

Assessment of the dynamics in nitrogen and carbon sequestration of European forest soils

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Alterra-Rapport 818

Alterra, Wageningen, 2003

ABSTRACT

Vries, W. de, C. van der Salm, G.J. Reinds, N.B. Dise, P. Gundersen, J.W. Erisman & M Posch, 2003. *Assessment of the dynamics in nitrogen and carbon sequestration of European forest soils*. Wageningen, Alterra, Alterra-Rapport 818. 148 blz.; 47 figs.; 24 tables.; 187 refs.

This report describes the major result of a research project that focused on the assessment of the dynamics in nitrogen and carbon sequestration of European forest soils by estimation of the: (i) retention or release of nitrogen species for selected Intensive Monitoring plots by comparing the input, based on measurements of throughfall and bulk deposition, with the soil output, obtained by multiplying soil solution concentration measurements with modelled soil water fluxes and (ii) carbon sequestration by relating the N and C dynamics in soils by the soil C/N ratio. Major results are that: (i) N leaching and sequestration is influenced by the soil C/N ratio in the organic layer, (ii) C sequestration in forest soils on a European scale is much less than C sequestration due to forest growth and (iii) the impact of N deposition on soil N leaching is fast but the impact on changes in soil C/N ratio is small.

Keywords: nitrate leaching, C/N ratio, forest, nitrogen deposition, dynamic modelling, carbon sequestration, forest, Europe.

ISSN 1566-7197

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Preface

This report describes the major result of a research project funded by DG Agriculture as a so-called article 4 project under the European Scheme on the Protection of Forests against Atmospheric Pollution (Council Regulation (EEC) No 3528/86). The study focused on the assessment of the dynamics in nitrogen and carbon sequestration of European forest soils by estimation of the: (i) retention or release of nitrogen species for selected Intensive Monitoring plots by comparing the input, based on measurements of throughfall and bulk deposition, with the soil output, obtained by multiplying soil solution concentration measurements with modelled soil water fluxes and (ii) carbon sequestration by relating the N and C dynamics in soils by the soil C/N ratio.

The project was carried out by Alterra Green World research in co-operation with:

- National Energy Research (ECN), P.O. Box 1, NL-1755 ZG Petten, the Netherlands: Dr Jan Willem Erisman
- Danish Forest and Landscape Research Institute (DFLRI), DK-2970 Hoersholm, Denmark: Dr Per Gundersen.
- Dept of Earth Science, The Open University (OU), Milton Keynes, UK : Dr Nancy Dise
- National Institute of Public Health and the Environment (RIVM), P.O. Box 1, NL 3720 BA, Bilthoven, the Netherlands: Dr Max Posch.

The research was carried out in the period 2000-2003. This report includes the papers resulting from this study. These papers are

- Kristensen, H.L., Gundersen, P., Callesen, I., Reinds, G., 2003. Throughfall N deposition influences soil solution nitrate concentration differently in European coniferous and deciduous forests. Accepted in *Ecosystems*.
- MacDonald, J.A. N.B. Dise, E. Matzner, M. Armbruster, P. Gundersen and M. Forsius, 2002. Nitrogen input together with ecosystem nitrogen enrichment predict nitrogen leaching from European forest. *Global Change Biology* 2002: 1028-1033.
- W. de Vries, C. van der Salm, G.J. Reinds and J.W. Erisman, 2003. Element fluxes through European forest ecosystems and their relationships with stand and site characteristics. Draft paper for submission to *Environmental Pollution*.
- W. de Vries, G.J. Reinds and P. Gundersen, 2003 Assessment of the impacts of nitrogen deposition on carbon sequestration on a European scale. Draft paper for submission to *Global Change Biology*.
- G.J. Reinds, M. Posch and W. de Vries, 2003. Long-term impacts of atmospheric nitrogen and sulphur deposition on soil solution chemistry at Intensively Monitored forest plots in Europe. Draft paper for submission to *Environmental Pollution*.

We thankfully acknowledge the various national Ministries, including the Dutch ministry of Agriculture, Nature and Fisheries, for co-financing the project and Mr Jan-Cees Voogd for data evaluation and text processing.

Extended summary

Background and aim

In the Kyoto Protocol, terrestrial sinks of CO₂ are recognised and may in the future be accounted for in the agreed international CO₂ emission reductions. This will require methods for reliable quantification of these C sinks. Information on C and N sequestration and their response to changes in N deposition on a European scale are limited. There are measurements of C fluxes above a range of forests across Europe but extrapolation of these results to a European scale is still prone to large uncertainties. The same is true for C sequestration in soils, where both simulation models and local data are available for a number of sites, but extrapolation to a European scale has not yet taken place.

By far the largest amount of C stored in forests in the northern hemisphere is stored in the soil. Nitrogen is often the limiting nutrient in terrestrial ecosystems, and thus sequestration of C is closely linked to the N cycle. Current hypotheses suggests that increased N deposition affects the rate of soil organic matter accumulation by increased leaf/needle biomass and litter production, and by reduced decomposition of organic matter. The increased net primary production in European forests, thereby increasing sequestration of CO₂ from the atmosphere, has been hypothesised as one of the links between N and C sequestration. N deposition may also have a negative effect on the decomposition of plant litter in later stages of decomposition, when litter has become almost humus. A low C:N ratio of the humus or litter may lead to retardation of humus decomposition and to an increased C-accumulation in soils. A major sink for the high N inputs from deposition in terrestrial ecosystem might thus be the accumulation of N-rich soil humus. Understanding the N cycle in semi-natural ecosystems is therefore the key to understanding sequestration of C and the long-term source or sink strength of soils for carbon.

This report describes major results of a project dyNamiC, focusing on the assessment of the dynamics in carbon sequestration based on the interaction of carbon (C) cycles, nitrogen (N) cycles in forests, using an interdisciplinary collaborative approach combining data integration and modelling. More specifically, the objectives were to:

- Develop and validate empirical models that allow extrapolation of N sequestration to regional and European scales, by evaluating European databases on N sequestration and leaching and ecosystem state indicators that may affect these processes. The first three articles focus on this aim by identifying indicators of N sequestration and N (nitrate) leaching such as climate, soil type, vegetation type, soil C/N ratios etc , to scale to allow predictions in time and space of changes in soil N pools and N leaching and improve calculations of critical N loads, which is of practical use to managers and policy makers.
- Develop empirical models that allow large scale extrapolation of C sequestration and apply this model on the European scale. The fourth article focuses on this aim by relating C and N sequestration to the soil C/N ratio and applying the

relationships derived in the earlier articles to estimated N sequestration on the European scale.

- Further develop and apply dynamic models that provide estimates of C sequestration and N retention at current conditions and in the future, given scenarios for environmental change, such as air pollution changes, on a European scale. The last article focuses on this aim but most emphasis is given to NO₃ leaching and soil acidification.

Impacts of nitrogen deposition on dissolved nitrate concentrations in European forests

The first paper investigates the influence of ecosystem characteristics on soil solution nitrate concentrations at 104 plots of the Pan European Programme for the Intensive and Continuous Monitoring of Forest Ecosystems, using time-series of soil solution chemistry from Dec. 1995 to Feb. 1998 at a plot scale for conifer and broadleaved forests with a statistical model. Soil solution nitrate concentrations varied by season, with summer concentrations being approx. 25% higher than winter concentrations. Soil solution nitrate concentrations increased strongly with throughfall (and bulk precipitation) N input for both broadleaves and conifers. However, at elevated throughfall N input (>10 kg N ha⁻¹ yr⁻¹) nitrate concentrations were higher in broadleaved than in coniferous stands. This tree-type difference was not observed in response to increase in bulk precipitation N input. In coniferous stands throughfall N input, foliage N concentration, organic layer C/N ratio, and nitrate concentrations covaried. Soil solution nitrate concentrations in conifer plots were best explained by a model with throughfall N and organic layer C/N as main factors, where C/N ratio could be replaced by foliage N. The organic layer 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 indicated low, intermediate, and high risk of nitrate leaching, respectively. In broadleaved forests, correlations between N characteristics were less pronounced and soil solution nitrate concentrations were best explained by throughfall N and soil pH (0-10 cm). The results suggest that the responses of soil solution nitrate concentration to changes in N input will be more pronounced in broadleaved than in coniferous forests, since broadleaf are located on the more fertile soils in European forests.

Nitrogen input together with Ecosystem Nitrogen Enrichment Predict Nitrate Leaching from European Forests

The second paper evaluates available information in the IFEF (Indicators of Forest Ecosystem Functioning) database, that has been developed on the basis of literature data. IFEF contains information on annual input-output fluxes of N for approximately 230 forested plots and catchments over the last two decades. Additional data like soil pH, organic horizon C:N ratios and soil chemistry are compiled for approximately 100 sites. Often, data such as C and N pools or concentrations in soil, vegetation, litterfall are measured as well. Previous analyses of small subsets of these data involved (15-35 sites) have suggested that the N input in deposition, together with the forest floor C:N ratio, are useful indicators for the magnitude of nitrate leaching from - and inversely the N sequestration in forests. However, predictions based on few sites have high uncertainties.

The complete IFEF database was analysed to evaluate the C/N ratio in the organic horizon as an indicator of nitrate leaching. In total 181 forests are examined, from countries across Europe ranging from boreal to Mediterranean regions, encompassing broadleaf and coniferous sites and plot and catchment studies. N input in throughfall ranges from less than 1 kg N.ha⁻¹.yr⁻¹ in northern Norway and Finland to greater than 60 kg N.ha⁻¹.yr⁻¹ in the Netherlands and Czech Republic. The amount of NO₃⁻ leached covers a smaller range, between 1 and 40 kg N.ha⁻¹.yr⁻¹. Nitrate leaching is strongly dependent on the amount of nitrogen deposited in throughfall (N input) and simply adding the C/N ratio in the organic horizon does not improve this relationship. However, when the data are stratified based on C/N ratios less than or equal to 25 and greater than 25, highly significant relationships ($p < 0.05$) are observed between N input and NO₃⁻ leached. The slope of the relationship for those sites where C/N ratio is ≤ 25 ('nitrogen enriched' sites) is twice that for those sites where C/N ratio is > 25 . These empirical relationships may be used to identify which forested ecosystems are likely to show elevated rates of nitrate leaching under predicted future nitrogen deposition scenarios. Elevated NO₃⁻ leaching also shows a relationship with soil pH, with high rates of NO₃⁻ leaching only being observed at sites with a pH < 4.5 and N inputs > 30 kg N.ha⁻¹.yr⁻¹. Tree age and species had no significant impact on the ecosystem response to N input at a regional scale.

Element fluxes through European forest ecosystems and their relationships with stand and site characteristics

The third paper uses more detailed data of the Pan- European Intensive Monitoring Programme to calculate N deposition and N leaching for more than 100 forest Intensive Monitoring plots (Level II plots). Unlike IFEF, the data are thus all based on the same type of calculation approach. The paper describes a European wide assessment of element budgets, using available data on deposition, meteorology and soil solution chemistry at Intensive Monitoring plots in this continent. 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. Element outputs from the forest ecosystem were derived by multiplying fortnightly or monthly measurements of the soil solution composition at the bottom of the root zone with simulated unsaturated soil water fluxes. Element retention or release was assessed from the difference between inputs and outputs.

Median values for SO₄ leaching were nearly equal to the median SO₄ deposition. On a considerable number of plots SO₄ leaching was, however, higher than SO₄ deposition, indicating systems that are releasing S stored in the soil in previous episodes of higher SO₄ input. 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 than the N leaching, reflecting N retention in the system. There was a significant relationship between N leaching and N deposition. Furthermore, N leaching was limited at high C/N ratios (> 30) in the organic layer. Due to the large N retention, the leaching flux of NO₃ was mostly lower than that of SO₄. The leaching

flux of BC (Ca+Mg+K) and Al increased significantly with an increase in SO_4 deposition and decreased strongly with an increase in soil base saturation.

Despite the uncertainties in the calculated budgets, considering the uncertainties in calculated water fluxes and measured element concentrations in view of spatial variability within a plot, the results indicate that: (i) SO_4 is still the dominant source of actual soil acidification despite the generally lower input of S than N, due to the different behaviour of S and N, (ii) base cation removal due to man-induced soil acidification is limited and (iii) Al release is high in areas with high S inputs and low base status.

Impacts of nitrogen deposition on carbon sequestration by forests in Europe

The fourth paper includes an estimation of C sequestration in European forest soils. In general, the interaction between N and C cycling can be used to derive estimates of C sequestration in forests on the basis of N sequestration. A recent estimate of the C sequestration in forest trees and forest soils over the world suggests that the sinks in both compartments is of equal magnitude. This estimate is, however, based on a total world N deposition estimate, averages values for the C/N ratio in stemwood and forest soils and equal N retention fractions in both compartments, based on the short-term fate (1-3 yr.) of ^{15}N labelled tracer experiments in nine temperate forests. Those assumptions strongly hamper an adequate estimate on a large scale. This paper presents an updated estimate of C sequestration in the soil using site specific estimates or measurements of N deposition, N uptake and C/N ratios at forest soils located in a systematic grid of 16 km x 16 km over Europe (excluding Russia) being representative for the approximately 1,5 million km^2 for Forests.

First, an estimate of net carbon pool changes in Intensive Monitoring plots was based on repeated forest growth surveys for trees. Carbon pool changes in the soil were based on calculated nitrogen retention (N deposition minus N leaching) rates in soils minus N uptake and multiplied by the C/N ratio of the forest soils. In order to scale up results to Europe, an estimate of soil carbon pool changes was calculated for more than 6000 level I plots using: (i) N deposition by model estimates, (ii) net N uptake by yield estimates as a function of site quality, (iii) N retention fractions in soil related to measured C/N ratios, based on results from level II plots and (iv) measured C/N ratios for forest soils. More specifically, carbon sequestration at all level 1 plots (approximately 6000) was calculated by: (i) multiplying modelled N deposition data minus a calculated N uptake at each plot by an N sequestration fraction, depending on the C/N ratio of the humus layer and (ii) multiplying this calculated N sequestration by the measured C/N ratio using available site specific C/N ratios. The allocation of C sequestration in the organic layer and the organic layer and the mineral layer was calculated as a function of the NH_4/NO_3 ratio in deposition and the C/N ratio of the organic layer, based on available results of tracer experiments. The N deposition was based on results of the EMEP model that were interpolated to all. The N uptake was derived from stand age and available site quality characteristics, using forest yield tables to estimate the actual forest growth and N accumulation in biomass.

As expected the changes in the carbon pool in tree due to forest growth increase going from Northern to Central Europe. The calculated changes in the carbon pool in soil are high in Central Europe and low in Northern and Southern Europe, since it follows the N deposition pattern. The carbon pool changes in the tree are generally 5-10 times as high as the estimated carbon pool changes in the soil. Net increases in the carbon pool by forests in Europe (both trees and soil) are in the range of 0.1-0.15 Gton.yr⁻¹, being an important part (about 50%) of the terrestrial carbon sink in Europe, derived from atmospheric inversion models. The results furthermore show that the C sequestration by forest is mainly due to a net increase in forest growth, since the longer term C immobilisation in the soil is limited. The contribution of N deposition to the increase in carbon in standing biomass is approximately 10 and 20 Mton.yr⁻¹. If one relates the additional growth to the estimated forest growth of approximately 280 Mton.yr⁻¹, the contribution varies between approximately 3.5 and 7%.

Modelling the long-term impact of deposition scenario's for nitrogen and acidity at intensively monitored forest plots

In the last article, the dynamic soil chemistry model SMART was applied to about 200 Pan-European Intensive Monitoring plots for which both element input (deposition) and element concentrations in the soil solution were available. The plots occur in a transect from South -Western Europe to Scandinavia, the majority being located in Western and Northern Europe. The reason for applying SMART is because the above mentioned article gives a steady state estimate of C sequestration, since all parameters (N deposition, N uptake and C/N ratio) are assumed to stay constant. In reality, N deposition may change thus affecting N uptake and C/N ratios, depending on tree age, soil N status etc. Furthermore, the decomposition may change as a function of temperature, which is influenced by global change. In order to gain insight in the long-term dynamics of C sequestration, it is important to have insight in the dynamics of N sequestration. Such information is also important to gain more insight in the time dependency of critical loads, which are also based on a steady-state concept.

SMART was amongst others applied to calculate NO₃ leaching and N sequestration for the Level II sites, using measured deposition and soil chemical characteristics. Most of the processes in the SMART model could be successfully calibrated. The chloride and sodium budgets show that the hydrology at the plots is generally well simulated. The nitrogen budget could, however, only be closed assuming a time independent N immobilisation for a number of plots. Sulphate adsorption could not be modelled with the available data and has thus been ignored in the model applications. There was generally a reasonable to good agreement between measured and simulated data for most of the plots, although some of the intra-annual variation in especially nitrate and aluminium concentrations could not be reproduced for a number of plots. Statistical measures for the goodness of fit indicate that pH is on average very well reproduced by the model, but not all variations within the year are accurately simulated. Relative deviations between measured and simulated nitrate and aluminium concentrations are sometimes considerable (mostly between -50 and +50

%), especially for plots with low average measured data, but absolute errors in the simulated concentrations are mostly low.

Evaluation of the emission reduction scenarios in the period 1970-2030 shows a very strong reduction in sulphate concentrations between 1980 and 2000 in the soil due to the high reductions in sulphur emissions. By the year 2010, a significant reduction in nitrate concentration is predicted for most plots, but the effect is most striking for the plots with the highest present N concentrations. Simulations also show that implementation of the Gothenburg protocol causes a reduction of the percentage of aluminium concentrations above an assumed critical value of $0.2 \text{ mol}_e\text{.m}^{-3}$ from 25 % in 1970 to about 5-10 % of the plots in 2030. Al/BC ratios above a critical value of 1 occur at about 5 % of the plots in 1970 and this percentage only slightly decreases towards 2010 because at a number of plots there occurs a decrease of base cation concentration, due to replenishment of the exchange complex. Base saturation improves over time for most plots but for a number of plots where acid inputs remains relatively high, base saturation will still decrease in the future. This shows the difference between the fast reactions in soil solution to emission reductions and the slower reactions of the soil solid phase.

Conclusions and outlook

Major results of this project are that: (i) N leaching and sequestration is influenced by the soil C/N ratio in the organic layer, (ii) C sequestration in forest soils on a European scale is much less than C sequestration due to forest growth and (iii) the impact of N deposition on soil N leaching is fast but the impact on changes in soil C/N ratio is small.

Further research is needed to gain more insight in the dynamics of N and C sequestration on a European scale. Consequently, within an additional project, called CENTER (Carbon - Nitrogen in TERactions in forest ecosystems), literature searches for additional sites and quality assurance checks to increase confidence of data will be continued and the number of parameters will be expanded to include climate, input-output of other major ions, litterfall and C and N pools. This database will be combined with results obtained from a separate project on the input and output of nitrogen in approximately 200 plots from the intensive forest monitoring programme on a European wide scale (level II plots). Measured and derived parameters will be further analysed by statistical methods to identify and validate empirical relationships. This includes correlation analysis, multiple regression (linear and non-linear) and principal component analysis to identify simple ecosystem parameters that are significantly correlated to nitrate leaching, N accumulation, C storage and C accumulation in the forest floor. Empirical models will be developed on a subset of the data and validated on the other subset. Data subsets will include a random split (e.g. 60% model creation 40% verification), Level II on IFEF, IFEF on Level II. The relationships will be further validated on regional forest soil surveys in 150 Dutch forest sites and 100 Danish forest sites

The combination of datasets and empirical relations in dyNamiC provide excellent opportunities to improve and validate SMART both at local and European scales.

The knowledge that will be obtained from the combined European monitoring databases will thus be included in SMART that will also be further developed by including a better description of forest growth and carbon sequestration. The results of both the empirical relations and the process-based model will be compared with measured data on the sites. The validated SMART model will be used to calculate time-dependent N and C sequestration loads for Level II sites. Finally, the SMART model will be used to evaluate the effects of different N deposition scenarios on changes in C and N sequestration for all level I sites. Results of the scenario analysis will provide insight the differences in effectiveness of various scenarios to reduce nitrate leaching from (increase N sequestration in) the soil and the associated effects on C sequestration in soils and biomass. It will also be possible to obtain insight in the number of plots where nitrate concentrations exceed thresholds for nitrate in drinking water.

1 Throughfall N Deposition Influences Soil Solution Nitrate Concentration Differently in European Coniferous and Deciduous Forests

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Keywords: C/N ratio, mixed linear model analysis, nitrate, nitrogen deposition, soil water, time series

Abstract

Increases of atmospheric N deposition are known to influence N cycling in forest ecosystems with potential negative consequences due to leaching of nitrate to ground water. The Pan European Programme for the Intensive and Continuous Monitoring of Forest Ecosystems measures forest conditions at a plot scale for conifer and broadleaved forests, including time-series of soil solution chemistry from Dec. 1995 to Feb. 1998. The influence of ecosystem characteristics on soil solution nitrate concentrations at these forest plots (n=104) was analysed with a statistical model. Soil solution nitrate concentrations varied by season, with summer concentrations being approx. 25% higher than winter concentrations. Soil solution nitrate concentrations increased strongly with throughfall (and bulk precipitation) N input for both broadleaves and conifers. However, at elevated throughfall N input (>10 kg N ha⁻¹ yr⁻¹) nitrate concentrations were higher in broadleaved than in coniferous stands. This tree-type difference was not observed in response to increase in bulk precipitation N input. In coniferous stands throughfall N input, foliage N concentration, organic layer C/N ratio, and nitrate concentrations covaried. Soil solution nitrate concentrations in conifer plots were best explained by a model with throughfall N and organic layer C/N as main factors, where C/N ratio could be replaced by foliage N. The organic layer 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 indicated low, intermediate, and high risk of nitrate leaching, respectively. In broadleaved forests, correlations between N characteristics were less pronounced and soil solution nitrate concentrations were best explained by throughfall N and soil pH (0-10 cm). The results suggest that the responses of soil solution nitrate concentration to changes in N input will be more pronounced in broadleaved than in coniferous forests, since broadleaf are located on the more fertile soils in European forests.

1.1 Introduction

Over the last half-century, anthropogenic emissions of nitrogen (N) compounds to the atmosphere have increased N deposition significantly in the industrialised countries. High N deposition, especially in Western and Central Europe, gave rise to concern over the eutrophying and acidifying impact of N on forest soils and waters (e.g. Malanchuk and Nilsson, 1989) as well as over the potential negative impact on forest health (Nihlgård, 1985; Schulze, 1989). Increased N deposition to forests may lead to a gradual build up of N in plants and soil and cause a range of changes in N cycling processes. This may lead to elevated nitrate leaching loss from forest ecosystems, a condition often referred to as nitrogen saturation (Aber et al., 1989; Gundersen, 1991).

Compilations of ($n > 60$) published input-output budgets from European forests have shown that many sites were leaching more than $5 \text{ kg nitrate-N ha}^{-1} \text{ yr}^{-1}$ (Dise and Wright, 1995; Gundersen, 1995). Nitrate leaching mainly occurred above a threshold of $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in throughfall input, however, the direct correlation between input and output of N was rather weak. These literature reviews were improved and updated with data compilations from studies in plots and catchments ($n = 139$) over the period 1970 to 1995 (Dise et al., 1998a, b) and in plots alone ($n = 77$) in a narrower time span 1985-95 (Gundersen et al., 1998a). Both data sets revealed correlations between N deposition, N concentrations in foliage, and the leaching of nitrate. The regression model that explained most of the variability in nitrate leaching included both N input and the C/N ratio of the organic layer, but this was based on only 30-40 sites, primarily from coniferous forests and with some overlap between the two data sets (Gundersen et al., 1998a; Dise et al., 1998a). Incomplete data sets hampered a thorough statistical analysis of all ecosystem parameters. Further, differences in methodology as well as in temporal and spatial scales may have contributed an unknown error in detecting relationships in these data compilations.

In 1994, the Pan European Programme for the Intensive and Continuous Monitoring of Forest Ecosystems was established, based on the EU Scheme on the Protection of Forests against Atmospheric Pollution and the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP-Forest). The major aim was to increase the understanding of the impact of air pollution and other stress factors on forest ecosystems (De Vries et al., 1998). For > 800 selected forest plots, forest stand, biogeochemistry, and meteorological data are collected based on a common manual in the ICP-Forest Intensive Monitoring (the so-called Level II) programme (UN-ECE, 1998). However, the full monitoring and data collection programme is only operated at approx. 200 sites. The programme includes intercalibration procedures, cross evaluation of methods between member countries as well as quality and reliability checks on the database (De Vries et al., 2001). Thus, the ICP-Forest overcomes some of the limitations of the literature compilations mentioned above. Furthermore it includes both conifer and broadleaf stands.

Soil water chemistry has been included in the Intensive Monitoring (Level II) since 1996, but because the programme is based on plot-scale monitoring, leaching fluxes of nitrate and other ions below the root zone are not readily available without detailed modelling of the sites' water balances. This is time consuming and the calculations add an unknown amount of error to the data set of estimated nitrate leaching fluxes.

In this paper, we therefore used the measured time series of soil solution nitrate concentrations from the Intensive Monitoring plots in a regional analysis of nitrate leaching. The temporal variation of nitrate concentrations (e.g. by season and with rainfall fluctuations) may be significant. An analysis of a comparable data set from a survey of soil solution nitrate concentrations in Denmark showed, however, that despite the temporal variability, site factors such as forest size (in ha), management type and soil texture significantly affected nitrate concentrations in soil solution (Callesen et al., 1999).

The aim of this paper was to explore the Intensive Monitoring data set for the influence of atmospheric N deposition and site-specific factors on soil solution nitrate concentrations and to compare the response of conifer and broadleaf stands. We used a statistical model (mixed linear model) in the analysis that takes into account the repeated sampling of soil solution. To further illustrate some of the main results, we present traditional linear regressions on average soil solution nitrate concentrations. Both sets of models were estimated for all plots as well as for conifer and broadleaved plots separately.

1.2 Methods

Sites and parameters

The Intensive Monitoring programme is carried out on forest plots at sites selected by each participating country in Europe and comprises mandatory surveys of crown condition, foliar chemistry, soil chemistry, and forest growth; and optional surveys on atmospheric deposition, meteorology, ground vegetation, and soil solution chemistry. The number of sites in the soil solution chemistry survey has been steadily increasing since the start in 1996 and currently measurements are performed at 250 sites (de Vries et al., 2001).

For this analysis quality assured soil solution chemistry data were available from the period Dec. 1995 to Feb. 1998 at 160 sites. Data from some sites/countries were excluded from the analyses due to low sampling frequency (e.g. 14 sites from the Netherlands with only one sampling per year) or due to short duration of measurements (< 1-year data). Remaining were 111 sites (Fig. 1.1) from 10 countries: Germany (55 sites), France (15 sites), Norway (15 sites), Belgium (6 sites), Denmark (6 sites), Finland (4 sites), UK (4 sites), Ireland (3 sites), Sweden (2 sites) and Austria (1 site). The sites were mainly from managed forests dominated by one tree species or from plantation monocultures. Three broadleaf species (*Quercus robur* L., *Quercus petraea* L. ex Liebl., *Fagus sylvatica* L.) and six conifer species (*Picea abies* (L.) Karsten,

Picea sitchensis (Bong.) Carrière, *Abies alba* Mill., *Pinus sylvestris* L., *Pinus nigra* Arnold, *Pseudotsuga menziesii* (Mirbel) Franco) were represented. Averages and ranges of selected site characteristics are given in Table 1.1 for the broadleaf and conifer groups. Details on sampling and chemical analyses are found in De Vries et al. (1998, 1999, 2000).

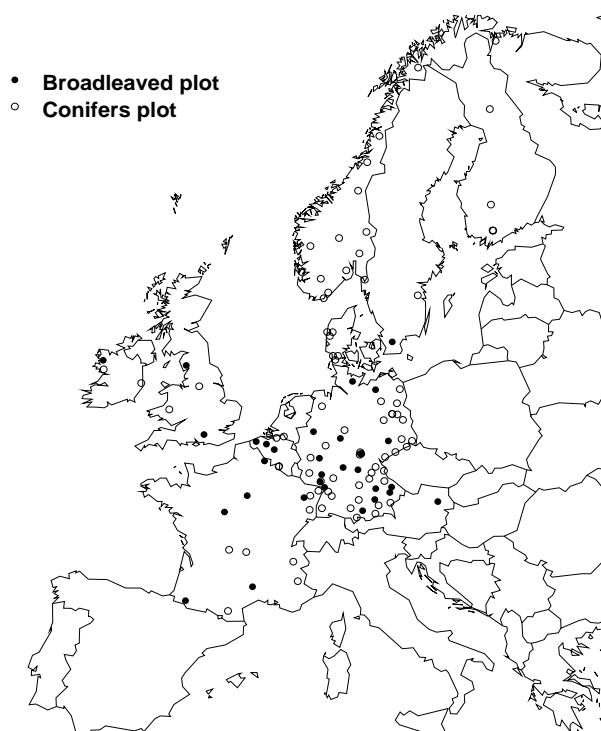


Figure 1.1 Location of sites included in the present study from the ICP-Forest Intensive Monitoring programme in Europe where soil solution chemistry was measured Jan. 1996 to Jan. 1998.

Table 1.1 Simple averages and ranges of selected ecosystem characteristics for conifer and broadleaf sites used in the present study from the Intensive Monitoring database.

	Conifers			Broadleaves		
	Sites (n)	Average	Range	Sites (n)	Average	Range
Latitude (°N)	80	53	43-69	31	50	43-56
Altitude (m)	80	375	25-1375	31	325	25-1375
Average annual air temperature (°C)	80	7	-3-13	31	9	6-14
Throughfall N input (kg N.ha ⁻¹ .yr ⁻¹)	73	14.2	0.3-42	31	14.2	2.3-23
Soil pH _{CaCl2} 0-10 cm	77	3.4	2.8-5.6	30	3.8	2.8-7.3
Soil pH _{CaCl2} 20-40 cm	61	4.3	3.2-6.3	26	4.2	2.9-7.6
Soil base saturation 0-10 cm (%)*	75	20	3-92	27	35	5-97
Soil base saturation 20-40 cm (%)*	57	14	1-95	22	32	3-96
Organic layer C/N	72	28.3	17-46	31	25.5	14-45
Soil C/N 0-10 cm	80	23.9	13-45	31	18.8	12-43
Organic layer (kg.m ⁻²)	52	6.0	0.5-15	29	4.5	0.7-31
Stand age (yr)	80	70	30-150	31	90	50-150
Current year foliage N (mg.g ⁻¹)	74	14.8	9.9-23	28	25.3	20-31
Soil solution nitrate concentration (mg.l ⁻¹)	80	1.54	0.0-15	31	2.62	0.0-18

*measured at soil pH (0.1 M BaCl₂) at 95% of the sites (De Vries et al., 1998).

At most sites soil solution nitrate concentrations were 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. Solutions were collected continuously in tension lysimeters (suction cups) using 5 to 25 samplers per site (De Vries et al., 1999).

For throughfall and bulk precipitation N input we calculated averages at each site for as long a period as possible (2-5 years) ending in 1997. Since the lifetime of N in the ecosystem may be several years, we used this longer average as a measure of 'pollution load' instead of only the N input in the actual two-year period with soil solution data. In the statistical analyses we preferred the use of throughfall N input as a measure for N input to the sites instead of bulk precipitation N input. Throughfall N input includes a large amount of dry deposition and relates therefore more closely to the actual N input to the system than does bulk precipitation N input (Ivens, 1990). Data on N input were missing at seven sites, thus leaving 104 sites for most of the statistical analyses.

In the analysis we considered 45 variables (including those displayed in Table 1.1) covering site, stand and soil characteristics, N input, N and P contents in soil and foliage, and climate.

Statistical models

Correlation and ANOVA analyses were used in a first step to identify significant correlations between average soil solution nitrate concentration and biogeochemical characteristics, and to limit the number of variables tested in more complex statistical models. Average soil solution nitrate concentration (Dec. 1995 to Feb. 1998) correlated with throughfall N input, bulk precipitation N, foliage N content, C/N ratio and total N in the organic layer, soil pH, and temperature and was influenced by climate zone (boreal/north, atlantic north, subatlantic, mediterranean/south) and humus type (mull, moder, mor, raw humus) (Table 1.2).

In the second step, these factors were examined in the construction of a mixed linear model (SAS Proc Mixed; Littell et al., 1996; 1998). A mixed linear model including random and fixed effects is a suitable method to analyse data from repeated samplings such as soil solution concentrations where the samplings are dependent (autocorrelated). The monitoring data fit a split-plot type design (Christensen, 1996) with sites as 'main plots' where site, stand and biogeochemical characteristics are measured once, and with the repeated samplings (time) as 'subplots'.

Sampling frequencies varied from biweekly to seasonal at the sites. To simplify the analysis we used seasonal averages (spring (March-May), summer (June-Aug.), autumn (Sept.-Nov.) and winter (Dec.-Feb.)) calculated on the available data from Dec. 1995 to Feb. 1998; that is, 3-9 repeated measurements per site. Soil solution nitrate concentrations were transformed prior to analysis by the function $y = \log(x + 0.05)$ to obtain homogeneity of variance. The value 0.05 (mg NO₃-N.l⁻¹) was added to avoid observations equal to zero, which can not be log-transformed. 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).

Table 1.2 Results of correlation and ANOVA statistical analyses of relationships between simple averages of soil solution nitrate concentrations, throughfall N input, and biogeochemical characteristics for all sites. In ANOVA, different letters indicate significant differences between estimated means for each climate and humus-type category.

Correlation analyses	Average soil solution nitrate concentration			Throughfall N input		
	n	R	p	n	R	p
Throughfall N input	104	0.54	0.0001	104	1	
Bulk precipitation N	104	0.35	0.0003	104	0.76	0.0001
Average annual air temperature	111	0.23	0.02	104	0.42	0.0001
Current year foliage N	102	0.33	0.0008	95	0.23	0.02
Total N in organic layer	81	0.34	0.002	74	0.16	*n.s.
Organic layer C/N	103	-0.26	0.01	96	-0.41	0.0001
Soil pH _{CaCl2} 0-10 cm	107	-0.12	n.s.	100	-0.38	0.0001
Soil pH _{CaCl2} 10-20 cm	93	-0.37	0.0004	88	-0.55	0.0001
ANOVA	Mean (mg N.l ⁻¹)			Mean (kg N.ha ⁻¹ .yr ⁻¹)		
Climate zone	111		0.0001	104		0.0001
Boreal/north	17	0.1 a		17	2.2 a	
Atlantic north	29	3.5 b		25	14 b	
Subatlantic	50	1.8 b		48	17 b	
Mediterranean/south	15	1.1 b		14	11 b	
Humus type	111		0.0001	104		p=0.0002
Raw humus	26	0.7 a		24	6.4 a	
Mor	24	3.3 b		20	12 ab	
Moder	39	2.0 b		39	18 b	
Mull	22	1.6 b		21	11 ab	

*n.s. = not significant

Since throughfall N correlated strongly with soil solution nitrate and several other factors (Table 1.2), each other factor was subsequently tested for significant effects on soil solution nitrate concentration in a model including throughfall N. The factors found to be significant were: tree-type, C/N ratio of the organic layer, humus type, and foliage N content. The model was furthermore used to test for interactions (covariance). The model best explaining soil solution nitrate was found in an iterative process for reducing insignificant factors and interactions. The resulting model for log-transformed soil solution nitrate observations at site (s) and season (t) was:

$$\text{Soil NO}_3^-(s,t) = \text{season}(t) + \text{throughfall N}(s) + \text{tree-type}(s) + \text{throughfall N} * \text{tree-type}(s) + \text{C/N organic layer}(s) + \text{site}(s) + \text{error}(s,t) \quad (1.1)$$

The estimates of intercept and coefficients for the model are given in Table 1.3. The terms 'site' and 'error' are random Gaussian variables. By taking 'site' as a random effect with expected mean zero and variance σ^2 , degrees of freedom were liberated for the analysis of biogeochemical site characteristics. These general features were the focus of the analysis, rather than predicting concentrations at specific sites. This represents the main difference from a multiple regression approach.

Table 1.3 Estimates of intercept and coefficients in the overall model (Eq. 1), conifers model (Eq. 2), and broadleaves model (Eq. 3) predicting $\log(\text{NO}_3 \text{ (mg N.l}^{-1}) + 0.05)$. For a categorical factor (tree-type), the coefficient is added in the equation and for continuous factors the coefficient is multiplied to the factor and added. As an example, in the overall model (Eq. 1) conifer in spring with throughfall 30 kg N.ha⁻¹.yr⁻¹ at C/N 25 will yield: $\log(\text{NO}_3+0.05) = -0.93 + 0.06 + 0.09*30 + 0.3 - 0.04*30 - 0.02*25 = 0.43$; back-transformed 1.5 mg NO₃-N.l⁻¹.

Effect	Level	All data (n=104)	Conifers (n=73)	Broadleaves (n=31)
Intercept		-0.93	-0.51	-2.84
Season	Autumn	0.02	0.03	-0.006
	Spring	0.06	0.08	0.03
	Summer	0.07	0.06	0.09
	Winter	0	0	0
Throughfall N		0.09	0.05	0.11
Tree-type	Conifers	0.30	*n.a.	n.a.
	Broadleaves	0	n.a.	n.a.
Tree-type*throughfall N	Conifers	-0.04	n.a.	n.a.
	Broadleaves	0	n.a.	n.a.
C/N organic layer		-0.02	-0.02	**n.s.
Soil pH 0-10 cm		n.s.	n.s.	0.29

*n.a. = not analysed. **n.s. = not significant

In Fig. 1.2, the ‘site’ term is illustrated for a specific site as the difference between model predictions including and excluding the random site effect. This particular site from Belgium has a large site effect and thus deviates strongly from the predictions by the main factors in the model. The deviation between observations and the solid line is the ‘error’. An $r^2=0.92$ for the model was calculated by use of sum of squares of observed values of soil solution nitrate concentrations and residuals from predicted values. This r^2 can not be interpreted like in a traditional regression model, since as illustrated in Fig. 1.2 part of the variability is captured in the ‘site’ term. When calculating r^2 by use of the residuals from model predictions excluding the random site effect, it was reduced to 0.58. Thus, approx. 34% of the variation was captured in the random ‘site’ term.

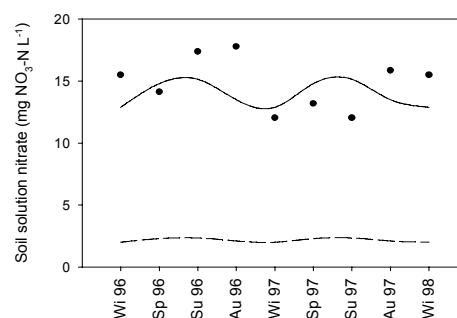


Figure 1.2 The observed nitrate concentration time series for plot 15 (Belgium, *Pinus sylvestris*, organic layer C/N ratio 34.9, and throughfall input 32.1 kg N.ha⁻¹.yr⁻¹) and the predicted concentrations found by use of the model (Eq. 1.1) including the random site effect (solid line) and excluding the random site effect (dashed line). Note that the predicted values are back-transformed (log) values which explains why the random site effect (the difference between the solid and the dashed line) not seems constant over time.

The model (Eq. 1.1) was used to estimate medians for each level of main factors. 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).

The same iterative 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 non-significant factors and interactions. The resulting models were:

Conifers ($r^2=0.93$; excluding the random site effect $r^2=0.59$):

$$\text{Soil NO}_3^-(s,t) = \text{season}(t) + \text{throughfall N}(s) + \text{C/N organic layer}(s) + \text{site}(s) + \text{error}(s,t) \quad (1.2)$$

Broadleaves ($r^2=0.87$; excluding the random site effect $r^2=0.58$):

$$\text{Soil NO}_3^-(s,t) = \text{season}(t) + \text{throughfall N}(s) + \text{soil pH}(0-10 \text{ cm})(s) + \text{site}(s) + \text{error}(s,t) \quad (1.3)$$

The estimates of intercept and coefficients in the equations for the models (Eq. 1.2 and 1.3) are given in Table 1.3.

In addition, to further illustrate the main effects found in the models and to focus on differences between conifer and broadleaf forests, we present scatter plots and results from regression analyses. Linear (and multiple) regressions between average soil solution nitrate concentrations and site properties were performed by use of SAS Proc GLM, as well as tests for homogeneity of slopes (SAS institute, 1990).

1.3 Results and Discussion

In this section we present and discuss results obtained with mixed linear models for all sites (Eq. 1.1) as well as for conifers (Eq. 1.2) and broadleaf sites (Eq. 1.3) separately, based on the time series of soil solution nitrate concentration from the ICP-Forest Intensive Monitoring sites. The differences in soil solution nitrate concentrations are discussed in relation to other ecosystem characteristics including the covariance of different N variables (throughfall N input, bulk N precipitation, C/N ratio of organic layer, foliage N) and temperature.

Overall results

The Intensive Monitoring data set available for this analysis covers the gradient found in N deposition from North to Central Europe (<1 to $40 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) and broad ranges in climate and soil conditions (Table 1.1). The sites represent North, West and part of Central Europe with the main cluster of sites in Germany (Fig. 1.1).

The overall median of soil solution nitrate concentration in the analysed data set was low, at 0.53 mg N.l⁻¹ (Table 1.4) despite the 0 to 18 mg N.l⁻¹ range in the data (Table 1.1). The distribution was skewed towards zero with 60% of the sites having concentrations below 1 mg N.l⁻¹ and only 2.8 % (3 sites) exceeding the European standard for nitrate in drinking water (11.3 mg N.l⁻¹). However, in this analysis 14 sites in the Netherlands with high N deposition (>25 kg N.ha⁻¹.yr⁻¹) had been excluded due to low sampling frequency. When these sites were included, the median was 0.7 mg N.l⁻¹ (De Vries et al., 2000) and the drinking water standard was exceeded at 10% of the sites (i.e. at half of the Netherlands sites).

Table 1.4 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)	Median nitrate concentration (mg N.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

Seasonal effects

Winter concentrations were significantly (p=0.011) lower than summer concentrations (Table 1.4), which may be explained by the diluting effect of increased water infiltration during winter due to higher rainfall and decreased evapotranspiration, as well as by decreased nitrifying activity during the cold season. In a similar study of dormant season soil solution nitrate concentrations in Danish forests, Callesen et al. (1999) observed the lowest concentrations in January and found that absolute water content could explain part of the variation in nitrate concentrations (lower concentration at higher water content). The seasonal pattern in soil solution (Table 1.4) is opposite to the concentration pattern usually observed in stream water where very low concentrations occur in the summer when plant uptake is high and higher concentrations occur in the winter (e.g. Stoddard, 1994). The reason for this difference in concentration pattern between soil solution and stream water datasets may be, apart from the possible effect of dilution in winter, that the sampling generally occurred below the main rooting zone limiting the influence of plant uptake from this layer. Thus nitrate leached down the profile in the dormant

season may remain in the subsoil in the summer where water movement is limited by evapotranspiration.

Although significant, the differences between seasons were relatively small (0.12 mg N.l⁻¹ or 25% at the median concentration, Table 1.4). The effect of years (1996, 1997) on soil solution nitrate concentrations was tested in the mixed model as well but it was not significant and thus not included in the model (Eq. 1.1).

Throughfall and bulk precipitation N input

Throughfall N input was the strongest predictor of soil solution nitrate concentrations ($p < 0.0001$). Nitrate concentrations above the limit of detection occurred (with a few exceptions) above a threshold of 7 kg N.ha⁻¹.yr⁻¹ in throughfall (Fig. 1.3a). Nitrate concentrations above 1 mg N.l⁻¹ occurred above 10 kg N.ha⁻¹.yr⁻¹ in throughfall. The later compare with the threshold observed in earlier studies of input-output budgets (Dise and Wright, 1995; Gundersen, 1995; Dise et al., 1998a; Gundersen et al., 1998a). Due to a significant interaction between throughfall N and tree-type ($p = 0.045$) broadleaves had significantly higher nitrate concentrations than conifers at average throughfall (14.2 kg N.ha⁻¹.yr⁻¹) (Table 1.4). This interaction indicates that the difference in soil solution nitrate concentrations between broadleaves and conifers depended on the level of throughfall N input, which is further illustrated by linear regression between throughfall N and the log-transformed average nitrate concentration in soil solution (Fig. 1.3a).

Broadleaves (at throughfall >10 kg N.ha⁻¹.yr⁻¹) had higher soil solution nitrate concentrations than conifers at the same throughfall N input level. The slopes of regression lines were significantly different for conifers and broadleaves ($p = 0.0069$), suggesting that nitrate concentration in soil solution under broadleaves will respond more to throughfall N input changes than under conifers. Earlier compilations of data from the literature have shown that nitrate leaching increase with increasing throughfall N input (Dise et al., 1998a; Gundersen et al., 1998a). However, no differences between tree-types were found, but this could be due to low sample size for broadleaves in these data compilations.

Bulk precipitation N input correlates with throughfall N input (Fig. 1.3c) and can usually replace throughfall N in the relationships found in this type of regional analysis (Dise & Wright, 1995; Gundersen, 1995; Tietema & Beier, 1995). When throughfall N was replaced by bulk precipitation N in the statistical model (Eq. 1.1) there was, however, no interaction between tree-type and bulk precipitation N input ($p = 0.73$) nor was there an effect of tree-type alone ($p = 0.64$) as also illustrated in Fig. 1.3b by simple regression analysis on site average nitrate values ($p = 0.32$). The other factors stayed significant in the mixed linear model (results not shown). However, the variation explained with bulk precipitation N in the statistical model was much less $r^2 = 0.33$ than with throughfall N ($r^2 = 0.58$) as also indicated in the difference in r^2 for regressions in Fig. 1.3a and Fig. 1.3b. The fact that the tree-type effect in eq. 1.1 disappear if throughfall N is replaced by bulk precipitation N indicates that the differences in soil solution nitrate between broadleaves and conifers at increasing

throughfall N input (Fig. 1.3a) may be a result of complex interactions between N input, cycling and retention.

