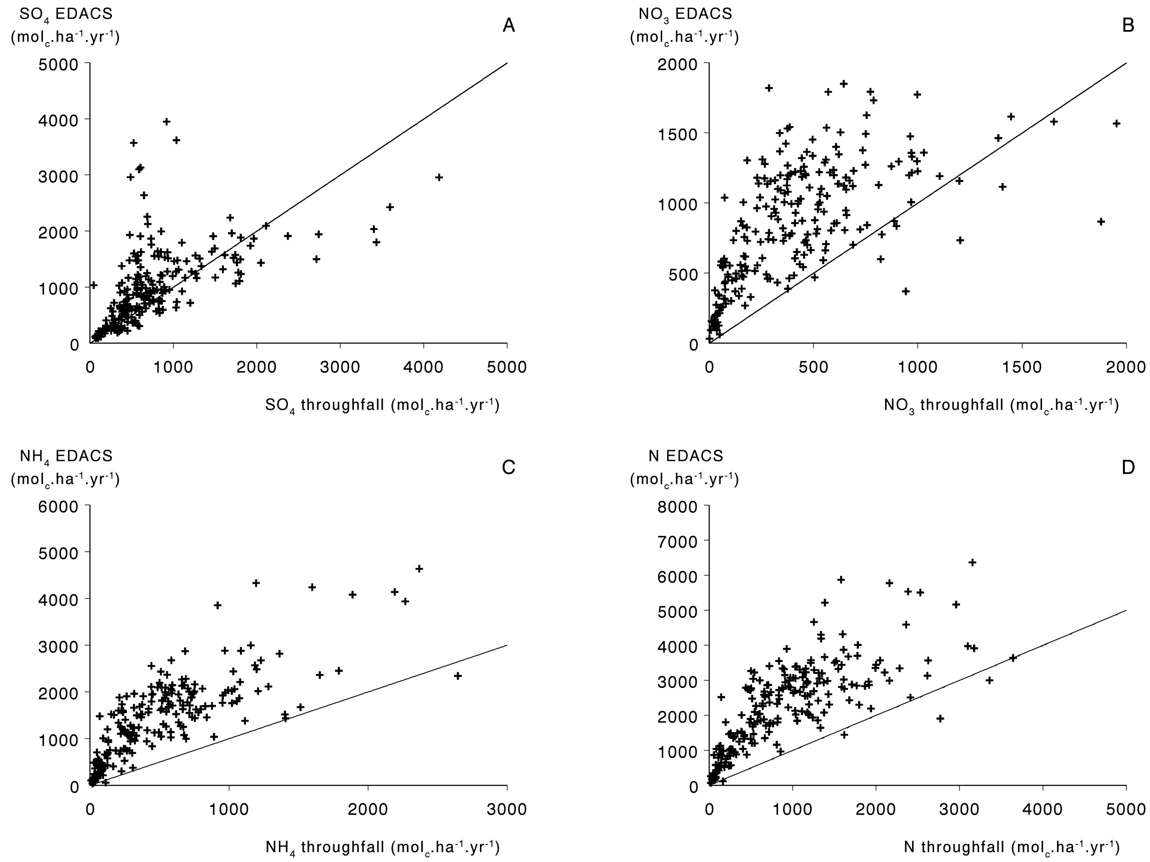

Figure E.2 Comparison of total deposition calculated with EDACS with throughfall measurements of SO_4 (A), NO_3 (B), NH_4 (C) and total N (D).

The throughfall data are not corrected for canopy exchange. Assuming that total deposition model estimates are correct, canopy exchange can be estimated by subtracting throughfall measurements from the model estimates. This estimate also includes input by stemflow. Results for canopy exchange thus obtained for NH_4 and NO_3 as a function of the input by throughfall are given in Figure E.3. Results show a decrease in claculated canopy uptake for NO_3 with increasing NO_3 input by throughfall (Fig. E.3A). Considering the fact that NO_3 exchange in the canopy is low, this result indicates a tendency to overestimate NO_3 deposition at low throughfall inputs and underestimate NO_3 deposition at high throughfall inputs. As expected, NH_4 exchange is nearly always positive, but at a large number of plots the exchange exeeds 800 $mol_c.ha^{-1}.yr^{-1}$ which is generally considered a maximum. This implies that NH_4 deposition seems to be overestimated at a large number of plots.

