Chemical composition of the humus layer, mineral soil and soil solution of 150 forest stands in the Netherlands in 1990

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ABSTRACT

Vries de, W. & 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.* Wageningen, Alterra, Green World Research. Alterra-rapport 424.1. 113 pp., 12 figs.; 84 tables; 129 refs.

A nation-wide assessment of the chemical composition of the humus layer, mineral topsoil (0-30 cm) and soil solution in both topsoil and subsoil (60-100 cm) has been made for 150 forest stands in the year 1990. The stands, that were part of the national forest inventory on vitality, included seven tree species and were all located on non-calcareous sandy soils. Results show increased levels of nitrogen, aluminium, lead and cadmium in at least one of the various soil compartments, indicating the occurrence of eutrophication, acidification and heavy metal pollution. Tree species and stand characteristics, such as tree height and canopy coverage, appear to be have the largest effect, on the concentration level of the various chemical parameters by influencing the input by atmospheric deposition. The various assessments allowed the calculation of various parameters related to aluminium dissolution, cation exchange and phosphate adsorption, to be used in simulation models.

Keywords: acid deposition, eutrophication, forest, heavy metals, humus layer, soil acidification

Contents

Preface

To examine the impact of atmospheric deposition on non-calcareous soils of Dutch forests, a survey of the chemical soil and soil solution composition below 150 forest stands, including seven major tree species, was carried out by Alterra (formerly the DLO Winand Staring Centre) in 1990. This research was financially supported by the Ministry of Agriculture, Nature Management and Fisheries and the Ministry of Housing, Physical Planning and Environment of the Netherlands.

It was foreseen that the results of the research would be presented in four reports with the common title: Effects of acid deposition on 150 forest stands in the Netherlands, with the following subtitles:
1. Chemical composition of the humus layer, mineral soil and soil solution;
2. Relationships between forest vitality characteristics and the chemical composition of foliage, humus layer, mineral soil and soil solution;
3. Input output budgets for sulphur, nitrogen, base cations and aluminium;
4. Assessments of the chemical composition of foliage, mineral soil, soil solution and ground water on a national scale.

Actually, the reports 2, 3 and 4 have been published already in 1994. This report contains the results of the chemical soil and soil solution composition below the 150 forest stands, and their relationship with deposition level, tree species, stand and site characteristics, that would be published as part 1 of the series. For various reasons, this report has been delayed extremely. Consequently, it is not published as SC report 69.1 as previously announced, but as Alterra Report 424.1. It now forms a series with another report (424.2) in which the chemical soil and soil solution composition below 200 forest stands is given in 1995, partly coinciding with the 150 forest stands where the same assessment took place in 1990.

Summary

Approach

Aim of the research
Research on soil acidification during the last decade has significantly increased our knowledge about the impact of atmospheric deposition on forest soils and forest vitality and the magnitude of critical loads to avoid such effects. However, nearly all research activities were carried out on a limited number of intensively monitored sites. In order to gain more insight in the regional variability of the soil and soil solution composition below forests in relation to forest vitality, a nation-wide assessment was made of the chemical composition of the leaves (needles), humus layer, mineral topsoil and soil solution in 150 forest stands. Here we report the results of the soil and soil solution composition.

Site selection
The choice of the locations was largely determined by 118 forest stands selected by the National Institute of Public Health and Environmental Protection (RIVM) for the determination of ground-water quality at the phreatic level in 1990. From this database, 89 stands were selected. The additional 61 stands were selected by aiming at (i) an optimal range in deposition level, (ii) inclusion of major tree species, proportional to the national occurrence and (iii) an optimal range in site conditions, i.e. soil type and ground-water level. The resulting forest stands include 45 stands of Scots pine, 30 stands of oak and 15 stands of black pine, Douglas fir, Norway spruce, Japanese larch and beech. A total of eleven stands were later selected to be part of the monitoring system in the context of the International Co-ordinated programme of Forests, being monitored since 1994. At each site an indication of stand characteristics, affecting the deposition, was made such as tree height, canopy coverage, distance to the forest edge and surrounding land use. Furthermore, a description of soil type and ground water class was made. Most forests were located on podzolic soils, i.e. Cambic, Carbic and Gleyic Podzols, and Haplic Arenosols and to a small extent on relatively rich sandy soils. Ground-water levels are mostly deep.