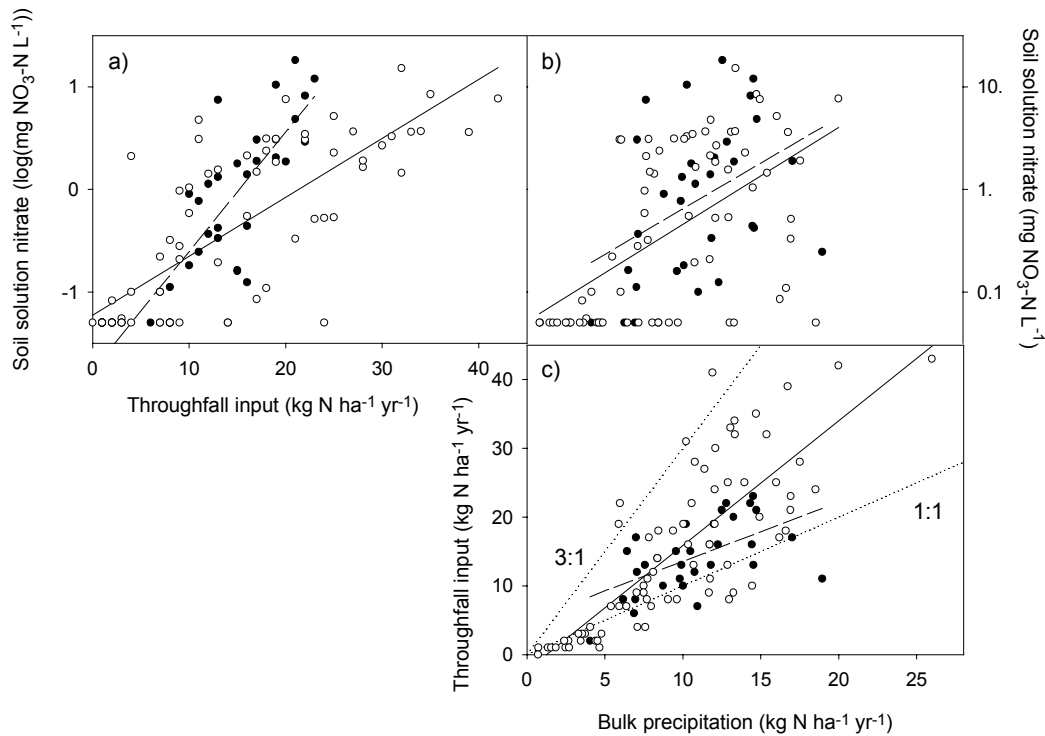


Figure 1.3 Nitrate concentrations in soil solution (log transformed averages Jan. 1996 to Jan. 1998) vs a) throughfall N input, and b) bulk precipitation N (both calculated averages 1993-1997 from Intensive Monitoring sites); as well as c) throughfall N input vs bulk precipitation N. The dashed lines show the 1:1 and 1:3 relationships. Conifers: ○; broadleaves: ●. The regressions are for a) conifers: $\log(y) = 0.06x - 1.2$ ($r^2=0.59$, $p=0.0001$); broadleaves: $\log(y) = 0.12x - 1.8$ ($r^2=0.65$, $p=0.0001$); for b) conifers: $\log(y) = 0.09x - 1.3$ ($r^2=0.32$, $p<0.0001$); broadleaves: $\log(y) = 0.09x - 1.18$ ($r^2=0.16$, $p=0.02$); for c) conifers: $y = 1.8x - 2.3$ ($r^2=0.65$, $p=0.0001$); broadleaves: $y = 0.86x + 4.9$ ($r^2=0.32$, $p=0.0008$).

Conifers are generally found to have higher throughfall N input than broadleaves at high levels of bulk precipitation N input (Rothe et al., 2002). This was also indicated in the present data set (Fig. 1.3c), although the slopes of regression lines for conifers and broadleaves were not significantly different ($p=0.11$). At some conifer sites throughfall N was more than 3 times bulk precipitation N (Fig. 1.3c). This effect 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., 2002). This difference is not observed at low N deposition levels ($<5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) where direct assimilation of N in the canopy may decrease throughfall N relative to bulk precipitation N input (Fig. 1.3c). With higher N input to conifers, one might expect higher nitrate concentration below conifers than below broadleaves. Accordingly, a compilation of data from adjacent pairs of Norway spruce and beech stands grown on the same soil (and receiving the same bulk precipitation N input) at 16 European sites showed that Norway spruce stands had higher throughfall N input and higher nitrate concentration in the subsoil than beech stands (Rothe et al., 2002). This is opposite

to the results presented here from the monitoring program (Fig 1.3a), where broadleaves had higher nitrate concentration than conifers at intermediate to high throughfall N input. We suspect this is due to a difference in soil conditions between the two tree-types more than an effect of the tree-types alone, since broadleaves had higher base saturation and lower C/N ratio in the mineral soil than conifers (Table 1.1). Naturally as well as in European plantation forestry, broadleaves are more abundant on the fertile and N rich soils, whereas conifers dominate on the less fertile and N poor soils, which was also reflected in the two groups of sites in our analysis. It was not possible to test if fertile soil conditions increase nitrate concentrations irrespective of tree-type, since fertile conifer sites in our dataset only existed at low throughfall N input. In a similar analysis of soil solution nitrate concentrations in Danish forests at 111 sites, Callesen et al. (1999) observed low concentrations at sandy infertile soils and higher concentrations at fertile loamy soils and could not detect an effect of tree species.

The organic layer C/N ratio

The C/N ratio of the organic layer was the only biogeochemical property besides throughfall N input that significantly explained nitrate concentrations in the common model (Eq. 1.1) for broadleaves and conifers (Table 1.4). When testing the same factors (throughfall N, tree-type and C/N organic layer) in the equivalent regression analysis on average nitrate concentrations, the C/N ratio was not a significant factor ($p=0.19$) in the linear model. This indicates that use of the information in the time series of seasonal fluctuations in nitrate concentrations increased the analytical power of the statistical models. This may also partly be due to the higher number of degrees of freedom which is obtained by use of time series in the Proc Mixed procedure.

The result that C/N ratio of the organic layer is a significant factor in the model (Eq. 1.1) is in line with previous work by Gundersen et al. (1998a) who, based on analysis of three independent data sets, found that nitrate leaching in forests was increasing with decreasing C/N ratio in the organic layer. They suggested that C/N ratio in the organic layer could be used as an indicator of the N status of the ecosystem and therefore as a predictor of the risk for nitrate leaching from the system. Gundersen et al. (1998a) proposed three C/N classes >30 , $25-30$ and <25 as characteristic for forests with a low, intermediate and high risk for nitrate leaching, respectively. We tested these C/N classes in the mixed model (Eq. 1.1) and found that weighted medians of nitrate concentration in the three C/N classes were significantly different increasing from 0.13 mg.l^{-1} in the >30 C/N class, over 0.49 mg.l^{-1} in the range $25-30$ to 1.24 mg.l^{-1} in the <25 C/N class, respectively (Table 1.4).

In the separate model analyses of the two tree-types (Eq. 1.2 and 1.3), C/N ratio of the organic layer entered the model for conifers ($p=0.029$), but not for broadleaves. Thus, only the results from conifers support the hypothesis that the organic layer C/N ratio may be a predictor of the risk for nitrate leaching from the system. In addition, the data in the previous work by Gundersen et al. (1998a) were mainly from coniferous forests.

In an European data set compile from literature Dise et al. (1998b) found that sites with throughfall N input 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. We observed similar results for the Intensive Monitoring data for conifers (Fig. 1.4): 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. Two sites had high nitrate concentrations at C/N ratios above 30 and both had deposition levels well above 30 kg N.ha⁻¹.yr⁻¹. Neither the general model (Eq. 1.1) nor the conifer model (Eq. 1.2) predicted high soil solution nitrate at these sites as illustrated for one of the sites in Fig. 1.2 by the high random site effect of 0.8. De Schrijver et al. (2000) suggested that nitrate leaching at the other site could be due to transport of throughfall ammonium down through the upper soil layers to deeper layers with lower C/N ratio and higher nitrifying activity.

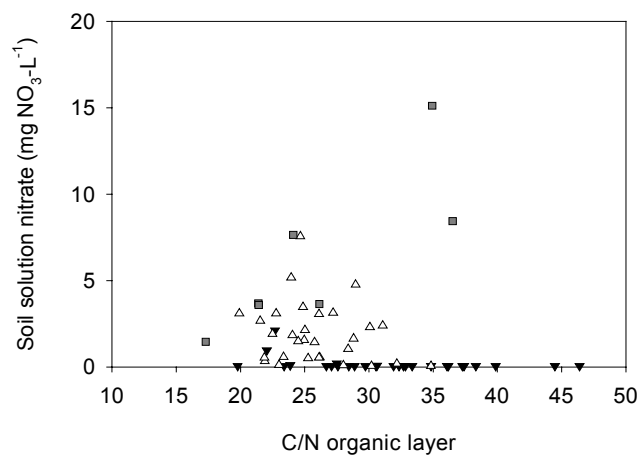


Figure 1.4 Nitrate concentrations in soil solution (averages Jan. 1996 to Jan. 1998) vs organic layer C/N ratio in conifers at low ($\blacktriangledown < 10 \text{ kg N.ha}^{-1}.\text{yr}^{-1}$), intermediate ($\triangle 10\text{-}30 \text{ kg N.ha}^{-1}.\text{yr}^{-1}$) and high ($\blacksquare > 30 \text{ kg N.ha}^{-1}.\text{yr}^{-1}$) throughfall N input at Intensive Monitoring sites.

Intercorrelations between C/N, throughfall N, foliage N, temperature and soil solution 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) and nitrate leaching (Gundersen et al., 1998a). With time, elevated N input may increase N concentrations in plants and soils and decrease the C/N ratio of the organic layer. The decades of elevated deposition seem to have influenced the C/N ratio of this layer in European forests, since the organic layer C/N ratio decreased with throughfall N input for both tree-types (Fig. 1.5c), although the slopes of the regression lines differed significantly by tree-type ($p=0.015$). The organic layer C/N decreased 2 units for conifers and 5 units for broadleaves per 10 kg N.ha⁻¹.yr⁻¹ increase in throughfall N (Fig. 1.5c). However, throughfall N input increased with average annual temperature due to similar north-south gradients in deposition and temperature for conifers in the data set ($r^2=0.30$, $p<0.0001$, results not shown) This

correlation was not found for broadleaves ($r^2=0.05$, $p=0.22$). Thus, the trend of decreasing C/N with N input may have a climatic component at least for conifers. In multiple regression analysis of the conifer data set, C/N ratio of the organic layer was predicted ($r^2=0.36$, $p<0.0001$) by throughfall N ($p<0.0001$), temperature ($p=0.02$) and interaction between the two ($p=0.0002$). The relative importance of temperature and throughfall input in relation to C/N ratio could not be explored further with the current data set, due to the distribution of average temperatures and the strong covariation between temperature and throughfall N input.

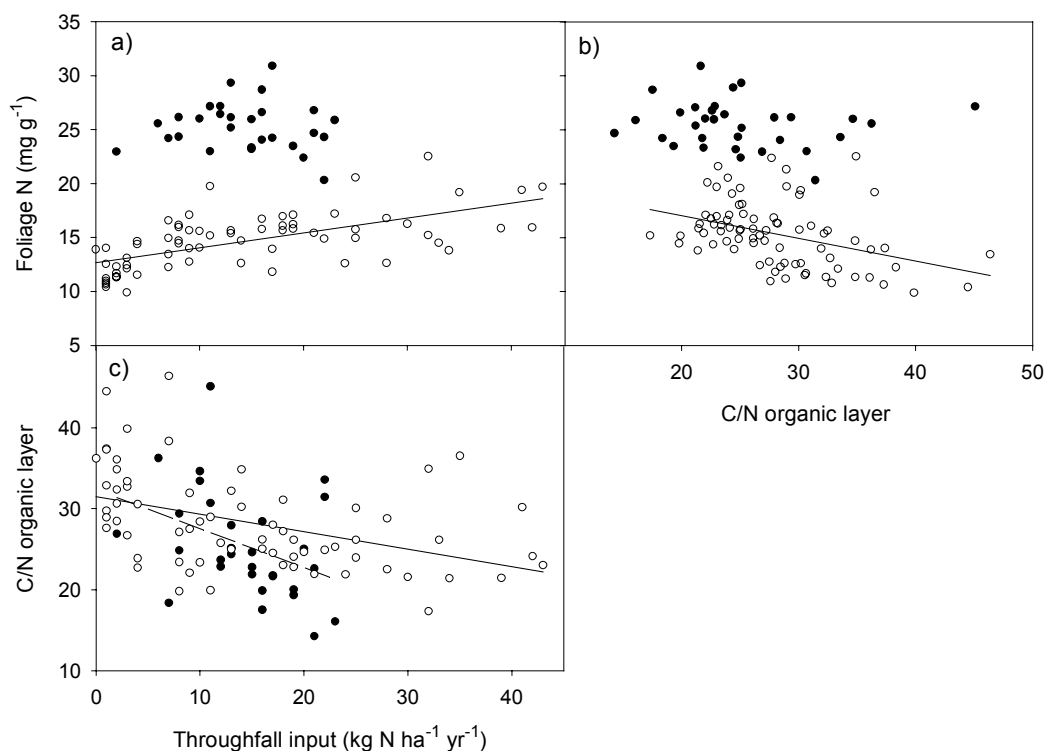


Figure 1.5 Foliage N concentration vs **a)** throughfall N input; and **b)** C/N ratio of the organic layer; and **c)** C/N ratio of the organic layer vs throughfall N input (averages 1993-1997) at Intensive Monitoring sites. Conifers: ○; broadleaves: ●. The regressions are for **a)** conifers: $y = 12.7 + 0.14x$ ($r^2=0.40$, $p<0.0001$); for **b)** conifers: $y = 21.2 - 0.21x$ ($r^2=0.16$, $p=0.0003$); and **c)** conifers: $y = 31.5 - 0.21x$ ($r^2=0.19$, $p=0.0002$); broadleaves: $y = 32.3 - 0.48x$ ($r^2=0.14$, $p=0.036$).

Another factor of importance for the C/N ratio is the N status of the litter input. Litterfall N was not measured at the Intensive Monitoring sites, although foliage N concentration was, which has been shown to correlate with litter N concentration (Tietema and Beier, 1995). Foliage N content was not included in the overall mixed model due to strong covariance with throughfall N and to species differences. Foliage N concentration decreased as the C/N of the organic layer increased for conifers (Fig. 1.5b) but not for broadleaves ($p=0.52$), and foliage N concentration differed between broadleaves (25.3 mg.g⁻¹) and conifers (14.8 mg.g⁻¹) (Fig. 1.5b, Table 1.1). In addition, foliage N content increased with throughfall N input for conifers (Fig. 1.5a), but not for broadleaves ($p=0.71$). A reason for these differences between conifers and broadleaves could be that retranslocation of N prior to senescence is a more important process in broadleaves which makes broadleaf foliage more

independent of N input. Another possibility as discussed above is that the broadleaves in general are found on the more fertile soils.

With the significant covariation between throughfall N, C/N ratio, and foliage N concentration for conifers, a correlation between soil solution nitrate concentration and foliage N content may be expected in conifers (Fig. 1.6). 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. Thus, the foliage N (mg N.g^{-1}) classes <13 , $13\text{--}17$ and >17 may indicate low, intermediate, and high risk of nitrate leaching, respectively. The threshold at 13 mg N.g^{-1} where nitrate start to occur in soil solutions corresponds surprisingly well with the thresholds $13\text{--}14 \text{ mg N.g}^{-1}$ where several conifers no longer give a significant growth response to fertiliser additions (Brockley, 2000 and ref. herein; Sikstrøm et al., 1998).

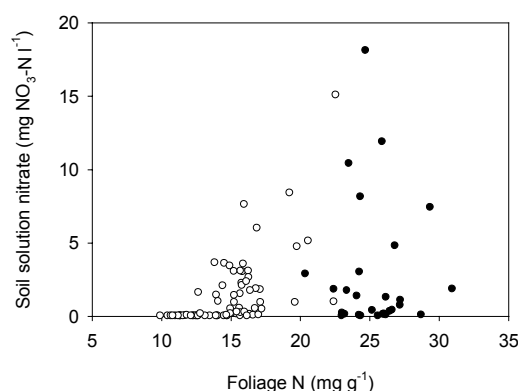


Figure 1.6 Nitrate concentrations in soil solution (averages Jan. 1996 to Jan. 1998) vs foliage N concentration at Intensive Monitoring sites. Conifers: ○; broadleaves: ●. The regression is for conifers: $y = 0.54x - 6.5$ ($r^2=0.34$, $p<0.0001$).

When replacing C/N ratio in Eq. 1.2 with foliage N content in the mixed model analysis of conifers, a significant relationship to nitrate concentration was also found ($p<0.0001$). For broadleaves neither the C/N ratio ($p=0.54$) nor the foliage N content ($p=0.89$) showed significant relationships to nitrate concentration in soil solution in the mixed model analysis.

Relations to soil pH

Previous studies have shown a negative correlation between pH of the B-horizon of European forests and nitrate leaching which may be explained by the acidifying effect from deposition and nitrification when nitrate is leached from the soil (Dise et al., 1998a). Such a negative correlation was also found in the present study (Table 1.2) but it was not significant in the overall model (Eq. 1.1). In addition, for conifers alone pH was only significant when throughfall N input was not included in the model (results not shown). In contrast, for broadleaves both throughfall N and soil pH entered the final model (Eq. 1.3). This may indicate that soil type and characteristics are more important for the response to N deposition in broadleaf than in coniferous forests. A non-linear effect of pH on nitrate concentration may be

expected with high nitrate both at low pH due to the acidifying effect of nitrate leaching as explained above and at high pH due to complete nitrification of N inputs. There was an indication of such an effect in the data for broadleaves, but the number of sites with high pH was not sufficient to substantiate such a relationship.

1.4 Conclusion

Soil solution nitrate concentrations are low ($<1 \text{ mg N.l}^{-1}$) at 60% of the Intensive Monitoring plots with soil solution measurements. Concentrations in winter are generally lower than in summer, but seasonal differences are small. Elevated nitrate concentrations occurred above a threshold of $7 \text{ kg N.ha}^{-1}\text{.yr}^{-1}$ in throughfall input. The response of coniferous and broadleaf forest to N deposition in throughfall is different and the tree-types need to be analysed separately.

In coniferous forests ($n=73$), N input with throughfall, foliage N concentration, organic layer C/N ratio, and nitrate leaching do covary. Soil solution nitrate concentrations are best explained by a model with throughfall N and organic layer C/N as main factors, though C/N ratio can be replaced by foliage N. The results confirm conclusions from previous literature reviews (Gundersen et al., 1998a; Dise et al., 1998b), that the organic layer C/N ratio classes >30 , 25-30 and <25 indicate low, intermediate, and high risk of nitrate leaching as well as the foliage N (mg N.g^{-1}) classes <13 , 13-17 and >17 , respectively.

In broadleaf forests ($n=31$), correlations among N characteristics are less pronounced than in conifers, but sample size is less than half of conifers. A model including throughfall N and soil pH (0-10 cm) as main factors best explains soil solution nitrate concentrations. The results suggest that the responses of soil solution nitrate concentration to changes in throughfall N deposition (if throughfall N is higher than $10 \text{ kg N.ha}^{-1}\text{.yr}^{-1}$) will be more pronounced in broadleaf than in coniferous forests in Europe, mainly because broadleaf forests grow on more fertile soils than coniferous forests.

Acknowledgements

This research was supported by the European Commission contract SG(99) D/10844) (HLK) and article 254 contract No 2000.60.NL, 3B; the DYNAMIC project (PGU). Special thanks are due to all the people involved in the Intensive Monitoring programme for the thorough work on all the monitoring plots.

References

- Aber JD, Nadelhoffer KJ, Steudler P, Melillo JM. 1989. Nitrogen saturation in northern forest ecosystems. *BioScience* **39**: 378-386.
- Brockley, RP. 2000. Using foliar variables to predict the response of lodgepole pine to nitrogen and sulphur fertilization. *Canadian Journal of Forest Research* **30**: 1389-1399.

- Callesen I, Raulund-Rasmussen K, Gundersen P, Stryhn H. 1999. Nitrate concentrations in soil solutions below Danish forests. *Forest Ecology and Management* **114**: 71-82.
- Christensen R. 1996. Analysis of variance, design and regression. Chapman and Hall London UK. Chapter 6. p146; Chapter 12. p344.
- De Vries W, Reinds GJ, Deelstra HD, Klap JM, Vel EM. 1998. Intensive monitoring of forest ecosystems in Europe. Technical report. EC-UN/ECE 1998, Brussels, Geneva. 104p.
- De Vries W, Reinds GJ, Deelstra HD, Klap JM, Vel EM. 1999. Intensive monitoring of forest ecosystems in Europe. Technical report. EC-UN/ECE 1999, Brussels, Geneva. 160p.
- De Vries W, Reinds GJ, van Kerkvoorde MS, Hendriks CMA, Leeters EEJM, Gross CP, Voogd JCH, Vel EM. 2000. Intensive monitoring of forest ecosystems in Europe. Technical report. EC-UN/ECE 2000, Brussels, Geneva. 191p. (http://europa.eu.int/comm/agriculture/fore/monitor/2000/tech_en.pdf).
- De Vries W, Reinds GJ, van der Salm C, Draaijers GPJ, Bleeker A, Auce J, Gundersen P, Kristensen HL, van Dobben H, De Zwart D, Derome J, Voogd JCH, Vel EM. 2001. Intensive monitoring of forest ecosystems in Europe. Technical report 2001. EC-UN/ECE 2001, Brussels, Geneva. 161p.
- De Schrijver A, van Hoydonck G, Nachtergale L, de Keersmaecker L, Mussche S, Lust N. 2000. Comparison of nitrate leaching under silver birch (*Betula pendula*) and Corsican pine (*Pinus nigra* ssp. *laricio*) in Flanders (Belgium). *Water, Air, and Soil Pollution* **122**: 77-91.
- Dise NB, Wright RF. 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management* **71**: 153-161.
- Dise NB, Matzner E, Gundersen P. 1998a. Synthesis of nitrogen pools and fluxes from European forest ecosystems. *Water, Air, and Soil Pollution* **105**: 143-154.
- Dise NB, Matzner E, Forsius M. 1998b. Evaluation of organic horizon C:N ratio as an indicator of nitrate leaching in conifer forests across Europe. *Environmental Pollution* **102 S1**: 453-456.
- Emmett BA, Gundersen P, Kjønaas OJ, Tietema A, Boxman AW, Schleppi P, Wright RF. 1998. Predicting the effects of atmospheric nitrogen deposition in conifer stands: evidence from the NITREX ecosystem-scale experiments. *Ecosystems* **1**: 352-360.
- Gundersen P. 1991. Nitrogen deposition and the forest nitrogen cycle: role of denitrification. *Forest Ecology and Management* **44**: 15-28.

- Gundersen P. 1995. Nitrogen deposition and leaching in European forests – preliminary results from a data compilation. *Water, Air, and Soil Pollution* **85**: 1179-1184.
- Gundersen P, Callesen I, De Vries W. 1998a. Nitrate leaching in forest ecosystems is related to organic top layer C/N ratios. *Environmental Pollution* **102 S1**: 403-407.
- Gundersen P, Emmett BA, Kjønaas OJ, Koopmans C, Tietema A. 1998b. Impact of nitrogen deposition on nitrogen cycling: a synthesis of NITREX-data. *Forest Ecology and Management* **101**: 37-55.
- Ivens W, 1990. Atmospheric deposition onto forests. Ph.D. thesis, University of Utrecht, The Netherlands. ISBN 9062660800. 153p.
- Littell RC, Milliken GA, Stroup WW, Wolfinger RD. 1996. SAS systems for mixed models. SAS Institute, Cary NC. Chap. 3-5. p87-177.
- Littell RC, Henry PR Ammerman CB, 1998. Statistical analysis of repeated measures data using SAS procedures. *J. Anim. Sci.* **76**: 1216-1231.
- Malanchuk JL, Nilsson J. 1989. The role of nitrogen in the acidification of soils and surface waters, Miljørapport 1989:10 (NORD 1989:92), Nordic Council of Ministers, Copenhagen, ISBN 8773033693.
- Nihlgård B. 1985. The ammonium hypothesis - an additional explanation to the forest dieback in Europe. *Ambio* **14**: 2-8.
- Parkin TB, Robinson JA. 1994. Statistical treatment of microbial data. Weaver et al., editors. *Methods of soil analysis. Part 2. Microbiological and biochemical properties.* SSSA Madison WI. SSSA Book Series 5. p15-40.
- Rothe A, Huber C, Kreutzer K, Weis W. 2002. Deposition and soil leaching in stands of Norway spruce and European Beech: Results from the Höglwald research in comparison with other European case studies. *Plant and Soil* **240**: 33-45.
- SAS institute, 1990. The GLM procedure. In: *SAS User's Guide: Statistics Version 6.* SAS Institute Inc., Cary, NC, USA, p891-996.
- Schulze E-D. 1989. Air pollution and forest decline in spruce (*Picea abies*) forest. *Science* **244**: 776-783.
- Sikström U, Nohrstedt H-Ö, Petterson F, Jacobson S. 1998. Stem-growth response of *Pinus sylvestris* and *Picea abies* to nitrogen fertilization as related to needle nitrogen concentration. *Trees* **12**: 208-214.

Stoddard JL. 1994. Long-term changes in watershed retention of nitrogen: Its causes and aquatic consequences. Baker LA, editor. Environmental Chemistry of Lakes and Reservoirs. Washington (DC), American Chemical Society. p223-284.

Tietema A, Beier C. 1995. A correlative evaluation of nitrogen cycling in the forest ecosystems of the EC projects NITREX and EXMAN. Forest Ecology and Management **71**: 143-151.

UN-ECE. 1998. Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests (4th edition). Hamburg, Geneva. (<http://www.icp-forests.org/Manual.htm>).

2 Nitrogen Input together with Ecosystem Nitrogen Enrichment Predict Nitrate Leaching from European Forests

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Keywords: nitrate leaching, C/N ratio, forest, nitrogen deposition

Abstract

The IFEF database (Indicators of Forest Ecosystem Functioning), consisting of nitrogen deposition, nitrate leaching fluxes, and soil and ecosystem characteristics, is analysed to evaluate the C/N ratio in the organic horizon as an indicator of nitrate leaching. One hundred and eighty one forests are examined, from countries across Europe ranging from boreal to Mediterranean regions, encompassing broadleaf and coniferous sites and plot and catchment studies. N input in throughfall ranges from less than 1 kg N.ha⁻¹.yr⁻¹ in northern Norway and Finland to greater than 60 kg N.ha⁻¹.yr⁻¹ in the Netherlands and Czech Republic. The amount of NO₃⁻ leached covers a smaller range, between 1 and 40 kg N.ha⁻¹.yr⁻¹. Nitrate leaching is strongly dependent on the amount of nitrogen deposited in throughfall (N input) and simply adding the C/N ratio in the organic horizon does not improve this relationship. However, when the data are stratified based on C/N ratios less than or equal to 25 and greater than 25, highly significant relationships ($p < 0.05$) are observed between N input and NO₃⁻ leached. The slope of the relationship for those sites where C/N ratio is ≤ 25 ('nitrogen enriched' sites) is twice that for those sites where C/N ratio is > 25 . These empirical relationships may be used to identify which forested ecosystems are likely to show elevated rates of nitrate leaching under predicted future nitrogen deposition scenarios. Elevated NO₃⁻ leaching also shows a relationship with soil pH, with high rates of NO₃⁻ leaching only being observed at sites with a pH < 4.5 and N inputs > 30 kg N.ha⁻¹.yr⁻¹. Tree age and species had no significant impact on the ecosystem response to N input at a regional scale.

2.1 Introduction

Forests across Europe receive a wide range of nitrogen inputs from the atmosphere as wet and dry deposition, typically at rates between 1 and 60 kg N.ha⁻¹.yr⁻¹. Most

forest ecosystems are naturally N limited and a wide range of ecosystem responses to this elevated N input has been recorded, including increased forest growth (Tamm, 1991), increases in foliar N concentration, and increased leaching of nitrate (Aber et al., 1995, Boxman et al., 1998). Deposition of N has also been implicated in forest decline (Nihlgård, 1985). This led to the development of the hypothesis of 'nitrogen saturation', variously defined as 'an ecosystem where N losses approximate or exceed the inputs of N' (Agren and Bosatta, 1988) or one where 'the availability of inorganic N is in excess of total combined plant and microbial nutritional demand' (Aber et al., 1989). Indicators of N saturation can provide valuable tools in the prediction of ecosystem response to elevated N inputs.

A large number of studies have monitored input and output fluxes of N and other major elements in forest ecosystems. In addition, experimental manipulation studies such as NITREX (Nitrogen saturation experiments) have measured ecosystem response to increases and decreases in N input (Wright and Rasmussen, 1998). Input/output studies provide valuable information about the response of a particular forest ecosystem to pollutant deposition. However, it is only by comparing the responses across a number of studies that the general response of forests to elevated N deposition can be determined. These regional responses can help set emission standards.

The IFEF (Indicators of Forest Ecosystem Functioning) database is the largest collection of input/output studies of N. In all, 181 forests across Europe are represented. The aim of this investigation is to examine the regional distribution and response of forest ecosystems to elevated N inputs and to evaluate the use of the organic layer C/N ratio as an indicator of NO_3^- leaching. This paper builds on the results of previous papers (Dise et al., 1998a and b, Gundersen et al., 1998) evaluating subsets or earlier versions of this dataset (65, 33 and 64 sites respectively).

2.2 Method

The IFEF database was collated from published sources, data questionnaires and the existing databases listed in Table 2.1.

Table 2.1 Summary sources of data used in IFEF (excluding individual site papers and personal communication sources).

ECOFEE	Gundersen et al., 1995
UNECE IMP	Forsius et al., 1996, Forsius et al., 2001
ENSF	Hauhs et al., 1989
GEOMON	Fottova and Skorepova, 1998
NITREX/EXMAN	Bredemeir et al., 1998, Kreutzer et al., 1998 Gundersen et al., 1998
Other	Matzner and Grosholz, 1997

The database consists of input (as throughfall) and output (as runoff or seepage water) fluxes of inorganic nitrogen (NO_3^- and NH_4^+) and other major elements, soil chemical data (such as pH (in H_2O), C/N ratio), as well as site characteristics including tree age and species, temperature and precipitation. Throughfall was

chosen over bulk deposition because it represents the total input to the soil: wet and dry deposition, canopy leaching, and assimilation. Additional information was noted, where available, on the land use history of a site. Not all data were available for all sites. A minimum of one year's data was used for element fluxes and the period of data collection ranged between 1980 and 1998.

In all, information on 251 sites was collated. The data were passed through several filters designed to check for data quality. Site data were discarded if the output of chloride was not within 50% of the chloride input, if the output of nitrate was larger than the input, both indicating ecosystem disturbance, or if the B horizon soil pH was greater than 6.5 (to restrict our analysis to acid-sensitive sites). It should be noted that sites were originally chosen for reasons specific to research organisations and therefore cannot be considered fully representative of European forests. Relationships between N input and output fluxes, soil parameters and site characteristics are examined using correlation, regression, and analysis of variance. Overall, 181 sites were included in the analysis.

Site Descriptions

Fifteen countries are represented, situated throughout central, northern and eastern Europe. The majority of sites are situated in central Europe, in particular in Germany and the Netherlands. Sites in southern Europe are scarce and no sites were included below 42°N. The sites incorporate several climatic regions from boreal to Mediterranean, and are composed of both plot-scale studies, where leached N was measured in seepage water, and catchment studies, where leached N was measured in an outflow stream. Of the sites used for this study, 76 were known to be plots and 64 were identified as catchment studies; the rest were unknown. Sites included a wide range of soil types and tree species, both deciduous and coniferous. The majority of sites (114) were coniferous with only 28 sites known to be dominated by broadleaved species. Site characteristics are shown in Table 2.2.

Table 2.2 Range of selected site characteristics

Site characteristic	min	max
Mean annual air temp. (°C)	-1.9	11.0
Precipitation (mm.yr ⁻¹)	395	2864
altitude (m asl)	8.2	2976
tree age (yr)	10	280

2.3 Results

2.3.1 Deposition and leaching of N

Throughfall N inputs range from less than 1 kg N.ha⁻¹.yr⁻¹ in northern Norway and Finland to greater than 60 kg N.ha⁻¹.yr⁻¹ in the Netherlands and Czech Republic. The majority of high deposition sites are situated in Central Europe, particularly in Germany and the Netherlands. The average input of N across Europe is 16.8 kg N.ha⁻¹.yr⁻¹ (Table 2.3). Approximately 40% of sites receive N deposition rates <10 kg N.ha⁻¹.yr⁻¹, 43 % receive 11-25 kg N.ha⁻¹.yr⁻¹ and 18% > 25 kg N.ha⁻¹.yr⁻¹.

Table 2.3 Mean, minimum and maximum values for selected parameters from the IFEF database.

Parameter	mean	min	max	n
N input (kg N ha ⁻¹ yr ⁻¹)	16.8	0.5	70	181
N output (kg N ha ⁻¹ yr ⁻¹)	5.8	0.0	43	181
C/N ratio	26.2	10.2	51	92
pH B horizon	4.52	3.3	6.28	114

The deposition of NH₄⁺ ranges from 0.2 to 51.5 kg N.ha⁻¹.yr⁻¹ and covers a much wider range than the deposition of NO₃⁻. The majority of sites with high N input are dominated by NH₄⁺ (Figure 1) and occurred mainly in the Netherlands, probably reflecting localised agricultural sources. For NO₃⁻ all sites receive less than or equal to 20 kg N.ha⁻¹.yr⁻¹ with the exception of one site in the Czech Republic that receives 47 kg N.ha⁻¹.yr⁻¹. The highest rates of NO₃⁻ deposition occur in Central Europe.

The majority of N leached is leached as NO₃⁻, with outputs ranging from less than 1 to greater than 40 kg N.ha⁻¹.yr⁻¹. The majority (64%) of sites leach less than 5 kg N.ha⁻¹.yr⁻¹, with 23% of sites leaching between 5 and 15 kg N.ha⁻¹.yr⁻¹ and 13% leaching more than 15 kg N.ha⁻¹.yr⁻¹. The spatial distribution of N leached follows a pattern similar to the throughfall N with the highest leaching in central Europe and the lowest in northern Scandinavia.

The relationship between throughfall N and leached NO₃⁻ is shown in Figure 2.1.

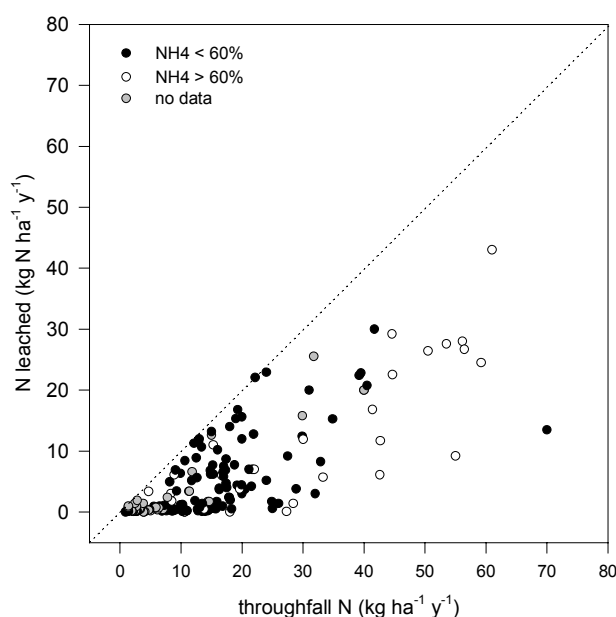


Figure 2.1 N input in throughfall versus NO₃⁻ leached (kg N.ha⁻¹.yr⁻¹). Leached NO₃⁻ = 0.46 * throughfall N - 1.87 ($n = 181$, $p < 0.05$, $r^2 = 0.62$). Open symbols represent sites where the input of N was dominated by ammonia (> 60%).

Low levels of NO₃⁻ leaching occur at input values between 0 and 8 kg N.ha⁻¹.yr⁻¹. At sites with intermediate inputs, between 8 and 30 kg N ha⁻¹ yr⁻¹, the leaching of N was highly variable with some sites showing almost complete retention and others

leaching large amounts of NO_3^- (Figure 2.1). NO_3^- was leached ($> 5 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) from all sites with an N input $> 30 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. Regression results for selected parameters are shown in Table 2.4.

Table 2.4 Regression results for selected parameters

Parameter	r^2	n	p
N input vs NO_3^- leached	0.62	181	0.05
NO_3^- leached vs C/N ≤ 25	0.80	45	0.05
NO_3^- leached vs C/N > 25	0.48	41	0.05

2.3.2 Soil parameters and site characteristics

In addition to N in throughfall, the C/N ratio of the organic horizon has been identified in other studies as a reasonable indicator of NO_3^- leaching (first shown by Matzner and Grosholz, 1997). Using subsets of the data used here, Gundersen et al. (1998) suggested that forests with a C/N of < 25 had a high risk of nitrate leaching, and Dise et al. (1998) showed that significant nitrogen leaching only occurred in forests with both high N deposition and N-enriched organic soils. Our expanded database supports this earlier conclusion (Figure 2.2), and warranted adding C:N to throughfall N as a predictor of N leaching.

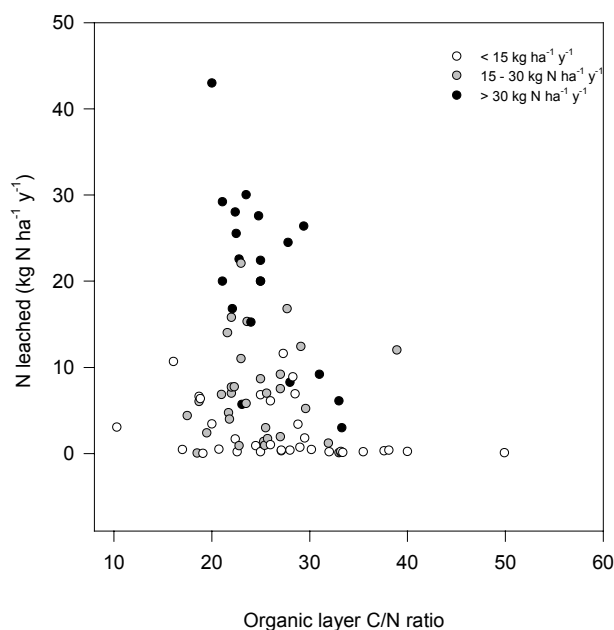


Figure 2.2 NO_3^- leached versus organic layer C/N ratio.

Simply adding C:N as a second continuous variable, however, did not increase the strength of the relationship between throughfall N and leached NO_3^- . The relationship between NO_3^- leaching and throughfall N is greatly improved, though, if only N-enriched sites (C:N < 25) are considered ($r^2=0.80, 0.42$ Figure 2.3a and b, Table 2.4). When the data are split into two groups based on the C/N ratio, the slope of Nout versus Nin for low C/N sites is twice as steep as that for high C/N sites.

For C/N ratios <25 leaching occurred at the majority of sites, and was strongly related to N input. For C/N ratios greater > than 25, overall nitrate leaching was significantly lower.

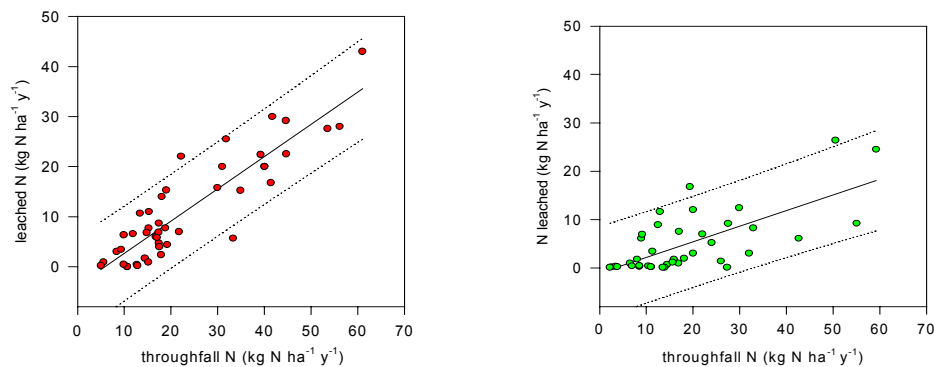


Figure 2.3 N input in throughfall versus NO_3^- leached ($\text{kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) at a) sites where the organic layer C/N ratio is less than or equal to 25 $\text{NO}_3^- \text{ leached} = 0.65 * \text{N throughfall} - 3.81$ ($r^2 = 0.80$, $p < 0.05$, $n=45$) and b) sites where the organic layer C/N ratio is greater than 25 $\text{NO}_3^- \text{ leached} = 0.32 * \text{N throughfall} - 1.05$ ($r^2 = 0.48$, $p < 0.05$, $n=41$).

A significant relationship was also observed between NO_3^- leached and soil pH in the B horizon ($r^2 = 0.24$, $p < 0.05$; Figure 4). NO_3^- leaching greater than approximately $10 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ only occurs where pH values are less than 4.6. At pH values greater than 4.6 leaching of NO_3^- is generally less than $10 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. The majority of high N deposition sites also show pH values less than 4.6.

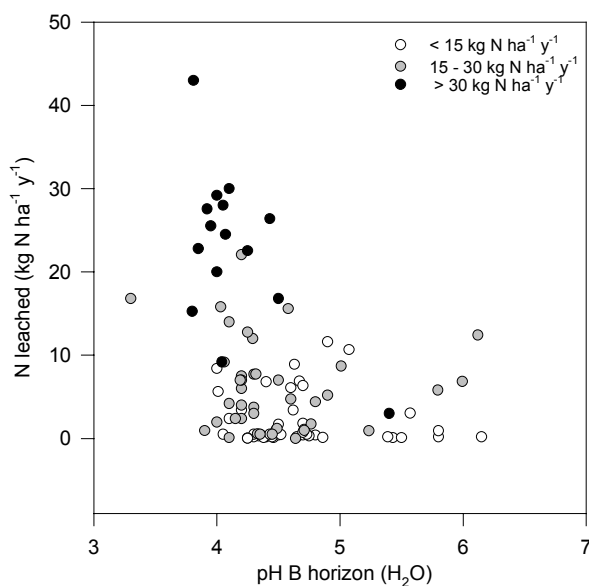


Figure 2.4 NO_3^- leached versus pH (H_2O) in the B horizon.

Both N input and output fluxes are significantly ($p < 0.05$) higher in plot compared to catchment studies. This is mainly due to their geographical location, since the majority of catchment studies are located in Scandinavia, where N inputs are low.

Most plot studies are located in central Europe where the largest inputs of N were observed.

No significant differences are observed for relationships between tree species or between coniferous and broadleaved sites for N input and output fluxes, C/N ratios or pH values, when considering the same range in data. The only significant difference between coniferous and broadleaved sites is in the thickness of the organic layer which averaged 3.5 cm in the broadleaved sites and 6.2 cm in the coniferous sites. Tree age had no significant impact on the ecosystem response to N at a regional scale; in fact, there is a slight inverse relationship with age (older trees leach less nitrogen) because most of the oldest trees are found in more remote areas of Europe, where N deposition is lowest (e.g. in northern Scandinavia).

2.4 Discussion and conclusion

The amount of N leached from a forest is strongly related to the amount of N deposited in throughfall: N input as throughfall explained just over 60% of the variation in NO_3^- leached. The overall regression is almost identical to that found by Dise and Wright (1995) indicating the robustness of this relationship. Also similar to earlier studies on smaller datasets (Dise and Wright 1995, Dise et al., 1998b, Gundersen 1995), the majority of sites retain most N at inputs below 10 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. Leaching does, however, occur at several sites receiving < 10 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$, where soils are acidic or with low to intermediate C/N ratios.

At N inputs > 10 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ the retention of N was highly variable between sites with similar N input. For example, retention of N between 11 and 25 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ ranged between < 1% and 100%. Many factors could contribute to this range, including the history of elevated N deposition, soil type, organic matter composition, tree age and soil buffering capacity. At inputs greater than 25 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$, deposition is dominated by NH_4^+ and significant NO_3^- leaching occurred at the majority of sites. At these sites proportionally more N is retained, most likely due to immobilisation within the soil horizons. Dise & Wright (1995) hypothesised that below inputs of 10 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ nitrification rates were not stimulated beyond the capacity of the ecosystem to retain N, between 10 and 25 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ nitrification and soil acidification may be stimulated with the amount of leaching depending on factors such as the amount of N stored in the soil and the severity of soil acidification, and above 25 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ the ecosystem cycling of N became decoupled resulting in NO_3^- leaching. The strong relationship between N input and output flux was demonstrated at the NITREX sites where experimentally excluding the input of N significantly reduced the output (Bredemeier et al., 1998)

In this study, at sites where C/N ratios were < 25, the risk of NO_3^- leaching is substantially higher than sites with a C/N ratio > 25, depending on the amount of N deposited. For example, for an N input of 30 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ the amount of NO_3^- leached is 9 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ for sites with C/N ratios > 25, and 15 kg $\text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ for sites < 25 (Table 2.5).

Table 2.5 Predicted rates of NO_3^- leaching from forests with a organic layer C/N ratio less than or equal to 25 and greater than 25.

Throughfall N ($\text{kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$)	C/N ratio organic layer	Leached N (low/high 95% CI)
10	≤ 25	3 (0-11)
10	> 25	2 (0-11)
20	≤ 25	8 (0-18)
20	> 25	4 (0-14)
30	≤ 25	15 (5-25)
30	> 25	9 (0-18)

Highly significant linear relationships are observed between N input and NO_3^- leached for each C/N category. The slope of the relationship for sites with a C/N ratio is < 25 is twice that for those sites where the C/N ratio is > 25 . The reason for this may be related to the capacity of the soil to assimilate added N. If low C/N ratio sites are a result of long-term elevated N deposition, then N inputs may be more readily matched by outputs because the system is saturated with respect to N. In comparison, sites with high C/N ratios are still able to assimilate added N through a number of processes such as immobilisation in soil horizons, uptake by microorganisms, or uptake by trees and vegetation. Table 2.5 shows the predicted amount of NO_3^- leached for N inputs in throughfall of 10, 20 and 30 $\text{kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ at C/N ratios above and below 25.