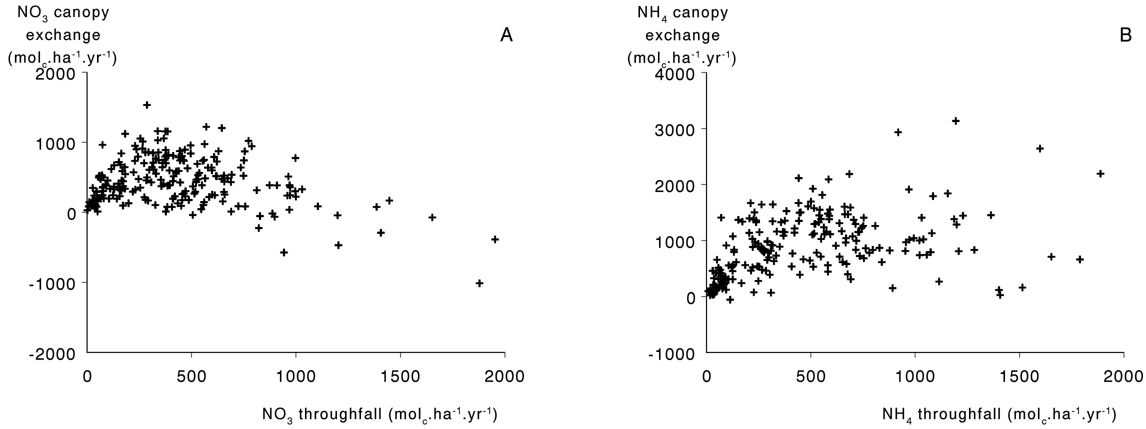

Figure E.3 *Comparison of canopy exchange calculated with from EDACS results and throughfall measurements as a function of throughfall for NO_3 (A) and NH_4 (B).*

These preliminary results show the potential for the EDACS model to be used for upscaling. There is, however, a need to improve the results. The most important improvement is the use of concentration data at a smaller grid. These will be available from the new EMEP model. Furthermore, tests with the Dutch LOTOS model and with the DEM model from Denmark will be done. Both models calculate concentrations at a much smaller scale. Finally, the deposition velocity parameterisation used in the model can be improved using micrometeorological measurements, which are made in several countries.

APPENDIX F RELATIONSHIPS BETWEEN SOIL NITRATE CONCENTRATIONS AND ENVIRONMENTAL FACTORS

F.1 Introduction

Increased nitrogen (N) deposition to forests may gradually change a range of N cycling processes and lead to nitrogen saturation of the ecosystem, i.e. elevated nitrate leaching will occur (Aber et al., 1995). Compilations of input-output budgets from European forests have shown that a major part of the investigated sites that received more than 10 kg $N.ha^{-1}.yr^{-1}$ in throughfall are leaching >5 kg $N.ha^{-1}.yr^{-1}$ (Dise and Wright, 1995; Gundersen, 1995). However, the relationships between input and output of nitrogen were rather weak. This variability in forest ecosystem response to N inputs was further studied in data compilations on element cycling and ecosystem characteristics from published European studies in plots and catchments (n=139) from 1970 to 1995 (Dise et al., 1998a, b) or in plots alone (n=80) in a more narrow time span 1985-95 (Gundersen et al., 1998a). Incomplete data sets hampered a thorough statistical analysis of all the parameters considered. Nevertheless, these data sets revealed relationships between N deposition, N concentrations in foliage, some ecosystem characteristics and leaching of nitrate. The regression model that explained most of the variability in nitrate leaching included both N input and C/N ratio of the forest floor, but this was based on only 30-40 sites with a strong bias towards the coniferous forests. Differences in methodology, as well as in temporal and spatial scales may contribute an unknown error in detecting relationships in these databases.

With the growing database from the Intensive Monitoring programme some of the drawbacks of the literature compilations can be avoided. However, in plot studies leaching fluxes can only be obtained by construction of a detailed water balance for each forest site (Appendix A). This is resource demanding for data collection and the calculations may add a considerable amount of error to the estimated fluxes. This may be a reason for the relative poor correlations found between element fluxes in Appendix B.

It may therefore be advantageous to use the measured soil solution nitrate concentrations directly in this kind of regional scale analysis. In a national survey in Denmark, Callesen et al. (1999) found significant relationships between nitrate concentrations in soil solution and forest characteristics such as management type and soil texture class. The approach, further made use of the concentration time series to extract information about seasonal and annual variations in nitrate concentrations.

The results of the Intensive Monitoring programme offer an opportunity for analyses of relationships between nitrate concentrations measured in soil solutions collected over time and a large number of site-specific factors. The purpose of the present study was to search for relationships between atmospheric N deposition, forest biogeochemistry and nitrate leaching based on the time series of nitrate concentrations in soil solution. The data was exploited by a statistical approach based on mixed linear model theory (Littell et al., 1996) as illustrated by Callesen et al. (1999).

F.2 Materials and Methods

Site and data description

The Intensive Monitoring programme is carried out on forest plots selected by each participating country in Europe. The forest plots included in the data base used in the present study were dominated by either broadleaf species (*Quercus robur, Quercus petraea, Fagus sylvatica*) or conifer species (*Picea abies, Picea sitchensis, Picea alba, Pinus sylvestris, Pinus nigra, Pseudotsuga menziesii*) with the average stand age ranging from 30 to 130 years. The plots are situated within the latitudes 43°N-69°N, at altitudes from 25 to 1375 m above sea level, and the $pH_{(0.01\ CaCl2)}$ was in the range of 2.8-7.3 in the top 0-10 cm layer of mineral soil. The N deposition in throughfall covered a range of 0-42 kg $N.ha^{-1}.yr^{-1}$. The Intensive Monitoring programme includes surveys of atmospheric deposition, meteorology, soil characteristics, tree species, foliar and soil solution chemistry among others. Details on sampling and chemical analyses are found in De Vries et al. (1998, 1999, 2000a, 2001). In the survey, the organic topsoil (forest floor) was defined as the O-horizon on top of the mineral soil (ICP-Forest Manual).