Sampling and analyses
At each site, composite samples were taken, consisting of 10 sub-samples for the humus layer (divided in a L& F and H horizon) and of 20 sub-samples for the mineral soil at depths of 0- 30 cm, 30 - 60 cm and 60 - 100 cm. The number of sub-samples (20) for each composite soil sample was based on the results from a comparative study of three methods to extract soil solution. The humus layer was sampled with a cylinder of steel with a diameter of 14.8 cm. For every sub-sample the thickness of the litter (L), fermented (F) and humus (H) horizon plus the total thickness was noted. Where the thickness of the humus horizon was more than 1 cm, the humus horizon was sampled.

Contents of all major nutrients, i.e. C, N, P, K, Ca, Mg and S were measured for the humus layer, whereas contents of C, N and P were also measured for the mineral layer. To gain insight in the buffer characteristics of the soil, the exchangeable cation contents (H, Al, Fe, Ca, Mg, K, Na and NH_4) and the CEC were measured both in the humus layer and the mineral topsoil. In the mineral layer the pools of readily dissolvable Al and Fe hydroxides were also measured, whereas the content of important heavy metals, i.e. Pb, Cd, Zn, Cu, Cr and Ni were determined for the humus layer. In the soil solution, all the major cations and anions were measured, i.e. H, Al, Fe, Ca, Mg, K, Na, NH_4, NO_3, SO_4, Cl and $RCOO^-$.

Chemical composition of the humus layer

Pools, thickness and bulk densities of organic matter
- Pools of organic matter in the humus layer varied mostly between 20–110 $ton.ha^{-1}$, indicating that parts of the forest stands are in the phase of organic matter accumulation.
- The humus layer mainly consisted of an F horizon with overlying freshly fallen leaves or needles (L horizon) with a much lower bulk density than the compacted humified H horizon. Thickest humus layers were found under Japanese larch, whereas thinnest median humus layers were found under black pine
- The median bulk density of the humus layer ($124\ kg.m^{-3}$) was slightly lower than data reported in the literature. This is most likely due to a relatively thick layer of loose fresh leaves or needless in the litter layer.

Contents, ratios and pools of organic carbon and nutrients
- Elevated S and N deposition is reflected by the chemical composition of the humus layer, with high contents of N and S, relatively low contents for P and Ca and very low contents for Mg and K.
- C/N ratios varied mostly between 20 and 30, which is relatively low, thus indicating the impact of high N inputs. Nevertheless, considerable N immobilisation may still take place in most of the sites. This is in accordance with results from input - output budgets, which indicate that on average ca 80% of the incoming N is retained in the ecosystem.
- C/S ratios varied mostly between 150 and 250, indicating that net S mineralisation is likely to be considerable. This is in accordance with results from input-output, which indicate that on average all the incoming SO_4 is leached from the system.
- C/P ratios were very high and varied mostly between 450 and 950, indicating that net mineralisation of P is likely to be very small, and that P deficiencies in these forest soils are likely. This is in accordance with the results of foliar P contents.
- The impact of humus layer horizon and tree species on nutrient contents and nutrient ratios was small. For oak the N, Ca, Mg and K contents were higher than for the other species. The median pools of carbon and nutrient in the LF horizon were, however almost three times the median pools found in the H horizon.

Soil acidity and exchangeable cations
- Results for the pH in a water extract and in a KCl extract generally varied between 3.5 and 5 and between 2.5 and 4, respectively. The pH values in the H horizon were lower than in the LF horizon. The impact of tree species was small.
- The cation exchange capacity (CEC) of the humus layer varied mostly between 200-400 $mmol_c.kg^{-1}$, whereas the CEC normalised to the organic matter content ranged between 2.4 and 8.0 $mmol_c.kg^{-1}$ per % organic matter, which is low compared to literature data. The CEC varied only slightly between humus layer horizons and tree species.
- Exchangeable cations on the adsorption complex were generally dominated by protons (on average approximately 50%) followed by Ca (on average approximately 25%). Exchangeable Al contents were relative low, since there is no mineral pool of Al in the organic layer. The H horizons had almost twice as low exchangeable Ca, Mg, K, Na and NH_4 contents as the LF horizons. Tree species, however, hardly affected exchangeable cation contents.
- The exchangeable pool of base cations varied mostly between 4 and 20 $kmol_c.ha^{-1}.yr^{-1}$. Considering a net acid input of ca 5.0 $kmol_c.ha^{-1}.yr^{-1}$ on Dutch forests in 1990, this pool is quite limited.