Organic layer C/N ratio is related to nitrification rates, with a ratio between 25 and 27 hypothesised to determine the onset of nitrate production (Gundersen & Rasmussen, 1990, Gundersen et al., 1998). Using ^{15}N , Tietema et al. (1998) attributed elevated N leaching at low C/N ratio NITREX sites to increased gross nitrification rates. Organic layer C/N ratio may be considered an indicator of the N saturation status of a site. We suggest from this study that at low C/N ratios a site is saturated with N, nitrification rates are stimulated, and the output of NO_3^- is strongly related to the input. At high C/N ratios the capacity of a site to assimilate N is not saturated and N will be retained within the system to an extent dependent on factors such as the capacity of the trees to assimilate N, the climate, and the proportion of NO_3^- versus NH_4^+ in precipitation.

The potential for C/N together with N input to serve as a robust indicator of N saturation is demonstrated by its correlation with NO_3^- leaching across Europe despite large variations in site characteristics including altitude, rainfall, plot versus catchment studies, tree species and age, and variations in sampling methods. The 95% confidence intervals of the relationship between N in throughfall and NO_3^- leached for both low and high C/N categories are $\pm 10 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$.

Soil pH in the B horizon was the only other parameter that showed a relationship with the amount of NO_3^- leached (Figure 2.4). Significant leaching of NO_3^- only occurs at sites with a pH less than approximately 4.6. It is not clear whether the acidic soils are a result of elevated N and other acidic inputs, or a cause of NO_3^- leaching due to acid production during nitrification. The contribution of N deposition to soil acidity at these sites cannot be quantified as it is dependent on the nature of the inputs and their subsequent transformations in the soil and uptake by

trees. It seems likely, however, that these sites have been acidified by either current deposition of N or past deposition of N and sulphur compounds.

The fact that other factors such as tree age and species were minor, and undetectable, compared with the impacts of N deposition and forest floor C/N ratio on the amount of NO_3^- leached at a regional scale does not mean that these are unimportant at a local scale. Nitrate leaching has been observed to increase with tree age in sitka spruce stands in Wales, for instance (Emmett et al., 1993). However, major differences in N deposition and soil N status at the European scale obscure these secondary effects.

Combined with the N input, the nitrogen enrichment status of a forest (as measured by the C/N ratio of the organic layer) is a good indicator of NO_3^- leaching, with strong correlations between N inputs and NO_3^- leached above and below a C/N ratio of 25. Validation of this empirical relationship is required, but potentially similar regression equations describing the observed correlations may be used to predict the regional response of NO_3^- leaching to deposition in forests across Europe.

References

Aber JD, Magill A, McNulty SG, Boone RD, Nadelhoffer KJ, Downs M and Hallett R (1995) Forest Biogeochemistry and primary production altered by nitrogen saturation. *Water, Air and Soil Pollution* **85**: 1665 - 1670.

Aber JD, Nadelhoffer KJ, Steudler P and Melillo J (1989) Nitrogen saturation in northern forest ecosystems. *BioScience* **39**, 378-386.

Aber JD, McDowell W, Nadelhoffer K, Magill A, Berntson G, Kamakea M, McNulty S, Currie W, Rustad L and Fernandez I (1998) Nitrogen saturation in temperate forest ecosystems; Hypothesis revisited. *BioScience* **48**, 924-934.

Ågren GI and Bosatta E (1988) Nitrogen saturation of terrestrial ecosystems. *Environmental Pollution*, **54**, 185-197.

Berg B and Matzner E (1997) Effect of N deposition on decomposition of plant litter and soil organic matter in forest systems. *Environmental Review*, **5**, 1-25.

Bredemeier M, Blanck K, Xu YJ, Tietema A, Boxman AW, Emmett B, Moldan F, Gundersen P, Schleppi P and Wright RF (1998) Input-output budgets at the NITREX sites. *Forest Ecology and Management* **101**, 57-64.

Boxman AW, Blanck K, Brandrud T, Emmett BA, Gundersen P, Hogervorst RF, Kjonaas, Persson H and Timmermann V (1998) Vegetation and soil biota response to experimentally-changed nitrogen inputs in coniferous forest ecosystems of the NITREX project. *Forest Ecology and Management* **101**: 65-79.

Dise NB and Wright RF (1995) Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management*, **71**, 153-161

Dise NB, Matzner E and Forsius M (1998a) Evaluation of organic horizon C:N ratio as an indicator of nitrate leaching in conifer forests across Europe. *Environmental Pollution* **102**, S1, 453-456.

Dise, N.B., Matzner, E. and Gundersen, P. (1998b) Synthesis of nitrogen pools and fluxes from European forest ecosystems. *Water, Air and Soil Pollution*, **105**: 143-154

Forsius M, Vuorenmaa J Kleemola S (1996) Assessment of nitrogen processes at ICP IM sites, pp 25-38, in Kleemola S and Forsius M (eds) *ICP IM Programme Annual Report*. The Finnish Environment 27. Finnish Environment Institute, Helsinki.

Forsius M, Kleemola S, Vuorenmaa J and Syri S (2001) Fluxes and trends of sulphur and nitrogen compounds at Integrated Monitoring Sites in Europe. *Water Air and Soil Pollution* (in press)

Fottova, D. and Skorepova, I. (1998) Changes in mass elements fluxes and their importance for critical loads: Geomon network, Czech Republic. *Water, Air and Soil Pollution* **105**: 365-376.

Gundersen P and Rasmussen L (1989) Nitrification in forest soils: effects of nitrogen deposition on soil acidification and aluminium release. *Review of Environmental Contamination and Toxicology* **13**, 1-45.

Gundersen P (1995) Nitrogen deposition and leaching in European forests - preliminary results from a data compilation. *Water, Air and Soil Pollution* **85**, 1179-1184.

Gundersen P, Emmett BA, Kjønås OJ, Koopmans CJ and Tietema A (1998) Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis on NITREX data. *Forest Ecology and Management* **101**, 37-55.

Gundersen P, Callesen I and de Vries W (1998) Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. *Environmental Pollution* **102** (S1), 403-407.

ICP IM Manual (1998) Finnish Environment Institute, Helsinki. www.vyh.fi/eng/intcoop/projects/icpim/manual/index.htm

Hauhs M, Rost-Siebert K, Paces T, Vigerust B and Raben G (1989) Summary of European data, in Malanchuk JL and Nilsson J (eds) *The role of nitrogen in the acidification of soils and surface waters*, Council of Nordic Ministers, Miljörapport 89,10,5.1-5.37.

Kreutzer K, Beier C, Bredemeier M, Blanck K, Cummins T, Farrell EP, Lammersdorf N, Rasmussen L, Rothe A, De Visser PHB, Weis W, Weiß T, and Xu YJ (1998) Atmospheric deposition and soil acidification in five coniferous forest ecosystems: a comparison of the control plots of the EXMAN sites. *Forest Ecology and Management* **101**, 125-142.

Matzner E and Grosholz C (1997) Beziehung zwischen NO₃-Austrägen, C/N-Verhältnissen der Auflage und N-Einträgen in Fichtenwald (*Picea Abies* Karst.) - *Ökosystemen Mitteleuropas. Forstw. Cbl.* **116**, 39-44.

Murphy D, Stockdale E, Dise NB and MacDonald JA (2001) Nitrogen supply and demand in agricultural and forest soils. In preparation.

Nihlgård B (1985) The ammonium hypothesis - an additional explanation to the forest dieback in Europe. *Ambio* **14**, 1-8.

Tamm CO (1991) Nitrogen in Terrestrial Ecosystems. Springer-Verlag.

Tietema A, Emmett BA, Kjonnas OJ and Koopmans CJ (1998) The fate of ¹⁵N-labelled nitrogen deposition in coniferous forest ecosystems. *Forest Ecology and Management*, **101**, 19-27.

de Vries W, Reinds GJ, Deelstra HD, Klap JM and Vel EM (1998) *Intensive monitoring of Forest ecosystems in Europe. EC-UN/ECE*, Geneva.

Wright RF and Rasmussen L (1998) Introduction to the NITREX and EXMAN projects. *Forest Ecology and Management* **101**, 1-7.

3 Element fluxes through European forest ecosystems and their relationships with stand and site characteristics

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Keywords:

Abstract

This paper describes a European wide assessment of element budgets, using available data on deposition, meteorology and soil solution chemistry at Intensive Monitoring plots in this continent. 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. Element outputs from the forest ecosystem were derived by multiplying fortnightly or monthly measurements of the soil solution composition at the bottom of the root zone with simulated unsaturated soil water fluxes. Element retention or release was assessed from the difference between inputs and outputs.

Median values for SO₄ leaching were nearly equal to the median SO₄ deposition. On a considerable number of plots SO₄ leaching was, however, higher than SO₄ deposition, indicating systems that are releasing S stored in the soil in previous episodes of higher SO₄ input. 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 than the N leaching, reflecting N retention in the system. There was a significant relationship between N leaching and N deposition. Furthermore, N leaching was limited at high C/N ratios (>30) in the organic layer. Due to the large N retention, the leaching flux of NO₃ was mostly lower than that of SO₄. The leaching flux of BC (Ca+Mg+K) and Al increased significantly with an increase in SO₄ deposition and decreased strongly with an increase in soil base saturation.

Despite the uncertainties in the calculated budgets, considering the uncertainties in calculated water fluxes and measured element concentrations in view of spatial variability within a plot, the results indicate that: (i) SO₄ is still the dominant source of actual soil acidification despite the generally lower input of S than N, due to the different behaviour of S and N, (ii) base cation removal due to man-induced soil acidification is limited and (iii) Al release is high in areas with high S inputs and low base status.

3.1 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 (S), nitrogen (N), base cations (BC) and aluminium (Al) 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 BC give information about the mechanisms buffering the acid input (e.g. Mulder and Stein, 1994; Wesselink, 1994; 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., 2000a).

Element budgets have already been carried out at Intensive Monitoring plots by several countries including: Ireland (Boyle et al., 2000; Farrell et al., 2001), Germany (Sprangenberg, 1997; Wetzel, 1998; Block et al., 1999) and Slovakia (FIMCI, 2000). Furthermore, there are several literature compilations of element budgets, focusing on the behaviour of N (e.g. Dise et al., 1998a; Dise et al., 1998b; Gundersen et al., 1998a; Gundersen et al., 1998b; MacDonald et al., 2001), base cations (Armbruster et al., 2002) and Al (Dise et al., 2001). A European wide assessment of element budgets, using all available data on deposition, meteorology and soil solution chemistry at Intensive Monitoring plots in this continent has, however, not yet been carried out.

This paper aims to fill this gap. It describes methods used to calculate output and retention or release of major elements (SO_4 , N, BC and Al) and gives results on the range and geographic variation of all these fluxes. In Van der Salm et al. (2004) the methods used to calculate water fluxes and the results obtained are described, whereas in Bleeker et al. (2004) more information is given on total atmospheric deposition, based on measurements of both throughfall and bulk deposition. Furthermore, relationships between leaching or retention/ release of elements and readily available environmental variables, such as stand and site characteristics, soil and foliar chemistry, precipitation and bulk deposition, are presented. Reliable relationships can be used for upscaling the results to the European scale.

3.2 Methods

3.2.1 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 Van der Salm et al., 2004);
- 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 3.1), located in Belgium, France, Denmark, Germany, Great Britain, Ireland, Norway, Sweden, Finland and Austria (Fig. 3.1). 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 3.1 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 (See Bleeker et al., 2004). Fig. 3.1 shows the geographic variation of (i) the 121 plots for which budgets could be calculated, (ii) the 83 plots (204-121; see Table 3.1) 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 3.1) with only data on bulk deposition and throughfall.

3.2.2 Data assessment and data quality assurance

Data assessment 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. Results from ring tests for the chemical analyses of atmospheric deposition (bulk precipitation and throughfall) generally indicated no large comparability problems for the concentrations of major ions (Lövblad, 1994).

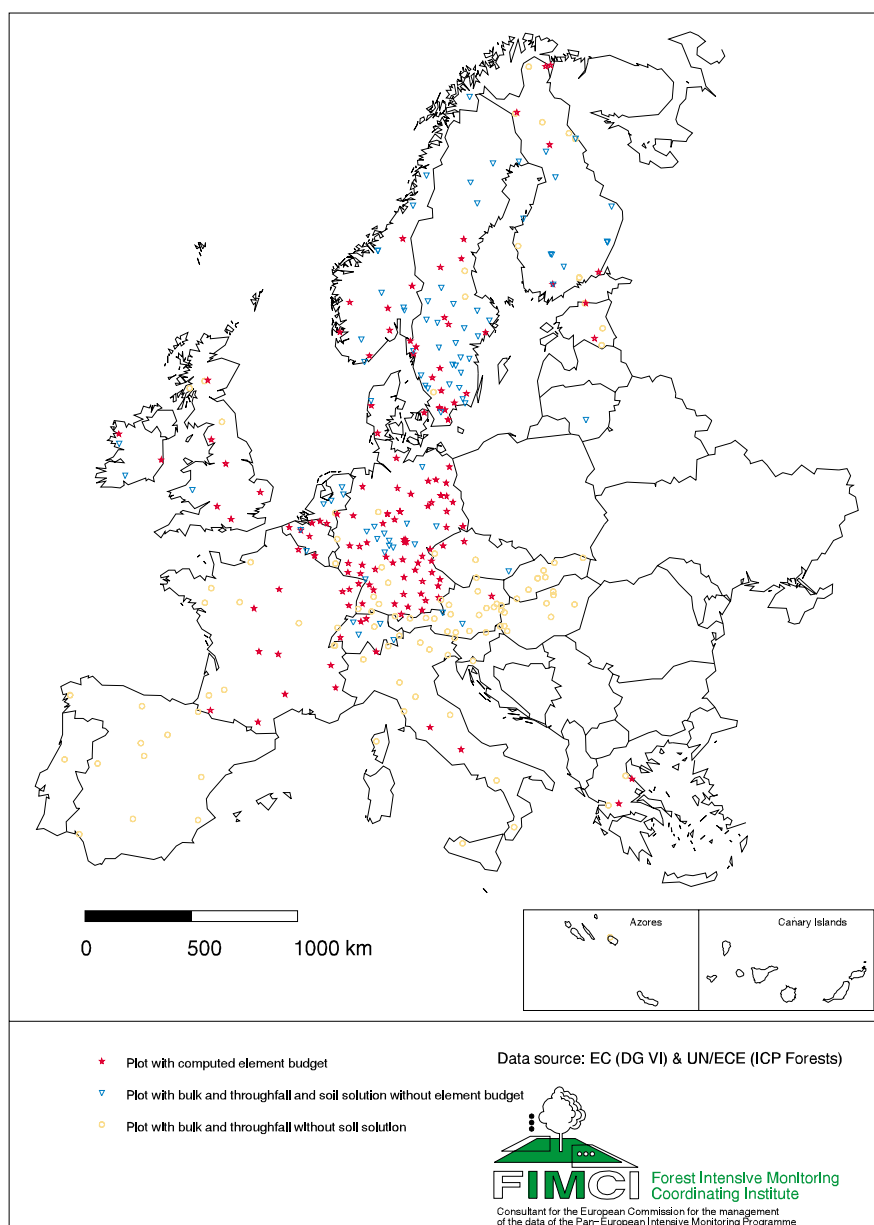


Figure 3.1 Geographical distribution of Intensive Monitoring plots for which element inputs (309 plots) and element budgets (121 plots) have been calculated.

Through Data Accompanying Report Questionnaires the participating countries submitted information on the applied methods for most of the plots. Comparable methods were used at most of the plots. For monitoring of throughfall data, use was mostly made of funnels. The number of funnels used usually ranged between 10 and 15 % (61%) but more than 15 funnels were used at 32% of the plots. Results of a joint field campaign, 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 showed that the spatial variability is such that 15-25 funnels are needed to estimate the deposition at a required accuracy of

10%. (Draaijers et al., 2001). For monitoring of the soil solution, use was made of suction cups (sometimes combined with zero tension lysimetry) at the majority the plots. The number of samplers ranged from 1-5 in the organic layer, 1-23 in the mineral topsoil and 1-12 in the mineral subsoil. The majority of used lysimeters is made of materials that are considered appropriate, such that the sample solution is not influenced by the sampler itself (De Vries et al., 2000b).

Quality assurance

Quality assurance and quality control (QA/QC) of the chemical composition of bulk deposition, throughfall, stemflow and soil solution was included by a check on (see De Vries et al., 2000b; De Vries et al., 2001; Bleeker et al., 2004):

- The balance between the sum of cations and the sum of anions. Approximately 50-60% of the measurements in bulk deposition, throughfall and stemflow appeared to fulfil the requirement
- that the percentage difference is less than 20%. For soil solution samples, the percentage of measurements in an acceptable range of $\pm 20\%$ was nearly 70%.
- The difference between measured and calculated electric conductivity. Those results were better than the difference between the sum of cations and anions. An allowable discrepancy between measured and calculated conductivity of 20% was fulfilled by approximately 62% of the measurements for bulk deposition, 69% for throughfall, 70% for stemflow and 79% for the soil solution.
- The ratio between Na and Cl concentrations. On average the Na/Cl ratio in bulk deposition, throughfall, stemflow and soil solution resembled those in seawater (0.858 eq.eq^{-1}). Very high Na/Cl ratios were hardly found, indicating that Na contamination due to Na release from the bottle in which solution samples are kept in the field, does not occur frequently.

Throughfall, stemflow, bulk precipitation and soil solution concentration data in the Intensive Monitoring database regularly did not pass the quality checks described above. For this reason a 'correction' procedure was implemented resulting in more data available for further analysis, as described in De Vries et al. (2001) and Bleeker et al. (2004).

3.2.3 Model evaluation

Calculation of element input, leaching fluxes and element retention

Total deposition was calculated according to a slightly adapted canopy budget model, correcting the input by both throughfall and stemflow for exchange processes, occurring within the forest canopy. A complete description of the model calculations is given in De Vries et al., (2001) and Bleeker et al. (2004). Leaching fluxes of the considered elements were calculated by multiplying the measured soil solution concentrations with estimated water leaching fluxes at the corresponding depth. For the calculation of water fluxes, we refer to Van der Salm et al. (2004) and De Vries et al. (2001). For sites with a thick soil profile ($> 1 \text{ m}$), 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 (Van der Salm et al., 2004). 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:

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

Results showed that the difference between both approaches was minimal (De Vries et al., 2001).

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. Supposed relationships were of the form:

$$\log y = \alpha_0 + \alpha_1 \cdot x_1 + \alpha_2 \cdot x_2 + \dots + \alpha_n \cdot x_n \quad (3.1)$$

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 were applied by using a so-called Select procedure. An overview of the predictor variables included in the various regression models is given in Table 3.2.

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; Dise et al., 1998b; Gundersen et al., 1998a). All stand and site characteristics were included as qualitative variables. For tree species 3 major groups were distinguished: pine, spruce and deciduous trees. Regarding soil type, 3 main groups were distinguished i.e.: acidic sandy soils (Podzols and Arenosols), slightly acidic loamy soils or clayey soils (Cambisols and Luvisols) and remaining non-calcareous soils. The humus types were distinguished in mor, moder and moder/mull and mull. 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 plots (121 at maximum). As a rule of thumb, the number of observations should exceed 4 times the degrees of freedom (Oude Voshaar, 1994).

Table 3.2 Overview of the predictor variables used to explain element leaching and element budgets at the 121 Intensive Monitoring plots, using the standard approach (stand.) and an alternative approach (alt.).

Predictor variables	S		N		BC		Al	
	Stand.	Stand.	Alt.	Stand.	Alt.	Stand.	Alt.	
<i>Site/Stand characteristics</i>								
Tree species	x	x	x	x	x	x	x	
Soil type group	x	x	x	x	x	x	x	
Humus type group	x	x	x	x	x	x	x	
Stand age	x	x	x	x	x	x	x	
Altitude	x	x	x	x	x	x	x	
<i>Climate</i>								
Climate zones ¹	x	x	x	x	x	x	x	
Precipitation ¹	x	x	x	x	x	x	x	
Temperature ¹	x	x	x	x	x	x	x	
<i>Deposition</i>								
Average S deposition 1995-1998 ²	x			x		x		
Accumulated S deposition 1960-1995 ³	x			x		x		
Average NH ₄ deposition 1995-1998 ²		x						
Average NO ₃ deposition 1995-1998 ²		x						
Average N deposition 1995-1998 ²			x	x		x		
Accumulated N deposition 1960-1995 ³		x	x	x		x		
Average S+N deposition 1995-1998 ²					x		x	
Accumulated S+ N deposition 1960-1995 ³					x		x	
Average BC deposition 1995-1998				x	x			
<i>Foliar chemistry</i>								
N-content		x	x					
<i>Soil chemistry</i>								
C/N ratio organic layer ⁴		x	x					
C/N ratio mineral topsoil ⁴								
pH organic layer								
pH mineral topsoil	x	x	x					
pH mineral subsoil	x			x	x	x	x	
Base saturation mineral topsoil								
Base saturation mineral subsoil				x	x	x	x	

¹ In the statistical analyses, use was made of either climate zones or the combination of precipitation and temperature to investigate the possible impact of climatic variables on the relation between element input and output.

² In the statistical analyses related to N leaching, use was made of both NH₄ and NO₃ deposition separately and the combined input of both elements. Similarly, In the statistical analyses related to BC and Al leaching, use was made of both S and N deposition separately and the combined input of both elements.

³ Accumulated deposition of S and N at each site was calculated by adding annual EMEP model estimates for the grid squares in which the plot was located, multiplied by the ratio between measured and modelled deposition for the period 1995-1998, for which measurements were available.

⁴ We also investigated whether the interaction of N deposition with C/N ratio was a significant contribution to the model, but this did not appear to be the case. Furthermore, both N leaching and N retention were not only related to the N deposition but also to the net N input (N deposition minus calculated net N uptake) but this did not lead to more significant relationships.

With respect to climatic variables, precipitation was based on three yearly average values for the bulk deposition, whereas temperature values were based on interpolation of 30-year averaged data on temperature (after Leemans and Cramer, 1991), which gives an impression of the average temperature at the site. Altitude,

which may affect temperature was also included as a quantitative variable with 50 m intervals. The climatic zones included were Atlantic (South and North), continental and sub Atlantic, boreal, boreal temperate and Mediterranean. With respect to atmospheric inputs, use was made of both measured throughfall and of the calculated total deposition using the canopy exchange model. Here we only report results related to total deposition. 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).

In the standard approach for N, the deposition of N was divided in NH_4 and NO_3 , whereas in an alternative approach, the difference was neglected to investigate the necessity of using separate N compounds in the regression analyses. Similarly, in the standard approach for BC and Al, the deposition of acidity was divided in S and N, whereas in an alternative approach, the difference was neglected to investigate the necessity of using separate S and N compounds (see Table 3.2).

Quality checks and statistical evaluation of results

In performing the analyses, use was made of results for all 121 plots and for plots passing a quality check with respect to the ration of Cl input and output. This ratio was then required to be between 0.5 and 1.5. In all other cases, the modelled hydrological fluxes (Van der Salm et al., 2004) were considered too inadequate. An additional check in case of N was that the ratio of N leaching and N input should be less than 1.1.

The statistical analyses was carried out using normal values and logarithmic transformations for the leaching and deposition flues. In order to evaluate the quality of the model predictions, a comparison was made with the measurements by an evaluation of the deviation between predictions and measurements by the Normalised Mean Error (NME) and the Normalised Mean Absolute Error (NMAE), as described below:

$$\text{NME} = \frac{\sum_{i=1}^N (P_i - O_i)}{\overline{NO}} \quad (3.2)$$

$$\text{NMAE} = \frac{\sum_{i=1}^N |P_i - O_i|}{\overline{NO}} \quad (3.3)$$

where P_i and O_i are the predicted and observed value I, \overline{O} is the average of the observations and N is the number of observations. The NME compares predictions and observations on an average level and expresses the bias in the average values of predictions compared to the observations (systematic underestimation or overestimation) but is rather sensitive to outliers. The NMAE is not so sensitive for outliers and does not allow for compensation of under- and overestimates, as the absolute value of the error is summed (Janssen and Heuberger, 1995). The closer the

values to 0, the better. Predictions were selected with minimal NME and NMAE values when comparing predictions and observations

3.3 Results and discussion

3.3.1 Ranges and geographic variation in deposition and leaching fluxes and element budgets

Comparison of deposition and leaching fluxes

A comparison of median deposition and median leaching fluxes (Table 12) shows that median SO_4 leaching fluxes are comparable to SO_4 deposition, whereas N leaching is generally much lower than N deposition. The high leaching fluxes for SO_4 compared to N 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 indicates a clear difference between S and N retention in the forest ecosystem. On average SO_4 behaves as a tracer, whereas N is strongly retained in the soil and/or denitrified.

Table 3.3 Median total input (atmospheric deposition), output (leaching from the rootzone) and budgets of SO_4 , N and total BC(Ca+Mg+K) as well as Al leaching: (in $\text{mol}_e\text{ha}^{-1}\text{yr}^{-1}$).

Tree species	Number of sites	SO_4			N			BC			Al	
		input	output	budget	input	output	budget	input	output	budget	output	
Pine	29	517	197	216	714	7	703	491	156	253	138	
Spruce	51	685	590	16	1198	112	1040	469	331	94	774	
Oak	15	637	1025	-256	962	212	686	519	2184	-911	30	
Beech	20	634	604	-22	1340	135	984	489	717	30	326	
Other	6	509	590	28	826	54	772	751	1149	-862	31	
All	121	592	509	21	995	60	871	482	377	86	294	

The median SO_4 deposition on trees is comparable but median SO_4 leaching fluxes vary considerably. Median SO_4 leaching fluxes decrease strongly going from oak > spruce and beech > pine, although the median input of SO_4 is almost equal for the considered tree species. The median budget for SO_4 is close to zero in coniferous forests, whereas it is slightly positive in deciduous forests (see Table 3.3). At approximately 50% of the plots SO_4 is retained.

Median N deposition varies considerably. Differences between tree species with respect to deposition 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. There is also a considerable difference in N leaching fluxes below the different tree species. The lowest median N leaching flux is found under pine trees which is partly caused by the low water flux. N leaching fluxes under Spruce are also lower compared to the fluxes under the deciduous tree species. N is retained in 90% of the sites and accordingly the median N budget is negative for all tree species. The median base cation budget is zero to slightly negative for the coniferous tree species and positive for the deciduous species.

Median BC deposition is again quite comparable for the various tree species. The high leaching fluxes of BC and consequently the high values for BC budgets under oak stands is partly due to calcareous parent material. The median leaching flux of BC is generally higher than for Al, 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 Spruce where the median leaching flux of Al is almost twice as high as for BC. Al is released at all plots, but this result may be slightly biased since Al deposition is not taken into account. The median ratio of Al and BC budget, in which the budget indicates the release of these elements by weathering and cation exchange buffering the soil system against acid atmospheric inputs, is near 3 being equal to the ratio of these elements in many primary minerals.

Ranges in element budgets

Results of element deposition and leaching fluxes obtained for the 121 investigated sites show a considerable variation causing a large range in element budgets. This is illustrated in Table 3.4 in which ranges in element budgets for chloride (Cl), SO₄, N, BC (Ca+Mg+K) and Al for the 121 monitoring sites are presented.

Table 3.4 Element budgets for chloride, sodium, SO₄, N, BC (Ca+Mg+K) and Al.

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
S	120	-672	21	540	57	43
N	111	159	871	1787	96	4
BC	121	-2240	86	517	57	43
Al	114	-1648	-294	-7	1	99

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 annual Cl budgets ranged from -560 to 830 mol_c.ha⁻¹.yr⁻¹ in a 30-year period (Van der Salm, 2004). Extremely high Cl deposition and leaching fluxes (above 2000-3000 mol_c.ha⁻¹.yr⁻¹) mainly occur near the coast in Ireland and Denmark. At continental sites the Cl deposition and leaching fluxes are generally less than 500 mol_c.ha⁻¹.yr⁻¹.

The median SO₄ budget is also close to zero but the range in SO₄ budgets is much broader than for Cl. Budgets for 80% of the sites range from approximately -675 to 550 mol_c.ha⁻¹.yr⁻¹. At a considerable number of sites SO₄ is released from the soil, indicating that these system are recovering from previous episodes of high SO₄ input. This is confirmed by the geographical differences in SO₄ budgets (See below).

For 80% of the sites N (NH₄ + NO₃) budgets range from approximately range from 160 to 1800 mol_c.ha⁻¹.yr⁻¹. At most sites (96%) the N input is higher then the N leaching. Remarkably are the strong differences in N leaching which is almost negligible in 50% of the soils, whereas the 90 percentile leaching flux is 1000 mol_c.ha⁻¹.yr⁻¹ (De Vries et al., 2001). This indicates that N is strongly retained or denitrified in the soil until a certain threshold in deposition levels is exceeded.

At 57% of the sites the BC balance is positive (retention) indicating that the input of BC 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 $-15000 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$). The Al balance is always negative (Al is leached) because the input of Al is negligible. The median Al balance is $-300 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$. This corresponds to a median leaching concentration of $0.25 \text{ mol}_c.\text{m}^{-3}$, which is above a critical limit of $0.2 \text{ mol}_c.\text{m}^{-3}$, indicated in the literature with respect to impacts on roots for the most sensitive tree species (Cronan et al., 1989).

Geographic variation in deposition and leaching fluxes and element budgets

There is a large geographic variation in deposition and leaching fluxes and the resulting budgets of SO_4 , N, BC and Al (De Vries et al., 2001). Here we concentrate on the geographical distribution of the leaching fluxes and the resulting budgets, with a special focus on N, since input fluxes are also presented in Bleeker et al. (2004).

Relatively high SO_4 input ($>800 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$) can be found everywhere in Europe, except for central and northern part of Scandinavia. Many sites with high SO_4 input are situated in central Europe. 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 (Fig 3.3 bottom) indicating the occurrence of an acid soil releasing mainly Al in response to the high input (leaching) of SO_4 . Sites with the highest SO_4 release are located in central Europe, where the strongest reduction in SO_4 deposition has taken place over the last decade (De Vries et al., 2001).

High N inputs ($>1800 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$) occur in central Europe. Total N input is generally much smaller in northern and southern Europe. High N leaching fluxes ($>1000 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$) do occur in Belgium and Central Germany where the input of N (specifically of NH_4) is also high (Fig 3.2 top). 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 ($< 200 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$). However, the geographic variation of N leaching is large (specifically in Germany), indicating that both N deposition and soil characteristics influence N leaching. Sites with a net release of N are found in Belgium and North-western Germany (Fig 3.2 bottom). This corresponds to the area which has received a high N deposition over a prolonged period of time. Remarkable is the high N retention in South-eastern Germany. According to the present calculations these sites still retain a lot of N despite relatively high depositions of N. This 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.

Base cation input is relatively high ($>800 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$) in southern Europe and Lithuania, which is consistent with findings of Draaijers et al. (1997), whereas the input of BC is low in Scandinavia. High BC release values are generally found in areas with a high N or S deposition such as Belgium, North western Germany and

the area around the German-Czech border. 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 leaching of Ca is high due to natural decalcification. At these sites the leaching of bicarbonate is also high.

3.3.2 Relationships between leaching and retention of elements and environmental factors

Relationships between element leaching and element deposition

The range in S and N leaching is generally comparable to the range in S and N deposition as illustrated in Figure 3.2. 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. 3.2A). At several sites the leaching of SO₄ is considerably higher than the deposition (up to 1500 mol_c.ha⁻¹.yr⁻¹), indicating a strong release of SO₄. Most of these sites are located in areas that received a high deposition over the past decades (Czech-German border).

The present high leaching fluxes at these sites are probably due to the release of SO₄, which has been adsorbed during previous decades.

In accordance with results found by e.g. Dise et al. (1998a; 1998b) and Gundersen et al. (1998a), the leaching of N is generally negligible below a throughfall or deposition input of 10 kg.ha⁻¹.yr⁻¹ (approximately 700 mol_c.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. 3.3B), indicating the occurrence of a disturbance in the N cycle. The range in Al leaching fluxes is quite comparable to the range in S and N deposition (Fig. 3.3C). At several sites, Al leaching fluxes are even higher than the acid deposition, indicating that the leaching of SO₄ 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. Sites where the Al leaching flux is lower imply that part of the potential acid input is buffered by S and/or N retention and/or base cation release.

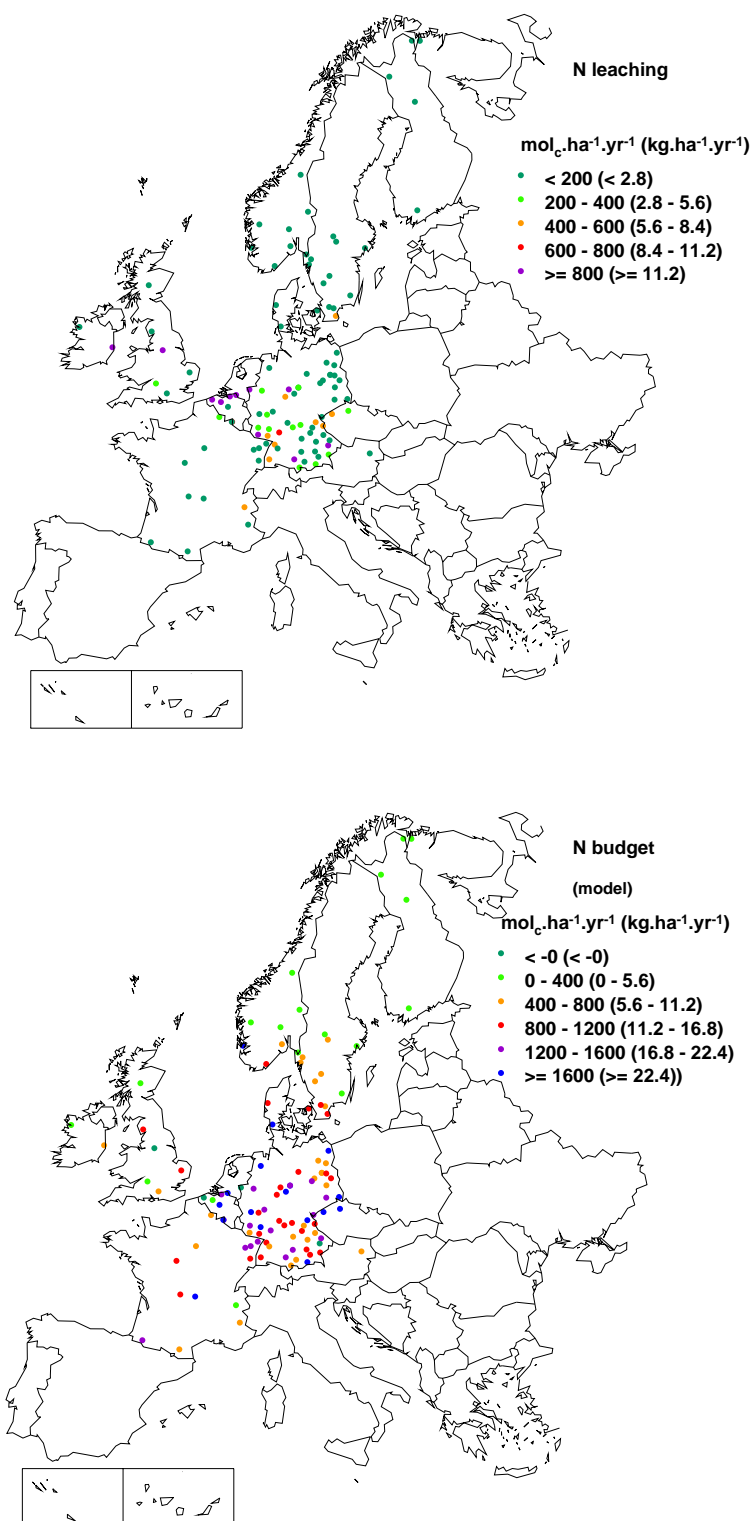


Figure 3.2 Geographical variation in leaching fluxes ($\text{mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$) (top) and budgets of N (bottom) at the Intensive Monitoring plots throughout Europe.

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, for example, illustrated by a site with a high input of S and N (near 5000 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. 3.3D). 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.

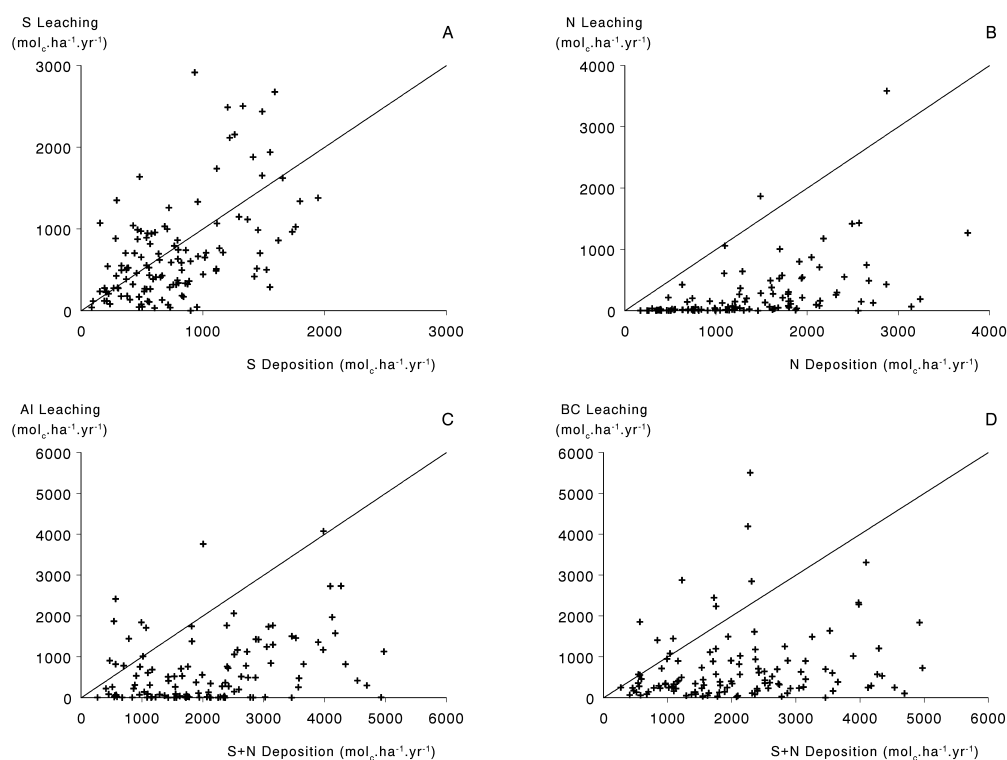


Figure 3.3 Relations between total deposition and leaching fluxes of S (A) and N (B) and between the Al leaching fluxes and the total deposition flux of S+N (C) and BC leaching and S+N deposition (D) at the 121 monitoring sites.

The clear increase in N leaching above a total N deposition of 10-15 kg.ha⁻¹.yr⁻¹ (above 1000 mol_c.ha⁻¹.yr⁻¹) is further illustrated in Fig. 3.4 in which the relationship between leaching and deposition has been presented for coniferous and deciduous forests separately, while limiting the budgets to those passing the quality control. Results show that N leaching is below 200 mol_c.ha⁻¹.yr⁻¹ at an N deposition below 1000 mol_c.ha⁻¹.yr⁻¹ with the exception of two coniferous plots and a clear increase in N leaching above this level, specifically in the deciduous sites.

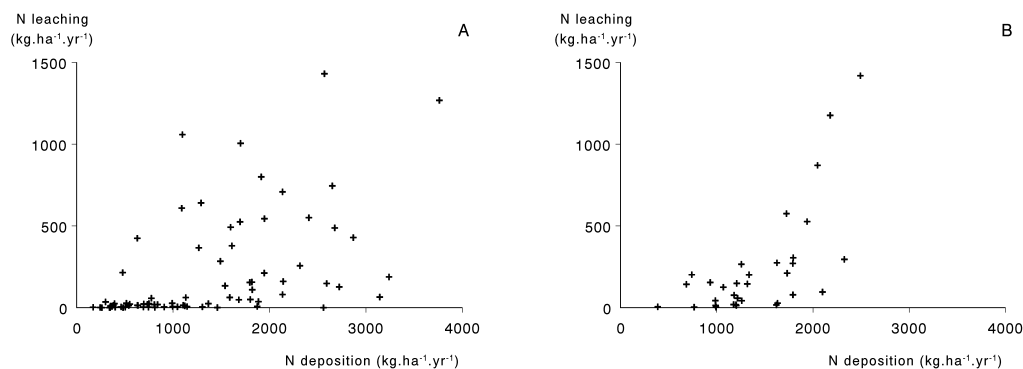


Figure 3.4 Relationships between N leaching and N deposition for coniferous forests (A) and deciduous forest (B) using data that passed the quality control related to the Cl balance.

Dise et al. (1998a; 1998b) and Gundersen et al. (1998a) found that apart from N deposition, the N leaching flux is influenced by the C/N ratio of the organic layer. A visual inspection of the relationship between N leaching against C/N ratio of this layer, with varying N deposition fluxes, showed that soils with very high C/N ratios (> 35) in the organic layer tend to have nearly negligible N leaching fluxes, but this situation is generally correlated with an N deposition that is low, i.e. below $1000 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$ (Fig. 3.5). Below C/N ratios of 35 and specifically below 30, however, the scatter is quite large. For example, the N leaching ranges between 150 and $1500 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$ at a C/N ratio of the organic layer of approximately 25 and a N deposition of more than $2000 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$.

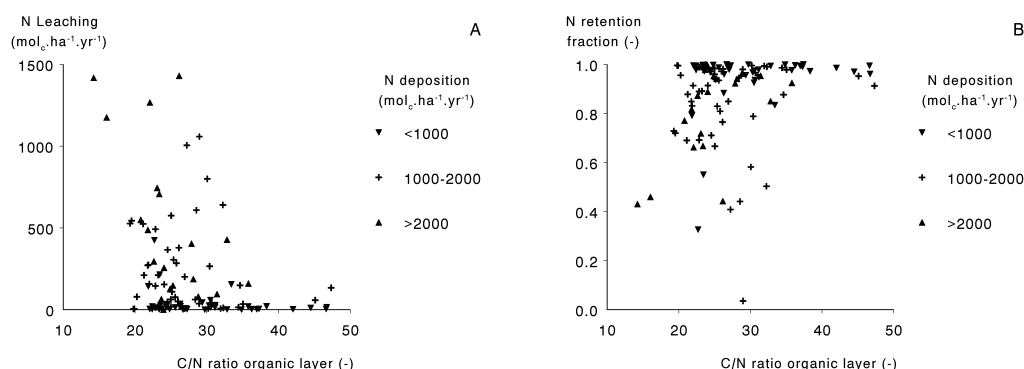


Figure 3.5 Relationships between N leaching (A) and N retention fraction (B) and the C/N ratio of the organic layer.

Multiple regression analyses for element leaching

Results of the best models derived with multiple regression analyses, relating various environmental factors to element leaching are presented in Table 3.5. The table also includes information on the percentage variance accounted for (R^2_{adj}) before and after quality control and also the NME, expressing the bias in the average values of predictions (systematic underestimation or overestimation), and the NMAE (see Eq. 3.2 and 3.3).

Table 3.5 Overview of the predictor variables explaining element leaching at the investigated Intensive Monitoring plots with the number of plots and the percentage variance accounted for before and after quality control.

Predictor variables	S _{le}		N _{le}		BC _{le}		Al _{le}	
	All data	Qual. control	All data	Qual. control	All data	Qual. control	All data	Qual. control
<i>Site/Stand characteristics</i>								
Tree species								
Soil type group								++
Humus type group	-							-
Stand age	++				+		+	+
Altitude							++	
<i>Climate</i>								
Precipitation								
Temperature					+			
Climate zone		++					++/--	+/-
<i>Deposition</i>								
Average S deposition 1995-1998	++	++					++	++
Accumulated S deposition 1960-1995							+	
Average NH ₄ deposition 1995-1998								
Average NO ₃ deposition 1995-1998								
Average N deposition 1995-1998			++	++				
Accumulated N deposition 1960-1995				++				
Average S+N deposition 1995-1998								
Accumulated S+ N deposition 1960-1995						++		
Average BC deposition 1995-1998 ¹					++	++		
<i>Foliar chemistry</i>								
N-content								
<i>Soil chemistry</i>								
C/N ratio organic layer ⁴			--					
C/N ratio mineral topsoil ⁴								
pH organic layer								
pH mineral topsoil			++	+				
pH mineral subsoil								
Base saturation mineral topsoil								
Base saturation mineral subsoil					++	++	--	--
N ¹⁾	125	59	111	49	92	40	93	41
R ² _{adj} (%) ²⁾	51	71	23	68	36	55	45	47
NMAE	0.51	0.37	0.98	0.50	0.62	0.54	0.61	0.54
NME	0.00	0.00	0.00	0.25	0.00	0.00	0.00	0.00

++ 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⁾ R²_{adj} = percentage variance accounted for.

In general, application of quality control, based on the Cl budget, caused a decrease of more than 50% of the data points. The explanation of the leaching results by

environmental factors increased strongly in the case of N, substantially in the case of SO₄ and Bc and hardly for Al (see the changes in R^2_{adj} and NMAE in Table 3.5). The average predicted leaching values were always correct (NME = 0) with the exception of N leaching after quality control. The major reason for this is that the data after quality control could best be described after a log transformation, but this caused a systematic bias in the predictions. The results show that variations in the element leaching fluxes are always related to the atmospheric deposition (the S input in case of Al, being the major source of acidification). Below we present and discuss the derived leaching equations before and after quality control.