All sites where soil solution nitrate concentration had been measured in the period Jan. 1996 to Jan. 1998 and where data on main biogeochemical properties were available were included in the analyses (n=111). The soil nitrate concentration was at most sites measured at several depths. The concentration measured in the depth closest to 100 cm was chosen to represent nitrate concentration in soil water leaching from the rhizosphere. The chosen depths ranged from 40-250 cm. The results were obtained from analysis of solution collected continuously in suction cups or zero tension lysimeters. The results from some sites/countries were excluded from the analyses due to the use of centrifugation for collection of soil solution or due to very limited time resolution of the results (e.g. the Netherlands). Soil centrifugation has been found to give higher results for nitrate concentration compared to suction cup lysimeters (De Vries et al., 1999). The countries included in the analysis were France (n=15), Germany (n=55), Belgium (n=6), Sweden (n=2), Norway (n=15), Finland (n=4), UK (n=4), Ireland (n=3), Austria (n=1) and Denmark (n=6). Throughfall and bulk deposition of N was calculated as an average of the estimated annual deposition rates per plot varying between 1-5 estimates in the period 1993-1997. We used this longer-term average as a measure of ‘pollution load’ instead of the throughfall N deposition from the actual soil solution time series alone, since the lifetime of N in the ecosystem may be several years. In the statistical analyses we preferred the use of throughfall N deposition as a measure for N input to the sites instead of bulk N deposition. Throughfall N deposition includes the major part of the dry deposition and relates therefore more closely to the actual N input to the system than does bulk N deposition. Estimates of total deposition derived in Chapter 6.2.5 were not considered, since we wanted to concentrate on directly measured parameters.

Statistical models

A preliminary statistical analysis was performed to indicate significant relationships between biogeochemical characteristics and soil solution nitrate concentration. Simple linear regression analyses and test of homogeneity of slopes (SAS proc glm) were performed on average soil nitrate concentration calculated for each site from measurements in the period Jan. 1996 to Jan. 1998. The factors found to be significantly related to average soil solution nitrate concentrations were climate, throughfall N, foliage N content, tree-type (conifers, broadleaves), stand age, C/N ratio of the organic layer, humus type (mull, moder, mor, raw humus), soil pH, phosphorous content of mineral soil (0-10 cm) and soil classification. These factors were subsequently examined in the construction of a mixed linear model (SAS proc mixed).

The data on soil nitrate concentrations (response variable) used in the mixed model were the same time series as averaged in the preliminary analyses. However, to overcome the problem that different sampling frequencies were used at the sites, an average nitrate concentration was calculated for each season (spring (March-May), summer (June-Aug.), autumn (Sept.-Nov.) and winter (Dec.-Feb.)) in the period winter 1996 to winter 1998; that is, 3-9 repeated measurements per site.

The longitudinal character of the data was taken into account by using a split-plot type design with sites as 'main plots' and season results as 'subplots' (Christensen, 1996). Equivalently this means that the factor site has a random effect in the model, or that a compound symmetry dependence structure is assumed for the series of observations at each site (Littell et al., 1996). The soil nitrate concentrations were transformed prior to analysis by the function y=log(x+0.05). The value 0.05 (mg NO_3-N.l^{-1}) was added to avoid observations equal to zero, which are not allowed for the transformation class. The log transformation was recommended by maximum likelihood estimation. Due to the transformation, the resulting estimates and confidence intervals were calculated by retransformation to the original scale and therefore correspond to median (midpoint) nitrate concentrations (Parkin and Robinson, 1994).

Throughfall N was found to have a strong relationship to soil nitrate when tested alone in the mixed model analysis. Each other factor was subsequently tested for significant effects on soil nitrate concentration in a preliminary model including throughfall N. The factors found to be significant were: tree-type, C/N ratio of the organic layer, humus type, phosphorous content of mineral soil (0-10 cm), and foliage N content. The factors that were found not to be significant were age, soil classification, climate and soil pH. The model was furthermore used to test for interactions (covariance). The significant factors and interactions were used to construct a common mixed model, which then was reduced for insignificant factors. The formal writing of the resulting model for soil solution nitrate observations at site s and time t is

$$\begin{aligned}\text{Soil NO}_3^-(\text{s},\text{t}) &= \text{season (t)} + \text{throughfall N (s)} + \text{tree - type (s)} + \\ &\text{throughfall N} \cdot \text{tree - type (s)} + \text{C/N organic layer (s)} + \text{site(s)} + \text{error(s, t)}\end{aligned} \tag{F.1}$$

Here the terms 'site' and 'error' are random Gaussian variables. An r^2 of 0.92 was calculated for the model by use of sum of squares of observed response variables and residuals from predicted response variables (SAS proc univariate). The r^2 is not a true coefficient of determination of the complex model, but it illustrates the impact of variation in the model factors on soil nitrate concentrations. The r^2 can not be interpreted like in a traditional regression model, since some of the variation is captured in the 'site' term.