Contents and pools of heavy metals
- Approximately 95% of the forest stands do have contents of Pb, Cd, Cu and Zn in the humus layer that are higher than those observed in unpolluted areas. High contents were mainly located in the strongly polluted Kempen area in the southern part of the Netherlands. Contents of Cd and Zn in the humus layers were highly correlated indicating co-emission and co-deposition of these metals.
- Differences between heavy metal contents in LF and H layers were relatively small. Contents of Pb, Cd, Cu and Zn, in humus layers generally decreased going from spruce forests to pine forests to deciduous forests, but such a trend was not found for the heavy metal pools
- In general, the humus layers are most strongly polluted with Pb, followed by Zn, Cd and Cu. Toxic effects of elevated metal contents on soil microbiota and soil invertebrates seems quite unlikely, except for Pb, but they may retard decomposition, thus lowering the availability of nutrients.
- Estimated average annual deposition rate of heavy metals, derived by dividing the heavy metal pool in the humus layer with the age of the trees, were generally higher than those simulated by atmospheric deposition models. This is likely due to the higher surface roughness of forests compared to low vegetation.

Chemical composition of the mineral topsoil

Contents and pools of organic matter, carbon and nutrients
- Compared to the humus layer, the organic matter and carbon contents in the mineral soil are much lower, but the pools of both organic matter and carbon are generally twice to thrice as large, because of the much higher bulk densities of the mineral soil. The organic carbon contents were higher in more wet or acid soils.

- Nitrogen contents in organic matter were slightly lower in the mineral soil (median value of 20 $g.kg^{-1}$), than in the humus layer (median value of 22 $g.kg^{-1}$), indicating the impact of N deposition on N contents in the humus layer.
- Despite the high N contents in the humus layer, the C/N ratio was generally lower in the mineral soil, indicating the stronger degree of humification. C/P and N/P ratios were much lower in the mineral soil, since P not only occurs in organic matter but also in mineral form.
- C and N contents and C and N pools generally increased in the direction Arenosols<Podzols<Anthrosols< Gleysols, reflecting partly the fertility of those soil types. Furthermore, the total P content and P pool was much larger in the Fimic Anthrosols, indicating the impact of long-term fertilisation in the past.

Soil acidity and exchangeable cations
- The pH in a water extract and in a KCl extract generally varied between 3.5 and 4.5 and between 2.5 and 4.0, respectively, in the mineral topsoil. Differences between pH-H_2O and pH-KCl were approximately 0.5, being less than in the humus layer.
- The CEC in the mineral topsoil (median of 32 $mmol_c.kg^{-1}$) was much lower than in the humus layer (median of 302 $mmol_c.kg^{-1}$) because of the much lower organic matter content in the mineral layer. The CEC, normalised to 1% of organic matter, was, however, higher in the mineral topsoil (median of 8.3 $mmol_c.kg^{-1}$) than in the humus layer (median of 4.7 $mmol_c.kg^{-1}$). This was also the case with the exchangeable cation pool because of the much higher bulk density of the mineral layer.
- The proton and base saturation was much lower and the Al saturation was much higher in the mineral topsoil compared to the humus layer. This indicates that Al mobilisation is the dominant buffer mechanism in the mineral topsoil, whereas exchange of protons with base cations dominates in the humus layer. The exchangeable cation pools generally decreased according to Al>H>Fe>Ca followed by Mg, K, Na and NH_4
- Al saturation was considerably higher in the more acidic Arenosols and Podzols (median of 65-75%) than in the more buffered Anthrosols and Gleysols (median of 40-55%).

Contents and pools of oxalate extractable aluminium, iron and phosphorus
- The readily available, oxalate extractable, Al pool varied mostly between 100- 1000 $kmol_c.ha^{-1}$. Considering the net acid input in 1990, this Al pool can be depleted within a period of within several decades to centuries.
- The ratio of oxalate extractable P to Al and Fe varied mostly from 0.02-0.18, implying a phosphate saturation percentage between 4-36%. This is much lower than in agricultural soils with a large input of P by animal manure. Highest percentages were found in the Fimic Anthrosols, in which the contents of oxalate extractable Al were low, whereas the oxalate extractable P contents were high.