Using all data, SO₄ leaching was mainly related to SO₄ deposition and stand age, being 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 SO₄ accumulation in the soils of the young stands is less compared to the mature stands. SO₄ deposition was also (weakly) related to the humus type, values being less in mor and moder type soils than in mull type soils (Eq. 3.4). The reason for this relationship is not so evident and may be an artefact. Using the data after quality control only, SO₄ leaching was only significantly related to SO₄ deposition and climate zone, values increasing from the Atlantic zone (reference situation) to boreal, boreal temperate, continental and sub Atlantic and Mediterranean (Eq. 3.5). This impact may be an artefact from the regional variation in deposition reduction and not a real impact of climate itself.

$$SO_{4,le} = -237 - 147 \cdot \text{moder} - 314 \cdot \text{mor} + 527 \cdot \text{Age}_{\text{mature}} + 0.9119 \cdot SO_{4,dep} \quad (3.4)$$

$$SO_{4,le} = -253 + 199 \cdot CZ_{\text{boreal}} + 317 \cdot CZ_{\text{boreal,temperate}} + 592 \cdot CZ_{\text{continental+sub-atlantic}} + 1279 \cdot CZ_{\text{mediterranean}} + 1.108 \cdot SO_{4,dep} \quad (3.5)$$

Using all data, N leaching is positively related to the N deposition and the pH in the mineral topsoil and negatively correlated with the C/N ratio of the organic layer (Eq. 3.6). The significant correlation between the calculated N leaching flux and the C/N ratio of the organic layer is in line with the results presented by Dise et al. (1998a; 1998b) and Gundersen et al. (1998a). We did also find a statistically significant impact of the C/N ratio on soil NO₃ concentrations for approximately 240 Intensive Monitoring plots. Using the data after quality control only, N leaching is not only positively related to the present N deposition, but also the historic N deposition in the period 1960-1995 and the pH in the mineral topsoil (Eq. 3.7). Unlike the results when using all data N leaching was not related any more to the C/N ratio of the organic layer. A more in-depth analysis, based on more input-output budgets of N is necessary to further investigate the possible role of the C/N ratio of the soil on the N dynamics.

$$N_{le} = -123 + 0.2319 \cdot N_{dep} - 15.91 \cdot C/N_{\text{organic layer}} + 133.5 \cdot pH_{\text{topsoil}} \quad (3.6)$$

$$\log N_{le} = -2.113 + 0.000917 \cdot N_{dep} + 0.000614 \cdot N_{\text{dep,historic}} + 0.561 \cdot pH_{\text{topsoil}} \quad (3.7)$$

Using tall data, variations in BC leaching were very significantly related to the BC input and the base saturation of the subsoil. As expected, variations in BC release from the soil were positively to these two variables, but also with temperature (may affect BC weathering rates in soils) and stand age (Eq. 3.8). The relation with stand age may be an artefact. Using the data after quality control only, BC is not only positively related to the present BC deposition, but also the historic acid (S and N) deposition in the period 1960-1995 and the base saturation of the subsoil (Eq. 3.9).

$$BC_{le} = -842 + 398 \cdot Age_{mature} + 76.4 \cdot T + 0.1376 \cdot BC_{dep} + 12.71 \cdot BS_{subsoil} \quad (3.8)$$

$$BC_{le} = -713 + 0.3141 \cdot AC_{dep,historic} + 0.2263 \cdot BC_{dep} + 17.48 \cdot BS_{subsoil} \quad (3.9)$$

Using tall data, Al leaching shows a positive relation with the present and historic SO_4 deposition and a negative relation with the base saturation of the subsoil. The strong relation between S deposition and soil acidification in terms of Al release is in line with the finding of the large N retention, implying that potential Al toxicity effects are still mainly driven by S. The Al release was further significantly related to stand age (possibly because of larger S accumulation in the past and thus larger release at present) and altitude (possibly because of poorer soils at higher altitudes). Furthermore, leaching was higher in Central and Northern Europe (boreal areas) than in the continental and sub Atlantic and Mediterranean areas (Eq. 3.10). This effect will be interlinked with effects of deposition and base saturation /soil type. Using the data after quality control only, Al leaching is not significantly related to altitude any more but to soil type and humus type which are related to altitude. Al leaching appears to be higher in mull type humus compared to mor and moder type humus (Eq. 3.11). This indicates that the solubility of Al is probably lower in soils with a mor type humus compared to more strongly decomposed humus types.

$$Al_{le} = -146 + 469 \cdot Age_{mature} + 0.758 \cdot ALT + 470 \cdot CZ_{boreal} + 180 \cdot CZ_{boreal,temperate} - 726 \cdot CZ_{continental+sub-atlantic} + -944 \cdot CZ_{mediterranean} + 0.572 \cdot SO_{4,dep} + 0.1372 \cdot S_{dep,historic} - 6.47 \cdot BS_{subsoil} \quad (3.10)$$

$$Al_{le} = 775 + 712 \cdot Age_{mature} + 1044 \cdot loam/clay + 241 \cdot remaining\ soils - 1554 \cdot moder - 981 \cdot mor + 1175 \cdot CZ_{boreal} + 377 \cdot CZ_{boreal,temperate} + 492 \cdot CZ_{continental+sub-atlantic} - 226 \cdot CZ_{mediterranean} + 0.908 \cdot SO_{4,dep} - 26.40 \cdot BS_{subsoil} \quad (3.11)$$

An overview of results obtained by the various relations before and after quality control and the real observations for the leaching of SO_4 , N, BC and Al is given in Fig. 3.6. The results show a reasonable correlation between predictions and observations but the errors can be large up to 1000-1500 $mol_c \cdot ha^{-1} \cdot yr^{-1}$, implying that the relationships are too weak to make reliable maps of the geographic variation in element leaching with available environmental data used in the relationships.

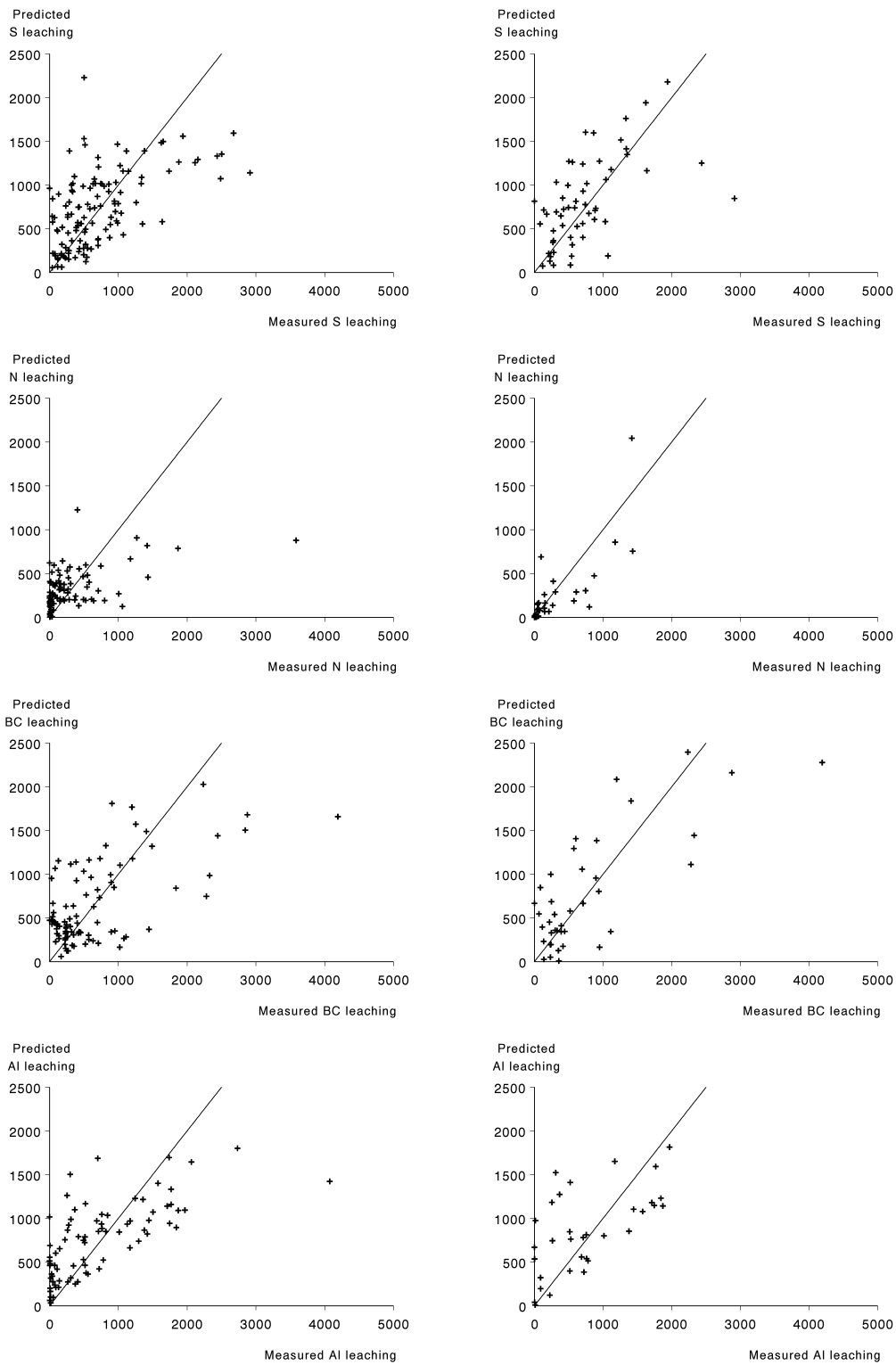


Figure 3.6 Comparison of results predicted by the various relations and the real observations for the leaching of SO_4 , N, BC and Al for all data (left) and after quality control related to Cl budgets (right).

Multiple regression analyses for element budgets

Results of the best models derived with multiple regression analyses, relating various environmental factors to element retention, before and after quality control, are presented in Table 3.6. As with Table 3.5, information is included on the percentage variance accounted for (R^2_{adj}), NME and NMAE (see Eq. 3.2 and 3.3).

Table 3.6 Overview of the predictor variables explaining element retention at 97-112 Intensive Monitoring plots with the number of plots and the percentage variance accounted for before and after quality control.

Predictor variables	S _{bu}		N _{bu}		BC _{bu}	
	All data	Qual. control	All data	Qual. control	All data	Qual. control
<i>Site/Stand characteristics</i>						
Tree species	-					
Soil type group				--		
Humus type group		++				
Stand age	--				-	
Altitude	--					
<i>Climate</i>						
Precipitation			-			
Temperature					-	
Climate zone						
<i>Deposition</i>						
Average S deposition 1995-1998	++					
Accumulated S deposition 1960-1995						
Average NH ₄ deposition 1995-1998						
Average NO ₃ deposition 1995-1998						
Average N deposition 1995-1998			++	++		
Accumulated N deposition 1960-1995						
Average S+N deposition 1995-1998						
Accumulated S+ N deposition 1960-1995						--
Average BC deposition 1995-1998 ¹					++	++
<i>Foliar chemistry</i>						
N-content						
<i>Soil chemistry</i>						
C/N ratio organic layer ⁴						
C/N ratio mineral topsoil ⁴						
pH organic layer						
pH mineral topsoil						
pH mineral subsoil						
Base saturation mineral topsoil						
Base saturation mineral subsoil					--	--
N ¹⁾	127	59	115	52	92	40
R ² _{adj} (%) ²⁾	23	19	74	92	88.5	87.6
NMAE	4.5	-4.0	0.16	0.14	0.45	0.49
NME	0.00	0.00	-0.037	-0.011	0.00	0.00

++ 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⁾ R²_{adj} = percentage variance accounted for.

Compared to the leaching estimates, the retention estimates were better explained in case of N and BC but worse for S. Furthermore, the effect of using more reliable data by skipping the plots with a strongly deviating Cl budget hardly improved the relationships. The average predicted retention values were always nearly correct (NME = 0 or very close to 0). As with leaching, the variations in the element relation are always related to the atmospheric deposition. Below we present and discuss the derived retention equations before.

The results show that S retention from the soil can hardly be explained from environmental variables. Before and after quality control, the explanation is near 20%, but the included variables do vary. Using all data, S retention increase with S deposition and decreases with stand age and altitude (Eq. 3.12), whereas the humus type is the only explaining variable after quality control (Eq. 3.13). Considering the low correlations, it is not very worthwhile to speculate about the possible impact of these variables.

$$SO_{4, bu} = -31 - 132 \cdot \text{Spruce} - 388 \cdot \text{Deciduous} - 378 \cdot \text{Age}_{\text{mature}} - 224.4 \cdot \log \text{altitude} + 394 \cdot \log SO_{4, dep} \quad (3.12)$$

$$SO_{4, bu} = -529 + 459 \cdot \text{moder} + 610 \cdot \text{mor} \quad (3.13)$$

Using all data, N retention increased with an increased N deposition and decreased with an increased precipitation (Eq. 3.14). The first relationship is trivial. The decrease in N retention with increased precipitation is also to be expected because of the elevated BN leaching at higher precipitation rates. Unlike N leaching, N retention was not significantly related to the C/N ratio of the organic or mineral layer. Using the data after quality control only, N retention also increased with an increased N deposition but now soil type has a significant impact instead of precipitation (Eq. 3.15). N retention seems to be lower in loamy/clayey soils compared to sandy soils (reference situation)

$$\log N_{bu} = 0.922 - 0.263 \cdot \log \text{Prec} + 0.9232 \cdot \log N_{dep} \quad (3.14)$$

$$\log N_{bu} = 0.388 - 0.0980 \cdot \text{loam/clay} + 0.0039 \cdot \text{remaining soils} + 0.8601 \cdot \log N_{dep} \quad (3.15)$$

As with BC leaching, variations in BC retention were significantly related to the BC input, the base saturation of the subsoil, temperature and stand age (Eq. 3.16), exactly in the reverse way (compare Eq. 3.8). Using the data after quality control only, BC retention is again the inverse of leaching being positively related to the present BC deposition, but negatively to the historic acid deposition in the period 1960-1995 and the base saturation of the subsoil (Eq. 3.17).

$$BC_{bu} = 842 - 398 \cdot \text{Age}_{\text{mature}} - 76.4 \cdot T + 0.8624 \cdot BC_{dep} - 12.71 \cdot BS_{\text{subsoil}} \quad (3.16)$$

$$BC_{bu} = 713 - 0.3141 \cdot AC_{\text{dep, historic}} + 0.7737 \cdot BC_{dep} - 17.48 \cdot BS_{\text{subsoil}} \quad (3.17)$$

An overview of results obtained by the various relations and the real observations for the budgets of SO_4 , N and BC is given in Fig. 3.7. The results show a good correlation between predictions and observations for N and BC but a very weak or nearly absent relationship for SO_4 . Apparently, we are not able to predict, nor do we really understand the fate of S in the soil. The relationships for N and BC, however, are such that reliable maps of the geographic variation in N and BC retention or release can be made when the environmental data used in the relationships are available.

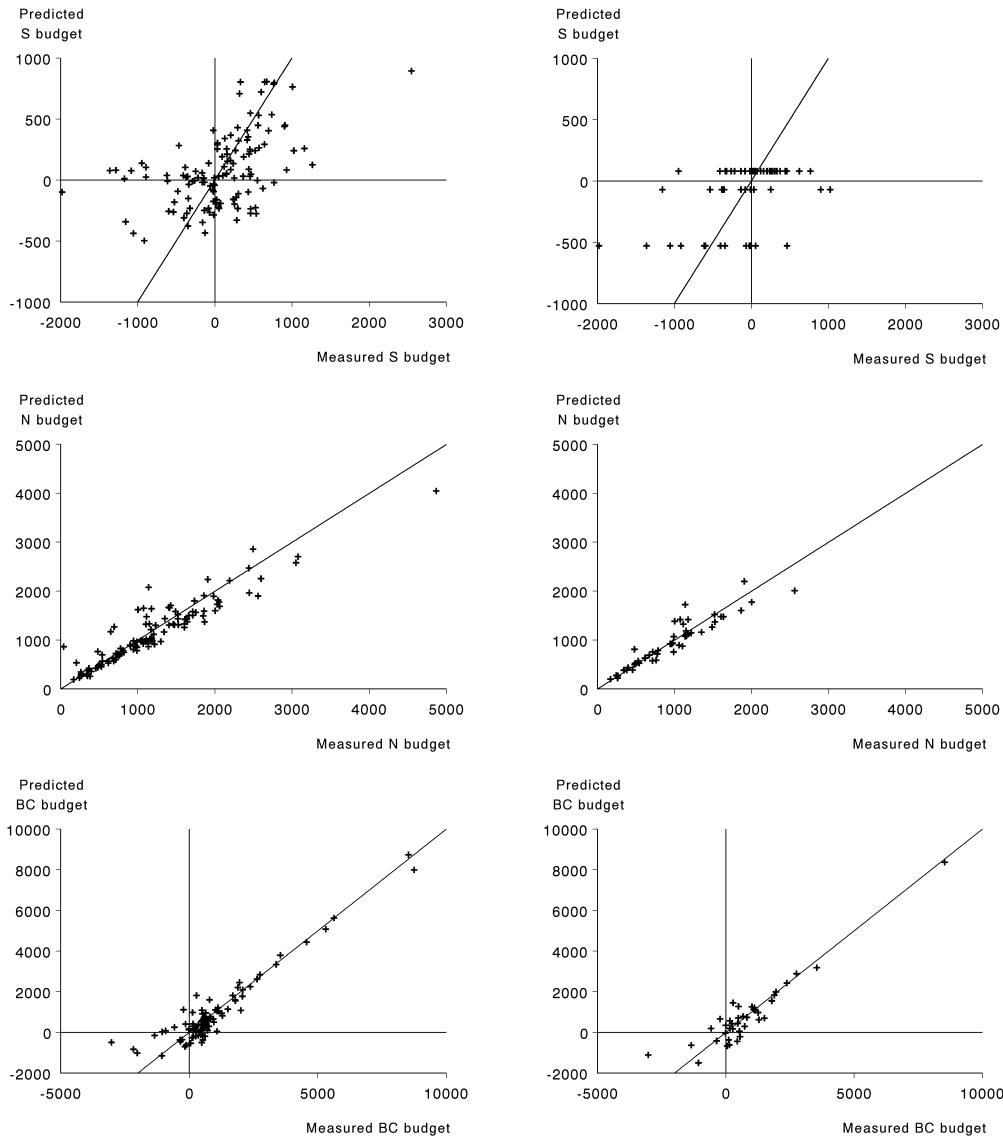


Figure 3.7 Comparison of results predicted by the various relations and the real observations for the budgets of SO_4 , N and BC for all data (left) and after quality control related to CI budgets (right)

3.4 Discussion and conclusions

Discussion

Results show large ranges in budgets for all the considered elements. This was to be expected considering the wide geographic range in locations with diverse circumstances with respect to deposition, hydrology and bio-geochemistry. There are, however, 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, and the relative short time period as discussed below.

In order to calculate water fluxes, meteorological data were needed on a daily basis. Only at part of the plots, those data were available but at most plots, the data were derived by interpolation from nearby meteorological stations (Van der Salm et al., 2004). 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. Van der Salm et al., 2004). 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 BC (De Vries et al., 2001). The differences 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%. The underestimation of leaching fluxes by using interpolated data instead of local measured meteorological data affects the calculated budgets in particular for elements where the output flux is comparable or higher than the input. N budgets are hardly affected at more than 50% of the sites, whereas S, Cl, Na and BC budgets are more strongly affected with a deviation of more than 20% at 50% of the sites (De Vries et al., 2001). 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 BC.

Furthermore 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) were 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 SO₄ and N at two sites is caused by extreme leaching in 1998, whereas the other years have a much lower release of SO₄ and N. Further improvements of the budgets can be expected when the time period increases.

Conclusions

Despite the various uncertainties, the following main conclusions can be drawn with respect to the leaching and retention of the different elements:

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. 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. Sites with the highest SO_4 release are also located in central Europe, where the strongest reduction in SO_4 deposition has taken place over the last decade. This indicates that these systems are releasing SO_4 stored in the soil in previous episodes of higher SO_4 input. 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 leaching of N is generally negligible below throughfall inputs of $10 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. 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. N budgets show that at most sites (90%) the N input is higher than the N leaching. Sites with a net release of N 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. Furthermore, N leaching was limited at high C/N ratios (>30) in the organic layer. A more in-depth analysis, based on 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 BC ($\text{Ca} + \text{Mg} + \text{K}$) is higher than that of Al. Extremely high leaching fluxes for BC (above $7000\text{--}8000 \text{ mol}_c \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) 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. 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 BC ($\text{Ca} + \text{Mg} + \text{K}$) increased significantly with an increase in the SO_4 (acid) input.
- 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 $370 \text{ mol}_c \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. High values are generally found in areas with a high N or S deposition.

References

- Armbruster, M., J.A. MacDonald, N.B. Dise and E. Matzner, 2002. *Throughfall and output fluxes of Mg in European forest ecosystems: a regional assessment*. For. ecol. manage. 164 (1-3), 137-147.
- Bleeker, A., G.P.J. Draaijers, J.W. Erisman and W. de Vries, 2004. *Canopy exchange modelling to estimate atmospheric deposition from throughfall measurements*. Environ. pollut. (this issue).
- Block, J., J. Eichborn, J. Gehrmann, C. Kolling, E. Matzner, K.J. Meiwes, K.v. Wilpert and B. Wolff, 1999. *Kernwerte zur Charakterisierung des ökochemischen Bodenzustandes des Gefährdungspotentials durch Bodenversauerung und Stickstoffsättigung an Level II-Waldökosystem-Dauerbeobachtungsflächen*. Bundesministerium für Ernährung, Landwirtschaft und Forsten, Arbeitskreis C der Bund-Länder Arbeitsgruppe Level II, 167 pp.
- Boyle, G.M., E.P. Farrell, T. Cummins and N. Nunan, 2000. *Monitoring of forest ecosystems in Ireland*. Forest Ecosystem research group Report 48. University College Dublin, Ireland.
- Cronan, C.S., R. April, R.J. Bartlett, P.R. Bloom, C.T. Driscoll, S.A. Gherini, G.S. Henderson, J.D. Joslin, J.M. Kelly, R.M. Newton, R.A. Parnell, H.H. Patterson, D.J. Raynall, M. Schaedle, C.T. Schofield, E.I. Sucoff, H.B. Tepper and F.C. Thornton, 1989. *Aluminum toxicity in forests exposed to acidic deposition: the ALBIOS Results*. Water Air Soil Poll. 48 (1-2), 181-192.
- De Vries, W., J.J.M. van Grinsven, N. van Breemen, E.E.J.M. Leeters and P.C. Jansen, 1995. *Impacts of acid deposition on concentrations and fluxes of solutes in acid sandy forest soils in the Netherlands*. Geoderma 67 (1-2), 17-43.
- De Vries, W., G.J. Reinds, J.M. Klap, E.P. van Leeuwen and J.W. Erisman, 2000a. *Effects of environmental stress on forest crown condition in Europe. Part III: Estimation of critical deposition and concentration levels and their exceedances*. Water, Air, and Soil Pollution 119 (1-4), 363-386.
- De Vries, W., G.J. Reinds, M.A. van Kerkvoorde, C.M.A. Hendriks, E.E.J.M. Leeters, C.P. Gross, J.C.H. Voogd and E.M. Vel, 2000b. *Intensive Monitoring of Forest Ecosystems in Europe. Technical Report 2000*. UN/ECE, EC, Forest Intensive Monitoring Coordinating Institute, 193 pp.
- De Vries, W., G.J. Reinds, C. van der Salm, G.P.J. Draaijers, A. Bleeker, J.W. Erisman, J. Aue, P. Gundersen, H.L. Kristensen, H. van Dobben, D. de Zwart, J. Derome, J.C.H. Voogd and E.M. Vel, 2001. *Intensive Monitoring of Forest Ecosystems in Europe. Technical Report 2001*. UN/ECE, EC, Forest Intensive Monitoring Coordinating Institute, Geneva and Brussels, 177 pp.

- Dise, N.B., E. Matzner and M. Forsius, 1998a. *Evaluation of organic horizon C:N ratio as an indicator of nitrate leaching in conifer forests across Europe*. Environ. pollut. 102 (Supp 1), 453-456.
- Dise, N.B., E. Matzner and P. Gundersen, 1998b. *Synthesis of Nitrogen Pools and Fluxes from European Forest Ecosystems*. Water Air Soil Poll. 105 (1-2), 143-154.
- Dise, N.B., E. Matzner, M. Armbruster and J.A. MacDonald, 2001. *Aluminium output fluxes from forest ecosystems in Europe: A regional assessment*. J. Environ. Qual. 30 (5), 1747-1756.
- Draaijers, G.P.J., E.P. van Leeuwen, P.G.H. de Jong and J.W. Erisman, 1997. *Base cation deposition in Europe - Part I. Model description, results and uncertainties*. Atmospheric Environment 31 (24), 4139-4157.
- Draaijers, G.P.J., A. Bleeker, D. van der Veen, J.W. Erisman, H. Möls and M. Geusenbroek, 2001. *Field inter-comparison of throughfall, stemflow and precipitation measurements performed within the framework of the Pan European Intensive Monitoring Program of EU/ICP forests*. report no. TNO-MEP-R2000/140. TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Apeldoorn, The Netherlands.
- Farrell, E.P., J. Aherne, G.M. Boyle and N. Nunan, 2001. *Long-Term Monitoring of Atmospheric Deposition and the Implications of Ionic Inputs for the Sustainability of a Coniferous Forest Ecosystem*. Water Air Soil Poll. 130 (3), 1055-1060.
- FIMCI, 2000. *Poster presentations of the Intensive Monitoring in the European forest ecosystems*. A composition of the posters presented by several countries at the combined SAG/NFC meeting 20-22 September 2000.
- Gundersen, P., I. Callesen and W. de Vries, 1998a. *Nitrate leaching in forest ecosystems is related to forest floor C/N ratios*. Environ. pollut. 102 (1), 403-407.
- Gundersen, P., B.A. Emmet, O.J. Kjønaas, C. Koopmans and A. Tietema, 1998b. *Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data*. For. ecol. manage. 101 (1-3), 37-55.
- Janssen, P.H.M. and P.S.C. Heuberger, 1995. *Calibration of process-oriented models*. Ecological Modelling 83 (1-2), 55-66.
- Leemans, R. and W.P. Cramer, 1991. *The ILASA database for mean monthly values of temperature, precipitation and cloudiness of a global terrestrial grid*. Research Report RR-91-18. International Institute of Applied System Analysis, Laxenburg, Austria, 61 pp.
- Lövblad, G. (Ed.) 1994. *Submanual on deposition for ICP-Forests level 2 plots*. Presented at the UN-ECE Task Force on Forest meeting in Lillehammer (Norway) May 1994.

- MacDonald, J.A., N.B. Dise, E. Matzner, M. Armbruster, P. Gundersen and M. Forsius, 2001. *Nitrogen input together with ecosystem enrichment predict nitrate leaching from European forests*. Glob. Change Biol. 8, 1028-1033.
- Mulder, J. and A. Stein, 1994. *The solubility of aluminum in acidic forest soils: Long-term changes due to acid deposition*. Geochim. Cosmochim. Acta 58 (1), 85-94.
- Oude Voshaar, J.H., 1994. *Statistiek voor onderzoekers: met voorbeelden uit de landbouw- en milieuwetenschappen*. Wageningen Pers, Wageningen, 253 pp.
- Sprangenberg, A., 1997. *Heterogenitat und Dynamik der Bodenlosungschemie am Beispiel verschiedener Nabhrelemente im Freiland und Tracer-transport an Bodensaulen*. Berichte des Forschungszentrum für Waldokosysteme Reihe A, Bd 149.
- Sverdrup, H. and P. Warfvinge, 1993. *The effect of soil acidification on the growth of trees, grass and herbs as expressed by the (Ca+Mg+K)/Al ratio. Reports in ecology and environmental engeneering*. Reports in Ecology and Environmental Engineering 1993: 2. Lund University, Department of Chemical Engineering II, 108 pp.
- Van Breemen, N., C.T. Driscoll and J. Mulder, 1984. *Acidic deposition and internal proton sources in acidification of soils and waters*. Nature 307, 599-604.
- Van der Salm, C., 2004. *Hydrological fluxes in forests: a comparison of different model concepts*. Environ. pollut. (this issue).
- Van der Salm, C., G.J. Reinds and W. de Vries, 2004. *Water balances in intensively monitored forest ecosystems in Europe*. Environ. pollut. (this issue).
- Wesselink, L.G., 1994. *Time trends and mechanisms of soil acidification*. PhD thesis, Agricultural University Wageningen, 129 pp.
- Wetzel, H., 1998. *Prozessorientierte Deutung der Kationendynamik von braunerden als Glieder von Acker- und Waldcatenen einer norddeutschen Jungmoränenlandschaft - Bornhöveder Seenkette*. Ecosys 25, 132 pp.

4 Impacts of nitrogen deposition on carbon sequestration by forests in Europe

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Keywords: C/N ratio, nitrogen retention carbon sequestration, nitrogen deposition, forest, forest soil, Europe

Abstract

An estimate of net carbon pool changes in Intensive Monitoring plots was based on repeated forest growth surveys for trees. Carbon pool changes in the soil were based on calculated nitrogen retention (N deposition minus N leaching) rates in soils minus N uptake and multiplied by the C/N ratio of the forest soils. In order to scale up results to Europe, an estimate of soil carbon pool changes was calculated for more than 6000 level I plots using: (i) N deposition by model estimates, (ii) net N uptake by yield estimates as a function of site quality, (iii) N retention fractions in soil related to measured C/N ratios, based on results from level II plots and (iv) measured C/N ratios for forest soils. As expected the changes in the carbon pool in tree due to forest growth increase going from Northern to Central Europe. The calculated changes in the carbon pool in soil are high in Central Europe and low in Northern and Southern Europe, since it follows the N deposition pattern. The carbon pool changes in the tree are generally 5-10 times as high as the estimated carbon pool changes in the soil. Net increases in the carbon pool by forests in Europe (both trees and soil) are in the range of 0.1-0.15 Gton.yr⁻¹, being an important part (about 50%) of the terrestrial carbon sink in Europe, derived from atmospheric inversion models. The results furthermore show that the C sequestration by forest is mainly due to a net increase in forest growth, since the longer term C immobilisation in the soil is limited. The contribution of N deposition to the increase in carbon in standing biomass is approximately 10 and 20 Mton.yr⁻¹. If one relates the additional growth to the estimated forest growth of approximately 280 Mton.yr⁻¹, the contribution varies between approximately 3.5 and 7%.

4.1 Introduction

The importance of assessing the terrestrial carbon sink

It is of importance to arrive at reliable estimates of CO₂ sequestration in forests since this may delay the rise in the atmospheric CO₂ concentration with implications for the speed of climate change. In the Kyoto Protocol, signed by 84 nations and ratified by 22 nations until January 2000, governments agreed to reduce emissions of CO₂ either by limiting fossil fuel consumption or by increasing net carbon sequestration in terrestrial sinks through afforestation and land use change or both. Even though increasing net carbon sequestration is still limited to strictly defined cases of

afforestation and land use change, it has been advocated (IGBP Terrestrial Carbon Working Group, Steffen et al., 1998) to use a full carbon budget, including all potential terrestrial sinks over a sufficiently long time period, to be accounted for in international CO₂ emission reductions. This requires methods for reliable quantification of these C sinks.

The possible impact of nitrogen deposition on carbon sequestration in forests

Important questions with respect to carbon sequestration are related to the cause of the large uptake of the mid-latitude forests and the time period in which the terrestrial sink will be saturated (Houghton et al., 1998). European forests have a role in net carbon sequestration of the biosphere (i.e. (Kauppi et al., 1992; Nabuurs et al., 1997). Apart from changes in standing growing stock (influenced by forest management), changes in net primary productivity may also play a role in this respect (Spiecker et al., 1996). Increased net primary productivity have been hypothesised to be due to increases in atmospheric CO₂ concentrations (e.g. Melillo et al., 1993; Friedlingstein et al., 1995), nitrogen deposition (Holland et al., 1997; Nadelhoffer et al., 1999) and temperature, increasing the growing season (e.g. Myneni et al., 1997). Increase in CO₂-concentrations on the other hand may favour growth as well as increase water use efficiency of trees. However, trees may adapt to changing CO₂-concentrations and the effect may diminish soon (Tognetti et al., 2000). Using a modelling approach, temperature has been claimed to be relatively unimportant, whereas the combination of CO₂ rise and elevated N deposition may account for a 15-20% increase in forest net primary productivity (Rehfuess et al., 1999). In this context, N deposition is claimed to be most important (Rehfuess et al., 1999, last ref recognition). The remaining explanation would then be the impact of forest management.

Furthermore an elevated carbon sequestration in the soil, due to an increased accumulation of soil organic matter in response to elevated N inputs, may play a role. By far the largest amount of C stored in forests in the northern hemisphere is stored in the soil. Carbon fixed by photosynthesis ultimately moves via litter fall to the soil, where it is only partially decomposed. Thus, over the long term the soil is the ultimate sink or source of CO₂ for these ecosystems. Nitrogen is often the limiting nutrient in terrestrial ecosystems, and thus sequestration of C is closely linked to the N cycle. Soil processes account for the most significant unknowns in the C and N cycle. Current hypotheses suggest that increased N deposition causes an increased rate of soil organic matter accumulation at least in two ways due to an increased leaf/needle biomass and litter production (e.g. Schulze et al., 2000) and a reduced decomposition of organic matter (Berg and Matzner, 1997; Harrison et al., 2000) The N-content of forest litter and humus might thus be an important indicator of the C-sequestration. Understanding the N cycle in semi-natural ecosystems is therefore the key to understanding the long-term source or sink strength of soils for carbon.

Since nitrogen often is the limiting nutrient in forests, nitrogen deposition may increase wood production and accumulation of soil organic matter, thus increasing carbon sequestration into the forest. Earlier estimates suggested that this mechanism could take up one third of the global CO₂ emission from fossil fuel (or $2 \times 10^{15} \text{ g.yr}^{-1}$)

if most of the deposition nitrogen was taken up by trees and used to form new woody biomass (Holland et al., 1997). Recent data on the distribution of deposition nitrogen between trees and soil (Nadelhoffer et al., 1999), however, suggest that a large part of the nitrogen is accumulated in the soil at low carbon to nitrogen ratio (10-40) and not in the trees at carbon to nitrogen ratio (200-500). Thus the increase in nitrogen deposition may cause a much smaller additional CO₂ sequestration in forests (0.25×10^{15} g.yr⁻¹). This issue is a matter of ongoing scientific debate (e.g. Jenkinson et al., 1999; Schindler, 1999; Sievering, 1999) and continued research and deserves further attention as described in this background document. When the large uptake is mainly due to elevated growth, it is likely that this is a short transitory phenomenon, whereas it could be a carbon sink for a long period if soil accumulation is the main cause, since below ground carbon has much lower turnover times than above ground carbon.

Upscaling of carbon sequestration research in forests to the European scale

Information on C and N sequestration and their response to changes in N deposition on a European scale is presently still limited. The EUROFLUX project provided measurements of C fluxes above a range of forests across Europe (Thenhunen et al., 1998), but extrapolation of these results to a European scale is still prone to large uncertainties. The aboveground CO₂ sequestration in the trees can also be estimated from yield tables and models on tree growth. Furthermore, the net C sequestration can be based on repeated forest surveys (e.g. Kauppi et al., 1992; Nabuurs et al., 1997). But the CO₂ sequestration in forest soils is difficult to estimate from direct measurements at European or global scale. Recent EU projects (EXMAN, NITREX, NIPHYS, CANIF) have increased the understanding of controls in the N and C cycle in forests (e.g. Berg and Matzner, 1997; Dise et al., 1998a; Dise et al., 1998b; Gundersen et al., 1998). However, the detailed process understanding has not yet led to major improvements on the ability to predict and extrapolate such impacts and to assess C sequestration on a European scale. Simulation models and local data are available for a number of sites, but extrapolation to a European scale has not yet taken place.

An example of upscaling forest ecosystem research to the continental and global scale (although based on rough generalisations) is the publication by Nadelhoffer et al. (1999). They calculated additional C sequestration on a global scale from additional N uptake by trees and N immobilisation in soils in response to N deposition. From their estimate, the authors conclude that C sequestration in forest trees and forest soils over the world is of equal magnitude. This estimate is, however, based on an estimated total world N deposition, averages values for the C/N ratio in stem wood and forest soils and constant N retention fractions in both compartments, based on the short-term fate (1-3 yr) of ¹⁵N labelled tracer experiments in nine temperate forests (Nadelhoffer et al., 1999). The upscaling of the results to a European scale (assumed constant N retention fractions and C/N ratios in stem wood and soil independent of the location) is extremely simple, thus hampering an adequate estimate on this large scale. The available data at level II and level I plots do allow for much better estimates as described below.

Contents of this chapter

This study presents an estimate of: (i) the current carbon sequestration in trees and soil in European forests for the year 2000, based on simple assumptions and empirical knowledge of the interaction of carbon (C) cycles and nitrogen (N) cycles in forests, and (ii) the likely impact of N deposition on the C sequestration rates in the last 40 years (the period 1960-2000). In making the calculations, use is made of data on N retention, N uptake and C/N ratios in soils, that were: (i) available at more than 100 Intensive Monitoring (level II) plots and (ii) estimated (N deposition, N uptake) and measured (C/N ratios) at more than 6000 Level 1 plots at a systematic grid, statistically representing approximately 2 million km² of forests in Europe (including part of Russia).

In Section 4.2, we describe the approaches that were used to calculate carbon sequestration both at Intensive Monitoring plots and at the European scale using Level I plot data. This includes a literature review of methods and results related to the assessment of the terrestrial carbon sink (Section 4.2.1) and the methods to calculate carbon sequestration at Intensive Monitoring plots (Section 4.2.2), extrapolate carbon sequestration to the European forested area (Section 4.2.3) and assessing nitrogen deposition impacts on the carbon sequestration for that area (Section 4.2.4). Results are described in Section 4.3. This again includes the carbon sequestration in soils at Intensive Monitoring plots (Section 4.3.1) and on the European scale (Section 4.3.2) and the impact of nitrogen deposition on carbon sequestration (Section 4.3.3). Finally, a discussion of the results and conclusions is presented in Section 4.4.

4.2 Methods

4.2.1 Methods and results related to the assessment of the terrestrial carbon sink

Measurements of atmospheric CO₂ indicate that from the estimated 7.1 Gton C released by man (5.5. fossil fuel and 1.6 from land use change and deforestation) only 3.4 Gton is found back in the atmosphere. From this, an estimated 1.5-2.0 Gton is being absorbed by the oceans (Bousquet et al., 1999). The remaining 1.5-2.0 Gton would be global terrestrial uptake (Ciais et al., 1995) but this estimate is also commonly referred to as the missing sink. Studies using global inversion models indicate that a significant portion of the net uptake of the terrestrial biosphere occurs at northern mid-latitude forest regions (Ciais et al., 1995; Fan et al., 1998; Bousquet et al., 1999).

Up to now, several studies have been carried out, to assess carbon sequestration in forests in Europe, but a direct comparison is hampered because of the measurement of different carbon sink terms. First of all, there is a difference in the assessment of the so-called net ecosystem production (NEP) or net ecosystem exchange (NEE), and the net biome production (NBP). The NEP or NEE stands for the total uptake of CO₂ by photosynthesis, corrected for plant and soil respiration, whereas the NBP equals the NEP corrected for CO₂ emissions due to harvest and forest fires. The

latter term is critical with respect to long-term carbon storage, since an aggrading forest may temporarily sequester large carbon amounts, but most of it is re-emitted to the atmosphere after logging. Secondly, a distinction can be made in sequestration in the trees and in the soil. Over the long term, the soil is the ultimate sink or source of CO₂ for these ecosystems.

An overview of various estimates of the carbon sequestration in Europe, focusing on different ecosystem compartments and using different methods is given in Table 4.1. Apart from a distinction in the type of flux and the forest compartment, a differentiation has been made in the quality of the upscaling methods, going from individual sites to the European scale. A systematic discussion related to the various approaches and results is given below.

NBP estimates at landscape scale based on Inversion modeling

Bousquet et al. (1999) estimated a carbon sink of 0.3 Gton C yr⁻¹ for Europe using a global inversion model including data on regional CO₂ emissions and tropospheric CO₂ concentrations. This is the main approach used up to now to assess C sinks on a regional scale, since it includes regionally distributed data and models. Similarly, Bousquet et al. (1999) estimated a C sink in North Asia of 1.5 Gton C yr⁻¹ and of 0.5 Gton C year⁻¹ in the Northern United States and Canada. Those models do not differentiate between forests and other land use types. In the Arctic and tropical Asia a net release of respectively 0.2 and 0.8 Gton C year⁻¹ was estimated.

NEE/NEP estimates of whole forests or trees from CO₂ net flux and tree growth measurements

An NEP estimate related to forests only is based on direct measurement of the net CO₂ exchange flux to the forest ecosystem at seventeen so-called EUROFLUX sites along a transect from North Sweden to Central Italy (Valentini et al., 2000). Tree species included were Norway spruce and beech. Results indicate that most forests act as sinks at present, and sequester CO₂ at an average rate of 3.03 ton.ha⁻¹.yr⁻¹. Scaling these results to the level of the continent remains difficult. Recently, Papale and Valentini (2003), used the net CO₂ exchange flux collected in the EUROFLUX network at sixteen of these sites to train a neural network to provide spatial (1 x 1km) estimates of carbon fluxes of European forests. By using this approach, they estimated the total NEE to equal 0.47 Gton C yr⁻¹. This is almost equal to an estimate that can be derived by simply multiplying the average net CO₂ exchange flux of 3.03 ton.ha⁻¹.yr⁻¹ with the forested area 149 million ha of forests, which is generally used as an estimate for forests in Europe excluding Russia (Nabuurs et al., 1997), that would lead to an NEE of 0.45 Gton C yr⁻¹. Earlier, Martin et al. (1998), estimated that only between 0.17 and 0.31 Gton C yr⁻¹ was sequestered by European forest in 1997, using an upscaling technique with forest maps, based on net CO₂ exchange fluxes ecosystem at eleven EUROFLUX sites. In both approaches, on an aerial basis the net sequestration was largest in Central Europe and lowest in Northern Europe, with Southern Europe in between.

Table 4.1 Overview of different estimates of carbon sequestration on a European wide scale.

Type of C flux	Compartment	Method	Estimated sink Gton.yr ⁻¹	Upscaling method	Reference
<i>NBP landscape</i>					
NBP	Landscape	Inversion modelling	0.30	Good	Bousquet et al. (1999)
<i>NEE/NEP Whole forest/ trees</i>					
NEE	Whole forest	CO ₂ net flux measurements	0.47	Neural networks	Papale and Valentini (2003)
			0.25	Forest maps	Martin et al. (1998)
NEP	Total above-ground biomass	Tree growth measurements	0.39-0.53 ¹	Multiply with forested area	Schulze et al. (2000)
<i>NBP whole forest/ trees</i>					
NBP	Trees (stem wood)	Repeated forest Inventories	0.10	Country inventory data	(Kauppi et al., 1992) (Nabuurs et al., 1997)
NBP	Trees (stem wood)	Modelling forest growth	0.08-0.12 ²	Country inventory data	Liski et al. (2002)
NEP con-tribution	Trees (above-ground biomass)	N retention	0.025 ³	World average values	After Nadelhoffer et al. (1999)
<i>NBP forest soil</i>					
NBP	Forest soil (below-ground biomass)	Carbon soil input minus carbon mineralisation	0.13	Multiply with forested area	Schulze et al. (2000)
NBP	Forest soil (below-ground biomass)	Modelling forest growth and decomposition	0.038-0.061 ²	Country inventory data	Liski et al. (2002)
NBP	Forest soil (below-ground biomass)	N retention	0.022 ³	World average values	After Nadelhoffer et al. (1999)

¹ The first estimates was derived by Schulze et al. (2000) based on a forested area in Europe of approximately 150 million ha, whereas the second estimate is based on an area of 200 million ha, used in this study

² These estimates were originally limited to the EU + Norway and Switzerland (approximately 138 million ha) but results were scaled to the European forested area, excluding most of Russia (approximately 200 million ha)

³ These estimates were originally global but were scaled to the European N deposition and forest area. Actually, Nadelhoffer et al. (1999) also estimated a NEP of 0.025 for carbon sequestration in trees but this was presented as the contribution of N deposition to NEP in trees and not the total growth

At 11 forest sites, two of them overlapping with the Euroflux sites (so called Canif sites), the current carbon sequestration by tree growth or NEP (by trees), based on process studies and inventories, was estimated to equal 2.64 ton.ha⁻¹.yr⁻¹ (Schulze et al., 2000). Schulze et al. (2000) multiplied this value by 149 million ha of forests, to estimate an NEP of 0.39 Gton C yr⁻¹ for Europe. Using a forested area of 200 million ha, applied in this study, it would lead to a sink of 0.53 Gton C yr⁻¹. Apart from the still relatively poor upscaling procedures, it should be noted that data on the present sequestration in the trees by uptake (and the same holds for the present CO₂

exchange) do overestimate the net carbon sink, as this approach does not account for C release after disturbances (NEE or NEP is larger than NBP).

NBP assessments for trees from repeated forest inventories and modelling forest growth

The net increase in carbon in forests (NBP) can be derived from repeated forest inventories on the standing biomass. Such data do indicate an increase in the period between 1970-1990 of 25% (Kauppi et al., 1992) leading to a net NBP in trees of approximately 0.1 Gton C yr⁻¹. A similar value was obtained by Nabuurs et al. (1997), using much more detailed information on forest inventories in most countries within Europe.

Liski et al. (2002) gave an estimate of the net carbon sequestration in trees based on a dynamic modelling exercises, using data on stem wood volumes from forest resource information over Europe. The growth of branches, foliage and roots is included by an additional allocation of dry matter increment, relative to the known stem wood increment data. The model was applied to the EU countries including Norway and Switzerland. The net carbon sequestration in trees was estimated at 390-600 kg.ha⁻¹.yr⁻¹ in 1990 and at 440-510 kg.ha⁻¹.yr⁻¹ in 2040. Considering the forested area of the included countries (138 million ha) this leads to a net carbon sequestration of 0.054-0.082 Gton.yr⁻¹ in 1990 and of 0.062-0.070 Gton.yr⁻¹ in 2040. Assuming that the average carbon sequestration is equal in the forests that are not considered, the net carbon sequestration equals 0.078-0.12 Gton.yr⁻¹ in 1990 and of 0.088-0.102 Gton.yr⁻¹ in 2040 for a forested area of 200 million ha.