The model was used to estimate medians for each level of main factors. The C/N of the organic layer was for this reason included in the model after classification into the levels C/N<25, 25<C/N<30, and C/N>30 based on the hypothesis of Gundersen et al. (1998a). Medians were calculated as weighted values based on the distribution of sites at different levels of main factors. Differences between weighted medians were tested by Student t-tests with Bonferroni correction for multiple comparisons (Christensen, 1996). Due to significant interaction in the model between throughfall N and tree-type, it is called a covariate by treatment interaction model (Littell et al., 1996). This means that differences between factors with covariates should be tested at different levels of the covariate. Therefore, differences between conifers and broadleaves were tested at the average throughfall N deposition calculated separately for conifers and broadleaves. Both averages happened to be at 14.2 kg N.ha^{-1}.yr^{-1}. Furthermore a low (4.0 kg N.ha^{-1}.yr^{-1}) and a high (22.8 kg N.ha^{-1}.yr^{-1}) value of throughfall N was tested. These values represented the minimum and maximum throughfall N measured at broadleaf sites. Foliage N content was not included in the mixed model analyses due to strong covariance with throughfall N and due to species specific differences.

The same procedure as described above was used to construct separate mixed models for conifers and broadleaves. The significance of all factors and interactions were tested followed by reduction of the resulting model by removal of insignificant factors and interactions. The formal writing of the resulting models is:

Conifers (r^2=0.93):

$$\text{Soil NO}_3^-(\text{s},\text{t}) = \text{season (t)} + \text{throughfall N (s)} + \text{C/N organic layer (s)} + \text{site(s)} + \text{error(s, t)} \quad \text{(F.2)}$$

Broadleaves (r^2=0.87):

$$\text{Soil NO}_3^-(\text{s},\text{t}) = \text{season (t)} + \text{throughfall N (s)} + \text{soil pH(0 - 10 cm) (s)} + \text{site(s)} + \text{error(s, t)} \quad \text{(F.3)}$$

F.3 Results and Discussion

Seasonal and annual effects

Differences in soil nitrate concentrations between seasons were significant (p=0.011) in the overall model (Eq. F.1) and a significant difference was found between winter and summer concentrations in the subsequent test between weighted medians (Table F.1). No difference between years was detected. Winter concentrations were lower than summer concentrations, which may be explained by the diluting effect of increased water infiltration due to decrease of evapotranspiration, as well as by decreased nitrifying activity during the cold season. Although significant, the differences between seasons were relative small. This may mean that the uncertainty due to modelled timing of water flow (Appendix A) may not add large errors to the estimates of nitrate leaching fluxes.

Table F.1 Estimated medians of nitrate concentration in soil solution and test of significant differences between estimates at the average throughfall of 14.2 kg N.ha^{-1}.yr^{-1} in the common mixed model for broadleaves and conifers. Different letters indicate significant differences between estimated medians for each main factor.

Variable		Sites (n)	Observations (n)	Estimate mg.l^{-1}	Confidence interval (95%)
Overall median		104	777	0.53	0.38 – 0.74
Season (p=0.011)					
	Winter	103	225	0.47 a	0.33 – 0.67
	Spring	104	183	0.55 ab	0.39 – 0.77
	Summer	104	185	0.59 b	0.41 – 0.82
	Autumn	103	184	0.52 ab	0.37 – 0.74
Throughfall N (p<0.0001)		104	777		
Tree-type (p=0.276)					
Tree-type·throughfall N (p=0.045)		104	777		
	Conifers	73	545	0.32 a	0.24 – 0.43
	Broadleaves	31	232	0.64 b	0.42 – 0.95
C/N organic layer (p=0.025)					
	>30	30	228	0.13 a	0.07 – 0.22
	25-30	25	188	0.47 b	0.24 – 0.88
	<25	49	361	1.23 c	0.84 – 1.78

Throughfall and bulk N deposition

The strongest relationship to nitrate concentrations was found for throughfall N deposition (p<0.0001). At the average throughfall of 14.2 kg N.ha^{-1}.yr^{-1} this resulted in significantly higher nitrate concentrations below broadleaves compared to conifers (Table A6.1). There was, however, also a significant interaction between throughfall N and tree-type (p=0.045). This interaction also appears from linear regression between throughfall N and the average nitrate concentration in soil solution (Fig. A6.1).

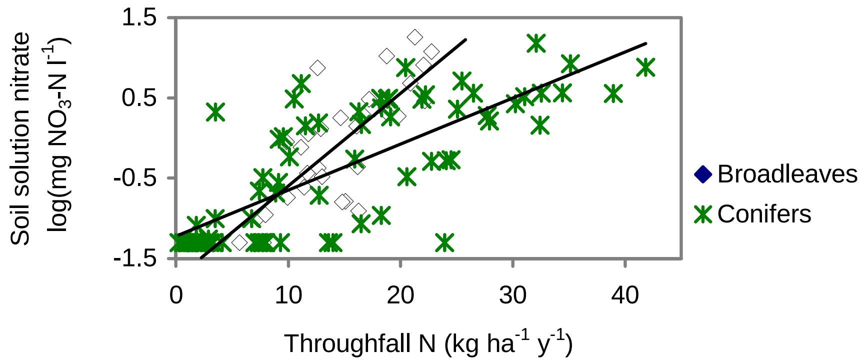

Figure F.1 *Average nitrate concentration in soil solution Jan. 1996 to Jan. 1998 (log transformed) vs throughfall N flux (1993-1997) at Intensive Monitoring plots. Linear regressions yield for broadleaves: log (y) = 0.12 x – 1.8; r^2=0.65; for conifers: log (y) = 0.06 x – 1.2; r^2=0.59.*