Chemical composition of the soil solution

Element concentrations
- SO_4 concentrations were higher than the NO_3 concentrations indicating the dominance of SO_4 in soil acidification.
- NO_3 concentrations were generally higher than a target value of 0.4 $mol_c.m^{-3}$, used in the Netherlands with respect to drinking water quality.
- Al concentrations were mostly above a critical value of 0.2 $mol_c.m^{-3}$, related to toxic effects on roots.
- Differences between ion concentrations in the topsoil and subsoil were small, except for the pH, which is lower in the topsoil.

Element ratios
- The $(NH_4 + NO_3)/SO_4$, indicating the contribution of both compounds to soil acidification, is mostly below 1.0 (median value was 0.57), whereas this ratio was larger than 1.0 in the atmospheric input in the Netherlands in 1990. This implies that a considerable amount of nitrogen is retained as a result of uptake, immobilisation and/or denitrification.
- The NH_4/NO_3 ratio, indicating the degree of nitrification, was mostly below 1.0 (median value was 0.21). This indicates a strong degree of nitrification and/or preferential NH_4 uptake, since the NH_4/NO_3 ratio in the atmospheric input in the Netherlands was (much) larger than 1.0 in 1990.
- The $Al/(SO_4 + NO_3)$ ratio, indicating the degree of Al mobilisation by acidic inputs, varied strongly (from 0.01-0.8 with a median value of 0.45). Most likely, the lower values for the $Al/(SO_4 + NO_3)$ ratio are the result of a high base cation (mainly Ca) input from the atmosphere. Liming/fertilisation in the past may also play a role.
- The median Al/RCOO ratio was 3.4, indicating that toxic free Al dominates the Al speciation compared to non-toxic organically complexed Al.
- Median values for the Al/Ca ratio are 1.1 in the topsoil and 1.4 in the subsoil. This is higher than the average critical value of 1.0. This implies that adverse effects of Al on roots are likely. The median Al/(Ca+Mg+K) ratios are 0.41 and 0.53 in the topsoil and subsoil, respectively.
- The ratio of NH_4 to K and of NH_4 to Mg nearly always remained below a critical value of 5. Median values are even near or below 1.0 for both ratios in topsoil and subsoil. This is likely due to preferential MH4 uptake and nitrification.

Relationships between soil solution chemistry and environmental factors
- The concentrations of most ions in soil solution were especially influenced by tree species. Lowest pH values and highest concentrations in NO_3, SO_4 and Al occur below Norway Spruce and Douglas Fir. The reverse is true for Oak and Beech, whereas Japanese Larch, Scots Pine and Black Pine occupy an intermediate position. Differences between tree species are probably caused by increased dry deposition and evapotranspiration.

- There impact of the estimated average deposition level in grids where the forest were located on concentrations in NO_3, SO_4 and Al, but it appeared to be smaller than the impact of tree species.
- For most ions, concentrations increased with an increase in tree height and canopy coverage, most likely due to an increase in dry deposition and evapotranspiration.

Relations between ion concentrations in soil and soil solution

Correlation between ion concentrations in soil and soil solution
- In the considered acidic sandy soils, there is a clear linear relationship between the H+Al concentration and the concentration of SO_4+NO_3, indicating that the net acidic input by S and N compounds is mainly neutralised by Al release, while the remaining part is leached as protons.
- In the mineral topsoils, there was a clear correlation between dissolved cation (H, Al, NH_4, Ca, Mg, K, Na) concentrations and exchangeable cation fractions at the adsorption complex (r= 0.4-0.7), with the exception of Al.
- There was no clear relationship between the dissolved nitrate concentration in the subsoil and the C/N ratio of the forest floor (humus layer), which is contrary to results published in the literature.

Aluminium dissolution and cation exchange
- In the mineral topsoil, Al concentrations in the soil solution can not be described with the Gibbsite equilibrium equation, that is generally used in soil acidification models. The slope of the pAl-pH relationship is near 1, which implies that Al release in the mineral topsoil is most likely dominated by equilibrium complexation reactions with organic matter.
- In the mineral subsoil, the slope of the pAl-pH relationship was close to 3.0, which would indicate equilibrium with Gibbsite, but the equilibrium constant was clearly lower than that of gibbsite (undersaturation).
- There is a large variation in exchange constants, specifically for H and Al. The affinity of the exchange complex is clearly much higher for protons than for the other monovalent cations. The influence of soil type appeared to be small with respect to the affinity for monovalent and divalent cations, but the affinity for Al and Fe was clearly lower in the two Gleysoils than in all other soils.