A comparable model was used by Nabuurs and Schelhaas (2002) who calculated the net carbon sequestration in trees for 16 typical forest types across Europe. The advancing mean of the net sink of all forests was calculated to equal 800 kg C.ha⁻¹.yr⁻¹. Multiplication of this amount by the European forested area is not allowed, since the calculations are just mean to give indicative values for representative forest types. If one, however, simply multiplies this average value with a forested area of 200 million ha, it would lead to a net carbon sequestration of 0.16 Gton.yr⁻¹.

NEP assessments for soil from carbon cycling measurements and modelling soil C dynamics

As with CO₂ sequestration in tree, the retention in forest soils can be derived from repeated soil inventories, but those data are hardly available. An example of results thus obtained is presented in Leeters and de Vries (2001), but the results show that the change is hard to detect within a short period of time, considering the large present pools with the possible exception of the organic layer (see also De Vries et al., 2000). One can also estimate the net C sequestration in the soil from direct measurements of the carbon input to the soil by litterfall and root decay and carbon release by mineralization, but this approach is again hampered by the fact that the result is based on subtracting large numbers with relative high uncertainties. Such an approach was used by Schulze et al. (2000) at eleven 'Canif' sites, mentioned above. These authors estimated an average C accumulation in soils of 0.86 ton C yr⁻¹. By

simply multiplying this figure with 149 million ha of forests, they calculated a sink of 0.128 Gton C yr⁻¹ at the European scale. Using a forested area of 200 million ha, as consistently applied in this study, it would lead to a sink of 0.172 Gton C yr⁻¹.

Apart from net carbon sequestration in trees, Liski et al. (2002) also gave an estimate of the net carbon sequestration in soil, based on the dynamic modelling exercise described before for the EU countries including Norway and Switzerland. The net carbon sequestration in soil was estimated at 190 kg.ha⁻¹.yr⁻¹ in 1990 and at 305 kg.ha⁻¹.yr⁻¹ in 2040. Considering the forested area of the included countries (138 million ha) this leads to a net carbon sequestration of 0.026 Gton.yr⁻¹ in 1990 and of 0.043 Gton.yr⁻¹ in 2040. Assuming that the average carbon sequestration is equal in the forests that are not considered, the net carbon sequestration equals 0.038 Gton.yr⁻¹ in 1990 and of 0.061 Gton.yr⁻¹ in 2040 for a forested area of 200 million ha. Nabuurs and Schelhaas (2002) also calculated the net carbon sequestration in soil for 16 typical forest types across Europe. The advancing mean of the net sink of all forests was calculated to equal 110 kg C.ha⁻¹.

Carbon sequestration derived from N retention

A completely different approach compared to all the former approaches is related to the possibility to assess C sequestration from N uptake by trees and N immobilisation in soils in response to N deposition. First estimates based on this approach suggested that this mechanism could take up one third of the global CO₂ emission from fossil fuel (or 2 Gton C yr⁻¹), being equal to the missing carbon sink (Holland et al., 1997). In this approach most of the deposition nitrogen was assumed to be taken up by trees to form new woody biomass. The assumption was that carbon and nitrogen accumulate in organic matter at the same relative rates through the same mechanisms. This means that nitrogen saturated forests with low nitrogen retention will have nearly no CO₂ sequestration in the soil.

Recent data on the distribution of deposition nitrogen between trees and soil, however, suggest that a large part of the nitrogen is accumulated in the soil at a low carbon to nitrogen ratio and not in the trees at a high carbon to nitrogen ratio. These results are based on the short-term fate (1-3 yr) of ¹⁵N labelled tracer experiments in nine temperate forests (Nadelhoffer et al., 1999). Using a total world N deposition estimate of 5.1 Mton.yr⁻¹, average N retention fractions in stem wood (0.05) and in the soil compartment (0.7) and averages values for the C/N ratio in stem wood (500) and forest soils (30), these authors thus came to a ten times lower global estimate, than estimated by Holland et al. (1997). In Table 4.1 the estimates by Nadelhoffer et al. (1999) have been scaled to an estimated N deposition for Europe of 1.1 Mton.yr⁻¹. The results suggest that the sinks in forest trees and forest soils are of equal magnitude.

This estimate by Nadelhoffer et al. (1999) of the C sequestration gave rise to statements about the 'mysterious' missing carbon sink (Schindler, 1999), since it would imply that forest are not responsible for the net uptake of the missing 1.5-2.0 Gton of CO₂ in the atmosphere. The estimated above-ground carbon sequestration is, however, likely to be underestimated since the authors neglected the effect of

direct foliar uptake (Jenkinson et al., 1999; Sievering, 1999). The repeated forest inventory data by Kauppi et al. (1992) and Nabuurs et al. (1997) for Europe, leading to a net NBP in trees of approximately 0.1 Gton C yr⁻¹ is already a strong indication for this. The problem in this discussion, however, is that Nadelhoffer et al. (1999) focused in principle on the additional C sequestration in response to N deposition and not on the total sequestration, as discussed further in Section 4.2.4.

4.2.2 Calculation of carbon sequestration in soils at Intensive Monitoring plots

An estimate of net C sequestration in Intensive Monitoring plots was based on the calculated nitrogen immobilisation (sequestration) in the soils, multiplied by the C/N ratio of the forest soils, distinguishing between the organic layer (forest floor) and mineral soil. As stated before, the basic assumption is that CO₂ sequestration can be calculated from nitrogen retention in the soils since carbon and nitrogen accumulation in organic matter occurs through the same mechanisms. N immobilisation (sequestration) was calculated as:

$$\text{N immobilisation} = \text{N deposition} - \text{N leaching} - \text{N uptake} \quad (4.1)$$

This approach is based on the assumption that denitrification can be neglected in the organic layer and the mineral topsoil, where both N and C sequestration is assumed to occur. Figure 4.1 shows the calculated N retention (N deposition minus N leaching) and N uptake for the Intensive Monitoring plots for which carbon pool changes in trees and soil were calculated (Fig 4.1). This included the plots with information on: (i) both bulk deposition and throughfall of N, thus allowing the calculation of total N deposition, and (ii) soil solution chemistry, thus allowing the calculation N leaching. Such budgets were only available for 124 plots, due to the limited availability of soil solution chemistry data. The budgets are an update of those described in De Vries et al. (2001) by including two additional years (the period 1995-2000). The plots were located in Belgium, France, Denmark, Germany, UK, Ireland, Norway, Sweden, Finland and Austria (Fig. 4.1). The actual N uptake was derived by multiplying changes in standing biomass in terms of stem wood, from repeated growth surveys in the period 1995-2000, as described in Chapter 5 with deposition dependent N contents in biomass. The uptake in branch wood was thus neglected. The results show that N uptake systematically increases going from Northern to Southern Europe while the N retention generally follows this pattern. In nearly all cases total retention (equal to uptake, denitrification and soil immobilisation) is larger than uptake implying that N is immobilised in the soil.

In multiplying the net N immobilisation with the C/N ratio, the variation of the C/N ratio with the depth of the soil profile must be accounted for. Especially there is often a large difference between C/N ratio in the organic layer (forest floor) and in the mineral soil. The retention of N in those layers is dependent on the transport of the mineral N input down the profile. From experiments simulating increased nitrogen deposition it is shown that nitrate is much more mobile than ammonium

(Nadelhoffer et al., 1995; Emmet et al., 1998) and some transport of nitrate down the profile even occur at sites with high C/N in the forest floor (Gundersen and Rasmussen, 1995; Moldan et al., 1998).

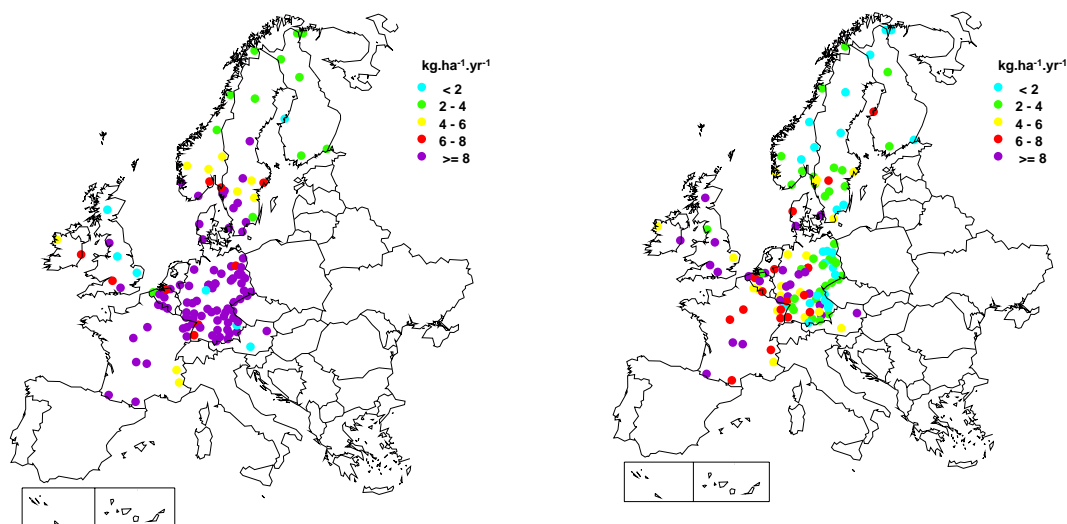


Figure 4.1 Nitrogen retention (N deposition minus N leaching; left) and N uptake (right) at the 121 Intensive Monitoring plots ($\text{kgN.ha}^{-1}.\text{yr}^{-1}$) that were used for the calculation of carbon sequestration in soils.

The fate of deposition N in forest soils has been studied by nitrogen tracer (^{15}N) technique. In an ammonium-nitrate addition study by Nadelhoffer et al. (1999) in oak and pine stands nitrate and ammonium were labelled separately. Spraying of a NH_4NO_3 solution monthly in the growing season was performed to simulate deposition of $58 \text{ kg N.ha}^{-1}.\text{yr}^{-1}$. Results of the experiment are shown in Table 4.2. Most of the retained ammonium (80%) was found in the forest floor, whereas the retention of nitrate was about equal in the forest floor and the first 20 cm of the mineral soil. The data in Table 4.2 show a higher retention of both N compounds in the red pine stand, which had a higher C/N ratio than the oak stand. This indicates that at higher C/N ratio, which determines the sink strength of the forest floor, less N is transported down to the mineral soil.

Table 4.2 The fraction of added N (ammonium or nitrate) retained in the forest floor relative to the total soil N retention of the compound in both the forest floor and the mineral soil (0-20 cm) in two stands at Harvard Forest, U.S.A. (Nadelhoffer et al., 1999).

Forest stand	N Labelling	Fraction N retained in the forest floor
Red Pine	Ammonium	0.82
(C/N = 26)	Nitrate	0.58
Oak	Ammonium	0.78
(C/N = 23)	Nitrate	0.52

Within the NITREX project, Tietema et al. (1998) performed ^{15}N tracer studies with various combinations of input levels (current deposition and simulated increase or decrease of deposition) and dominating N compounds (NH_4 -fractions from 0.1 to 0.8). Based on the fate of N added over one year, 40 to 75 % of soil N retention occurred in the forest floor. The lowest percentages were found at the highest nitrate

depositions rates (lowest NH_4 -fraction). In nitrifying soils (lower C/N ratio soils) labelled NH_4 may over time be transformed to nitrate and leached down the profile, which makes the interpretation of these numbers difficult. Based on these results we modelled the partitioning of N retention between forest floor and mineral soil as a function of the N input and the C/N ratio of the forest floor according to:

$$\text{C sequestration} = \text{N immobilisation} \cdot (\text{fret}_{\text{ff}} \cdot \text{C/N}_{\text{ff}} + (1 - \text{fret}_{\text{ff}}) \cdot \text{C/N}_{\text{ms}}) \quad (4.2)$$

Where C/N_{ff} and C/N_{ms} are the C/N ratios of the forest floor and the mineral soil (up to a depth of 20 cm), and fret_{ff} is the N retention fraction in the forest floor, being the ratio of the N retention in the forest floor and the N retention in the complete soil profile (forest floor and mineral soil). The N retention fraction in the forest floor was calculated as a function of the NH_4 -fraction in the N input and the C/N ratio of the forest floor, by multiplication of two factors t and r according to:

$$\text{fret}_{\text{ff}} = t \cdot r \quad (4.3)$$

With t and r are being values depending upon the NH_4 -fraction in the N input and the C/N ratio of the forest floor, according to:

$$\begin{aligned} t &= 0.5 && \text{if } \text{NH}_4 \text{ fraction} < 0.5 \\ t &= \text{NH}_4 \text{ fraction} && \text{if } 0.5 < \text{NH}_4 \text{ fraction} < 0.75 \\ t &= 0.75 && \text{if } \text{NH}_4 \text{ fraction} > 0.75 \end{aligned} \quad (4.4)$$

$$\begin{aligned} r &= 1.0 && \text{if } \text{C/N ratio} < 20 \\ r &= 1.0 + 0.033 \cdot (\text{C/N ratio} - 20) && \text{if } 20 < \text{C/N ratio} < 30 \\ r &= 1.33 && \text{if } \text{C/N ratio} > 30 \end{aligned} \quad (4.5)$$

A comparison of calculated N retention fractions in the forest floor for sites and treatments included in Tietema et al. (1998) and the observed partitioning from the tracer experiments is presented in Fig. 4.2A. The figure shows a reasonable comparison, but the simple relationships may give a slight overestimation of the fraction of N retained in the forest floor. Values for the N retention fraction in the forest floor thus calculated for the intensive monitoring plots considered are presented in Fig 4.2B. In general the N retention fraction is higher than 50%.

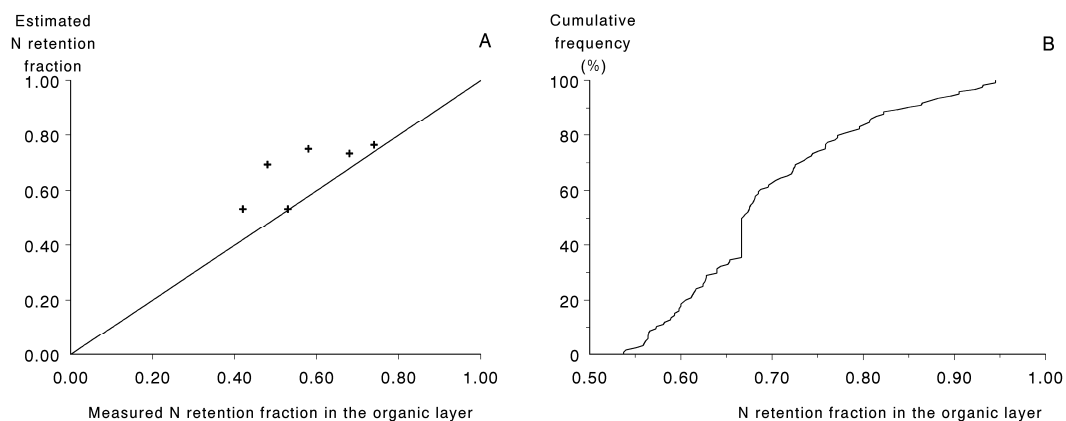


Figure 4.2 Comparison of predicted and measured N retention fractions in the organic layer of six forest plots (A) and predicted N retention fractions in the forest floor of the 121 Intensive Monitoring plots (B)

The C/N ratio of both organic layer and the mineral topsoil for the intensive monitoring plots is given in Figure 4.2. The figure shows that generally, the C/N ratios of the forest floor are much higher than in the mineral soil. Specifically in the Nordic countries the difference can be large with C/N ratios in the organic layer often being higher than 35 and in the mineral layer varying between 20-30 (compare Fig. 4.2 left and right).

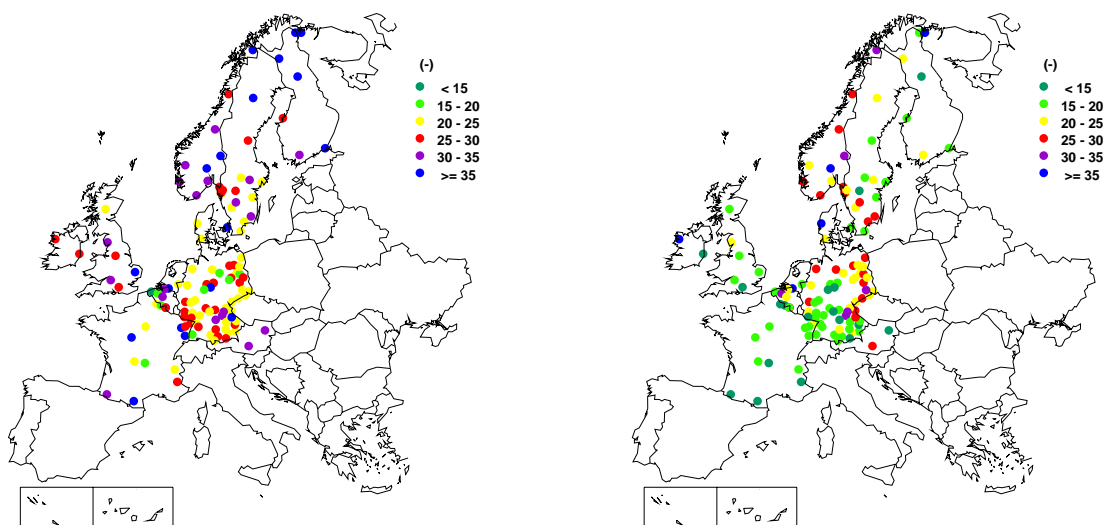


Figure 4.3 C/N ratios in the organic layer (left) and mineral topsoil (right) at the 121 plots that were used for the calculation of carbon sequestration in soils.

4.2.3 Extrapolation of carbon sequestration to the European forested area

In order to scale up results to the European scale, an estimate of net C sequestration for more than 6000 forest soils located in a systematic grid of 16 km x 16 km (level I plots) was made, being representative for approximately 2,0 million km² for Forests in Europe, including part of Russia (each plot represents approximately 256 km²).

The assumed representative forest area of each grid cell in a country was scaled to the total forested area in each country given in the Annexes of the executive reports of ICP forests. As with the Intensive Monitoring plots, the calculation was based on calculated nitrogen retention in the soils, multiplied by the C/N ratio of the forest soil considered (see Eq. 4.1). N immobilisation (sequestration) was now calculated as a fraction of the N deposition corrected for N uptake, according to:

$$\text{N immobilisation} = \text{frN}_{\text{im}} \cdot (\text{N deposition} - \text{net N uptake}) \quad (4.6)$$

The fraction frN_{im} was calculated as a function of the C/N ratio of the forest soil and the fraction NH_4 in deposition, using presently available results on this relationship given in e.g. Matzner and Grosholz (1997), Dise et al. (1998a; 1998b) and Gundersen et al. (1998) and newly derived results from the Intensive monitoring plots. This relationship was derived by plotting the relation between N retention/N deposition and C/N ratio for several plots for which those data are available, including the Intensive Monitoring plots.

A relationship between the output (nitrate leaching)/input (throughfall N) ratio and C/N ratios in the forest floor in more than 30 forest conifer plots is presented in Figure 4.4A (after Gundersen et al., 1998). It should be noted that the estimates of output are relative uncertain and that throughfall N underestimate the total N input due to canopy uptake. N leaching appears to be negligible at all sites with an N input $< 10 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. Based on those data, Gundersen et al. (1998) presented a range in retention fractions as a function of the N status of the ecosystem, including C/N ratios, as given in Tabel 4.3

Table 4.3 An overview of ranges in N retention fractions as a function of the N status of the ecosystem based on results from Gundersen et al. (1998; 2003) and De Vries et al. (2001).

Nitrogen status	Low (N limited)	Intermediate	High (N saturated)
Input ($\text{kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$)	0-15	15-40	40-100
Needle N%	< 1.4	1.4-1.7	1.7-2.5
Soil N flux density (litterfall + throughfall) ($\text{kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$)	< 60	60-80	> 80
C/N ratio ($\text{g C} \cdot \text{g N}^{-1}$)	> 30	25-30 or 20-30 ¹	< 25 or < 20 ¹
Proportion of input retained (%)	> 90	40-100	0-70

¹ the first criterion is based on Gundersen et al. (1998) and the second on De Vries et al. (2001).

The reliability of the suggested N retention fractions as a function of C/N ratio is only partly substantiated by the results of the Intensive Monitoring plots as presented in Figure 4.4B. The results show indeed that N retention is nearly complete (above 90%) at C/N ratios above 30-35 and very low at low C/N ratios (below 20) but in between it is highly variable. However, the Intensive Monitoring data include many sites with low input and low C/N (e.g. boreal forests in Scandinavia) that exhibit full retention simply because the input is low as illustrated in Dise et al. (1998b).

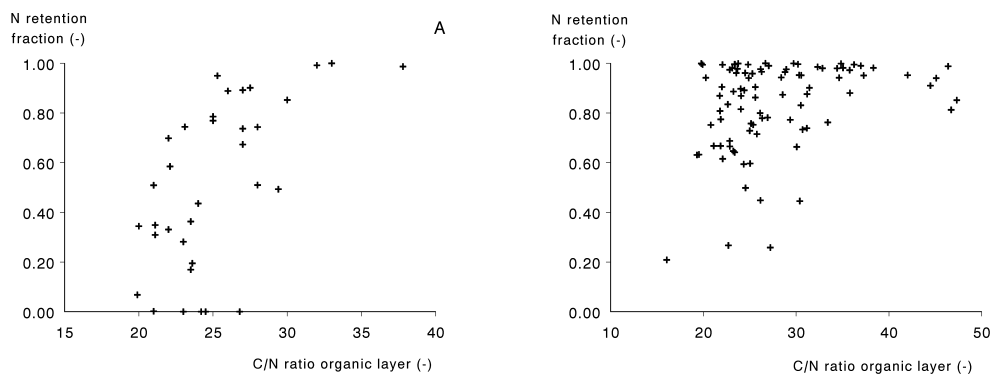


Figure 4.4 Relationship between N retention fraction and C/N ratios in the organic layer. The left graph refers to 34 forest plots of mainly conifers using ECOFEE-data from Gundersen et al. (1998) with N input being (throughfall of N and N output referring to nitrate only (A). The right graph refers to 121 Intensive Monitoring plots with available data on total N deposition and N leaching (B).

Using the average fractions at each C/N ratio a logistic function of the N retention fraction as a function of C/N ratio was used in the calculations of N immobilisation as given in the following formula:

$$\text{frN}_{\text{im}} = \frac{1}{1 + \alpha^{(\beta(\text{CN}-25))^{\gamma-1}}} \quad (4.7)$$

where $\alpha = 0.95$, $\beta = 0.4$ and $\gamma = -0.95$.

In the calculation use was made of site specific estimates for the more than 6000 forest soils in a systematic grid of 16 km x 16 km (level I) of

- N (NH_4 , NO_3) deposition: EDACS model estimates
- Net N uptake: yield estimates as a function of stand age and site quality as described in Klap et al. (1997) multiplied by deposition dependent N contents in biomass.
- frNret: related to measured C/N ratios forest soil and modelled fraction NH_4 in deposition
- C/N ratios for forest soils: measurements, partly extrapolations

An overview of the calculated N deposition in 1960, 1990 and 2000 is given in Fig 4.5. Results show the large increase in N deposition in that period. The data for 2000 were used to calculate the carbon sequestration in the soil for that year. The data for the whole period 1960-2000 (data at 5 year intervals that were linearly interpolated) were used to assess the contribution of elevated N deposition in that period on the increase in carbon pools in standing biomass in that period (see the methodology described in Section 4.2.4 below).

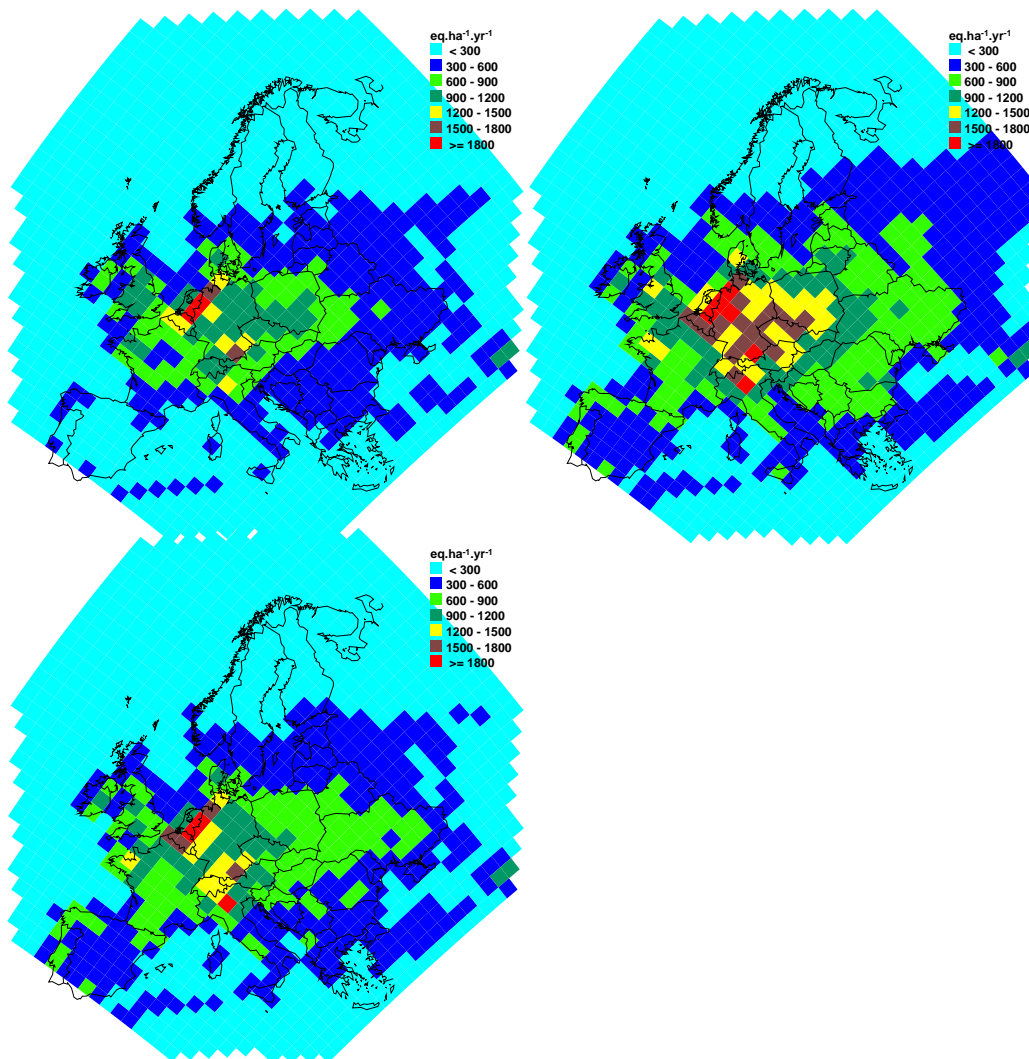


Figure 4.5 N deposition ($\text{mol N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) for the year 1960, 1990 and 2000 as calculated by EMEP. Those data were allocated to the approximately 6000 level I plots based on a direct overlay

In this study, an estimate of C sequestration in stem wood of European forests (NEP) was derived from stand age and available site quality characteristics, using forest yield tables to estimate the actual forest growth (Klap et al., 1997), using a C content of 50%. This estimate was assumed to equal the baseline growth without impact of elevated N deposition. This estimate was increased with additional growth due to elevated N deposition as described in the following section. The net C sink (NBP) in stem wood was calculated by assuming that NBP equals 33% of the NEP. This percentage is based on an estimated average NBP/NEP ratio for Europe, implying a net increase in standing forest biomass of 33% of the growth since 67 % is removed by harvesting or forest fires (Nabuurs and Schelhaas, 2003).

4.2.4 Assessing nitrogen deposition effects on carbon sequestration by European forests

The methodology used to calculate the impact of elevated nitrogen deposition on carbon sequestration by European forests is inspired by the approach of Nadelhoffer et al. (1999). These authors assessed additional C sequestration on a global scale from additional N uptake by trees and N immobilisation in soils in response to N deposition. Actually, the paper is sometimes rather unclear whether it derives the additional carbon sequestration due to N deposition, above the C sequestration due to 'normal' forest growth, or whether it calculates the total C sequestration using N retention as the indicator. This ambiguity is also partly reflected in the reactions on the paper debate (e.g. Jenkinson et al., 1999; Schindler, 1999; Sievering, 1999) and follows from the calculation. The estimate by Nadelhoffer et al. (1999), which suggest that C sequestration in forest trees and forest soils over the world is of equal magnitude is based on the following assumptions:

- Present total world N deposition estimate.
- Constant N retention fractions in trees (uptake; a fraction of 0.05) and soil (immobilisation; a fraction of 0.70), based on short-term fate (1-3 year) of ^{15}N labelled tracer experiments in nine temperate forests
- Averages values for the C/N ratio in stem wood (500) and forest soils (30).

Apart from the rough generalisation, the confusing aspect in this approach is that the present total world N deposition is used, whereas the paper discusses the possible impact of elevated N deposition. The 'unaffected' growth figures should be related to a certain N deposition as well. This implies that one should discuss the impact with reference to the increase in carbon pool in trees in the last decades, as presented by Kauppi et al. (1992) and Nabuurs et al. (1997). Those authors estimated a net increase in the C pool in trees in Europe of approximately 0.1 Gton C.yr⁻¹ in the period 1970-1990. This implies that one has to estimate what the impact of increased N deposition in that period is on the C sequestration. In this study we used this approach but we extended the period to 1960-2000, assuming that the net C pool change in trees in that period is also 0.1 Gton C.yr⁻¹.

An overview of all differences used in this approach and those used by Nadelhoffer et al. (1999) is presented in Table 4.4. First of all, we used 1960 as the reference for N deposition (this leads to 'normal' growth) and calculated what the additional N deposition was in the period 1960-2000 compared to that reference year. Nadelhoffer et al. (1999) implicitly assumed that the reference N deposition is negligible. Unlike those authors we included the spatial differences in N deposition on the plots (EMEP estimates). Furthermore, we assumed that the additional N uptake due to N deposition is (uptake fraction) is a function of the N deposition, with values being higher in low deposition areas, because of N deficiencies, and lower in high deposition areas. Actually, the uptake fraction was assumed to vary from 10% in areas below 300 mol.ha⁻¹.yr⁻¹ (approximately 5 kg.ha⁻¹.yr⁻¹) to 5% (the constant value used by Nadelhoffer et al. (1999) in areas above 1500 mol.ha⁻¹.yr⁻¹ (approximately 20 kg.ha⁻¹.yr⁻¹). Similarly, the N immobilisation fraction was assumed to be a function of

the C/N ratio of the organic layer and the NH_4/NO_3 in deposition, as described before, and not a constant of 70%.

Similar to the uptake fraction, the C/N ratios in trees were assumed to vary with the N deposition, values being higher in low deposition areas and lower in high deposition areas. This was based on the idea that luxury consumption takes place at a high N availability, meaning that the additional N uptake is only partly leading to additional growth (C pool change) since part is just leading to higher N contents (lower C/N ratios) in stem wood. Actually, the C/N ratio was assumed to vary from 500 (the constant value used by Nadelhoffer et al. (1999) in areas below $1500 \text{ mol.ha}^{-1}.\text{yr}^{-1}$ (approximately $20 \text{ kg.ha}^{-1}.\text{yr}^{-1}$) to 250 in areas above $5000 \text{ mol.ha}^{-1}.\text{yr}^{-1}$ (approximately $70 \text{ kg.ha}^{-1}.\text{yr}^{-1}$). This relation is based on a variation of N contents between 0.1 and 0.2% (at a constant C content of 50%) in comparatively low deposition areas (Scandinavia) to high deposition areas (The Netherlands). For the C/N ratio in the organic layer and mineral layer, we used the measured values at all Level I plots, instead of using a constant value of 30.

Table 4.4 Overview of differences between the approach used by Nadelhoffer et al. (1999) and in this study to calculate the impacts of N deposition on carbon sequestration.

Nadelhoffer et al. (1999)	Our approach
Reference N deposition is negligible	Reference N deposition is 1960
Constant average N deposition	Spatially distributed and time dependent N deposition ¹⁾
N uptake fraction is constant	N uptake fraction is $f(\text{N deposition})$
N immobilisation is constant	N immobilisation fraction is $f(\text{C/N ratio humus layer/soil, } \text{NH}_4/\text{NO}_3 \text{ in deposition})$
C/N ratio tree is constant	C/N ratio tree varies in space and time as $f(\text{N deposition}_{x,t})$ ¹⁾
C/N ratio soil is constant in space and time	C/N ratio organic and mineral layer varies in space ²⁾

¹⁾ Based on calculated EMEP N deposition

²⁾ Based on the measured C/N ratio data at approximately 6000 forested plots

The above described methodological approach is presented below in mathematical terms. First the N sequestration in the tree is calculated from the additional N input in the period 1960-200 and the related C sequestration is calculated by multiplication with an N deposition dependent C/N ratio in the tree according to:

$$N_{\text{seqtree}}(\text{extra}) = \sum_{t=1960}^{t=2000} (\text{Ndep}_{(t)} - \text{Ndep}_{(1960)}) \cdot \text{frup}_{(t)} \quad (4.8)$$

$$C_{\text{seqtree}}(\text{extra})_{(t)} = N_{\text{seqtree}}(\text{extra})_{(t)} \cdot \frac{C}{N} \text{tree}_{(t)} \quad (4.9)$$

with the uptake fraction by stem wood being dependent on N deposition according to:

$$\text{frup}_{(t)} = 0.10 - 0.05 \cdot \frac{(\text{Ndep}_{(t)} - 300)}{1200} \quad (4.10)$$

for $300 < N_{dep} < 1500$, with $frup_{(t)} = 0.1$ if $N_{dep} < 300$ and $frup_{(t)} = 0.05$ if $N_{dep} > 1500$

and with the C/N ratio in the tree being dependent on N deposition according to:

$$\frac{C}{N}_{tree(t)} = 500 - 250 \cdot \frac{(N_{dep(t)} - 1500)}{5000} \quad (4.11)$$

for $1500 < N_{dep} < 5000$, with $C/N_{(t)} = 500$ if $N_{dep} < 1500$ and $C/N_{(t)} = 250$ if $N_{dep} > 5000$

Then, the N immobilisation (sequestration) in the soil is calculated from the additional N input (N deposition in a given year minus the N deposition in 1960, corrected for the additional N uptake due to this increased N availability) for the period 1960-2000, multiplied with the N immobilisation fraction, according to (see Eq. 4.2):

$$N_{imsoil}(extra) = \sum_{t=1960}^{t=2000} (\delta N_{dep(t)} - \delta N_{up(t)}) \cdot frN_{im} \quad (4.12)$$

with frN_{im} being calculated according to Eq. (4.7). Finally, the related C sequestration in the soil is calculated by multiplication of the calculated N immobilisation with the C/N ratio in the soil (organic and mineral layer), according to:

$$C_{seqsoil}(extra)_{(t)} = N_{imsoil}(extra)_{(t)} \cdot f(CN_{soil}) \quad (4.13)$$

with $f(CN_{soil})$ being equal to the description of given in Eq. (4.2).

4.3 Results

4.3.1 Carbon pool changes in trees and soils at Intensive Monitoring plots

The result of the calculated annual carbon sequestration at the Intensive Monitoring plots obtained using Eq. (4.2) is given in Figure 4.6, together with the estimated sequestration due to forest growth in the last five years (see the previous chapter).

The results show that the carbon pool changes in the tree are generally 5-10 times as high as the estimated carbon pool changes in the soil. As expected, the changes in the carbon pool in tree due to forest growth increase going from Northern to Central Europe and decrease again in Southern Europe. In line with the calculation procedure, the calculated changes in the carbon pool in soil do follow the N deposition pattern being high in Central Europe and low in Northern and Southern Europe (Fig. 4.6). Interestingly, however, the same kind of pattern is found by Papale and Valentini (2003), presenting spatial (1 x 1km) estimates of carbon fluxes of

European forests based on the net CO₂ exchange flux collected at sixteen of sites in the EUROFLUX network, using neural networks for the spatial extrapolation.

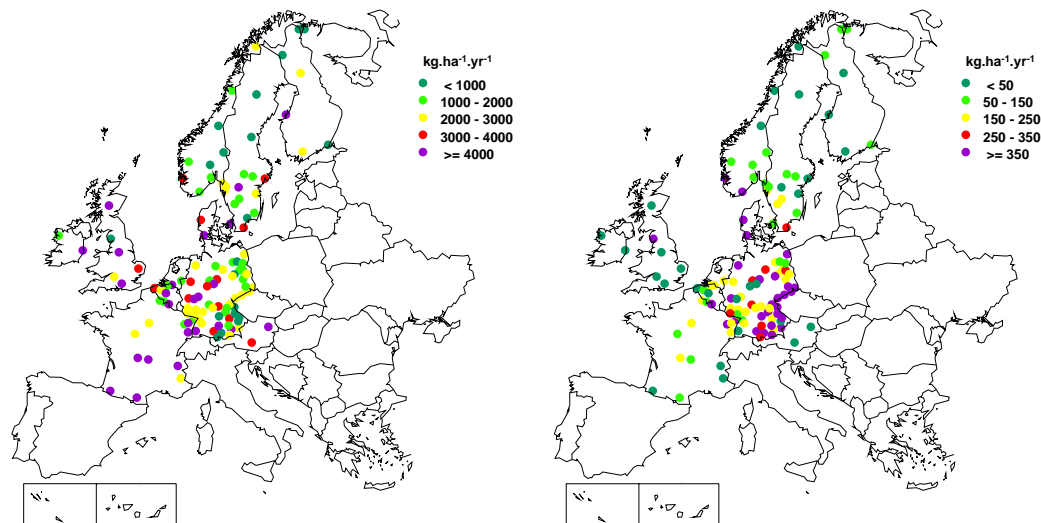


Figure 4.6 Calculated carbon pool changes ($\text{kgC.ha}^{-1}.\text{yr}^{-1}$) in trees (left) and soils (right) at the 121 Intensive Monitoring plots for the year 2000

4.3.2 Carbon sequestration in soils and trees on the European scale

The estimated actual carbon sequestration in the tree wood (NEP) during the period 1960-2000 is given in Table 4.5. This estimate was based on the use of standard forest yield tables related to available site quality characteristics for each level I plot, while correcting for stand age increased with additional growth due to elevated N deposition as described before. Table 4.4 also includes an assessment of the net C sink (NBP) assuming that the latter value equals 33% of the NEP. The calculated carbon sequestration in stem wood due to forest growth equals approximately 0.28 Gton.yr^{-1} . Using a forested area of 200 million ha, the mean carbon sequestration rate in tree stem wood based on uptake is approximately $1400 \text{ kg.ha}^{-1}.\text{yr}^{-1}$. Assuming that NBP is 33% of the NEP, gives results close to 0.1 Gton.yr^{-1} , being equal to a mean net sequestration rate of approximately $450 \text{ kg.ha}^{-1}.\text{yr}^{-1}$.

Table 4.5 Estimated total and net carbon sink for European forests due to tree growth (NEP) and increase in standing biomass (NBP, being 33% of the NEP) for the year 1960 and 2000.

Region	Carbon sequestration in wood (Gton.yr^{-1})			
	NEP 1960 -2000		NBP1960 -2000	
	No N impact	With N impact	No N impact	With N impact
EU	0.184	0.194	0.061	0.064
Candidate member states	0.036	0.038	0.012	0.013
Other European countries	0.059	0.063	0.020	0.021
Total	0.279	0.295	0.093	0.098

Note that total N uptake related to the above mentioned NEP growth figures is much higher than the additional N uptake mentioned by Nadelhoffer et al. (1999), which some authors related to total N uptake. The total estimated N uptake was

0.663 Mton.yr⁻¹ at an estimated total deposition of 1.096 Mton.yr⁻¹. This implies a percentage uptake of 60% if one would relate N uptake to N deposition only, whereas Nadelhoffer et al. (1999) used a value of 5% for the additional N uptake related to N deposition. The impact of additional N input is 0.016 Gton.yr⁻¹ (see also Section 4.3.3).

Estimated net carbon sequestration by accumulation in forest soils is given in Table 4.6. A distinction was made in the standard calculation with respect to N uptake and N accumulation (based on Eq. 4.2 and the extrapolation methods in section 4.2.3) and an alternative in which all the net incoming N was assumed to accumulate (total immobilisation, no leaching).

Table 4.6 Estimated net carbon sink by accumulation in European forest soils, for two different calculation scenarios for the year 2000.

Region	Net carbon sequestration in soil (Gton.yr ⁻¹)	
	Standard run	Total immobilisation
EU	0.0104	0.0183
Candidate member states	0.0013	0.0036
Other European countries	0.0020	0.0016
Total	0.0138	0.0235

The results using the standard run were lower than those derived by Nadelhoffer et al. (1999) (0.0138 vs. 0.022 Gton.yr⁻¹; compare Table 4.1 and 4.5). This is to be expected since these authors assumed a constant low net uptake (5%) and a constant high soil accumulation of 70% in the forest soil. Using the assumption that all the net incoming N is retained gives an estimate that is comparable to the estimate by Nadelhoffer et al. (1999), while the upper limit in this study appeared to be nearly twice as high compared than those derived by Nadelhoffer et al. (1999). Despite these possible uncertainties,

The geographic variation in carbon sequestration in trees and soils is illustrated in Fig. 4.74. The pattern in forest soil sequestration general follows the pattern of N deposition over Europe. It shows that C sequestration is small in Northern Europe, where the N input is low and nearly all incoming N is retained by the vegetation, and higher in Central and Eastern Europe where the N input is larger. This can, however, be a slight overestimate since part of the N accumulation may occur as a dilution of the C/N ratio at high deposition. The finding that C sequestration is negligible in northern boreal forest is in line with results from Martin et al. (1998) based on flux measurements for CO₂.

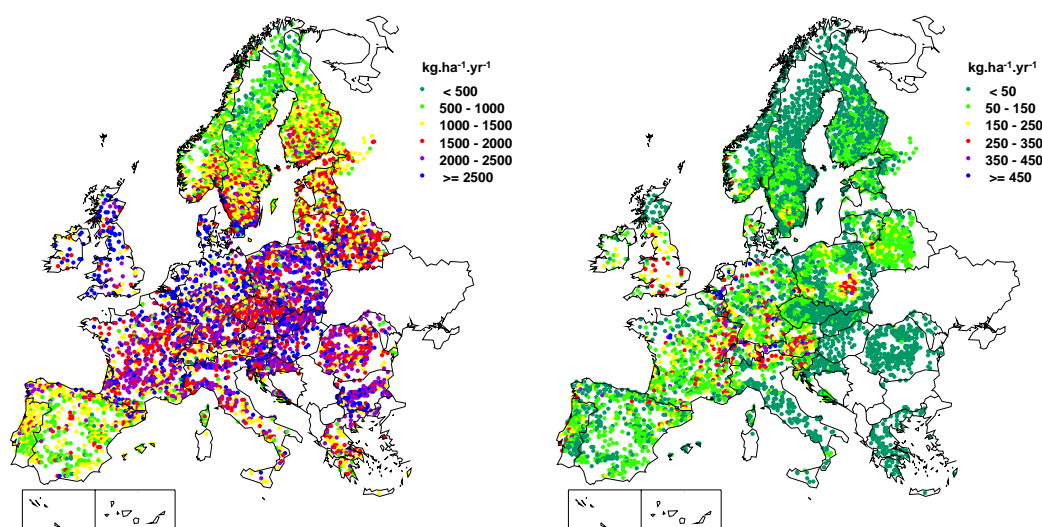


Figure 4.7 Geographic variation of the calculated carbon sequestration in trees and soil over Europe, using the standard run.

4.3.3 The impact of nitrogen deposition on carbon sequestration in European forests

Results obtained with respect to the total carbon sequestration in tree and soil using different assumptions regarding the parameters determining N retention are given in Table 4.7. Using the standard run, leads to an additional C sequestration in trees of approximately 16 Mton.yr^{-1} in the last 40 years. Comparing this estimate with the net increase in carbon pool in standing biomass of approximately 100 Mton.yr^{-1} (0.1 Gton.yr^{-1}) implies that 16% of this increase can be explained by an increase in N deposition. This contribution is however only the case if one relates the additional growth completely to the increase in standing biomass. If one relates it to the estimated growth without an impact of N deposition the contribution is only $16/279$ is only 6% (see Table 4.4). The sensitivity analyses showed that the contribution varies between approximately 10 and 20 Mton.yr^{-1} implying a potential contribution of N deposition to the increase in standing biomass pool of 10-20 % (NBP) or 3.6-7% of the total growth (NEP).

The additional carbon sequestration in the soil is approximately 40% of the amount sequestered in the tree when using the standard with a variation between approximately 30-70% for the various alternatives. Using the standard Nadelhoffer approach, the additional sequestration in tree and soil is nearly equal (Table 4.6).

Table 14.7 Overview of the additional C sequestration in view of elevated N deposition in this period compared to the annual net carbon sequestration (Mton.yr⁻¹).