Thus the difference between nitrate concentrations below broadleaves and conifers depended on the level of throughfall N deposition and was therefore tested further for significant differences at a low and high level of throughfall N (see explanation in the Materials and Methods section). In accordance with the tree-type differences illustrated in Fig. F.1, the test found the nitrate concentration to be higher below broadleaves compared to conifers (Table F.2) both at average and high throughfall N deposition (14.2 and 22.8 kg $N.ha^{-1}.yr^{-1}$), while no difference was found at low deposition level (4.0 kg $N.ha^{-1}.yr^{-1}$). The regression lines in Fig. F.1 indicate that nitrate concentration in soil solution under broadleaves will respond much more to deposition changes (at the double exponential rate) than under conifers.

Table F.2 *Estimated medians of nitrate concentration in soil solution (mg $N.l^{-1}$) and test of significant differences between estimates at three different levels of throughfall N in the common mixed model for broadleaves and conifers. Different letters indicate significant differences between estimated medians.*

Tree type	Low throughfall N (4.0 kg $N.ha^{-1}.yr^{-1}$)	Average throughfall N (14.2 kg $N.ha^{-1}.yr^{-1}$)	High throughfall N (22.8 kg $N.ha^{-1}.yr^{-1}$)
Conifers	0.04	0.33 a	0.97 a
Broadleaves	0.01	0.64 b	4.03 b

Bulk N deposition correlates with throughfall N deposition (Fig. F.2) and can usually replace throughfall N deposition in the relationships found in this type of regional analysis (Dise and Wright, 1995; Gundersen, 1995; Tietema and Beier, 1995).

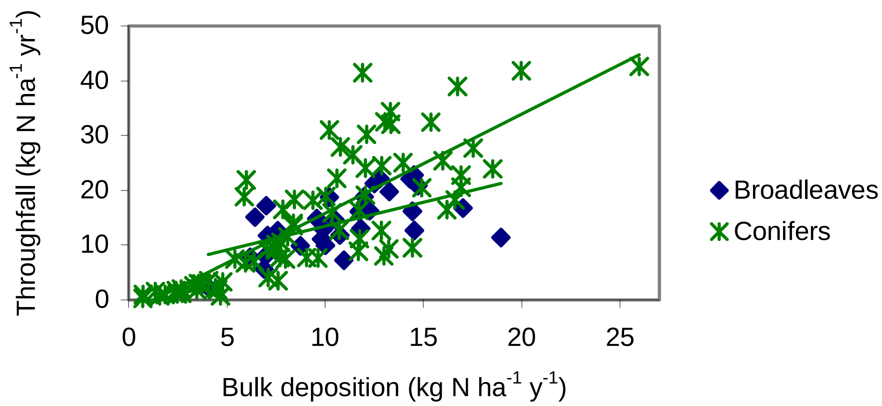

Figure F.2 Throughfall vs bulk precipitation average N fluxes (1993-1997) at Intensive Monitoring plots (r^2=0.64 for conifers; r^2=0.33 for broadleaves).

When throughfall N deposition was replaced by bulk N deposition in the statistical model (Eq. F.1) there was no interaction between tree-type and bulk N deposition (p=0.93) and neither was there an effect of tree-type alone (p=0.73). The other factors stayed significant in the model (results not shown). The differences found between nitrate concentrations below broadleaves and conifers may be interpreted as a result of the complex interactions between N deposition, forest biogeochemistry and nitrate leaching. Conifers are found to have higher throughfall N deposition than broadleaves at high levels of bulk N deposition (Fig. F.2). This is due to the larger filtering effect of the conifer canopy compared to that of broadleaves caused by the larger canopy surface and roughness as well as the evergreen nature of conifers (e.g. Rothe et al., 2001). This difference is not observed at low N deposition levels where direct assimilation of ammonium in the canopy decrease throughfall N relative to bulk N deposition (Fig. F.2). Ammonium is known to constitute a relatively larger part of throughfall N deposition compared to nitrate at higher deposition levels (Dise et al., 1998a), which is also apparent in the present dataset (Fig. F.3).

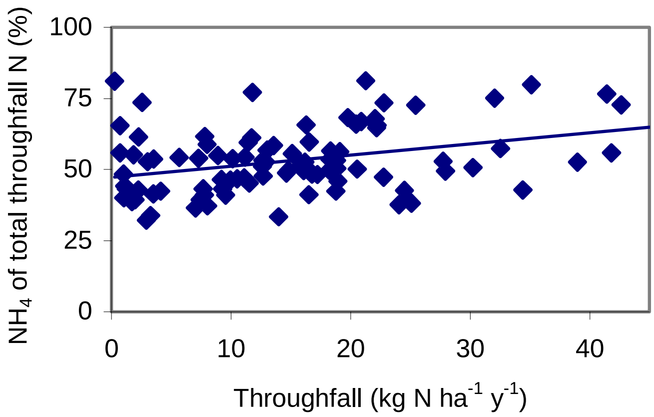

Figure F.3 Ammonium contribution in throughfall in relation to the total throughfall N flux (average 1993-1997) at Intensive Monitoring plots.