Phosphate adsorption
- In forest soils, with low dissolved inorganic P concentrations (up to 2 mg.l^{-1}), the interaction between soil solid phase and soil description can best be described with a non-linear Freundlich equation. This gives a better prediction of the dissolved inorganic P concentration than the Langmuir description used in agricultural soils.
- P adsorption is lower in acidic forest soils than in slightly acid agricultural soils. There was, however, no relationship between the range in adsorption constants and the pH or organic matter content.

1   Introduction

Impacts of elevated deposition levels of SO_x, NO_x and NH_x on the chemical composition of forest soils, and its effect on forest vitality, has received much attention in the Netherlands during the period 1980-1990 (Heij and Schneider, 1991). However nearly all research activities have been carried out on a limited number of intensively monitored forest sites. These sites are not representative for Dutch forest as far as deposition level, stand characteristics, such as tree species, and site characteristics, such as soil type, are concerned.

The major aim of this report is to give:
(1) A nation-wide overview of the chemical composition of non-calcareous sandy forest soils occurring below major tree species and
(2) Insight in the relationship with deposition level, stand characteristics and site characteristics.

1.1   Soil acidification research in the Netherlands in the period 1985-1990

Research on soil acidification and nitrogen accumulation at various forest sites in the Netherlands has mainly been carried out within the Dutch Priority Programme on Acidification that started in 1985. Major aims of these research efforts were the assessment of (i) the impact of atmospheric deposition on the soil and soil solution chemistry and (ii) the indirect (soil mediated) effects of atmospheric deposition on forest vitality, as discussed below.

Impact of atmospheric deposition on the soil and soil solution chemistry
Impacts of atmospheric deposition on the soil have been derived by the determination of input-output budgets of major ions, i.e. sulphate (SO_4), nitrate (NO_3), ammonium (NH_4), aluminium (Al), base cations (Ca, Mg, K, Na) and protons (H). This was done to gain insight in (1) the fate of S and N in the ecosystem and (2) the buffer mechanism in the soil to neutralise the acid input associated with it. Input fluxes were derived from fortnightly and monthly measurements of the chemical composition of throughfall water, multiplied by the throughfall flux. Output fluxes were derived by multiplying monthly measurements of the soil solution composition at various depths with simulated unsaturated soil water fluxes (Van Grinsven et al., 1987). An overview of the budget studies thus carried out is given in Van Breemen and Verstraten (1991). Research results of nine intensively monitored sites showed that the average SO_4 input equals the average SO_4 output, suggesting that the forests are sulphur-saturated. Nitrogen saturation only occurred at one site. On average about 1.5 kmol (± 20 kg) $N.ha^{-1}.yr^{-1}$ was removed from the soil, either by uptake or denitrification, or retained in organic matter by immobilisation. Furthermore, on average 70% of the amount of SO_4 and NO_3 leaching from the system was accompanied by Al. This indicates that Al mobilisation is a major buffer mechanism

in non-calcareous sandy forest soils in the Netherlands (Van Breemen and Verstraten, 1991; Heij et al., 1991).

Input-output budgets were also obtained for eight Douglas stands. This was done by comparing the input by throughfall with the output calculated by multiplying the concentration at the bottom of the root zone in April with the annual precipitation surplus simulated by a hydrologic model (Reurslag et al., 1990). Results, which are also given in Van Breemen and Verstraten (1991), showed that four of the eight Douglas stands are nitrogen saturated. Nitrogen saturation appeared to be correlated with an increased nitrogen deposition level.

The dominating role of Al-mobilisation in the investigated forest sites was due to the low base saturation of the adsorption complex (nearly always less than 20%). Laboratory experiments with soil samples from these sites showed that the Al-pool responsible for buffering is mainly limited to organically bound Al and amorphous Al-hydroxides (Mulder et al., 1989). This implies that major physical and chemical soil changes are presently taken place by the depletion of this limited pool.