Variation	Assumptions	Extra C sequestration 1960-2000 (Mton.yr ⁻¹)	
		Tree	Soil
1 This study: standard		16.1	6.2
- Uptake fraction	N dependent 5-10% ¹		
- Immobilisation fraction	N dependent 0-100% ¹		
- C/N ratio tree	N dependent 250-500 ¹		
- C/N ratio soil	Site dependent ¹		
2 This study alternatives			
- Uptake fraction	Constant 5% ²	9.9	5.6
- Uptake fraction	Constant 10% ²	19.7	5.3
- Immobilisation fraction	Constant 70% ²	14.6	6.3
- Immobilisation fraction	Constant 100% ²	14.6	9.0
C/N ratio tree	Constant 500 ²	14.4	5.4
C/N ratio tree	Constant 400 ²	11.5	5.4
C/N ratio soil	Constant 30 ²	14.6	9.7
C/N ratio soil	Constant 25 ²	14.6	4.6
3 Nadelhoffer standard	Constant fractions and C/N ratios ³	9.8	7.8
4 Nadelhoffer alternative	Adapted constant fractions and C/N ratios ⁴	15.6	8.8

¹ The variation in fractions and C/N ratios depends amongst others on N deposition as described in the main text

² This variation implies that all other parameters are standard according to variation 1

³ The standard Nadelhoffer calculation includes constant fractions for tree uptake (5%) and soil immobilisation (70%) and constant C/N ratios in tree (500) and soil (30)

⁴ The alternative Nadelhoffer calculation includes adapted constant fractions for tree uptake (10%) and soil immobilisation (100%) and constant C/N ratios in tree (400) and soil (25)

4.4 Discussion and conclusions

Comparison of calculated carbon sequestration estimates in stem wood with literature values

NEP: The average carbon pool change at all plots due to forest growth equals approximately 1400 kg.ha⁻¹.yr⁻¹, being approximately 1.5 times as low as the median change in carbon pool at all Intensive monitoring plots during a five year period (approximately 2175 kg.ha⁻¹.yr⁻¹; see Table 5.10). Apart from the fact that the Intensive Monitoring plots are not representative for the whole of Europe, this difference is most likely due to the fact that the calculated growth rates for the level I plots are average values over the total rotation period. For a total forested area in Europe of 200 million ha, the calculated carbon sequestration in stem wood due to forest growth (NEP) equals approximately 0.28 Gton.yr⁻¹.

Results of the NEP appear to be comparable to those based on CO₂ exchange fluxes (NEE) derived by Martin et al. (1998) based on the Euroflux sites (0.28 Gton.yr⁻¹), but the value is less (nearly twice as low) than the NEE value derived by Papale and Valentini (2003) from net CO₂ exchange fluxes collected at sixteen EUROFLUX sites. These fluxes do, however, include sequestration by trees and soil. The values are also twice as low as the NEP value derived from carbon flux data in forest at eleven 'Canif' sites along a North –south transect through Europe (Schulze et al.,

2000); compare Table 4.1). This illustrates that a simple extrapolation of results at a limited number of plots is highly questionable.

NBP: Assuming that NBP is 33% of the NEP, gives results close to 0.1 Gton.yr^{-1} , being comparable to the estimates derived from repeated forest inventories (Kauppi et al., 1992; Nabuurs et al., 1997). Using a forested area of 200 million ha, the mean net carbon sequestration rate in tree stem wood is approximately $465 \text{ kg.ha}^{-1}.\text{yr}^{-1}$. This is close to net carbon sequestration rates in trees calculated by Liski et al. (2002) based on a dynamic modelling exercise, as described before. These authors calculated a net carbon sequestration in trees was at $390\text{--}600 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ in 1990 and at $440\text{--}510 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ in 2040. Upscaling their results to a forested area of 200 million ha, also gives results for the NBP near 0.1 Gton.yr^{-1} (see table 16). The average value is approximately twice as low as the average value of $800 \text{ kg C.ha}^{-1}.\text{yr}^{-1}$ obtained by Nabuurs and Schelhaas (2002) for 16 typical forest types across Europe, but this in a comparable order of magnitude

Comparison of calculated carbon sequestration estimates in soil with literature values

The calculated net carbon sequestration in the soil of approximately $0.014 \text{ Gton.yr}^{-1}$, being equal to an average accumulation of $70 \text{ kg.ha}^{-1}.\text{yr}^{-1}$, is much higher than the value derived by Schulze et al. (2000) based on the C retention in eleven sites ($0.13\text{--}0.17 \text{ Gton C.yr}^{-1}$). The latter estimate is likely to be an overestimate, as it would imply that the C/N ratio of European forest soils is strongly increasing. There are no indications that this is the case. To the reverse, it is more likely that C/N ratios are decreasing, especially in areas with an elevated N deposition. This result thus illustrates that it is dangerous to make estimates on a European scale based on a limited number of plots using a simple upscaling procedure.

The result is more in line with those derived by Liski et al. (2002), based on the dynamic modelling exercise described before, with net carbon sequestration in soil estimated at $190\text{--}305 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ in 1990 and 2040, respectively. Even though this leads to clearly higher values on a European scale, the difference (see also Table 16) is by far not so large as with Schulze et al. (2000). Furthermore, the results are in line with the net carbon sequestration in soil for 16 typical forest types across Europe derived by Nabuurs and Schelhaas (2002), being equal 110 kg C.ha^{-1} . If one would, again, simply multiply this average value with a forested area of 200 million ha, it would lead to a net carbon sequestration of $0.022 \text{ Gton.yr}^{-1}$, being comparable to the upper estimate in this study.

The conclusion that net sequestration potential of the below ground carbon in the soil, which has much lower turnover times than above ground carbon, is only small in forests is also in line with field data, showing that soil C sequestration is even small after afforestation on arable fields (Vesterdal et al., 2002). This implies that the terrestrial carbon sink can only be viewed as 'buying variable time to address the most significant perturbation of the carbon cycle: fossil fuel emissions' (Steffen et al., 1998).

Impacts of nitrogen deposition on carbon sequestration

The basic assumption for carbon pool changes in both tree and soil was that the additional N uptake or immobilisation is reflected in carbon pool changes due to growth or organic matter accumulation according to the C/N ratio of the tree or the soil. The calculation focused on CO₂ sequestration in the soil from nitrogen retention assuming that nitrogen retained in the soil form organic matter with a constant carbon to nitrogen ratio. Most likely, the estimate constitutes an upper limit since nitrogen deposition tends to decrease the carbon to nitrogen ratio over time.

The conclusion that the increase in forest growth in trees is very small, about 5% only, seems contradictory with a generic more sophisticated modelling approach, in which the combination of CO₂ rise and elevated N deposition was estimated to account for a 15-20% increase in forest net primary productivity (Rehfuess et al., 1999). In this study, model predictions were made of carbon sequestration in view of changes in climatic variables, temperature and precipitation, CO₂ concentrations and nitrogen deposition. Results showed that the impact of temperature was much less important than that of CO₂, whereas N deposition was claimed to be most important (Rehfuess et al., 1999, last ref recognition). This contradiction is however due to the upscaling of the model to the European scale. The net impact of additional N deposition on forest growth was estimated at approximately 15/25 kg C per kg N by the various sophisticated forest growth models, being comparable to the result of the model applied in this study. It implies that in Central European areas with a large additional N input (e.g. of 10/20 kg.ha/1), the impact is large but not in Northern and Southern Europe, where the additional N input is generally low.

The predicted impact of N deposition in high deposition areas might even be overestimated. A positive effect can indeed be expected in areas where forest growth is limited by N availability, but a continuous high input of N may lead to a situation where other growth factors, such as other nutrients and water, become limiting for the growth of forest. The relation between water shortage and N surplus can be explained by the fact that a high N input favours growth of canopy biomass, whereas root growth may be relatively unaffected (shown only for seedlings). The increase in canopy biomass will lead to a higher demand for water and therefore to an increased risk of water shortage (drought). It also causes an increased demand of base cation nutrients (Ca, Mg, K) whereas the availability of these cations can be reduced by increased dissolved levels of NH₄ and/or Al (induced by NO₃ and SO₄). This effect may reduce the fertilising effect of high N deposition.

Conclusions and outlook

Based on soils data collected at the Level I and Level II monitoring plots and modelled nitrogen deposition data an estimate of CO₂ sequestration for European forests, divided in trees and soils could be made. Furthermore, the contribution of N deposition to forest growth and soil carbon sequestration could be assessed. Using the above mentioned approach, the following conclusions can be drawn from this study:

- Carbon pool changes in the tree are generally 5-10 times as high as the estimated carbon pool changes in the soil. As expected the changes in the carbon pool in tree due to forest growth increase going from Northern to Central Europe. The

calculated changes in the carbon pool in soil do follow the N deposition pattern being high in Central Europe and low in Northern and Southern Europe. This follows from results at both level I and level II plots.

- Net increases in the carbon pool by forests in Europe (both trees and soil) are in the range of 0.1-0.15 Gton.yr⁻¹, being an important part (about 50%) of the terrestrial carbon sink in Europe, derived from atmospheric inversion models. The results furthermore show that the C sequestration by forest is mainly due to a net increase in forest growth, since the longer term C immobilisation in the soil is limited.
- The contribution of N deposition to the increase in carbon due to forest growth is approximately 10 and 20 Mton.yr⁻¹, being 3.5-7% of the carbon pool increase due to the average estimated forest growth in that period (approximately 280 Mton.yr⁻¹).

The result of this study implies that the impact of forest management is most important in explaining the carbon pool changes in forest in Europe. Combined with the conclusion that the increase in carbon pools in trees is mainly responsible for carbon sequestration in Europe, it implies that the current sequestration is only a transitory phenomenon. It is a gain due to the fact that forests in Europe are aggrading because the removal by harvesting and forest fires is less than the net growth. A further contribution to C sequestration on the forest area may come from earlier and recent afforestations on fields or grasslands. Effects of such land use change are not included in the calculations. On these areas the build up of C stock in trees may be substantial but still a transitory phenomenon lasting a forest generation.

For future predictions, models that are able to describe the effects of CO₂, water and nutrients on tree growth (Van Oijen et al., 2003a, b; Van Oijen et al., 2003c) are important tools. Simultaneously, many stress-factors tend to cause defoliation and decrease tree growth in European forests. Shortage of water, high pollutant concentrations in air, e.g. ozone, and high inorganic aluminium concentration in soil water are potential causes of defoliation. Process based models can be used to assess the importance of water shortage to photosynthesis and growth, as well as the importance of climate and water stress to defoliation and subsequently growth. Such models can also be used to describe tree growth and flows and accumulation of carbon, nitrogen, other nutrients and water in forests ecosystems. The lack of quality checked test data has considerably hindered model development. The large variation in climate and nitrogen deposition within Intensive Monitoring sites in Europe now enables the use of versatile and informative data sets to the testing of the models and testing of our understanding of the processes explaining tree growth and forest health. Such models combined information at level II and level I plots do form an important tool for future more elaborated studies on the prediction of carbon sequestration in Europe in response to changing environmental conditions.

References

- Berg, B. and E. Matzner, 1997. Effect of N deposition on decomposition of plant litter and soil organic matter in forest systems. *Environ. rev.* 5, 1-25.
- Bousquet, P., P. Ciais, P. Peylin, M. Ramonet and P. Monfray, 1999. Inverse modelling of annual atmospheric CO₂ sources and sinks 1. Methods and control inversion. *Journal of Geophysical Research* 104, 26161-26178.
- Ciais, P., P.P. Tans, J.W.C. White, M. Trolier, R.J. Francey, J.A. Berry, D.R. Randall, P.J. Sellers, J.G. Collatz and D.S. Schimel, 1995. Partitioning of ocean and land uptake of CO₂ as inferred by ¹³C measurements from the NOAA Climate Monitoring and Diagnostics Laboratory global air sampling network. *Journal of Geophysical Research* 100, 5051-5070.
- De Vries, W., G.J. Reinds, M.A. van Kerkvoorde, C.M.A. Hendriks, E.E.J.M. Leeters, C.P. Gross, J.C.H. Voogd and E.M. Vel, 2000. Intensive Monitoring of Forest Ecosystems in Europe. Technical Report 2000. UN/ECE, EC, Forest Intensive Monitoring Coordinating Institute, 193 pp.
- De Vries, W., G.J. Reinds, C. Van der Salm, G.P.J. Draaijers, A. Bleeker, J.W. Erisman, J. Auee, P. Gundersen, H.L. Kristensen, H. Van Dobben, D. De Zwart, J. Derome, J.C.H. Voogd and E.M. Vel, 2001. Intensive Monitoring of Forest Ecosystems in Europe. Technical Report 2001. UN/ECE, EC, Forest Intensive Monitoring Coordinating Institute, Geneva and Brussels, 177 pp.
- Dise, N.B., E. Matzner and M. Forsius, 1998a. Evaluation of organic horizon C:N ratio as an indicator of nitrate leaching in conifer forests across Europe. *Environ. pollut.* 102 (Supp 1), 453-456.
- Dise, N.B., E. Matzner and P. Gundersen, 1998b. Synthesis of nitrogen pools and fluxes from European forest ecosystems. *Water Air Soil Poll.* 105, 143-154.
- Emmet, B.A., D. Boxman, M. Bredemeier, P. Gundersen, O.J. Kjønaas, F. Moldan, P. Schleppi, A. Tietema and R.F. Wright, 1998. Predicting the effects of atmospheric nitrogen deposition on coniferous stand: evidence from the NITREX ecosystem-scale experiments. *Ecosystems* 1, 352-360.
- Fan, S.M., M. Gloor, J. Mahlman, S. Pacale, J. L.Sarmiento, T. Takahashi and P.P. Tans, 1998. A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models. *Science* 282, 442-446.
- Friedlingstein, P., I. Fung, E. Holland, J. John, G. Brasseur, D. Erickson and D. Schimel, 1995. On the contribution of CO₂ fertilization to the missing biospheric sink. *Global biogeochemical cycles* 9 (4), 541-556.

Gundersen, P. and L. Rasmussen, 1995. Nitrogen mobility in a nitrogen limited forest at Klosterhede, Denmark, examined by NH_4NO_3 addition. *For. ecol. manage.* 71, 75-88.

Gundersen, P., I. Callesen and W. de Vries, 1998. Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. *Environ. pollut.* 102 (1), 403-407.

Gundersen, P., K. Raulund-Rasmussen and I.K. Schmidt, 2003. Leaching of nitrogen from temperate forests - effects of air pollution and forest management. In: R. Vertessy and H. Elsenbeer (Eds). *Forests and Water*. IUFRO (In press).

Harrison, A.F., D.D. Harkness, A.P. Rowland, J.S. Garnett and P.J. Bacon, 2000. Annual carbon and nitrogen fluxes in soils along the European forest transect determined using ^{14}C -bomb. In: E.D. Schulze (Ed). *Carbon and nitrogen in forest soils*. Ecological Studies 142. Springer Verlag, Heidelberg.

Holland, E.A., B.H. Braswell, J.F. Lamarque, A.R. Townsend, J. Sulzman, J.F. Muller, F. Dentener, G. Brasseur, H. Levy, II, J.E. Penner and G.J. Roelofs, 1997. Variations in the predicted spatial distribution of atmospheric nitrogen deposition and their impact on carbon uptake by terrestrial ecosystems. *Journal of Geophysical Research* 102, 15849-15866.

Houghton, R.A., E.A. Davidson and G.M. Woodwell, 1998. Missing sinks, feedbacks and understanding the role of terrestrial ecosystems in the global carbon balance. *Cycles* 12, 25-34.

Jenkinson, D.S., K. Goulding and D.S. Polson, 1999. Reply to Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. *Nature* 400, 629.

Kauppi, P.E., K. Mielikäinen and K. Kuusela, 1992. Biomass and carbon budget of European forests, 1971 to 1990. *Science* 256, 70-74.

Klap, J.M., W. de Vries, J.W. Erisman and E.P. van Leeuwen, 1997. Relationships between forest condition and natural and anthropogenic stress factors on the European scale; pilot study. Report 150. DLO Winand Staring Centre for Integrated Land, Soil and Water Research, Wageningen, the Netherlands.

Leeters, E.E.J.M. and W. de Vries, 2001. Chemical composition of the humus layer, mineral soil and soil solution of 200 forest stands in the Netherlands in 1995. *Alterra rapport 424.2*. Alterra, Green World Research, Wageningen (Netherlands), 108 pp.

Liski, J., D. Perruchoud and T. Karjalainen, 2002. Increasing carbon stocks in the forest soils of western Europe. *For. ecol. manage.* 169 (1-2), 159-175.

Martin, P.H., R. Valentini, M. Jacques, K. Fabbri, D. Galati, R. Quarantino, J.B. Moncrieff, P. Jarvis, N.O. Jensen, A. Lindroth, A. Grelle, M. Aubinet, R. Ceulemans,

A.S. Kowalski, T. Vesala, P. Keronen, G. Matteucci, A. Grainer, P. Berbingier, D. Loustau, E.D. Schulze, J. Tenhunen, C. Rebman, A.J. Dolman, J.E. Elbers, C. Bernhofer, T. Grunwald, H. Thorgeirsson, P. Kennedy and S. Folving, 1998. New estimate of the carbon sink strength of EU forests integrating flux measurements, field surveys, and space observations : 0.17-0.35 Gt (C). *Ambio* 27 (7), 582-584.

Matzner, E. and C. Grosholz, 1997. Beziehung zwischen NO₃-Austrägen, C/N-Verhältnissen der Auflage und N-Einträgen in Fichtenwald (*Picea abies* Karst.) - Ökosystemen Mitteleuropas. *Forstw. Cbl.* 116, 39-44.

Melillo, J.M., A.D. McGuire, D.W. Kicklighter, B. Moore, III, C.J. Vorosmarty and A.L. Schloss, 1993. Global climate change and terrestrial net primary production. *Nature* 363, 234-240.

Moldan, F., R.F. Wright, K.W. van der Hoek, J.W. Erisman, S. Smeulders and J.R. Wisniewski, 1998. Episodic behaviour of nitrate in runoff during six years of nitrogen addition to the NITREX catchment at Gardsjon, Sweden. *Environ. pollut.* 102 (Supp 1), 439-444.

Myneni, R.B., C.D. Keeling, C.J. Tucker, G. Asrar and R.R. Nemani, 1997. Increased plant growth in the northern high latitudes from 1981 to 1991. *Nature* 386, 698-702.

Nabuurs, G.J. and M.J. Schelhaas, 2002. Carbon profiles of typical forest types across Europe assessed with CO2FIX. *Ecological Indicators* 1 (3), 213-223.

Nabuurs, G.J. and M.J. Schelhaas, 2003. Spatial distribution of whole tree carbon stocks and fluxes of forests in Europe; where are the options for bio-energy? *Biomass & Bioenergy* 24, 311-320.

Nabuurs, G.J., R. Päivinen, R. Sikkema and G.M.J. Mohren, 1997. The role of European forests in the global carbon cycle-A review. *Biomass and bioenergy* 13 (6), 345-358.

Nadelhoffer, K.J., M.R. Downs, B. Fry, J.D. Aber, A.H. Magill and J.M. Melillo, 1995. The fate of ¹⁵N labelled nitrate additions to a northern hardwood forest in eastern Maine, USA. *Oecologia* 103, 292-301.

Nadelhoffer, K.J., B.A. Emmett, P. Gundersen, O.J. Kjønaas, C.J. Koopmans, P. Schleppi, A. Tietema and R.F. Wright, 1999. Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. *Nature* 398, 145 -148.

Papale, D. and R. Valentini, 2003. A new assessment of European forests carbon exchanges by eddy fluxes and artificial neural network spatialization. *Glob. Change Biol.* 9 (4), 525-535.

Rehfuess, K.-E., G.I. Ågren, F. Andersson, M.G.R. Cannell, A. Friend, I. Hunter, H.-P. Kahle, J. Prietzel and H. Spiecker, 1999. Relationships between recent changes of

growth and nutrition of Norway spruce, Scots pine and European beech forests in Europe-RECOGNITION. Working Paper 19, European Forest Institute, 94 pp.

Schindler, D.W., 1999. The mysterious missing sink. *Nature* 398, 105-106.

Schulze, E.D., L. Höglberg, H. van Oene, T. Persson, A.F. Harrison, D. Read, A. Kjoller and G. Matteucci, 2000. Interactions between the carbon and nitrogen cycle and the role of biodiversity: A synopsis of a study along a North-south transect through Europe. In: E.D. Schulze (Ed). *Carbon and nitrogen in forest soils*. Ecological Studies 142. Springer Verlag, Heidelberg.

Sievering, H., 1999. Reply to Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. *Nature* 400, 629-630.

Spiecker, H., K. Mielikäinen, M. Köhl and J.P. Skovsgaard (Eds.), 1996. *Growth trends in European forests*. Springer-Verlag, Berlin, Heidelberg, 372 pp.

Steffen, W., I. Noble, J. Canadel, M. Apps, E.-D. Schultze, P. Jarbis, D. Baldocchi, P. Ciais, W. Cramer, J. Ehleringer, G. Farquhar, C.B. Field, R. Gifford and M. Heimann, 1998. The terrestrial carbon cycle: implications for the Kyoto protocol. *Science* 280, 1393-1394.

Thenhunen, J.D., R. Valentini, B. Kostner, R. Zimmermann and A. Granier, 1998. Variation in forest gas exchange at landscape to continental scales. *Annales des Sciences Forestieres* 55 (1-2), 1-11.

Tietema, A., B.A. Emmett, P. Gundersen, O.J. Kjønaas and C. Koopmans, 1998. The fate of ¹⁵N labeled nitrogen deposition in coniferous ecosystems. *For. ecol. manage.* 101, 19-27.

Tognetti, R., P. Cherubini and J.L. Innes, 2000. Comparative stem-growth rates of Mediterranean trees under background and naturally enhanced ambient CO₂ concentrations. *New Phytologist* 146, 59-74.

Valentini, R., G. Matteucci, A.J. Dolman, E.D. Schulze, C. Rebmann, E.J. Moors, A. Granier, P. Gross, N.O. Jensen, K. Pilgaard, A. Lindroth, A. Grelle, C. Bernhofer, T. Grünwald, M. Aubinet, R. Ceulemans, A.S. Kowalski, T. Vesala, Ü. Rannik, P. Berbigier, D. Loustau, J. Gudmundsson, H. Thorgeirsson, A. Ibrom, K. Morgenstern, R. Clement, J. Moncrieff, L. Montagnani, S. Minerbi and P.G. Jarvis, 2000. Respiration as the main determinant of carbon balance in European forests. *Nature* 404 (20 April), 861-865.

Van Oijen, M., G.I. Ågren, O. Chertov, S. Kellomäki, A. Komarov, D.C. Mobbs and M.B. Murray, 2003a. Evaluation of past and future changes in European forest growth by means of four models (including underlying processes and uncertainties). In: T. Karjalainen and A. Schuck (Eds). *Causes and Consequences of Forest Growth Trends in Europe - Results of the RECOGNITION Project*, Chapter 4.4.

Van Oijen, M., G.I. Ågren, O. Chertov, S. Kellomäki, A. Komarov, D.C. Mobbs and M.B. Murray, 2003b. Identification of the major factors which determine forest response to environmental change: A methodology using multiple simulation models. In preparation.

Van Oijen, M., J. Prietzel, G.I. Ågren, O. Chertov, H.P. Kahle, S. Kellomäki, A. Komarov, K.H. Mellert, H. Spiecker and R. Straussberger, 2003c. Comparison of the results of the different approaches. In: T. Karjalainen and A. Schuck (Eds). Causes and Consequences of Forest Growth Trends in Europe - Results of the RECOGNITION Project, Chapter 5.1.

Vesterdal, L., E. Ritter and P. Gundersen, 2002. Change in soil organic carbon following afforestation of former arable land. For. ecol. manage. 169, 137-147.

5 Modelling the long-term impact of deposition scenario's for nitrogen and acidity at intensively monitored forest plots

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Keywords: dynamic soil model, deposition scenario's, model calibration, forest soils, monitoring, nitrogen, sulphur, acidification

Abstract

The dynamic soil chemistry model SMART was applied to about 200 Pan-European Intensive Monitoring plots for which both element input (deposition) and element concentrations in the soil solution were available. The plots occur in a transect from South-Western Europe to Scandinavia, the majority being located in Western and Northern Europe. Most of the processes in the SMART model could be successfully calibrated. The chloride and sodium budgets show that the hydrology at the plots is generally well simulated. The nitrogen budget could, however, only be closed assuming a time independent N immobilisation for a number of plots. Sulphate adsorption could not be modelled with the available data and has thus been ignored in the model applications. There was generally a reasonable to good agreement between measured and simulated data for most of the plots, although some of the intra-annual variation in especially nitrate and aluminium concentrations could not be reproduced for a number of plots. Statistical measures for the goodness of fit indicate that pH is on average very well reproduced by the model, but not all variations within the year are accurately simulated. Relative deviations between measured and simulated nitrate and aluminium concentrations are sometimes considerable (mostly between -50 and +50 %), especially for plots with low average measured data, but absolute errors in the simulated concentrations are mostly low.

Evaluation of the emission reduction scenarios in the period 1970-2030 shows a very strong reduction in sulphate concentrations between 1980 and 2000 in the soil due to the high reductions in sulphur emissions. By the year 2010, a significant reduction in nitrate concentration is predicted for most plots, but the effect is most striking for the plots with the highest present N concentrations. Simulations also show that implementation of the Gothenburg protocol causes a reduction of the percentage of aluminium concentrations above an assumed critical value of $0.2 \text{ mol} \cdot \text{m}^{-3}$ from 25 % in 1970 to about 5-10 % of the plots in 2030. Al/BC ratios above a critical value of 1 occur at about 5 % of the plots in 1970 and this percentage only slightly decreases towards 2010 because at a number of plots there occurs a decrease of base cation concentration, due to replenishment of the exchange complex. Base saturation improves over time for most plots but for a number of plots where acid inputs remains relatively high, base saturation will still decrease in the future.

5.1 Introduction

The relevance of dynamic soil models

Decisions on emission reductions policies require insight in the effectiveness of abatement strategies. In this respect, models are important tools to assist decision makers in their evaluation of strategies to control sulphur and nitrogen emissions. Up to now critical loads derived by steady-state models have been used in the negotiations of emission reductions in Europe; together with technical and economical aspects of emission reductions this had lead to cost-effective emission reductions based on effects on ecosystems. To gain insight into the time delay between the time-point of non-exceedance and actual chemical (and biological) recovery, however, dynamic models are needed.

In the causal chain from acid deposition to ecosystem-damage (damage to key indicator organisms) there are two major sources of response-delay. Biogeochemical processes can delay the chemical response in soil to acid deposition, and biological processes can further delay the response of indicator organisms, such as damage to trees in forest ecosystems. The static critical load model considers only the steady-state condition, in which the chemical and biological response to a change in deposition is complete. Dynamic models on the other hand, attempt to estimate the time evolution of soil (and biological) responses to changes in acid deposition and can be used to assess the time required for a new (steady) state to be achieved.

Relationships between critical load models and dynamic soil models

With critical loads, i.e. in the steady-state situation, only two cases can be distinguished when comparing them to deposition: (1) the deposition is below or equal to critical load(s), i.e. no exceedance, and (2) the deposition is greater than critical load(s), i.e. critical load exceedance. In the first case there is no (apparent) problem, so no reduction in deposition is necessary. In the second case there is, by definition, an increased risk of damage to the ecosystem, and therefore the deposition should be reduced to safeguard the ecosystem. Sometimes it is assumed that reducing deposition to (or below) critical loads immediately removes the risk of 'harmful effects', i.e. the chemical parameter (e.g. the Al/Bc ratio), which links the critical load to the effect(s), immediately attains a non-critical ('safe') value and that there is immediate biological recovery as well. But the reaction of soils, especially their solid phase, to changes in deposition is delayed by (finite) buffers, the most important being the cation exchange capacity (CEC). These buffer mechanisms can delay the recovery of e.g. chemical parameters, and it might take decades or even centuries before 'safe' values for a parameter or steady state is reached.

These finite buffers are not included in the critical load formulation, since they do not influence the steady state, but only the time to reach it. Therefore, dynamic models are needed to estimate the times to attain a certain chemical state in response to changes in acid deposition induced by agreements on emission reductions. In addition to the delay in chemical recovery, there is probably a further delay before the 'original' biological state is reached, i.e. even if the chemical criterion is met (e.g. $Al/Bc < 1$), it will take time before full biological recovery is achieved. More

information on the relationship between critical load models and dynamic soil models is given in Annex 5.1.

The role of ICP forests in dynamic modelling

Dynamic modelling is a relatively new topic for the effects-oriented work under the LRTAP Convention. Within the ICP on Integrated Monitoring, existing dynamic models have been applied in the mid-nineties at a few sites for which a sufficient amount of input data was available. By applying dynamic soil models at about two hundred Intensive Forest Monitoring sites, a picture appears of a transect through Europe going from southern France to northern Scandinavia. Especially the validation of dynamic soil models on those data is crucial since the new challenge within the ICP on Modelling and Mapping is to develop and apply dynamic model(s) on a European scale and to link them with the integrated assessment work under the LRTAP Convention in support of the review and potential revision of the Gothenburg Protocol.

Contents of this chapter

This chapter first presents the methods (locations, modelling approaches, model validation procedure and input data including deposition scenarios) that are needed to perform dynamic model calculations (Section 5.2). The dynamic modelling concepts and data requirements presented in the following are an extension of those employed in deriving the Simple Mass Balance (SMB) model, used in the previous Technical Report (De Vries et al., 2002) to derive critical loads for nitrogen and acidity. Results are described in Section 5.3. This includes results of a comparison of model results with measurements at more than 100 plots with both deposition and soil solution chemistry data (Section 5.3.1) and an application of the model to the same plots, using various relevant emission deposition scenarios (Section 5.3.2). Finally, a discussion of the results and conclusions is presented in Section 5.4.

5.2 Methods

5.2.1 Locations

For the dynamic modelling, validated information on bulk deposition, throughfall and soil solution chemistry is needed. In Fig 5.1 a map of the plots is presented for which these data are available and that were used for the dynamic model to predict the long-term impact of deposition scenario's for nitrogen and acidity. Only for these plots a (partial) calibration of the model can be performed as both input (total deposition) and response (soil solution concentrations) are needed.

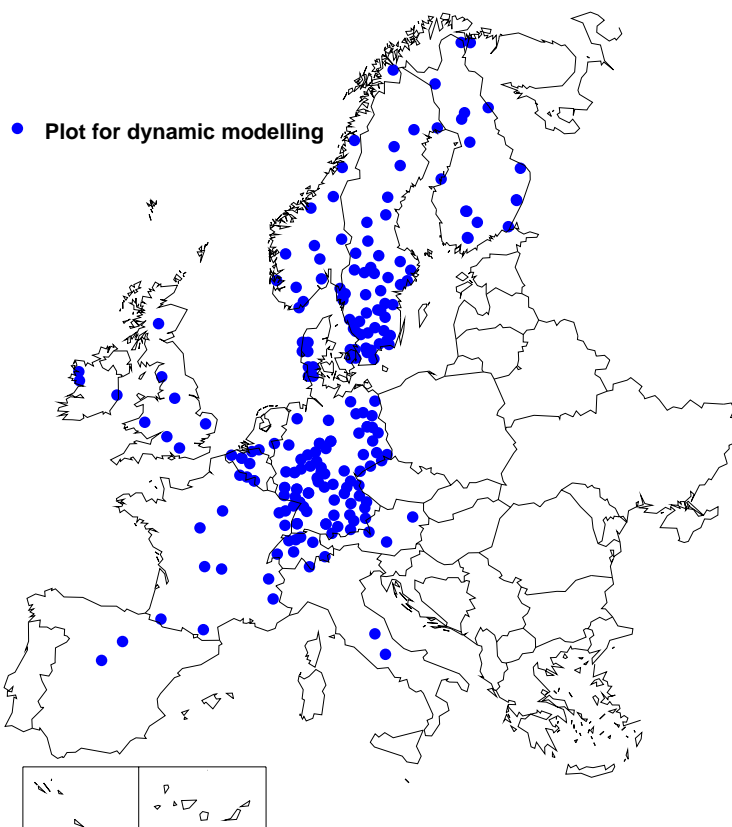


Figure 5.1 Locations of the Intensive Monitoring plots used for calibration and application the dynamic SMART model.

5.2.2 Modelling approach

Available dynamic soil models

For nearly 15 to 20 years, scientists have already been developing, testing and applying dynamic models to simulate the acidification of soils or surface waters. There is thus no shortage of soil (acidification) models, but most of them are not designed for regional applications. A comparison of 16 models can be found in a special issue of the journal 'Ecological Modelling' (Tiktak and van Grinsven, 1995). These models emphasise either soil chemistry (such as SMART, SAFE and MAGIC) or the interaction with the forest (growth).

In addition to the large number of dynamic model applications to individual sites over the past 15 years, there are several examples of dynamic soil models that were developed and applied for application on a (large) regional scale. Earlier versions of the RAINS model (Alcamo et al., 1990) contained an effects module which simulated soil acidification on a European scale (Kauppi et al., 1986). De Vries et al. (1994b) employed the SMART model to simulate soil acidification in Europe, and Hettelingh and Posch (1994) used the same model to investigate recovery delay times on a

European scale. Furthermore, De Vries et al. (1994a) used the RESAM model to simulate soil acidification in the Netherlands, while Alveteg et al. (1995) and Kurz et al. (1998) used the SAFE model to assess temporal trends in soil acidification in southern Sweden and Switzerland.

Constraints for dynamic models used in this study

Up to now critical loads, derived by steady-state models have been used to negotiate emission reductions in Europe. Thus the dynamic models to be used in the assessment of recovery under the LRTAP Convention have to be compatible with the steady-state models used for calculating critical loads. In other words, when critical loads are used as input to the dynamic model, the (chemical) parameter chosen as criterion in the critical load calculation has to attain the critical value once the dynamic simulation has reached steady state. But this also means that concepts used in the dynamic model have to be a continuation and extension of the concepts employed in deriving the steady-state model.

In order to meet this constraint the dynamic modelling concepts and data requirements presented in this chapter, are an extension of those employed in deriving the Simple Mass Balance (SMB) model. The SMB model is described in detail in the previous Technical report (De Vries et al., 2002). Earlier descriptions of the SMB model can be found in Sverdrup et al. (1990), De Vries (1991), Sverdrup and De Vries (1994) and Posch et al. (1995).

A model that does meet the constraints given above is the model SMART, described in De Vries et al. (1989) and Posch et al. (1993). This model contains basic extensions of the SMB model into a dynamic soil acidification model. An even simpler model, called Very Simple Dynamic (VSD) model, has recently been developed (Posch and Reinds, 2003).

The SMART model

The SMART model (Simulation **M**odel for **A**cidification's **R**egional **T**rends) is a relatively simple extension of the SMB model for critical loads. As with SMB, in the SMART model, the various ecosystem processes have been limited to a few key processes. Processes that are *not* taken into account are: (i) canopy interactions, (ii) nutrient cycling processes, (iii) N fixation and NH_4 adsorption, (iv) uptake, immobilisation and reduction of SO_4 and (v) complexation of Al with OH, SO_4 .

The SMART model consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. The soil solution chemistry in SMART depends solely on the net element input from the atmosphere (deposition minus net uptake minus net immobilisation) and the geochemical interaction in the soil (CO_2 equilibria, weathering of carbonates and silicates, and cation exchange). Soil interactions are described by simple rate-limited (zero-order) reactions (e.g. uptake and silicate weathering) or by equilibrium reactions (e.g. cation exchange and sulphate adsorption). It models the exchange of Al, H and $\text{Ca}+\text{Mg}+\text{K}$ with Gaines-Thomas equations and sulphate adsorption with a Langmuir equation. Furthermore, it does

include a balance for carbonate and Al, thus allowing the calculation from calcareous soils to completely acidified soils that do not have an Al buffer left. In this respect, SMART is based on the concept of buffer ranges expounded by Ulrich (1981). Recently a description of the complexation of aluminium with organic acids has been included. The interaction of Al with organic acids can be described as mono-, di- or tri-protic. A graphic representation of these processes is given in Figure 5.2.

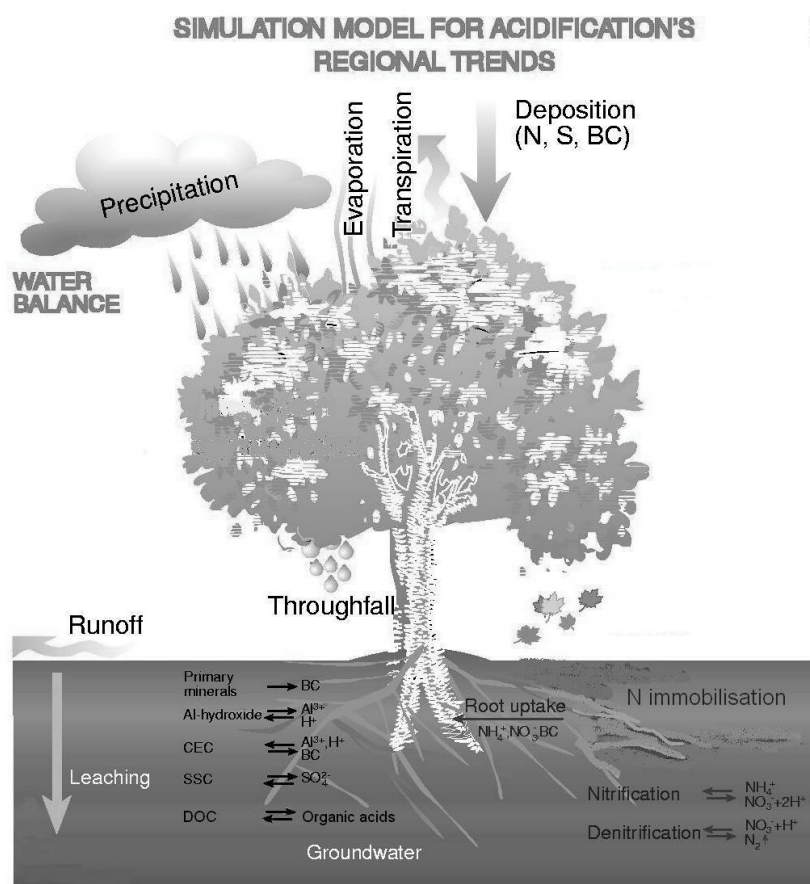


Figure 5.2 Graphic representation of the SMART model

Solute transport is described by assuming complete mixing of the element input within one homogeneous soil compartment with a constant density and a fixed depth. Since SMART is a single layer soil model neglecting vertical heterogeneity, it predicts the concentration of the soil water leaving this layer (mostly the root zone). The annual water flux percolating from this layer is taken equal to the annual precipitation excess. The time step of the model is one year, i.e. seasonal variations are not considered. A detailed description of the SMART model can be found in De Vries et al. (1989) and Posch et al. (1993). The SMART model has been developed with regional applications in mind, and an early example of an application to Europe can be found in De Vries et al. (1994b).

The guiding principle of SMART is the compatibility with the critical load model SMB, since the steady-state solutions of the dynamic model employed should be the critical loads derived earlier. Dynamic models of acidification are based on the same

principles as steady-state models: the charge balance of the ions in the soil solution, mass balances of the various ions, and equilibrium equations. However, whereas in steady-state models (SMB) only sources and sinks are considered which can be assumed infinite (such as base cation weathering), the dynamic model SMART includes finite sources and sinks of major ions, i.e. cation exchange, sulphate adsorption and nitrogen retention and a mass balance for cations, nitrogen and sulphate, in addition to the equations included in the SMB model. These are the three most important processes involving finite buffers and time-dependent sources/sinks. These finite buffers have not been included in the derivation of critical loads, since they do not influence the steady state. However, when investigating the chemistry of soils over time as a function of changing deposition patterns, these processes govern the long-term (slow) changes in soil (solution) chemistry. For example after an increase in acidifying input, cation exchange (initially) delays the decrease in the acid neutralisation capacity (ANC) by releasing base cations from the exchange complex, thus delaying the acidification of soil solution until a new equilibrium is reached (at a lower base saturation). On the other hand, cation exchange delays recovery since 'extra' base cations are needed to 'replenished' base saturation instead of increasing ANC of soil solution.

5.2.3 Model parameterisation and model calibration

Data needs

The input data needed to run dynamic models can be grouped into input- and removal fluxes and soil properties. Part of the input- and removal fluxes are also described in the previous technical Report (De Vries et al., 2002), since they were also needed in the SMB model, but for this study an update of those fluxes was made and the new results are shortly summarised. This includes the input of element by atmospheric deposition, the water fluxes through the forest ecosystems, the net uptake of nutrients by forests and the base cation weathering from the soil.

Furthermore this section describes how the (soil) data were derived that is needed to run dynamic models. Most important soil parameters are the cation exchange capacity (CEC) and base saturation and the exchange (or selectivity) constants describing cation exchange, as well as parameters describing sulphate adsorption or desorption, since these parameters determine the long-term behaviour (recovery) of soils. Also the parameters that determine nitrogen immobilisation, denitrification and nitrification were estimated.

Ideally, all input data are derived directly from measurements at the site for which the model is applied. This, however, is not always feasible for all input data. In this chapter we provide information on how the input data needed for SMART were derived, either derived directly from measurements at the sites or indirectly from model calibration.

Deposition of acidity and base cations

Total deposition of sulphur for the period 1995-2000 was computed by adding measured throughfall and measured or estimated stemflow values below the forest canopy, assuming that the effects of foliar sulphur uptake by the forest canopy is negligible. Base cation (Ca, Mg, K and Na) and nitrogen deposition data for each stand for the period 1995-2000 were derived on the basis of throughfall and bulk deposition data, accounting for canopy exchange, as described in De Vries et al. (2002).

Water fluxes

Water fluxes were calculated using the WATBAL model (Starr, 1999). This relatively simple water balance model uses a one-layer approach and monthly time-steps. Input data required are soil properties such as the available water content (AWC), rooting depth and texture dependent ratio's of the critical soil water content to the available water content, meteorological variables (rainfall, global radiation (or sunshine duration) and temperature), a number of generic site variables such as latitude, altitude, initial amount of snow on the ground and forest cover, and generic constants such as snow albedo. Measured throughfall was used as the water input at the top of the soil compartment, whereas monthly values of temperature and global radiation were derived from a data base with interpolated daily values for 50*50 km grid cells. AWC was estimated as function of soil type and texture class according to Batjes (1996) who provides texture class dependent AWC values for all FAO soil types based on an extensive literature review. Critical soil water: AWC ratios (the ratio between actual soil water content and AWC at which transpiration is reduced) were computed as a function of soil texture according to the standard WATBAL procedure.

The reliability of the water fluxes was checked by comparing the leaching of chloride (Cl) and sodium (Na) against the deposition. Both chloride and sodium can be considered as tracers (Cl) or nearly tracers (Na), i.e. the (long-term average) leaching computed from the modelled downward water flux and the measured concentration should match the deposition. In the case of Na, the leaching flux can be somewhat higher than the deposition flux due to weathering and cation exchange but generally these fluxes are negligible compared to the deposition of Na. The measurements of Na and Cl in deposition and soil solution thus allow checking whether the hydrology is modelled accurately.

Figure 5.3 shows the deposition-leaching relations for Cl and Na for plots with at least 2 years of measurements. As can be seen, the average slope for Cl is close to the perfect 1, indicating that there is no overall bias in the hydrological model. However, the graphs also show that there are several plots with rather unbalanced inputs and outputs. In the case of Na this could partly be explained by weathering. Part of the plots where chloride leaching is higher than chloride deposition are located close to the sea, which may cause imbalances in the budget due to sea-salt input on the soil that is not collected in the deposition samplers.

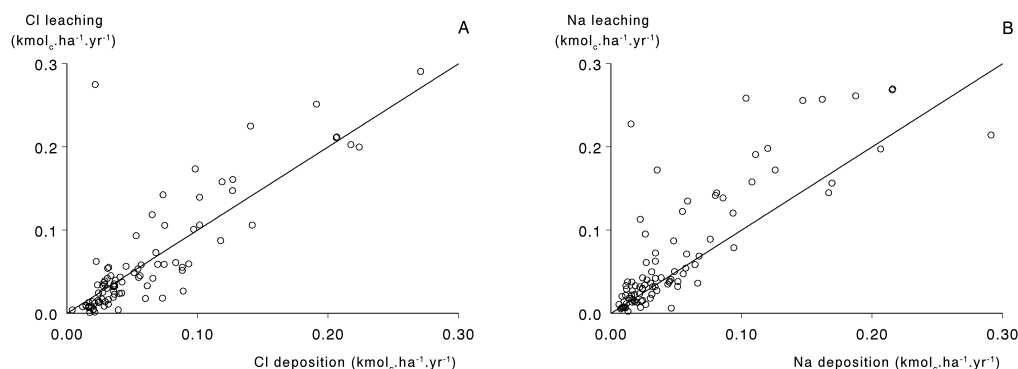


Figure 5.3 Cl and Na input-output (deposition-leaching) relationships.

Uptake of nitrogen and base cations

In SMART, nitrogen and base cation uptake is the net growth uptake, i.e. the net uptake by vegetation that is needed for long-term average growth. Input by litterfall and removal by maintenance uptake (needed to re-supply nitrogen and base cations to leaves) is thus not considered, assuming that both fluxes are equal in a steady-state situation. Thus the net uptake is calculated, being equal to the annual average removal in harvested biomass. In this calculation we assumed that this includes the removal of stems and branches.

Net growth uptake of N, N_{gu} , and base cations, Ca_{gu} , Mg_{gu} and K_{gu} , was computed by multiplying the current growth at the site with the densities of stem wood and standard element contents in stems and branches. For the densities of stem wood and the nitrogen and base cation contents in stems use was made of literature data (e.g. Kimmins et al., 1985; De Vries et al., 1994b), as presented in Table 5.1

Table 5.1 Average values used for the densities of stem wood and the N and BC (Ca+Mg+K) contents in stem wood of the considered main tree species

Tree species	Stem density (kg.m ⁻³)	N content in stem wood (g.kg ⁻¹)	BC content in stem wood (g.kg ⁻¹)
Scots Pine	510	1.2	1.6
Norway Spruce	460	1.2	1.2
Oak	700	1.7	2.5
Beech	700	1.4	2.4

Annual growth for the period 1995-2000 (for which the model was validated) was estimated from repeated surveys on stem diameter and tree height; as described in Chapter 5. Past and future growth, used in scenario analyses was derived by scaling the calculated yield for the period 1995-2000 with standard logistic growth curves available for combinations of species, climate and yield (Klap et al. (1997)). Stem to branch ratios were estimated as a function of tree species and stand age as described in Klap et al. (1997). Monthly net growth uptake was then derived by distributing the annual growth over the months within the growing season, weighted by the monthly fraction of temperature sum over the growing season. Begin and end of the growing season were computed as a function of climate zone, altitude and latitude according to Klap et al. (1997).