Thus conifer stands experience higher throughfall N deposition levels and relatively higher contributions of ammonium N compared to stands dominated by broadleaves. Input-output budgets indicate that ammonium from atmospheric deposition is better retained in forest ecosystems compared to nitrate probably due to differences in mobility of the two ions (Gundersen, 1995; Dise et al., 1998a). This may explain why conifers (at throughfall >8 kg N.ha^{-1}.yr^{-1}) have lower soil nitrate concentrations than broadleaves at the *same throughfall N deposition* level (Fig. A6.1) and further that this differences is absent when compared at the *same bulk N deposition*.

The forest floor C/N ratio

The C/N ratio of the organic topsoil was the only biogeochemical property that together with throughfall N deposition contributed significantly to explain nitrate concentrations in the common model (Eq. F.1) for broadleaves and conifers (Table F.1). In the preceding regression analysis on average nitrate concentrations the C/N ratio was not a significant factor (p=0.19) in a linear model with throughfall N. This indicates that use of the time series information (seasonal fluctuations in nitrate concentrations) increase the analytical power of the statistical models.

Weighted medians of nitrate concentration in the three C/N classes were significantly different increasing from 0.13 over 0.49 to 1.24 mg.l^{-1} in the >30, 25-30 and <25 class, respectively

(Table A6.1). In the separate model analysis of the two tree-types (Eq. F.2 and F.3) C/N ratio of the organic topsoil entered the model for conifers ($p=0.029$), but not for broadleaves. The results from conifers support the hypothesis of Gundersen et al. (1998a) based on analysis of published European data mainly from coniferous forests. The hypothesis says that the C/N ratio in the organic topsoil may be an indicator of the N status of the ecosystem and therefore also a predictor of the risk for nitrate leaching from the system. Gundersen et al. (1998a) suggested that a C/N ratio above 30 characterises forests with a low risk for nitrate leaching, a ratio between 25-30 characterises an intermediate risk, while a ratio below 25 characterises forests with a high risk for nitrate leaching. In an extended European dataset including also catchment studies Dise et al. (1998b) found that sites with throughfall N deposition below 10 kg $N.ha^{-1}.yr^{-1}$ had low nitrate leaching regardless of C/N. At sites with deposition levels of 10-30 kg $N.ha^{-1}.yr^{-1}$ nitrate leaching increased with decreasing C/N ratio. With deposition levels above 30 kg $N.ha^{-1}.yr^{-1}$ the results were more variable and nitrate leaching was observed at all sites including those with C/N ratio above 30. Using the same deposition classes on the Intensive Monitoring data for conifers similar relations between average soil nitrate concentrations and C/N ratio of the organic topsoil was observed (Fig. F.4):

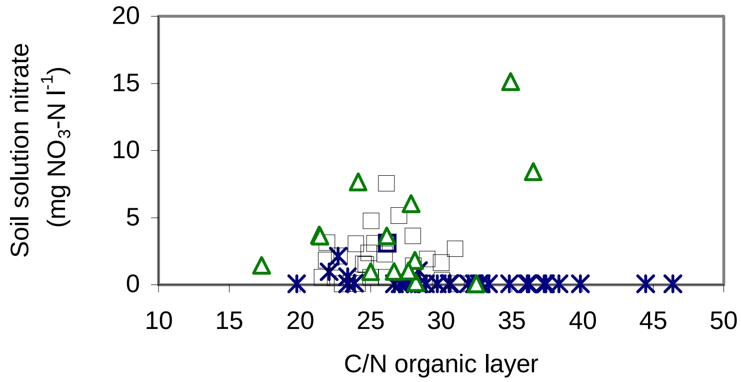

Figure F.4 Average nitrate concentrations in soil solution Jan. 1996 to Jan. 1998 vs forest floor C/N ratio at low (✷ < 10 kg $N.ha^{-1}.yr^{-1}$), intermediate (10-30 kg $N.ha^{-1}.yr^{-1}$) and high (Δ >30 kg $N.ha^{-1}.yr^{-1}$) throughfall N deposition at Intensive Monitoring plots.

Sites with deposition levels below 10 kg $N.ha^{-1}.yr^{-1}$ in general had soil solution nitrate concentrations close to zero irrespective of C/N ratio. Sites with high nitrate concentrations at C/N ratios above 30 all had deposition levels well above 30 kg $N.ha^{-1}.yr^{-1}$. One of these sites (C/N ratio 36.5, nitrate concentration 8.4 $mg.l^{-1}$) has been studied in detail by De Schrijver et al. (2000). They suggest that the mechanism behind leaching of nitrate at this high C/N ratio is due to transport of throughfall ammonium down through the upper soil layers to deeper layers with lower C/N ratio and higher nitrifying activity.

Intercorrelations between C/N, throughfall N, foliage N and soil nitrate concentrations

The C/N ratio of the organic layer is related to other ecosystem N fluxes and concentrations and may as such be an indicator of ecosystem N status (Gundersen et al., 1998b) as well as of the risk of nitrate leaching (Gundersen et al., 1998a). With time the elevated N input may increase N concentrations and fluxes in the ecosystem and the C/N ratio of the forest floor may thus decrease. The decades of elevated deposition seem to have influenced the C/N ratio of this layer in European forests, since a significant negative linear relationships was found between the throughfall N deposition and the C/N ratio for both tree-types (Fig. F.5).