Impacts of atmospheric deposition on the soil solution can also directly be inferred from these studies i.e. high concentrations of Al, SO_4 and NO_3 increasing with depth and low pH values (generally below 4). In the topsoil NH_4 concentrations were also relatively high, but nearly negligible below the root zone. Furthermore distinct seasonal patterns were observed i.e. high concentrations in the summer period, due to evapotranspiration and relatively low concentrations in the winter period (Van Breemen and Verstraten, 1991). Analyses of the data of several intensively measured sites indicated that the concentration in early spring (March, April) is generally most representative for the annual flux weighted solute concentration.

Indirect effects of atmospheric deposition on forest vitality
The indirect effects of atmospheric deposition have been studied by assessing the relationship between the soil and soil solution composition and forest vitality characteristics such as needle loss, needle colour and needle composition and root characteristics such as mycorrhizae frequency and root length. This type of research has been carried out on eight Douglas stands, mainly on podzolic soils, during the period 1986-1987 (Kleijn et al., 1989).

The soil solution composition was measured four times i.e. in June, September and December 1986 and in April 1987. Unlike the intensively monitored sites, where the soil solution was extracted with porous cups permanently installed in the field, soil solution was extracted by centrifugation from a previously sampled soil. This was done to enable measurements in mid-summer and to put more emphasis on spatial variability in the field. Forest vitality characteristics, needle composition and root characteristics were measured only twice in this period. Results on the soil and soil solution composition are given in Kleijn and De Vries (1987) and Kleijn et al. (1989). As with the intensively monitored sites, high concentrations of Al, SO_4 and NO_3 were found, especially in the summer. Furthermore spatial variability appeared to be high indicating that at least 5 measurements are needed to estimate the mean log-

concentration with an error below 20% (Kleijn and De Vries, 1987). Needle composition was characterised by high N contents and relatively low Mg, K and P contents. Fine roots were characterised by a low mycorrhizae frequency and a low (specific) root length.

Comparison of the various results gave an indication that a decrease in forest and root vitality characteristics is associated with high N contents in the needles and high Al and NH_4 concentrations in the topsoil. In this context, the ratio of Al and NH_4 to the nutrient base cations Ca, Mg and K appeared to be important. A similar conclusion was made by Roelofs et al. (1985) who compared the chemical composition of water extracts from the forest topsoil with forest vitality characteristics of black pine at 58 locations. The effect of increased ratios of Al, and NH_4 to Ca, Mg and K on forest vitality is also proven by laboratory experiments, which show that it causes a decrease in the uptake of nutrient base cations (Boxman and Van Dijk, 1988).

Modelling research
The results obtained from the various field and laboratory studies have been used to (i) determine the long term impact of atmospheric deposition on soils using simulation models and (ii) assess critical loads for nitrogen and sulphur (total acid) on forest soils, as discussed below.

Long term impacts of atmospheric deposition on forest soils have been derived using dynamic soil acidification models. An overview of the results thus derived is given in De Vries and Kros (1991). Results show that the present deposition level may cause depletion of Al-hydroxides in the forest topsoil within several decades (De Vries and Kros, 1989b). Furthermore, a reduction on the deposition level appears to cause a relative fast improvement in the chemical composition of the soil solution (De Vries and Kros, 1989a).

Critical loads for nitrogen and total acid on forest soils have been derived from critical values for the Al concentration and the ratio of Al and NH_4 to base cations, using steady-state soil acidification models. Again an overview of the results is given in De Vries and Kros (1991). Results show that the present acid deposition level is much higher than the critical load for non-calcareous forest soils.

1.2   Aim of the present research

Present knowledge and gaps therein
Soil acidification research conducted so far has greatly increased our knowledge about the present impact of atmospheric deposition on non-calcareous sandy forest soils. However the sites that were studied are not representative for the Dutch forests. First of all, most sites were located in areas with intensive animal husbandry with a bias towards high N loads. Secondly, the tree species studied was mainly Douglas fir, since the Dutch Priority Programme on Acidification was particularly focused on this tree. However Douglas fir is not representative for needle forest as

far as hydrological characteristics are concerned. The high needle amount (and canopy coverage) causes a large rate of interception evaporation leading to low water fluxes and a relatively large input of elements by dry deposition, thus increasing soil solution concentrations. Finally, both soil type and ground water level of most intensively studied sites are not representative for sandy forest soils in the Netherlands. They are either too loamy or too wet.