Figure 5.4 show the cumulative frequency distribution of computed N and BC uptake (in $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) for the considered plots. It clearly show that the uptake of especially N by broadleaved forest (median 5 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) is much higher than for conifers forest (median value 2.7 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$), due to higher growth rates and higher N contents in stem- and branch wood.

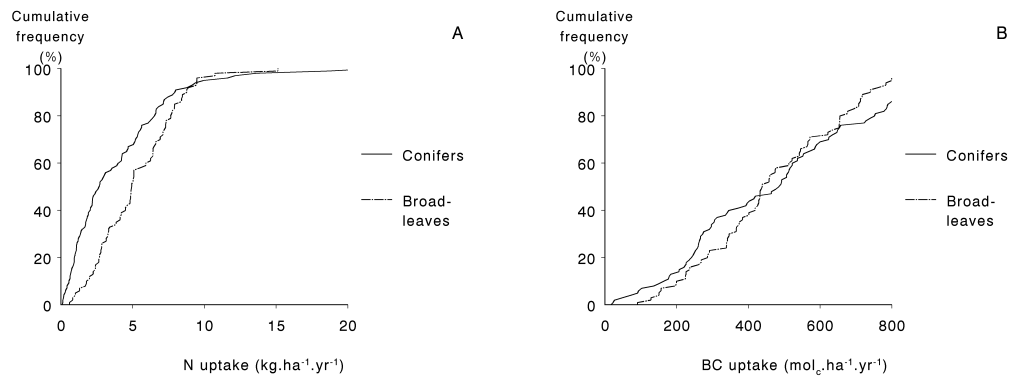


Figure 5.4 N uptake (left) and BC uptake (right) for conifers and broadleaved plots

Weathering of base cations

There are various possibilities to assess weathering rates including (UN/ECE, 1996):

- Estimation of the depletion of base cations in the soil profile by chemical analyses of different soil horizons including the parent material. This method, in which an extremely resistant mineral, such as zirconium, is often used as an internal standard, gives the average weathering rate over the period of soil formation (De Vries and Breeuwsma, 1986; Starr et al., 1998).
- Correlation between the weathering rate and the total Ca and Mg content in the parent material multiplied by the present day effective temperature sum (Olsson and Melkerud, 1991). As with the previous approach, this gives the average weathering rate over the period of soil formation.
- The weathering rate model PROFILE, which calculates actual field weathering rates based on the soil mineralogy (Sverdrup, 1990; Sverdrup and Warfvinge, 1993).
- Assignment of an actual field weathering based on the parent material and texture class of a given soil (dominant) soil unit (De Vries et al., 1994b).

Apart from the last method, total cation concentrations in either the parent material (C horizon) or even in the complete soil profile, are needed to estimate the weathering rate. At present, PROFILE is most frequently used when detailed mineralogical data are available or when such data can be derived from a total cation analyses. Becker et al. (2000), for example, used PROFILE to calculate the weathering of Intensive Monitoring plots in Germany for the assessment of critical loads for those plots. Data on the total cation contents are, however, either not available for the plots or not submitted to FIMCI.

Since no measurements of weathering are available, the weathering of the base cations Ca, Mg, K and Na was estimated from the budget (the average of the

differences between deposition and leaching corrected for base cation uptake) of the respective elements at the sites. If the budget yields a negative base cation weathering, the base cation uptake was adapted to close the budget and the weathering was set to zero. Simulations with Smart show that in many cases the contribution of cation exchange (release or adsorption) to the monthly budget can be considered negligible. Only for plots with a large base cation pool and rapidly changing acid input would it be of importance. However, the measurements do not allow an accurate assessment of the amount of base cations exchanged (only Ca +Mg in SMART) as only one observation of base saturation in time is available.

Thus the weathering of a base cation Y , Y_{we} , becomes:

$$Y_{we} = Y_{le} + Y_{gu} - Y_{dep} \quad (5.1)$$

where the subscripts le , gu and dep stand for leaching, net growth uptake and deposition of element Y . If Y_{we} calculated from Eq. 5.1 is negative, it is set to zero and Y_{gu} (for $Y=Ca, Mg, K$) is set to $Y_{dep} - Y_{le}$. Eq. 5.1 was applied to averages over the measurement period.

Figure 5.5 shows the cumulative frequency distributions of computed weathering rates for soil with sandy, clayey and calcareous parent materials. It shows that the median value for sandy soils is about half that of clayey soils. As to be expected, weathering rates for calcareous soils are much higher and generally range between 1700 and 10000 eq.ha⁻¹.yr⁻¹.

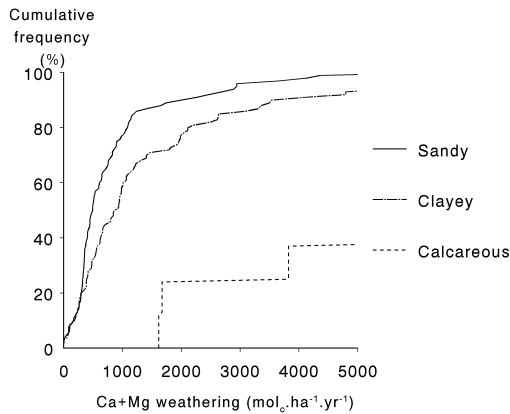


Figure 5.5 Base cation weathering for sandy, clayey and calcareous parent materials.

In the previous Technical Report, base cation weathering rates for the root zone were derived by a relationship with parent material class and texture class (either available or derived from soil type information). The estimates thus derived were updated on the basis of either the measured annual average temperature in the considered period 1995-1998 or interpolated annual average values for the 10-year period 1985-1995. More information on the reliability of this approach is given in the previous Technical Report (De Vries et al., 2002). A comparison of the results obtained from the present and the previous approach shows that there is only a very

weak relationship between the base cation weathering rates based on classes and those based on calibration. This can partly be explained by the fact that the calibrated weathering is computed from a rest-term from the base cation input-output budget that includes uncertain terms as base cation uptake and leaching. Furthermore, base cation release from the exchange complex is now considered as weathering which, in some cases, might lead to unrealistic weathering rates. Most likely, the weathering rates of sandy soils above $1500 \text{ mol}_c\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ are due to cation release from the exchange complex and the same is true with weathering rates of clayey soils above $3000 \text{ mol}_c\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$.

Parameters describing aluminium release

In SMART the concentration of free (uncomplexed) Al is modelled by a relationship with the H concentration according to:

$$[\text{Al}] = K_{\text{Al}_{\text{ox}}} \cdot [\text{H}]^{\alpha} \quad (5.2)$$

where $\alpha > 0$ is a site-dependent exponent and where $K_{\text{Al}_{\text{ox}}} =$ the Al dissolution constant. For $\alpha=3$ this is the familiar gibbsite equilibrium ($K_{\text{Al}_{\text{ox}}} = K_{\text{gibb}}$) used in the SMB model.

The equilibrium constant $K_{\text{Al}_{\text{ox}}}$ and the exponent α are determined by linear regression after taking logarithms in eq. 5.2. For each plot for which observations of $[\text{H}]$, $[\text{Al}_{\text{tot}}]$ and DOC were available, the concentration of free Al was first calculated. This was done by using a triprotic model for the dissociation of DOC and a simple complexation model with Al, as implemented in the latest version of the SMART model, described in detail in Annex 5.2. For plots without DOC data constants were derived for the relation between pH and total Al.

Figure 5.6 show the relationships between pH and pAl ($-\log(\text{Al})$) for total Al (left) and free Al (right). This figure clearly shows that the relationship between free Al and pH is better than between total Al and pH especially for pH values greater than 5 where most Al is complexed. The horizontal line at pAl 5.82 in the leftmost graph represents an aluminium concentration of $0.04 \text{ mg}\cdot\text{l}^{-1}$; for some countries this is the lowest value they submit (apart from 0) and might thus be the analytical detection limit for these countries. Figure 5.7 shows the correlation coefficient between pAl and pH for plots with an average pH lower than 5. This also illustrates the better correlation between pH and free aluminium than between pH and total aluminium as the median correlation coefficient between free Al and pH is about 0.7, whereas between total Al and pH it is about 0.4.

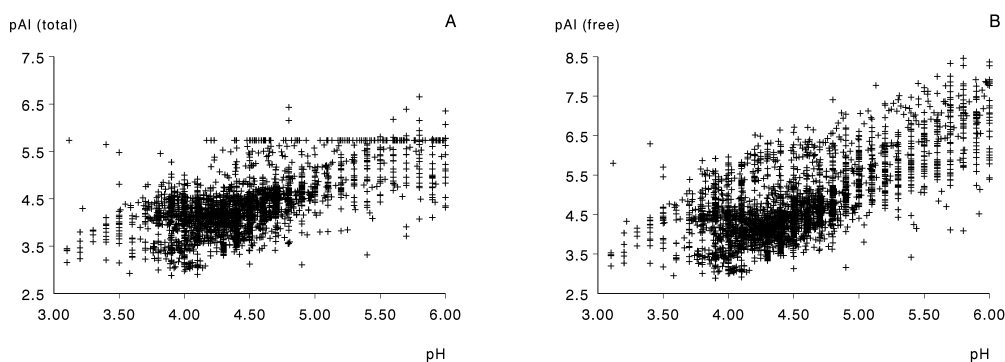


Figure 5.6 Relation between pH and pAl for total (A) and free Aluminium (B).

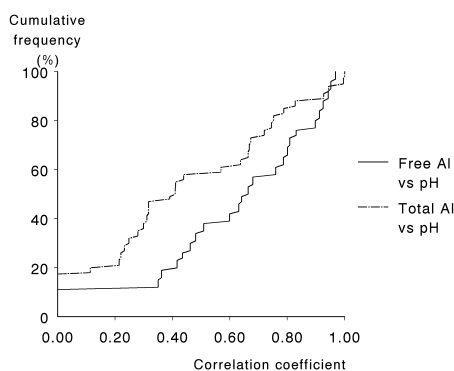


Figure 5.7 Cumulative frequency distribution of the correlation coefficient between pH and total and free Al

Figure 5.8 show the calibrated values of K_{Alox} and α in equation 5.2 for several selections from the data set. This figure shows α varies between 1 and 2.5 for plots with a good correlation between Al and pH ($r > 0.5$). Values for K_{Alox} are highly variable and mostly range between -5 and 3.

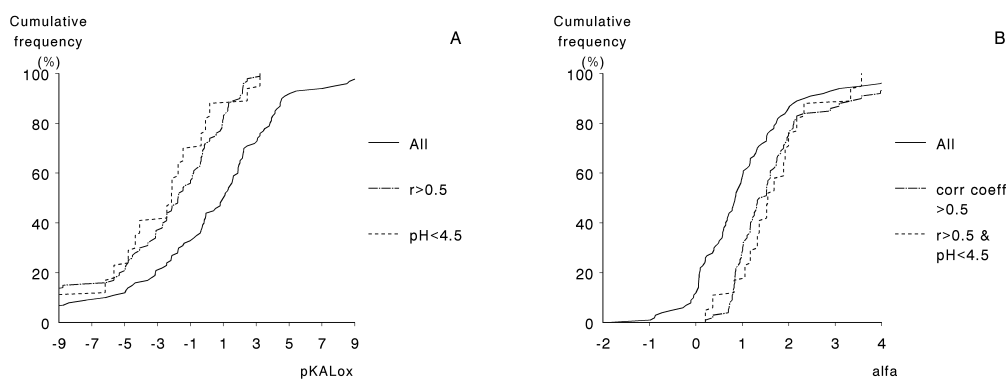


Figure 5.8 Cumulative frequency distribution of the logarithmic Al dissolution constant (A) and the exponent α (B) in the free Al-pH relationship using the whole data set (all) and plots with a good correlation between Al and pH ($r > 0.5$) including all soil or acid soils only ($\text{pH} < 4.5$).

Plotting α against pK_{Alox} (Figure 5.9 reveals a very strong relationship between these two parameters. This, at first sight remarkable relationship, is explained by the fact that for smaller α , K_{Alox} has to increase to get the same aluminium concentration in

other words there is, of course, a strong relationship between the intercept from the regression of pK_{Alox} against pH and the slope. It also shows that the simple gibbsite equilibrium with a $-pK$ value of about 8 and $\alpha=3$ holds only for a very few plots.

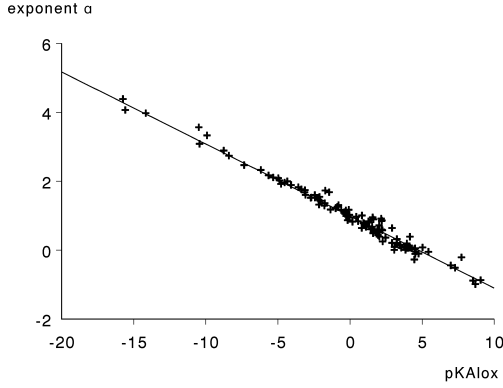


Figure 5.9 Relationship between α and pK_{Alox} .

Cation exchange constants

In SMART the exchange reactions in non-calcareous soils are described by Gaines-Thomas equations using concentrations instead of activities:

$$\frac{f_H^2}{f_{BC}} = K_{HBC} \cdot \frac{[H^+]^\beta}{[BC^{2+}]} \quad \text{and} \quad \frac{f_{Al}^2}{f_{BC}^3} = K_{AlBC} \cdot \frac{[Al^{3+}]^2}{[BC^{2+}]^3} \quad (5.3)$$

where K_{HBC} and K_{AlBC} are the Gaines-Thomas selectivity constants for H-BC exchange and Al-BC exchange, respectively. Since the exchange complex is assumed to comprise H^+ , Al^{3+} and BC^{2+} only, charge balance requires that

$$f_{BC} + f_{Al} + f_H = 1 \quad (5.4)$$

Dividing the Eqs. 5.3, inserting the relationship between Al and H (Eq. 5.2) and taking the square root one can express f_{Al} as function of f_H and $[H]$ alone:

$$f_{Al} = K \cdot [H]^{-\gamma} \cdot f_H^3 \quad \text{with} \quad K = \sqrt{\frac{K_{AlBC} \cdot K_{Alox}}{K_{HBC}^3}} \quad \text{and} \quad \gamma = 3\beta/2 - \alpha \quad (5.5)$$

which allows to eliminate f_{Al} from eq. 5.4:

$$f_H + K \cdot [H]^{-\gamma} \cdot f_H^3 = 1 - f_{BC} \quad (5.6)$$

For a plot for which observations of $[H]$, $[Al]$ (as derived from $[H]$, $[Al_{tot}]$ and DOC), $[BC]$, f_{Al} and f_{BC} (and thus also f_H) are available, one could easily compute the site-specific values of K_{HBC} and K_{AlBC} . For the Intensive Monitoring plots, however, $[H]$, $[Al]$ and $[BC]$ are generally available but at the adsorption complex only f_{BC} (base

saturation) is known. The values of K_{HBC} and K_{AIBC} can thus only be computed if one, e.g., assumes the pH-dependent relationship of eq. 5.5 between f_H and f_{Al} to be valid for all plots. Taking the logarithm of eq. 5.5,

$$\log_{10} \frac{f_{Al}}{f_H^3} = \gamma \cdot \text{pH} + \log_{10} K \quad (5.7)$$

and using the values on f_{Al} , f_H and $[H]$ from Dutch measurements for 531 forest soils layers (De Vries and Leeters, 2001; De Vries and Posch, 2003a), values of $\log_{10} K = -3.53$ and of $\gamma = 1.04$ were obtained by linear regression.

Using those values of γ and K and measurements of $[H]$ and f_{BC} from the Intensive Monitoring plots, the cubic eq. 5.6 was solved to obtain f_{HB} and then f_{Al} from eq. 5.5. The exchange equations (eq. 5.3) were then used to estimate the exchange constants, using measurements of $[H]$, $[Al]$ and $[BC]$ in soil solution. The exponent β was obtained as $\beta = 2(\gamma + \alpha)/3$, with α derived earlier.

Figure 5.10 shows the cumulative frequency distributions of the calibrated values for the exchange constants and β . The figures show that the exchange constants are highly variable, but similar ranges in K_{AIBC} have been found comparing data for about 200 plots in the Netherlands (De Vries and Leeters, 2001) for which the 5, 50 and 95 percentile are plotted in the graph as well. The variability in β is much smaller; it varies mostly between 1 and 2.5 with a median value of about 1.5.

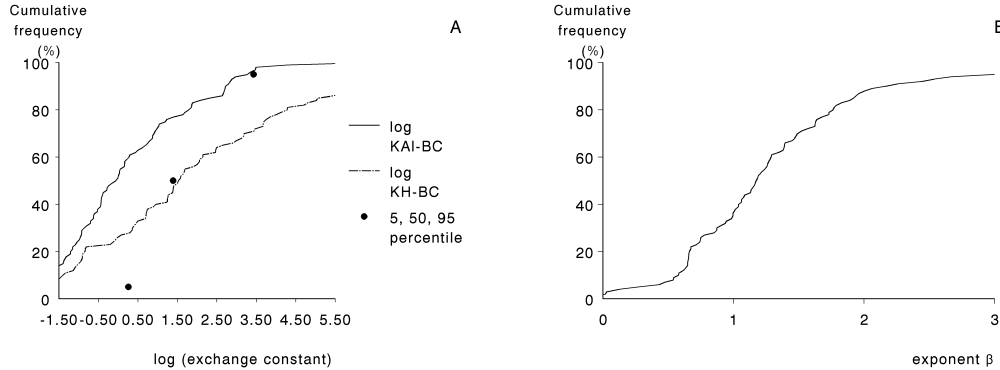


Figure 5.10 Cumulative frequency distributions of the calibrated exchange constants (A) and the exponent β (B)

Figure 5.11 shows that the relationship between exchange constants and soil texture, which is sometimes assumed (especially for K_{AIBC}), is not really confirmed by the results from the calibration.

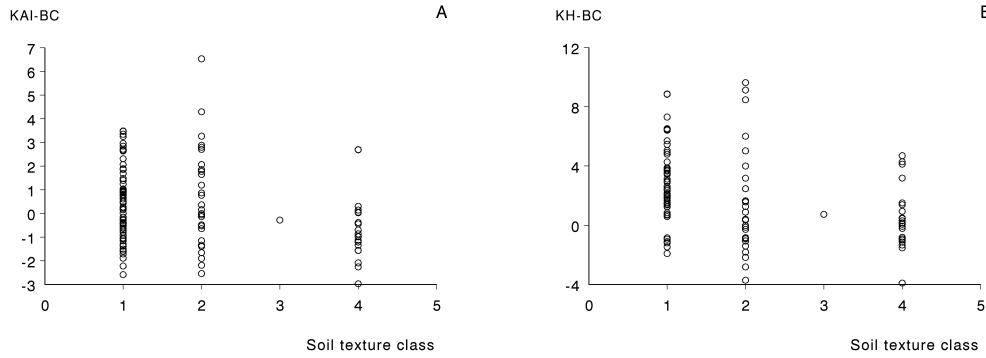


Figure 5.11 Exchange constants of Al against base cations (A) and protons against base cations (B) versus texture class

Nitrogen transformation parameters

In SMART the leaching of the nitrogen compounds NO_3 and NH_4 is calculated from the difference between input by deposition and the removal by growth uptake, immobilisation and denitrification, while accounting for the effect of nitrification. Denitrification and nitrification are modelled as fractions of the net nitrate and ammonium input, respectively. Growth uptake and immobilisation fluxes of both ions (NO_3^- or NH_4^+) are assumed proportional to their share in the deposition. The equations describing the nitrogen transformations in SMART are described in Annex 5.3.

Using the data from the Intensive Monitoring sites, the different N fluxes were estimated in the following way: Total deposition of NO_x and NH_3 was computed from bulk and throughfall measurements according to the procedure described in De Vries et al. (2001). The net growth uptake of N, N_{gu} , was derived as described earlier. The leaching fluxes of nitrate, ammonia, $\text{NO}_{3,le}$ and $\text{NH}_{4,le}$ were computed by multiplying (on a monthly basis) the measured concentrations of NO_3 and NH_4 with simulated downward water fluxes. Leaching of dissolved organic nitrogen, DON_{le} , was computed by multiplying the leaching of dissolved organic carbon (DOC) with the measured C/N ratio of the organic matter of the solid phase of the topsoil as this ratio gives a reasonable estimate of the C/N ratio of the dissolved organics (Michalzick and Matzner, 1999; Smolander et al., 2001).

In SMART the total N balance is given as:

$$N_{td} - N_{gu} - N_{im,t} - N_{im,acc} - N_{de} = N_{le} \quad (5.8)$$

The time (C/N ratio) dependent N immobilisation is computed from the immobilisation fraction f_{im} through:

$$N_{im,t} = f_{im} \cdot (N_{td} - N_{gu} - N_{im,acc}) \quad (5.9)$$

Observational and experimental evidence (e.g. Gundersen et al., 1998b) shows a correlation between the C/N ratio and the amount of N retained in the soil organic

layer. According to Dise et al. (1998) and Gundersen et al. (1998a) the forest floor C/N ratios may thus be used to assess risk for nitrate leaching. Gundersen et al. (1998a) suggested threshold values of >30, 25 to 30, and <25 to separate low, moderate, and high nitrate leaching risk, respectively. This information has been used in SMART to calculate nitrogen immobilisation as a fraction of the net N input, linearly depending on the C:N ratio between a minimum and maximum value (see Annex 5.3). Below a C/N ratio of 15 there is no net immobilisation ($f_{im} = 0$), whereas above a C/N ratio of 40 f_{im} equals 1.

Denitrification is (in case of complete nitrification) computed by:

$$N_{de} = f_{de} \cdot (N_{td} - N_{gu} - N_{im,t} - N_{im,acc}) \quad (5.10)$$

The denitrification fraction f_{de} was assigned a default value depending on soil texture and gleyic features of the site according to Table 5.2

Table 5.2 Denitrification fraction f_{de} as a function of texture and gley class.

Gley class	Denitrification fraction (-) per texture class				
	1	2	3	4	5
0	0.1	0.3	0.3	0.5	0.5
1	0.3	0.5	0.5	0.6	0.6
2	0.5	0.6	0.7	0.7	0.7
3	0.7	0.8	0.8	0.8	0.8

Using the measurements, N_{td} , N_{gu} , and N_{le} were computed as average values over the observation period, f_{im} was computed from the C:N ratio in the upper 20 cm of the soil and f_{de} was assigned according to Table 1. Then $N_{im,acc}$ being the constant N immobilisation that is assumed to be associated to the build-up of organic matter is obtained by combining the equations 5.8, 5.9 and 5.10:

$$N_{im,acc} = N_{td} - N_{gu} - \frac{N_{le}}{(1 - f_{im}) \cdot (1 - f_{de})} \quad (5.11)$$

Although in the above derivations complete nitrification is assumed, one can compute the actual nitrification fraction (f_{ni}) from the measurements according to (see Annex 5.3):

$$f_{ni} = 1 - \frac{NH_{4,le}}{f_{td} \cdot NH_{3,td}} \quad \text{where} \quad f_{td} = \frac{N_{td} - N_{gu} - N_{im,t} - N_{im,acc}}{N_{td}} \quad (5.12)$$

Figure 5.12 shows the cumulative frequency distributions of the denitrification fraction (estimated from texture and gley class), time-dependent immobilisation fraction (estimated from C:N ration in the topsoil) and computed nitrification fraction (c.f. Eq. 5.12). This figure shows that the denitrification fraction is low at most plots (mostly below 0.3) indicating that most soils are reasonably well drained. Immobilisation fractions vary between 0 (for C:N ratio's below 15) to 0.9 (C:N ratio's close to 40) illustrating the range in N saturation over the various plots over

Europe. The nitrification fraction exceeds 0.9 at 80 % of the plots which shows that assumption of complete nitrification (used in the derivation of Eq. 5.11) is valid for the vast majority of the plots.

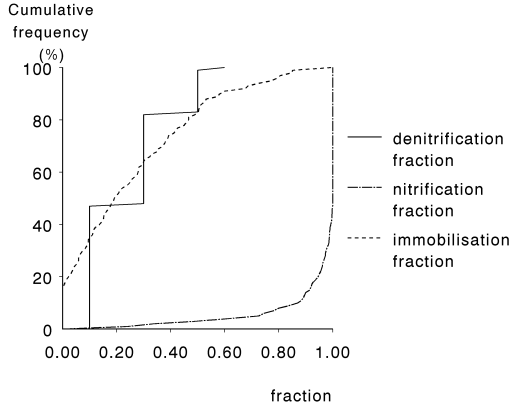


Figure 5.12 Cumulative frequency of estimated denitrification and time-dependent immobilisation fractions and of computed nitrification fraction at the plots

Time independent N immobilisation strongly varies between the plots. At about 20 % of the plots time independent N immobilisation equals 0 whereas the median value is about 5 kg.ha⁻¹.yr⁻¹. This shows that at many plots a substantial amount of N-loss cannot be explained by the assumed fractions of denitrification and C:N dependent N immobilisation. It must be kept in mind that this N immobilisation is a sort of rest-term in the N balance and therefore inherits all the uncertainties in the other terms such as leaching, uptake and total input.

Sulphate adsorption parameters

The amount of sulphate adsorbed, $SO_{4,ad}$ (meq.kg⁻¹), is assumed to be in equilibrium with the solution concentration and is described in SMART by a Langmuir isotherm (e.g. Cosby et al., 1986):

$$SO_{4,ad} = \frac{[SO_4]}{S_{1/2} + [SO_4]} \cdot S_{max} \quad (5.13)$$

where S_{max} is the maximum adsorption capacity of S in the soil (meq.kg⁻¹) and $S_{1/2}$ the half saturation concentration (eq.m⁻³). The parameters S_{max} and $S_{1/2}$ are not known, nor are there measurements of $SO_{4,ad}$. A *change* in $SO_{4,ad}$, i.e. the amount ad- or desorbed during one timestep, can in principle be estimated by looking at *differences* between S deposition and the amount of sulphur leached. However, the data available did not allow identifying meaningful values of S_{max} and $S_{1/2}$. For example, in many cases the estimated amount adsorbed increased despite a decrease in the concentration, in contradiction to the basic model assumption. Consequently, sulphate adsorption was neglected in the SMART simulations.

Soil properties

Data on soil properties that are needed are bulk density, cation exchange capacity (CEC) and sulphate sorption capacity (SSC) but the latter value was ultimately not used (see above). Values for the soil bulk density were taken from the voluntary soil physical data or, if not available, related to the organic carbon and clay content of the plot according to:

$$\rho = \begin{cases} 1 / (0.625 + 0.05 \cdot C_{\text{org}} + 0.0015 \cdot \text{clay}) & \text{if } C_{\text{org}} \leq 5\% \\ 1.55 - 0.0814 \cdot C_{\text{org}} & \text{if } 5\% < C_{\text{org}} < 15\% \\ 0.725 - 0.0337 \cdot \log_{10}(C_{\text{org}}) & \text{if } C_{\text{org}} \geq 15\% \end{cases} \quad (5.14)$$

where ρ is the bulk density ($\text{g}\cdot\text{cm}^{-3}$), C_{org} is the organic carbon content (%) and clay is the clay content (%). Equation 5.14 is based on data by Hoekstra and Poelman (1982) for mineral soils and from Van Wallenburg (1988) for peat soils. The middle part of equation 5.14 is a linear interpolation.

Values for cation exchange capacity (CEC) were taken from the soil survey data to arrive at a total value for the root zone. For plots where CEC was measured in an unbuffered solution, the CEC at pH 6.5 was calculated by assuming a relation between CEC, pH (in solution), clay and organic carbon (OC) according to (Helling et al., 1964):

$$\text{CEC} = (0.44 \cdot \text{pH} + 3.0) \cdot \% \text{clay} + (5.1 \cdot \text{pH} - 5.9) \cdot \% \text{OC} \quad (5.15)$$

Cation exchange capacity at pH 6.5 was then computed by scaling the measured CEC with the ratio between computed CEC at pH 6.5 and computed CEC at the soil solution pH according to:

$$\text{CEC}_{\text{updated}(\text{pH}6.5)} = \text{CEC}_{\text{measured}(\text{pHactual})} \cdot (\text{CEC}_{\text{calculated}(\text{pH}6.5)} / \text{CEC}_{\text{calculated}(\text{pHactual})}) \quad (5.16)$$

Evaluation of the modelling adequacy

In order to evaluate the quality of the model predictions, a comparison was made with the measurements by: (I) visual inspection for selected plots using monthly values, (ii) a scatter plot comparing the annual predictions and measurements for all plots and (iii) an evaluation of the deviation between predictions and measurements by various statistical measures. The measures used were the Normalised Mean Error (NME) and the Mean Absolute Error, as described below:

$$\text{NME} = \frac{\sum_{i=1}^N (P_i - O_i)}{NO} \quad (5.17)$$

$$MAE = \frac{\sum_{i=1}^N |P_i - O_i|}{N} \quad (5.18)$$

where P_i and O_i are the predicted and observed value i , \bar{O} is the average of the observations and N is the number of observations.

The NAE compares predictions and observations on an average level and expresses the bias in the average values of predictions compared to the observations (systematic underestimation or overestimation) but is rather sensitive to outliers. The closer the value to 0, the better. The mean absolute error is not so sensitive for outliers and does not allow for compensation of under- and overestimates, as the absolute value of the error is summed (Janssen and Heuberger, 1995)

5.2.4 Deposition scenarios used in model predictions

For the simulations, the trends in SO_2 , NO_x and NH_3 deposition were derived using RAINS country emissions (Cofala and Syri, 1998a, b) and transfer matrices derived from the EMEP long-range transport model (Bartnicki et al., 2002) for 1960 to 2010. After 2010 deposition is assumed constant. These trend curves were scaled by the average computed total deposition (based on bulk and throughfall measurements) for the period 1996-2000 so that the EMEP time series coincide with the plot-specific deposition for that period. Base cation deposition was assumed constant over the entire simulation period and was set equal to the total deposition (based on bulk and throughfall measurements) for each plot. After 2000, two scenario's were used (1) the implementation of the Gothenburg Protocol by 2010 and (2) the implementation of maximum technically feasible reduction measures by 2010 (MFR). The Gothenburg protocol signed in 1999 is the latest of eight protocols that have been adopted under the Convention on Long-range Transboundary Air Pollution which set national emission ceilings. It aims to abate acidification, eutrophication and ground-level ozone. Once this Protocol is fully implemented, Europe's sulphur emissions should be cut by at least 63% and NO_x emissions by 41% compared to 1990.

Figure 5.13 shows the historical and predicted future emissions of S and N for the two protocols.

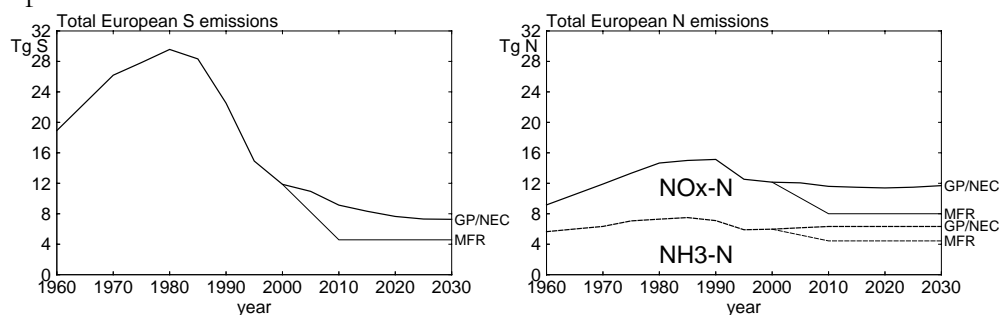


Figure 5.13 Emission reduction scenarios for S and N

The figure clearly shows that for sulphur large reductions have been achieved and that future reductions are planned. For N some emission reduction occurred, but only with the MFR scenario a significant decrease in N emissions can be expected.

5.3 Results

5.3.1 Model calibration

Comparison of model runs for selected plots

The model Smart was applied for the period 1960 to 2030. This means that initial estimates are needed (for the year 1960) for base saturation and C:N ratio. C:N ratio for 1960 was recomputed from the observed C:N ratio at the plots (mostly somewhere in the period 1990-1995) and the historical N input and uptake between 1960 and this time-point. For each plot, the base saturation in 1960 was calibrated by running the model between 1960 and the year with the observation of base saturation thereby adjusting the initial base saturation in 1960 until the observed base saturation is correctly reproduced. Figures 5.14 and 5.15 show examples of SMART model output compared with observations for various soil solution concentrations for two example plots in Germany (with a better than average fit) and Sweden (with a worse than average fit). Figure 5.14 shows a good agreement between (trends in) simulations and observations for all variables, especially for nitrate and aluminium.

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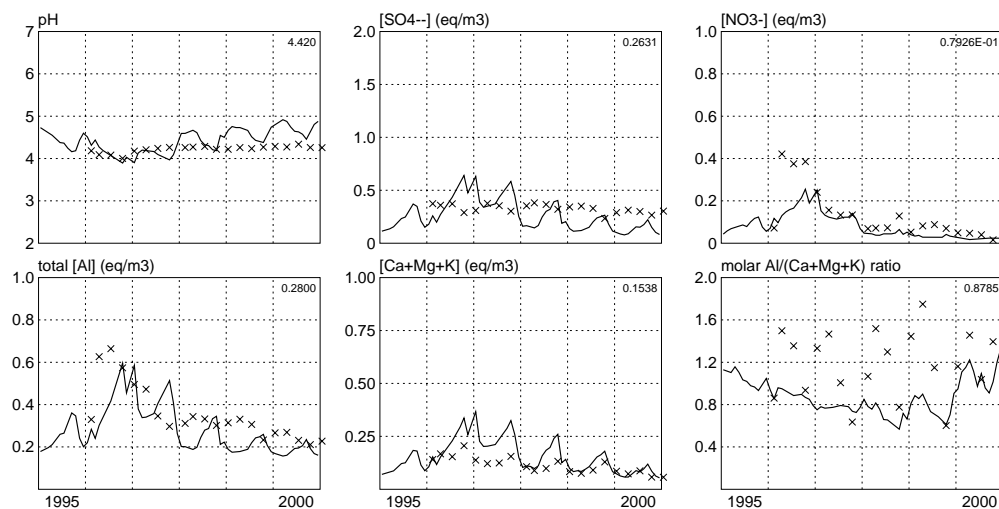


Figure 5.14 Observed (crosses) and simulated monthly soil solution concentrations for a plot in Belgium

Figure 5.15 shows the results of SMART for a plot in Sweden. For this plot pH and base cations are well simulated but not all peaks in Al concentration could not be reproduced and SO_4 is underestimated.

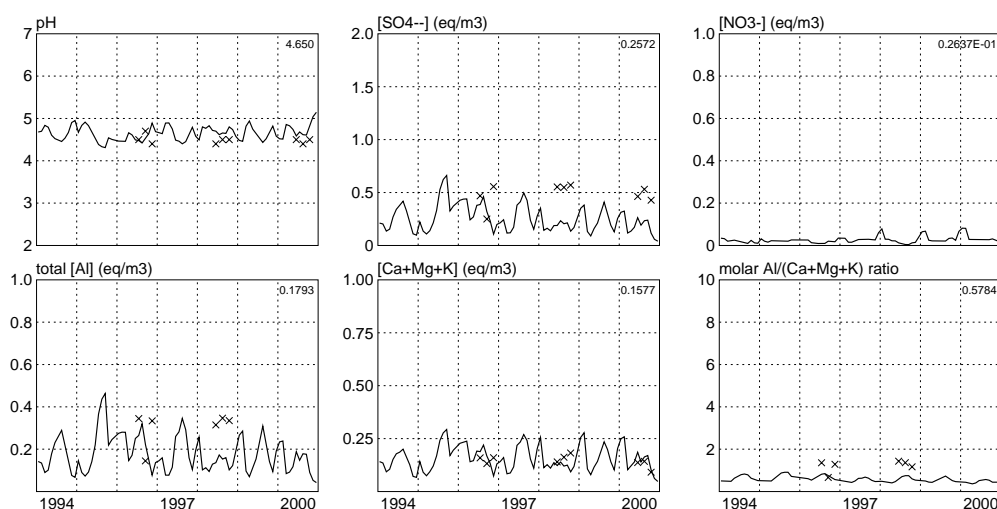


Figure 5.15 Observed (crosses) and simulated monthly soil solution concentrations for a plot in Sweden

Comparison of model runs for all plots:

Figure 5.16 shows the goodness-of-fit computed for all plots with at least 24 concentration measurements (two years of monthly data). Figure 5.16a shows the distribution of the Normalised Mean Error (NME) which gives a crude impression whether the simulations are an underestimate (negative NME) or an overestimate (positive NME). Ideally NME should be close to zero. This figure shows that pH is well simulated only for a low percentage of plots pH is underestimated by about 20-30 %. For sulphate and nitrate the median NME is close to 0 (no systematic under or overestimation) but high discrepancies between observations and model results occur for a number of plots. For sulphate and aluminium the deviation lies mostly between -50 and 50 %, for nitrate much higher overestimations occur. Very high errors in the simulated sulphate concentrations occur for some plots where sulphate is 'generated' in the soil itself due to weathering of parent material containing sulphate (Gypsum) or, for one plot, due to pyrite oxidation (!), processes not accounted for in the model.

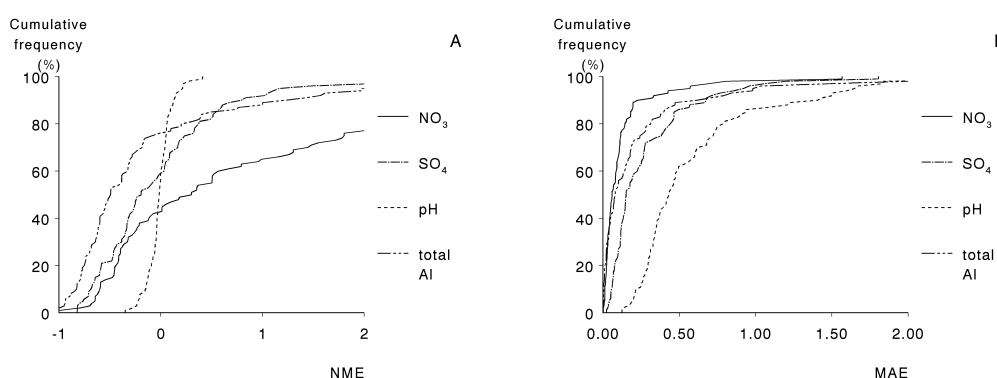


Figure 5.16 Goodness-of-fit expressed by the NME (A) and MAE (B) measures

Because the NME is the difference between modelled and observed values divided by the mean of the observations, low mean values can create high NME's.

Furthermore this measure is rather sensitive to outliers which often occur for nitrate and aluminium, as for many plots the measurements show high variations over short time periods that cannot be reproduced by the model (see Figure 5.15). Therefore Figure 5.16b shows the Mean Absolute Error (MAE) that simply gives the average absolute difference between observed and simulated values (for concentrations in eq.m^{-3} and for pH in pH units). This figure shows that the absolute error in simulated nitrate concentrations is low, mostly below 0.1 eq.m^{-3} . For pH the median average absolute error over all plots is about 0.45 pH units: in combination with figure 5.16a this shows that on average the pH is well simulated (expressed by an NME close to zero) but that both under- and over estimations occur during the simulation (expressed by a median MAE of about 0.45 pH units).

Figure 5.17 shows the observed values averaged over the entire measurement period for each plot versus the simulated concentrations for this period for sulphate, nitrate, pH and total aluminium.

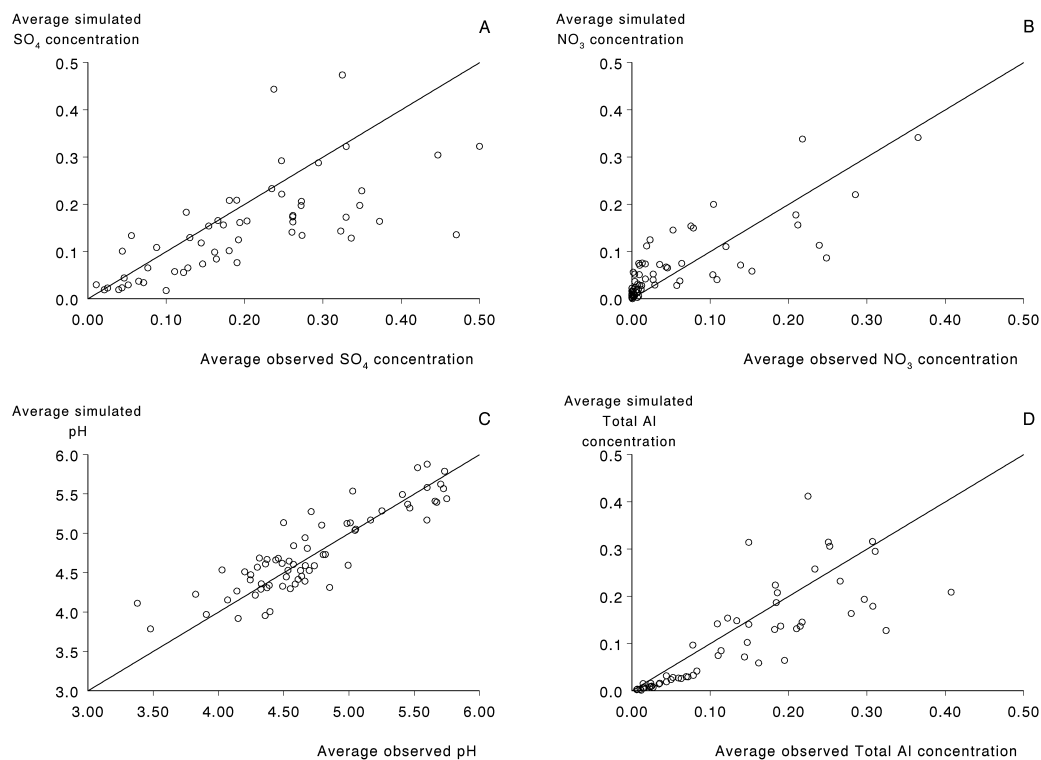


Figure 5.17 Observed versus simulated values for SO_4 (A), NO_3 (B), pH (C) and total Al (D) for 75 fully calibrated plots

Only those plots are shown for which nitrogen transformations, cation exchange and the free aluminium equilibrium could be calibrated. In practice this means that these are the 75 plots with measurements of all major cations and anions in both deposition and soil solution (including DOC in soil solution). The graphs show that there is a good correlation between measured and observed concentrations for most plots especially for pH and aluminium. Sulphate is for some plots clearly underestimated which might be due to weathering of sulphate containing parent

material or release of sulphate by sulphate desorption, processes not accounted for in the simulations. Underestimation of the aluminium concentration mainly occurs at plots with a high variation in measured concentrations that include peaks in Al concentration that the model cannot reproduce.

5.3.2 Model application for the period 1970-2030

Model runs for selected plots

Figure 5.18 shows an example of SMART model predictions for the period 1970-2030 for the same example plot in Germany for which we previously compared output with observations for various soil solution concentrations. The figure shows that recovery of the chemical soil status takes place under both the Gothenburg protocol and the Maximum Feasible Reduction (MFR) scenario as illustrated by the increase in pH and the decrease in Al/BC ratio. The MFR scenario is more effective than the Gothenburg scenario, but differences are small. The strongest effect of the MFR scenario is on the nitrate concentration: by 2030 the concentration simulated for the MFR scenario is much lower than simulated for the Gothenburg scenario.

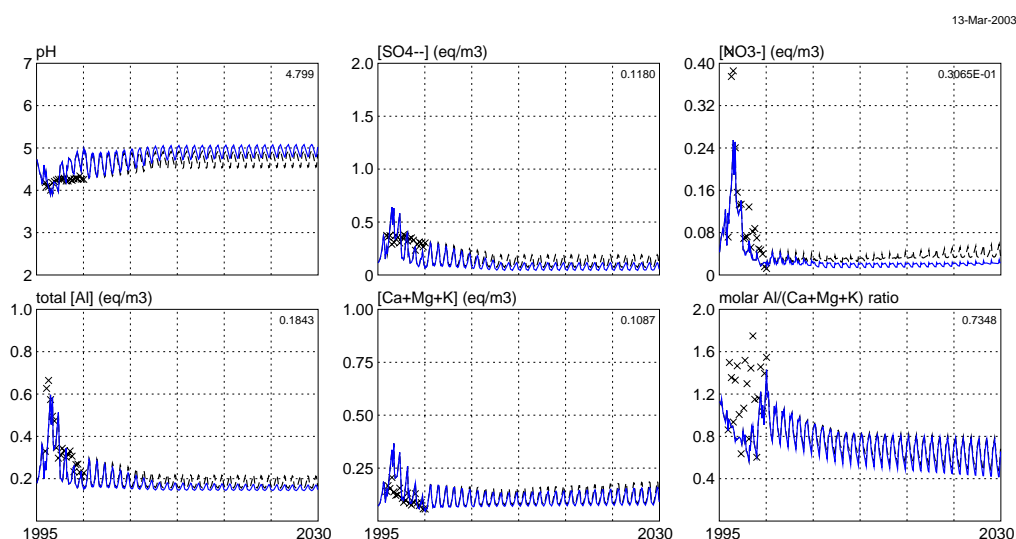


Figure 5.18 Scenario analysis for the plot of Figure 38 for the Gothenburg scenario (black lines) and the Maximum Feasible Reduction scenario (blue lines)

Model runs for all plots

Figure 5.19 and 5.20 shows the temporal evolution of 7 percentiles (5, 25, 50, 75 and 95) for 7 output variables of SMART for the period 1970 - 2030. The non-smooth behaviour of the lines between 1996 and 2000 reflects the use of year-specific data within this period (especially precipitation surplus), whereas for the other years average values were used. The figure shows a steep decline in SO_4 concentration caused by the strong reduction of sulphur deposition over Europe during the last two decades. This is accompanied by a decline in the loss of divalent base cations from the exchange complex. Patterns for pH are less distinct, only the lowest percentiles show a clear improvement over time. Aluminium follows the pH pattern;

here the high percentiles show the most improvement (fewer high Al concentrations over time). Nevertheless about 25% of the plots have Al concentrations above the critical value of 0.2 meq.l⁻¹. About 5 % of the plots have Al/BC ratios above 1.0 in 1970 but this percentage decreases towards 2010. Nitrate concentrations also decline between 1990 and 2030 but at a number of plots high concentrations persist. At a few plots nitrate concentrations will even increase as a result of reduced forest growth, and thus reduced N uptake, due to ageing of the forest that exceeds the (limited) reduction in N input.