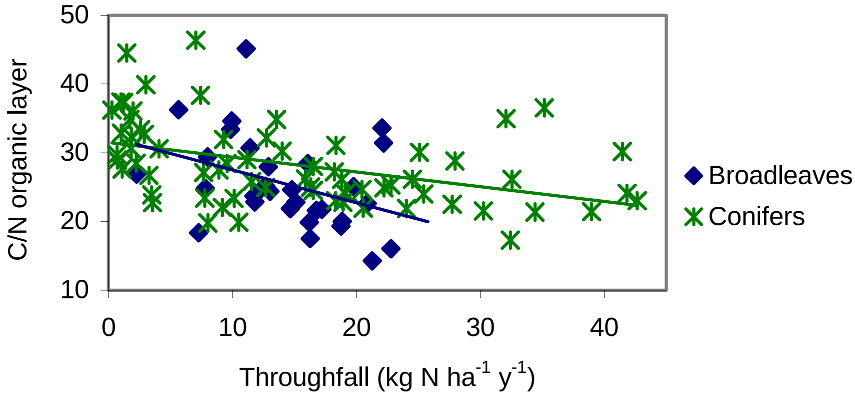

Figure F.5 *C/N ratio of the organic layer vs throughfall N flux (1993-1997) at Intensive Monitoring plots. The regressions are conifers: y= 31.5 – 0.21x (r^2= 0.19, p= 0.0002); broadleaves: y= 32.3 – 0.48x (r^2= 0.14, p= 0.036).*

The relationships suggest a 2 unit decrease of forest floor C/N in conifers and a 5 unit decrease in broadleaves per 10 kg $N.ha^{-1}.yr^{-1}$ increase in throughfall N (Fig. F.5). However, since the deposition gradient decrease northward like temperature, the decreasing trend in C/N with deposition may have a climatic component as well. Also the relationship for broadleaves was rather weak.

Another factor of importance for the C/N ratio is the N status of the litter input. This was not measured at the sites, but so was foliage N concentration, that have been shown to correlate with litter N concentration (Tietema and Beier, 1995). A significant negative correlation between foliage N concentrations and the C/N of the organic topsoil was found for conifers (Fig. F.6), however, not for broadleaves (p=0.52).

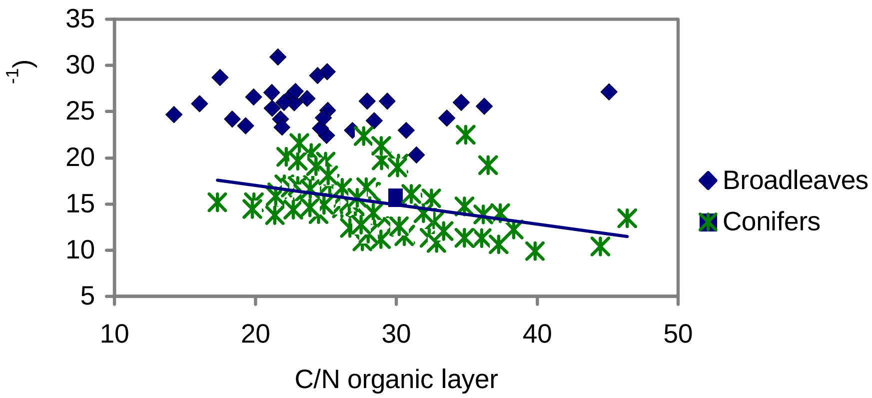

Figure F.6 *Foliage N concentration vs organic layer C/N ratio at Intensive Monitoring plots. The regression for conifers is y= 21.2 - 0.21x (r^2= 0.16, p= 0.0003).*

The figure further shows that the foliage N content differed between broadleaves and conifers with an average of 25.3 and 14.8 $mg.g^{-1}$, respectively. The foliage N content was then again for conifers significantly related to the throughfall N deposition (Fig. F.7), but not for broadleaves (p=0.71).

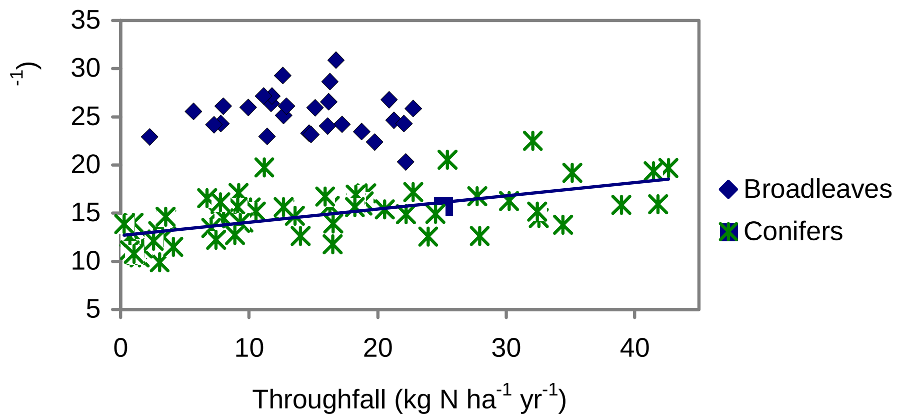

Figure F.7 *Foliage N concentration vs throughfall N flux (1993-1997) at Intensive Monitoring plots. The regression for conifers is: y = 12.7 + 0.14x (r^2=0.40, p<0.0001).*

With the significant intercorrelation between throughfall N, C/N ratio and foliage N concentration for conifers a relationship between soil nitrate concentrations and foliage N content may be expected in conifers as shown in Fig. F.8.