Furthermore, the research carried out until now has increased our insight in the relationship between forest vitality characteristics and the soil and soil solution composition. However, the amount of sites studied has been too few to establish really convincing correlations. The necessity to gain insight in such relationships is also pointed out in an international context by the International Co-ordinated Programme (ICP) on Assessment and Monitoring of Air pollution effects on Forests, that is part of the Working Group on Effects of the UN-ECE Convention on Long Range Transboundary Air Pollution.

Finally, model simulations, using the various field and laboratory data, have improved our knowledge about the long-term impacts of atmospheric deposition on soil and about the magnitude of critical loads. However, in order to evaluate emission-deposition reductions and to establish critical loads on a regional scale, more insight is needed in the regional variability of soil and soil solution composition below forest.

Research aims
In order to overcome the various limitations of the research carried out so far a national assessment has been made of the chemical composition of the needles, humus layer, mineral (top)soil and soil solution of forest ecosystems. The various characteristics were measured in 150 stands for seven major tree species in The Netherlands (Scots pine, black pine, Douglas fir, Norway spruce, Japanese larch, oak and beech) on non-calcareous sandy soils. The limitation to these soil types is because they are most sensitive to acidification and N accumulation and most Dutch forests (about 85%) are located on these soil types (De Vries et al., 1989). Forest vitality characteristics were known for the stands as they are part of the forest vitality study by the State Forestry Service.

Major aims of the research are the determination of the:
- Variability in soil and soil solution composition in relation to deposition level, stand characteristics and site characteristics.
- Relationship between soil and soil solution composition and forest vitality characteristics for major tree species.
- Regional assessment of input-output budgets for sulphur, nitrogen, aluminium and base cations.
- Mapping of soil and soil solution parameters on a national scale using relationships with stand and site characteristics available in GIS systems.

In this report, results of the inventory are given related to the first major aim. Results related to the other aims are given in Hendriks et al. (1994), De Vries and Jansen

(1994) and Leeters et al. (1994). Originally, the reported was aimed to be part of a series with the above-mentioned reports. However, due to its extreme delay, it is now part of a series of two reports in which the second report focuses on the variability in soil and soil solution composition of 200 forest stands in 1995 (Leeters and De Vries, 2001). This is specifically done because approximately 125 stands are overlapping in 1990 and 1995, thus allowing a direct comparison between the results obtained.

1.3   Contents of the report

Chapter 2 gives an overview of the methodological approach. This includes the choice of the locations, the description of stand and site characteristics in the field and the methods used for soil sampling, solution extraction and chemical analyses. Chapter 3 gives an overview of the locations of the various forest stands with a description of the deposition level, stand and site characteristics. Results for the humus layer are given in chapter 4. This includes the variation in total contents of major nutrients (N, P, K, Ca, Mg, S), exchangeable cation contents (H, Al, Ca, Mg, K, Na, and NH_4) and important heavy metals (Pb, Cd, Cu, Zn, Ni and Cr). The chemical composition of the forest topsoil (0 - 30 cm) is reported in chapter 5. This includes the total contents of N and P and the buffer characteristics of the soil, i.e. the exchangeable cation contents and the amount of readily dissolvable Al (and Fe). Chapter 6 gives an overview of the variation in the soil solution composition (H, Al, Ca, Mg, K, Na, NH_4, NO_3, SO_4, Cl, HCO_3 and RCOO) for the forest topsoil (0 - 30 cm) and subsoil (60 - 100 cm). Here, special emphasis is given to the relation with deposition level, tree species, and stand and site characteristics. Relations between the chemical composition of the solid phase in different layers and between the soil solution and the soil solid phase in the mineral topsoil are given in chapter 7. Finally, a discussion with conclusions is given in Chapter 8.

2 Methods

2.1 Selection of the locations

Criteria
The soil solution composition is mainly a result of the composition of precipitation and throughfall water (deposition) and the interaction with the mineral soil. Locally the deposition on the soil is determined by stand characteristics such as tree species (Ulrich, 1984), canopy coverage (Draayers et al., 1992), structure of the stand (Van Ek and Draayers, 1991), height of the trees (Stevens, 1987), distance of trees to the forest edge (Hasselrot and Grennfelt, 1987; Draayers et al., 1988) and surrounding land use (Boumans and Beltman, 1991). The soil interaction depends on site characteristics such as buffer capacity of the soil and ground water level. Buffer characteristics such as CEC and base saturation strongly determine the ratio of Al to base cations in the soil solution, whereas the ground-water level may influence nitrogen transformation processes, i.e. mineralisation, nitrification and denitrification. Furthermore the occurrence and coverage of forest vegetation might influence these processes through effects of light and temperature.