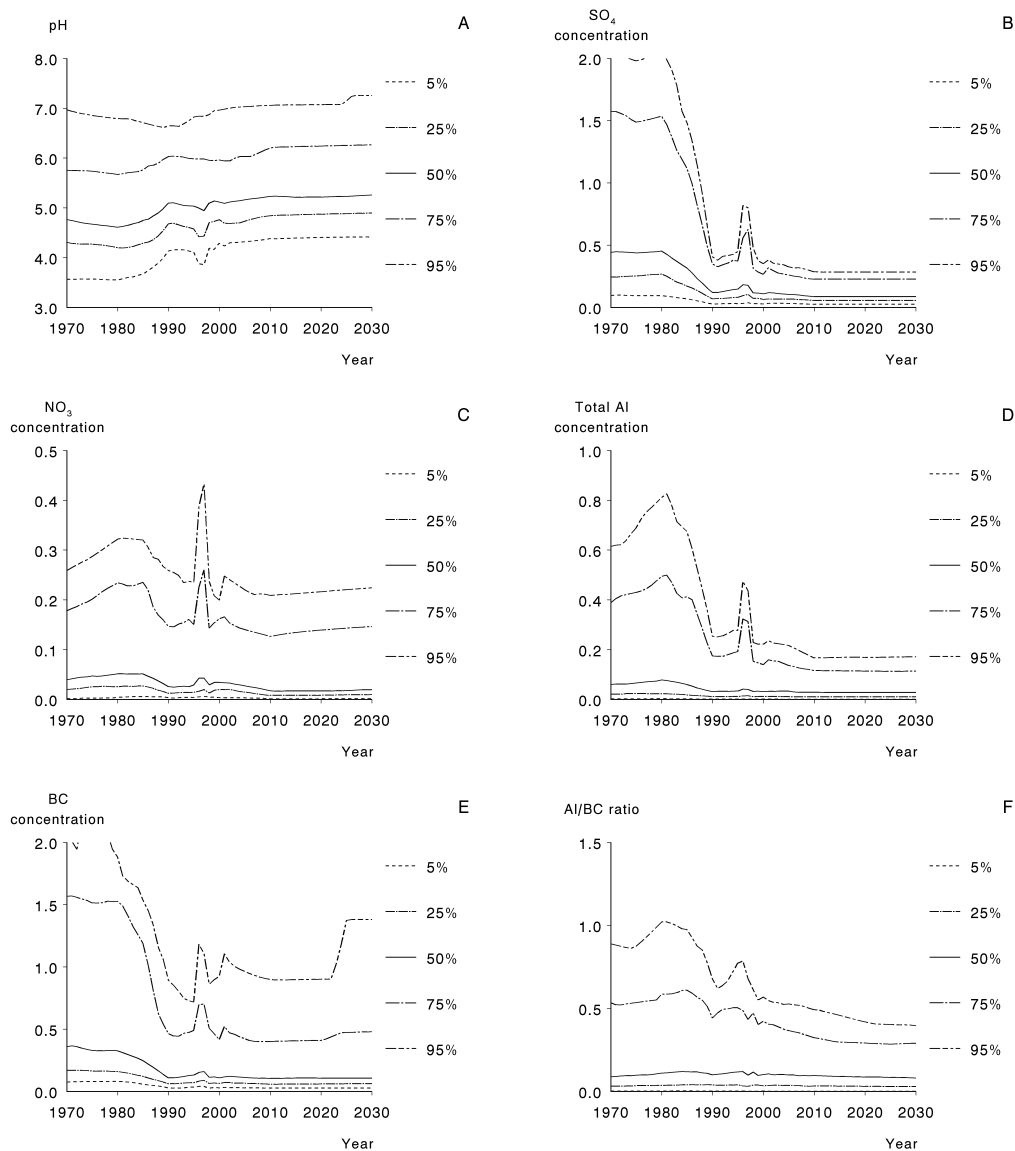


Figure 5.19 Graphs of the 5th, 25th, 50th, 75th and 95th percentiles of the distributions of 6 output variables of SMART between 1970 and 2030 for about 200 plots.

Base saturation (fBC, figure 5.20) improves over time for most plots but for a number of plots where acid inputs remains relatively high, base saturation will still decrease in the future as illustrated by the lines for the 25 and 5 percentile.

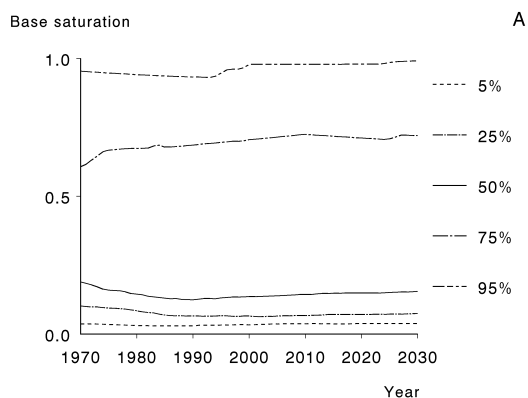


Figure 5.20 Graph of the 5th, 25th, 50th, 75th and 95th percentiles of the distributions of base saturation simulated by SMART between 1970 and 2030 for about 200 plots.

Figure 5.21 shows the time development of the median sulphate, nitrate and aluminium concentrations and pH for the two emission reduction scenarios.

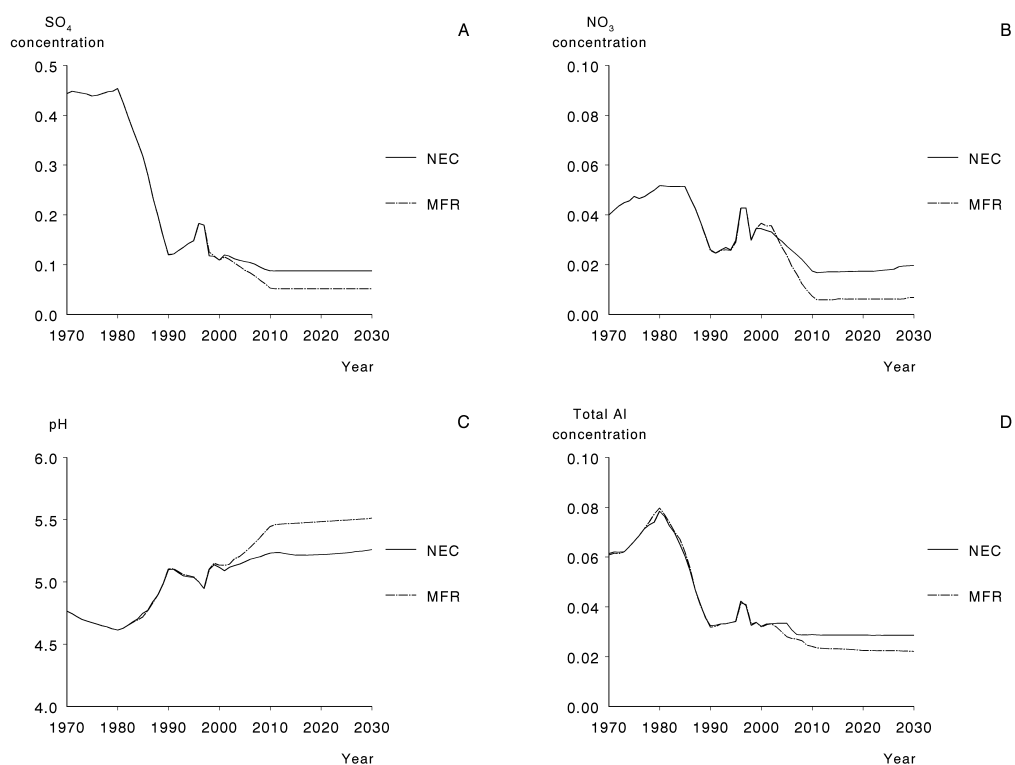


Figure 5.21 Graphs of the median values for SO_4 , NO_3 , Al and pH simulated by SMART between 1970 and 2030 for about 200 plots using two different emission reduction scenarios.

It shows that the MFR scenario leads to lower aluminium concentrations and higher pH values in 2010 than the Gothenburg scenario. The most pronounced difference occurs for nitrate as the median concentration over all plots in 2010 under the MFR scenario is less than half the median concentration under the Gothenburg scenario. This is due to the fact that under the Gothenburg scenario reductions in especially N emissions are much lower than when all available technology would be applied (MFR). The increase in median concentrations between 1995 and 2000 is an artefact caused by the use of year-specific hydrology for this period.

Geographic variation of predicted soil solution chemistry over time

Figure 5.22 shows the sulphate and nitrate concentrations at the modelled sites for the years 1970 and 2030 for the Gothenburg protocol.

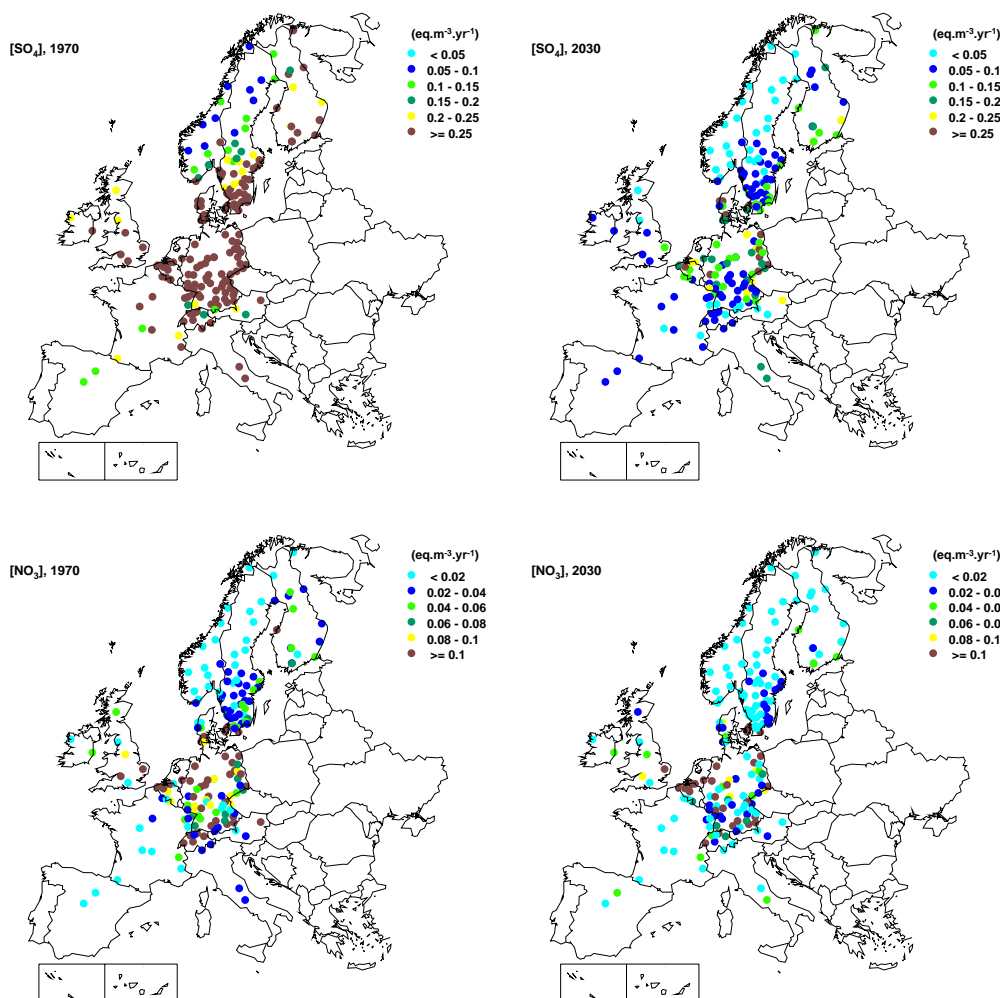


Figure 5.22 Annual mean soil solution concentrations of SO_4 and NO_3 at the modelled sites in 1970 and 2030 for the Gothenburg protocol

This figure illustrates the strong decline in sulphur concentrations also seen in Figure 5.19. It also shows the high spatial variability in SO_4 soil solution concentration with the highest values in Central Europe. It also shows that the reduction in N emissions leads to lower nitrate concentrations at the plots, but that the decrease in concentration is much less than for sulphate (see also figure 5.19). Highest nitrate concentrations are found in Belgium and parts of Germany, the United Kingdom and Denmark.

Figure 5.23 shows the time development in pH and the total Al concentration. It shows that for many plots simulated pH in 2030 is substantially higher than in 1970. For Al only the higher concentrations are strongly reduced over time (see also figure 5.19). It also shows that the number of plots where Al concentrations are above the critical value of 0.2 meq.l^{-1} hardly reduces over time.

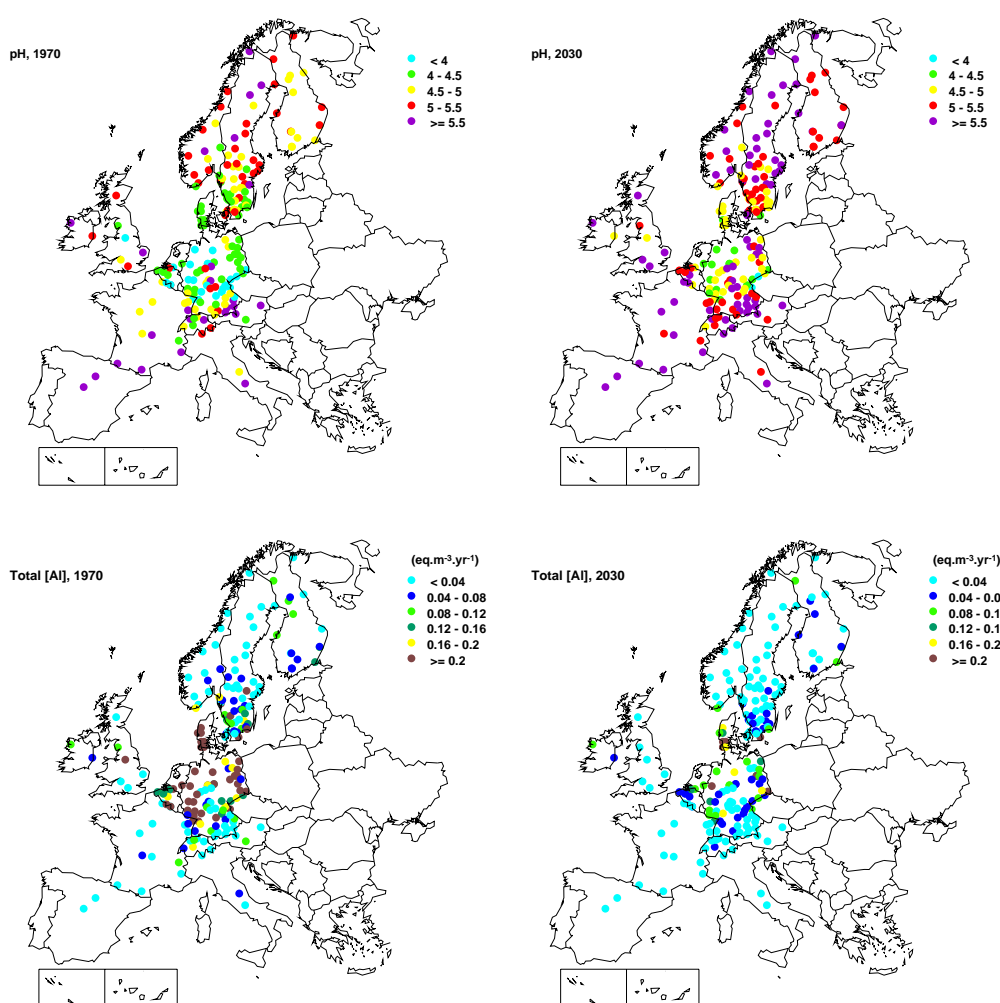


Figure 5.23 Annual mean pH and soil solution concentration of total Al at the modelled sites for 1970 and 2030 for the Gothenburg protocol

5.4 Discussion and conclusions

To evaluate effects of future deposition scenario's on Intensively Monitored plots, the model SMART was applied to about 200 sites where data on deposition, soil and soil solution were available. A number of parameters in the model could be computed from the measurements of element input (total deposition) and element concentrations in the soil solution. These plot-specific parameters were then used to apply the model at the sites. The computation of plot-specific model-parameters showed e.g.:

- The relationship between pH and free Al is better than between pH and total Al, especially for pH values greater than 5, and can for most plots be well described by an equilibrium reaction using a variable exponent. This exponent is mostly lower than 3 (as it is assumed in a gibbsite equilibrium).
- Exchange constants for Al-BC and H-BC are highly variable, but the exponent β in the relationship is mostly between 1 and 2. This high variability in exchange constants was also observed within the Netherlands (De Vries and Posch, 2003b).
- The total N budgets reveals that for many plots the loss (removal) of N cannot be described by uptake, leaching, denitrification and C:N dependent N immobilisation alone. Only when a time-independent N immobilisation is assumed the budget can be closed. Uncertainties in the various terms within this budget are, however, high.
- Nitrification is almost complete at most of the plots, i.e. hardly any ammonia is leached.
- Parameterisation of the sulphur adsorption process in SMART was not possible with the available data on S input and -output.
- On average pH values are very well simulated although the model is not able to simulate all intra-year variability. There is no systematic deviation in simulated sulphate and nitrate concentrations but at some plots the model cannot accurately predict measured concentrations. For a number of plots peaks in the, on average low, aluminium concentration cannot be reproduced by the model leading to an underestimation of average Al concentrations. However, nitrate and aluminium concentrations on many plots are very low, leading to high relative errors in the simulations but absolute errors in the model predictions are often very low.

Evaluation of the Gothenburg protocol on emission reductions for the period 1970-2030 shows:

- A very strong reduction in sulphate concentrations between 1980 and 2000 in the soil due to the high reductions in sulphur emissions
- A reduction of the nitrate concentrations by the year 2010 for most plots but most striking for the plots with the highest present N concentrations
- A reduction in the aluminium concentrations over time, most clearly for those plots where aluminium concentrations are currently (very) high.
- Aluminium concentrations above $0.2 \text{ mol}_e\text{m}^{-3}$ occur for about 25 % of the plots in the beginning of the simulation period; this percentage decreases to about 5-10 % of the plots in 2030.
- Al/BC ratios above a critical value of 1 occur at about 5 % of the plots in 1970 and this percentage even decreases towards 2010.

It should be kept in mind, however, that it not sure whether the planned reductions foreseen in the Gothenburg protocol will be reached in 2010 as a number of countries still needs to strongly decrease emissions to attain the targets set.

Comparison of the Gothenburg protocol with the maximum feasible reduction scenario shows:

- that the MFR scenario leads to lower sulphate and aluminium concentrations in 2030 than the Gothenburg scenario
- that the MFR scenario is much more effective in reducing nitrate concentrations than the Gothenburg scenario

References

Alcamo, J., R. Shaw and L. Hordijk, 1990. *The RAINS model of acidification*. Science and Strategies in Europe, Kluwer Academic Publishers, Dordrecht, 402 pp.

Alveteg, M., 1998. *Dynamics of forest soil chemistry*. PhD thesis, Reports in Ecology and Environmental Engineering 3:1998, Department of Chemical Engineering II, Lund University, Lund, Sweden, 81 pp.

Alveteg, M. and H. Sverdrup, 2002. *Manual for regional assessments using the SAFE model (draft version 8 April 2002)*. Department of Chemical Engineering II, Lund University, Lund, Sweden.

Alveteg, M., H. Sverdrup and P. Warfvinge, 1995. *Regional assessment of the temporal trends in soil acidification in southern Sweden, using the SAFE model*. Water Air Soil Poll. 85, 2509-2514.

Bartnicki, J., K. Olendrzynski, E.J. Jonson, E. Berge and S. Junger, 2002. *Description of the Eulerian acid deposition model*. EMEP/MS-CW.

Batjes, N.H., 1996. *Development of a world data set of soil water retention properties using pedotransfer rules*. Geoderma 71, 31-52.

Becker, R., J. Block, C.-G. Schimming, T. Spranger and N. Wellbrock, 2000. *Critical loads für Waldökosysteme - Methoden und ergebnisse für Standorte des Level II-Programms*. Bundesministerium für Ernährung, Landwirtschaft und Forsten, Bonn, Germany (in German).

Cofala, J. and S. Syri, 1998a. *Sulfur Emissions, Abatement Technologies and Related Costs for Europe in the RAINS Model Database*. IIASA Interim Report IR-98-35 (update 19.10.1998).

Cofala, J. and S. Syri, 1998b. *Nitrogen Oxides Emissions, Abatement Technologies and Related Costs for Europe in the RAINS Model Database*. IIASA Interim Report IR-98-88.

Cosby, B.J., G.M. Hornberger, R.F. Wright and J.N. Galloway, 1986. *Modeling the effects of acid deposition: Control of long-term sulfate dynamics by soil sulfate adsorption*. Water resour. res. 22 (8), 1283-1291.

De Vries, W., 1991. *Methodologies for the assessment and mapping of critical loads and the impact of abatement strategies on forest soils*. Staring Centre Report 46. Wageningen, 109 pp.

De Vries, W. and A. Breeuwsma, 1986. *Relative importance of natural and anthropogenic proton sources in soils in the Netherlands*. Water Air Soil Poll. 28 (1), 173-184.

De Vries, W. and E.E.J.M. Leeters, 2001. *Chemical composition of the humus layer, mineral soil and soil solution of 150 forest stands in the Netherlands in 1990*. Alterra rapport 424.1. Alterra, Green World Research, Wageningen (Netherlands), 113 pp.

De Vries, W. and M. Posch, 2003a. *Critical Levels and Critical Loads as A Tool For Air Quality Management*. In: C.N. Hewitt and A. Jackson (Eds). Handbook of Atmospheric Science. Principles and Applications. Blackwell Publishing, in press, London, UK, pp. 656.

De Vries, W. and M. Posch, 2003b. *Derivation of cation exchange constants for sand, loess, clay and peat soils on the basis of field measurements in the Netherlands*. Alterra Report (in press).

De Vries, W., M. Posch and J. Kämäri, 1989. *Simulation of the long-term soil response to acid deposition in various buffer ranges*. Water Air Soil Poll. 48 (3), 349-390.

De Vries, W., J. Kros and C. Van der Salm, 1994a. *Long-term impacts of various emission deposition scenarios on Dutch forest soils*. Water Air Soil Poll. 75 (1-2), 1-35.

De Vries, W., G.J. Reinds, M. Posch and J. Kämäri, 1994b. *Simulation of soil response to acidic deposition scenarios in Europe*. Water Air Soil Poll. 78, 215-246.

De Vries, W., G.J. Reinds, H. Van Dobben, D. De Zwart, M. Posch, J.C.H. Voogd, J. Auee and E.M. Vel, 2002. *Intensive Monitoring of Forest Ecosystems in Europe. Technical Report 2002*. UN/ECE and EC, Forest Intensive Monitoring Coordinating Institute, Geneva and Brussels, 175 pp.

De Vries, W., G.J. Reinds, C. Van der Salm, G.P.J. Draaijers, A. Bleeker, J.W. Erisman, J. Auee, P. Gundersen, H.L. Kristensen, H. Van Dobben, D. De Zwart, J. Derome, J.C.H. Voogd and E.M. Vel, 2001. *Intensive Monitoring of Forest Ecosystems in Europe. Technical Report 2001*. UN/ECE, EC, Forest Intensive Monitoring Coordinating Institute, Geneva and Brussels, 177 pp.

Dise, N.B., E. Matzner and P. Gundersen, 1998. *Synthesis of nitrogen pools and fluxes from European forest ecosystems*. Water Air Soil Poll. 105, 143-154.

Fumoto, T. and H. Sverdrup, 2001. *Implementation of sulfate adsorption in the SAFE model*. J. Environ. Qual. 30, 45-57.

Gundersen, P., I. Callesen and W. de Vries, 1998a. *Nitrate leaching in forest ecosystems is related to forest floor C/N ratios*. Environ. pollut. 102 (1), 403-407.

Gundersen, P., B.A. Emmet, O.J. Kjønaas, C. Koopmans and A. Tietema, 1998b. *Impact of nitrogen deposition on nitrogen cycling: a synthesis of NITREX- data*. For. ecol. manage. 101, 37-55.

Helling, C.S., G. Chesters and R.B. Corey, 1964. *Contribution of organic matter and clay to soil cation exchange capacity as affected by the pH of the saturating solution*. Soil Sci. Soc. Am. J. 28, 517-520.

Hettelingh, J.-P. and M. Posch, 1994. *Critical loads and a dynamic assessment of ecosystem recovery*. In: J. Grasman and G. Van Straten (Eds). Predictability and Nonlinear Modelling in Natural Sciences and Economics. Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 439-446.

Hoekstra, C. and J.N.B. Poelman, 1982. *Dichtheid van gronden gemeten aan de meest voorkomende bodemeenheden in Nederland*. Rapport nr. 1582. Stichting voor Bodemkartering, Wageningen, 47 pp.

Janssen, P.H.M. and P.S.C. Heuberger, 1995. *Calibration of process-oriented models*. Ecological Modelling 83, 55-66.

Kauppi, P., J. Kämäri, M. Posch, L. Kauppi and E. Matzner, 1986. *Acidification of forest soils: Model development and application for analyzing impacts of acidic deposition in Europe*. Ecological Modelling 33, 231-253.

Kimmins, J.P., D. Binkley, L. Chatarpaul and J. de Catanzaro, 1985. *Biogeochemistry of temperate forest ecosystems Literature on inventories and dynamics of biomass and nutrients*. Information Report PI-X-47E/F. Petawawa National Forestry Institute, Canada, 227 pp.

Klap, J.M., W. de Vries, J.W. Erisman and E.P. van Leeuwen, 1997. *Relationships between forest condition and natural and anthropogenic stress factors on the European scale; pilot study*. Report 150. DLO Winand Staring Centre for Integrated Land, Soil and Water Research, Wageningen, the Netherlands.

Kurz, D., M. Alveteg and H. Sverdrup, 1998. *Acidification of Swiss forest soils - Development of a regional dynamic assessment*. Environmental Documentation No.89, SAEFL, Berne, Switzerland, 115 pp.

Michalzik, B. and E. Matzner, 1999. *Dynamics of dissolved organic nitrogen and carbon in a Central European Norway spruce ecosystem*. Eur. J. Soil Sci. 50, 579 - 590.

Olsson, M. and P.A. Melkerud, 1991. *Determination of weathering rates based on geochemical properties of the soil*. In: E. Pulkinen (Ed). Environmental geochemistry in Northern Europe. Proceedings of a Symposium held in Rovaniemi, Finland, 17-19 October, 1989. Geological Survey of Finland, Special paper 9. pp. 69-78.

Posch, M. and G.J. Reinds, 2003. *VSD - User Manual of the Very Simple Dynamic soil acidification model*. Coordination Center for Effects, National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands (in preparation).

Posch, M., G.J. Reinds and W. de Vries, 1993. *SMART: A Simulation Model for Acidification's Regional Trends. Model Description and User Manual*. Mimeograph Series of the National Board of Waters and the Environment 477, Helsinki, Finland, 43 pp.

Posch, M., P.A.M. de Smedt, J.P. Hettelingh and R.J. Downing, 1995. *Calculation and mapping of critical thresholds in Europe: CCE status report 1995*. Report 259101004. Coordination Center for Effects, National Institute of Public Health and the Environment, Bilthoven, the Netherlands, 198 pp.

Posch, M., J.P. Hettelingh, W. de Vries, H. Sverdrup and R.F. Wright, 2002. *Manual for dynamic modelling of soil response to atmospheric deposition*. RIVM-CCE report (in press).

Santore, R.C., C.T. Driscoll and M. Aloii, 1995. *A model of soil organic matter and its function in temperate forest soil development*. In: W.W. McFee and J.M. Kelly (Eds). Carbon forms and functions in forest soils. Soil Sci. Soc. of America, Madison, Wisconsin, pp. 275-298.

Smolander, A., V. Kitunen and E. Mälikönen, 2001. *Dissolved organic nitrogen and carbon in a Norway spruce stand and an adjacent clear-cut*. Biol. fertil. soils 33, 190-196.

Starr, M., 1999. *WATBAL: a model for estimating monthly water balance components, including soil water fluxes*. In: S. Kleemola and M. Forsius (Eds). 8th Annual report 1999. UN ECE ICP Integrated Monitoring. The Finnish Environment 325. Finnish Environment Institute, Helsinki, Finland, pp. 31-35.

Starr, M., A.J. Lindroos, T. Tarvainen and H. Tanskanen, 1998. *Weathering rates in the Hieta jarvi integrated monitoring catchment*. Boreal Environment Research 3, 275-285.

Sverdrup, H. and P. Warfvinge, 1993. *The effect of soil acidification on the growth of trees, grass and herbs as expressed by the (Ca+Mg+K)/Al ratio*. Reports in ecology and environmental engineering. Reports in Ecology and Environmental Engineering 1993: 2. Lund University, Department of Chemical Engineering II, 108 pp.

Sverdrup, H. and W. de Vries, 1994. *Calculating critical loads for acidity with the simple mass balance method*. Water Air Soil Poll. 72 (1/4), 143-162.

Sverdrup, H., W. de Vries and A. Henriksen, 1990. *Mapping critical loads. A guidance manual to criteria calculation methods data collection and mapping*. Miljø rapport 1990: 14. Nordic Council of Ministers Copenhagen 1990, 124 pp.

Sverdrup, H.U., 1990. *The kinetics of base cation release due to chemical weathering*. Lund University Press, Sweden, 246 pp.

Tiktak, A. and J.J.M. van Grinsven, 1995. *Review of sixteen forest-soil-atmosphere models*. Ecological Modelling 83, 35-54.

Ulrich, B., 1981. *Ökologische Gruppierung von Boden nach ihrem chemischen Bodenzustand*. Z. Pflanzenernähr. Bodenk. 144, 289-305.

UN/ECE, 1996. *Manual on methodologies and criteria for mapping critical levels/loads and geographical areas where they are exceeded*. Texte 71/96 Umweltbundesamt, Berlin, Germany, 144+lxiv pp.

Van Wallenburg, C., 1988. *De dichtheid van moerige gronden*. Internal Report Stichting voor Bodemkartering, Wageningen, the Netherlands, 5 pp.

Warfvinge, P. and H. Sverdrup, 1992. *Calculating critical loads of acid deposition with PROFILE ? A steady-state soil chemistry model*. Water Air and Soil Pollution 63, 119-143.

Warfvinge, P., U. Falkengren-Grerup, H. Sverdrup and B. Andersen, 1993. *Modelling long-term cation supply in acidified forest stands*. Environ. pollut. 80, 209-221.

Annex 5.1 Relationships between critical load models and dynamic soil models

To illustrate the relationships between critical load models and dynamic soil models, Figure A5.1.1 summarises the possible development of a (soil) chemical and biological variable in response to a ‘typical’ temporal deposition pattern (after Posch et al., 2002).

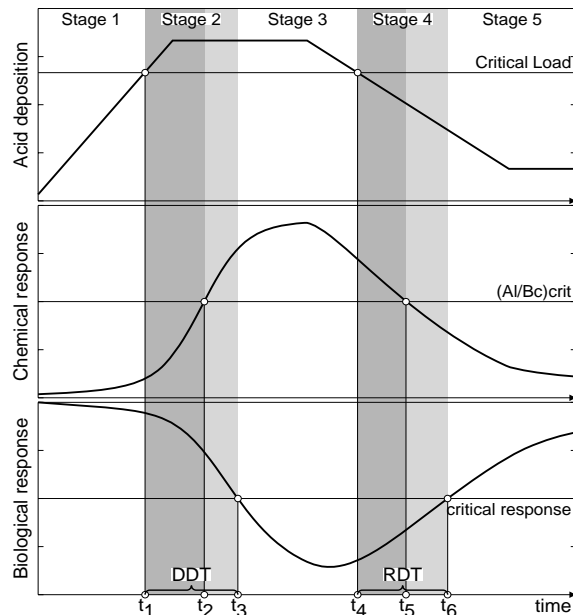


Figure A5.1.1 ‘Typical’ temporal (past and future) development of the deposition (top), a soil chemical variable and the corresponding biological response. Also depicted are the critical values of those (chemical and biological) variables and the critical load derived from them. The delay between the (non-)exceedance of the critical load, the (non-)violation of the critical chemical criterion and the crossing of the critical biological response is indicated in grey shades, highlighting the Damage Delay Time (DDT) and the Recovery Delay Time (RDT) of the system.

Five stages can be distinguished:

Stage 1: Deposition was and is below the critical load (CL) and the chemical and biological variables do not violate their respective criteria. As long as deposition stays below the CL, this is the ‘ideal’ situation.

Stage 2: Deposition is above the CL, but (chemical and) biological variables still don’t violate their respective criteria; there is a delay before this happens. Therefore, no damage is likely at this stage, despite the exceedance of the CL. We call the time between the first exceedance of the CL and first violation of the biological criterion the *Damage Delay Time* ($DDT=t_3-t_1$).

Stage 3: The deposition is above CL and both the chemical and biological criteria are violated. Measures have to be taken to avoid a (further) deterioration of the ecosystem.

Stage 4: Deposition is below the CL, but the chemical and biological criteria are still violated, and thus recovery has not yet occurred. We call the time between the first non-exceedance of the CL and the subsequent non-violation of both criteria the *Recovery Delay Time* ($RDT=t_6-t_4$).

Stage 5: This stage is similar to Stage 1. Deposition is below the CL and both criteria are no longer violated. Only at this stage can one speak of full ecosystem recovery. Stages 2 and 4 can be further subdivided into two sub-stages each: Chemical delay times ($DDT_c = t_2 - t_1$ and $RD T_c = t_5 - t_4$; dark grey in Fig.A.1) and (additional) biological delay times ($DDT_b = t_3 - t_2$ and $RD T_b = t_6 - t_5$; light grey).

Annex 5.2 The VSD, SMART and SAFE soil models

An overview of VSD, SMART and SAFE, being soil models of increasing complexity, is given in Table A5.2.1. Only a short description of the models can be given, but details can be found in the references cited. It should be emphasised that the term ‘model’ used here refers, in general, to a model system, i.e. a set of (linked) software (and databases) which consists of pre-processors for input data (preparation) and calibration, post-processors for the model output, and - in general the smallest part - the actual model itself.

Table A5.2.1 Overview of dynamic models that may be applied on a regional scale.

Model	Essential process descriptions	Layers	Essential model inputs
VSD	ANC charge balance Mass balances for BC and N (complete nitrification assumed)	One	CL input data + CEC, base saturation C/N ratio
SMART	VSD model + SO ₄ sorption Mass balances for CaCO ₃ and Al Separate mass balances for NH ₄ and NO ₃ , nitrification Complexation of Al with DOC	One	VSD model + S _{max} and S _{1/2} Ca-carbonate, Al _{ox} Nitrification fraction, f _{ni} pK values
SAFE	VSD model + Separate weathering calculation Element cycling by litterfall, root decay, mineralisation and root uptake	Several	VSD model + Input data for PROFILE Litterfall rate, parameters describing mineralisation and root uptake

The VSD model: The VSD model can be viewed as the simplest extension of the SMB model for critical loads. It only includes cation exchange and N immobilisation, and a mass balance for cations and nitrogen as described above, in addition to the equations included in the SMB model. In the VSD model, the various ecosystem processes have been limited to a few key processes. Processes that are *not* taken into account are: (i) canopy interactions, (ii) nutrient cycling processes, (iii) N fixation and NH₄ adsorption, (iv) interactions (adsorption, uptake, immobilisation and reduction) of SO₄, (v) formation and protonation of organic anions, (RCOO) and (vi) complexation of Al with OH, SO₄ and RCOO.

The VSD model consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. The soil solution chemistry in VSD depends solely on the net element input from the atmosphere (deposition minus net uptake minus net immobilisation) and the geochemical interaction in the soil (CO₂ equilibria, weathering of carbonates and silicates, and cation exchange). Soil interactions are described by simple rate-limited (zero-order) reactions (e.g. uptake and silicate weathering) or by equilibrium reactions (e.g. cation exchange). It models the exchange of Al, H and Ca+Mg+K with Gaines-Thomas or Gapon equations. Solute transport is described by assuming complete mixing of the element input within one

homogeneous soil compartment with a constant density and a fixed depth. Since VSD is a single layer soil model neglecting vertical heterogeneity, it predicts the concentration of the soil water leaving this layer (mostly the root zone). The annual water flux percolating from this layer is taken equal to the annual precipitation excess. The time step of the model is one year, i.e. seasonal variations are not considered. A detailed description of the VSD model can be found in Posch and Reinds (2003) and Posch et al., (2002).

The SMART model: The SMART model (**S**imulation **M**odel for **A**cidification's **R**egional **T**rends) is similar to the VSD model, but somewhat extended and is described in De Vries et al. (1989) and Posch et al. (1993). As with the VSD model, the SMART model consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. It includes most of the assumptions and simplifications given for the VSD model; and justifications for them can be found in De Vries et al. (1989). As with the VSD and SAFE model, it models the exchange of Al, H and divalent base cations, but describes them with Gaines-Thomas equations. Additionally, sulphate adsorption is modelled using a Langmuir equation (as in MAGIC) and organic acids can be described as mono-, di- or tri-protic. Furthermore, it does include a balance for carbonate and Al, thus allowing the calculation from calcareous soils to completely acidified soils that do not have an Al buffer left. In this respect, SMART is based on the concept of buffer ranges expounded by Ulrich (1981). Recently a description of the complexation of aluminium with organic acids has been included. The SMART model has been developed with regional applications in mind, and an early example of an application to Europe can be found in De Vries et al. (1994b).

The SAFE model: The SAFE (**S**oil **A**cidification in **F**orest **E**cosystems) model has been developed at the University of Lund (Warfvinge et al., 1993) and a recent description of the model can be found in Alveteg (1998) and Alveteg and Sverdrup (2002). The main differences to the SMART and MAGIC models are: (i) weathering of base cations is not a model input, but it is modelled with the PROFILE (sub-)model, using soil mineralogy as input (Warfvinge and Sverdrup, 1992); (ii) SAFE is oriented to soil profiles in which water is assumed to move vertically through several soil layers (usually 4), (iii) Cation exchange between Al, H and (divalent) base cations is modelled with Gapon exchange reactions, and the exchange between soil matrix and the soil solution is diffusion limited, (iv) SAFE assumes no retention of S in the soil (although a sulphate adsorption model depending on sulphate concentration and pH has been tested, Fumoto and Sverdrup, 2001). The SAFE model has been applied on many sites and more recently also regional applications have been carried out for Sweden (Alveteg and Sverdrup, 2002) and Switzerland (Kurz et al., 1998).

Annex 5.3 Calculation of aluminium complexation, nitrogen transformations and sulphate adsorption in SMART

Calculation of the free aluminium concentration in SMART

In SMART the concentration of free (uncomplexed) Al can be calculated from observations of the concentrations of $[H]$, $[Al_{tot}]$ and DOC using relatively simple models for the dissociation of DOC and complexation of Al with organic anions. The dissociation of DOC is described by a triprotic model for soil organic acids, according to:



or in mathematical form:

$$\begin{aligned} [H^+] \cdot [H_2A^-] &= K_1 \cdot [H_3A] \\ [H^+] \cdot [HA^{2-}] &= K_2 \cdot [H_2A^-] \\ [H^+] \cdot [A^{3-}] &= K_3 \cdot [HA^{2-}] \end{aligned} \quad (A5.3.2)$$

This system of equations for the concentrations of organic anions is easily solved, yielding (assuming that $m \cdot DOC$ is the sum of all organic species):

$$\begin{aligned} [H_2A^-] &= \frac{m \cdot DOC \cdot K_1 \cdot [H]^2}{[H]^3 + K_1 \cdot ([H]^2 + K_2 \cdot ([H] + K_3))} \\ [HA^{2-}] &= [H_2A^-] \cdot K_2 / [H] \\ [A^{3-}] &= [HA^{2-}] \cdot K_3 / [H] \end{aligned} \quad (A5.3.3)$$

The complexation of Al with organic anions is modelled according to (Santore et al., 1995):



In their mathematical form these equations read:

$$\begin{aligned} [AlA] &= K_{31} [Al^{3+}] [A^{3-}] \\ [AlHA^+] &= K_{32} [Al^{3+}] [A^{3-}] [H^+] \end{aligned} \quad (A5.3.5)$$

where K_{31} and K_{32} are the equilibrium constants. Defining $pK = -\log_{10}(K)$ (with K expressed in mol.l^{-1} or powers thereof), we use $pK_{31} = -7.89$, $pK_{32} = -12.86$ (Santore et al., 1995). Note that $[Al^{\hat{p}+}]$ refers to the concentration of *free* aluminium. From measurements the only quantity known is the concentration of *total* aluminium, $[Al_{tot}] = [Al^{\hat{p}+}] + [\Sigma Al_{org}]$, where $[\Sigma Al_{org}]$ is the sum of the organically complexed Al-species, $[\Sigma Al_{org}] = [AlA] + [AlHA^+]$. Combining the various equations, the concentration of free aluminium is obtained as:

$$[Al^{3+}] = \frac{[Al_{tot}]}{1 + [A^{3-}](K_{31} + K_{32}[H^+])} \quad (\text{A5.3.6})$$

Calculation of nitrogen transformations in SMART

In SMART the balance for the nitrogen compounds NO_3 and NH_4 is defined as:

$$\text{NO}_{3,le} = \text{NO}_{x,td} + \text{NH}_{4,ni} - \text{NO}_{3,de} - \text{NO}_{3,gu} - \text{NO}_{3,im} \quad (\text{A5.3.7})$$

and

$$\text{NH}_{4,le} = \text{NH}_{3,td} - \text{NH}_{4,ni} - \text{NH}_{4,gu} - \text{NH}_{4,im} \quad (\text{A5.3.8})$$

where the subscripts *le*, *td*, *ni*, *gu*, *de* and *im* stand for leaching, total deposition, nitrification, net growth uptake, denitrification and immobilisation, respectively. Adding equations A5.3.7 and A5.3.8 one obtains the mass balance for total nitrogen:

$$N_{le} = N_{td} - N_{gu} - N_{de} - N_{im,t} - N_{im,acc} \quad (\text{A5.3.9})$$

where nitrogen immobilisation has been split into a time-dependent part $N_{im,t}$ and a constant part $N_{im,acc}$.

Denitrification and nitrification are modelled as fractions of the net nitrate and ammonium input, respectively:

$$\text{NO}_{3,de} = f_{de} \cdot (\text{NO}_{x,td} + \text{NH}_{4,ni} - \text{NO}_{3,gu} - \text{NO}_{3,im}) \quad (\text{A5.3.10})$$

and

$$\text{NH}_{4,ni} = f_{ni} \cdot (\text{NH}_{3,td} - \text{NH}_{4,gu} - \text{NH}_{4,im}) \quad (\text{A5.3.11})$$

where f_{de} and f_{ni} are the denitrification and nitrification fractions, respectively. For complete nitrification adding Eqs. A3.10 and A3.11 yields the equation for the denitrification of total N:

$$N_{de} = f_{de} \cdot (N_{td} - N_{gu} - N_{im}) \quad (\text{A5.3.12})$$

Assuming no preference in the uptake and N immobilisation of NO_3^- and NH_4^+ , growth uptake and immobilisation fluxes is calculated according to:

$$\text{NO}_{3,\text{gu}} = \text{N}_{\text{gu}} \cdot \frac{\text{NO}_{\text{x,td}}}{\text{N}_{\text{td}}} \quad , \quad \text{NH}_{4,\text{gu}} = \text{N}_{\text{gu}} \cdot \frac{\text{NH}_{3,\text{td}}}{\text{N}_{\text{td}}} \quad (\text{A5.3.13})$$

and

$$\text{NO}_{3,\text{im}} = \text{N}_{\text{im}} \cdot \frac{\text{NO}_{\text{x,td}}}{\text{N}_{\text{td}}} \quad , \quad \text{NH}_{4,\text{im}} = \text{N}_{\text{im}} \cdot \frac{\text{NH}_{3,\text{td}}}{\text{N}_{\text{td}}} \quad (\text{A5.3.14})$$

Combining Eqs. A5.3.7 to A5.3.14, one obtains for the balances:

$$\text{NO}_{3,\text{le}} = f_{\text{td}} \cdot (1 - f_{\text{de}}) \cdot (\text{NO}_{\text{x,td}} + f_{\text{ni}} \cdot \text{NH}_{3,\text{td}}) \quad (\text{A5.3.15})$$

and

$$\text{NH}_{4,\text{le}} = f_{\text{td}} \cdot (1 - f_{\text{ni}}) \cdot \text{NH}_{3,\text{td}} \quad (\text{A5.3.16})$$

where

$$f_{\text{td}} = \frac{\text{N}_{\text{td}} - \text{N}_{\text{gu}} - \text{N}_{\text{im}}}{\text{N}_{\text{td}}} \quad (\text{A5.3.17})$$

While f_{de} and f_{ni} are inputs to SMART, the fraction f_{im} of N immobilised is computed as a function of the C:N ratio in the topsoil according to (De Vries et al., 1994b):

$$f_{\text{im}} = \begin{cases} 0 & \text{if } \text{CN} \leq \text{CN}_{\min} \\ \frac{\text{CN} - \text{CN}_{\min}}{\text{CN}_{\max} - \text{CN}_{\min}} & \text{if } \text{CN}_{\min} < \text{CN} < \text{CN}_{\max} \\ 1 & \text{if } \text{CN} \geq \text{CN}_{\max} \end{cases} \quad (\text{A5.3.18})$$

where CN_{\min} and CN_{\max} are given limit values.