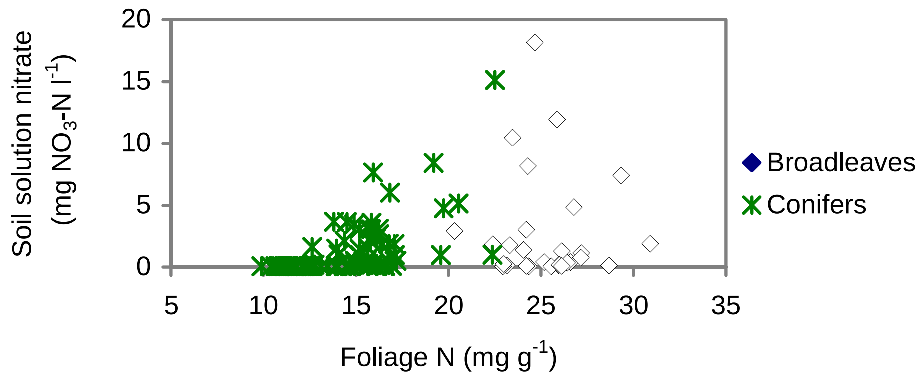

Figure F.8 *Average nitrate concentrations in soil solution Jan. 1996 to Jan. 1998 vs foliage N concentration at Intensive Monitoring plots. For conifers the correlation is significant (r^2=0.34, p<0.0001).*

The results in Fig. F.8 further show that a threshold can be set for conifer foliage N content of 12.6 mg.g^{-1} below which no nitrate was found in soil solution, and of 17.0 above which the nitrate concentration was always above detection limit. These limits correspond well with those suggested by Gundersen (1999) from other European data. When replacing the C/N ratio in Eq. A6.2 with foliage N content in the mixed model analysis of conifers a significant relationship to nitrate concentrations (p<0.0001) was also found.

In accordance with the lack of correlation for broadleaves in Fig. F.6, F.7 and F.8, neither the C/N ratio (p=0.54) nor the foliage N content (p=0.89) showed significant relationships to nitrate concentration in soil solutions in the mixed model analysis for broadleaves.

Relations to soil pH and humus type

The pH of the mineral soil (0-10 cm depth) contributed to explain soil nitrate concentrations in the separate mixed model for broadleaves (Eq. F.3). Previous studies have shown a relationship between pH of the B-horizon of European forests and nitrate leaching which may be explained by the acidifying effect on the soil of nitrification and leaching of nitrate from deposition (Dise et al., 1998a). Such relation was also found for conifers in the present study but only when throughfall N deposition was not included in the model (results not shown). Differently for broadleaves the pH was indicated to relate to nitrate concentrations more than what could be explained by the acidifying effect of N deposition, since both soil pH and throughfall N are included in the final model (Eq. F.3). This may mean that soil type and characteristics are more important for the response to N deposition in broadleaf than in coniferous forests.

A biogeochemical property of humus type of the organic topsoil was found to be significantly related to nitrate concentrations when included in the common model for broadleaves and conifers ($p=0.032$) as well as in the separate model for conifers ($p=0.035$) (results not shown). The humus types of forest sites were classified as raw humus, mor, moder and mull. The estimated medians of nitrate concentration for the classes decreased in the order mor>moder>mull>raw humus. This result has no clear relation to the ecological function of the organic topsoil as based on present knowledge. The effect may further be questioned as the reliability of the humus classification is low (Vanmechelen et al. 1997).

F.4 Conclusion

The mixed model analysis of the level II time series of soil nitrate concentrations increases the analytical power above that of correlation and regression statistics on concentrations means. Soil nitrate concentrations in winter are generally lower than in summer, but differences are small. The response of coniferous and broadleaf forest to N deposition is different and the tree-types need to be analysed separately.

In coniferous forests N input with throughfall, foliage N concentration, forest floor C/N ratio and nitrate leaching are interrelated variables. Soil nitrate concentrations are best explained by a model with throughfall N and forest floor C/N as main factors, though C/N ratio could be replaced by foliage N. The results confirm conclusions from other datasets, that the forest floor C/N ratio classes >30, 25-30 and <25 as well as the foliage N (mg $N.g^{-1}$) classes <13, 13-17 and >17 indicate low, intermediate and high risk of nitrate leaching, respectively.

In broadleaved forests, correlations between N characteristics are less pronounced. A model including throughfall N and soil pH (0-10 cm) as main factors best explained soil nitrate concentrations. The responses of soil nitrate concentration to changes in N deposition will probably be more pronounced in broadleaf than in coniferous forests.