In order to isolate all different influences, data from all possible combinations of stand and site characteristics are needed. This is practically impossible because several stand and site characteristics are correlated, so not all possible combinations do really exist. Furthermore the capacity of laboratory, time and money was limited. The number of locations was fixed to 150.

Starting with all forest stands on non-calcareous soils belonging to the forest inventory on vitality in 1988 or 1989, we decided to choose our locations by logical judgement. Since we aimed to gain insight in the relationship of the soil (solution) composition with deposition level, stand characteristics, such as tree species, and site characteristics, such as soil type and ground-water level, we used the following criteria:
(1) A large range in atmospheric deposition levels.
(2) Inclusion of all major tree species, covering at least 80% of Dutch forests i.e. Scots pine, black pine, Douglas fir, Norway spruce, Japanese larch, oak and beech, with an optimal range in forest vitality.
(3) A large number of different soil types and ground water levels to ensure a large range in buffer capacity of the soil.

Information about the atmospheric deposition of SO_x, NO_x and NH_x for the year 1989 was derived from the National Institute of Public Health and Environmental Protection (RIVM). Data were provided for each 5 km x 5 km gridcell on the basis of calculations with the model DEADM (Erisman, 1991). Data about the deposition of base cations and chloride, which partly neutralise the acid input, were also provided by the RIVM for each 10 km x 10 km gridcell. These data were derived by inverse distance interpolation of values from 22 monitoring stations for the period

1978-1985 (KNMI-RIVM, 1985). Information about the vitality of the forests, which has been gathered since 1984 by the State Forestry Service, was derived from this institute. We used the data of the inventories of 1988 and 1989. Information about soil type and ground water levels was available at the Winand Staring Centre (SC). We used the soil map of the Netherlands scale 1 : 50 000.

When we started this research the laboratory for soil and ground water of the RIVM already had chosen about 200 locations on non-calcareous sandy soils covered with forest or natural vegetation, in order to determine the quality of the phreatic ground water. They had chosen their locations by ensuring an optimal range in atmospheric N deposition (Boumans and Beltman, 1991). We used their locations as a start for the choice of our locations. Consequently we first describe their method, used to select (forest) sites.

Pre selection of the locations by RIVM
In order to select their locations a database of 500 m. x 500 m. gridcells was build, containing information about the total atmospheric deposition of nitrogen and land use. Land use was included because of its influence on the locale emission and deposition. When there is more agriculture within a grid, NH_4 emission is likely to be higher and through that the deposition. Furthermore, grids with more forest will have a greater input of dry deposition than those with more low vegetations, such as heather.

For every 500 m x 500 m gridcell the land use was given as the area of agriculture, forest and other non-agricultural lands using data from the national soil statistics (CBS, 1987). Since the emission and deposition in the surrounding gridcells influence the deposition within a gridcell, the area of agriculture, forest and other nature grounds was accounted for as the sum of the areas in the gridcell itself and the areas of the eight surrounding gridcells. The areas of the different land uses were divided into five classes i.e. 0 - 45, 45 - 90, 90 - 135, 135 - 180 and 180 - 225 ha. The total deposition of nitrogen ($NH_x + NO_x$) per 500 m x 500 m gridcell was also divided into five classes i.e. < 2.5, 2.5 - 3, 3 - 3.5, 3.5 - 4 and >4 $kmol.ha^{-1}.year^{-1}$. Estimates of the atmospheric N deposition were not derived from present information (see before). In this case data of 1984 were used based on TREND model calculations (Asman and Van Jaarsveld, 1990).

The so built database with of 500 m x 500 m gridcells was used for the selection of the locations (gridcells) using two criteria: (1) they should be representative for the Netherlands and (2) they must show as much as possible difference in nitrogen deposition levels. Furthermore, grids containing sites where throughfall monitoring was performed or sites with forest stands surveyed for vitality in 1988 or 1989 were preferentially selected. A detailed description of the selection procedure used is given in Boumans and Beltman (1991). Finally they chose 193 locations. From these 193 locations, 25 where dropped because either they did not belong to the property of the State Forestry Service (for the practical reason of getting permission for sampling) or because the ground-water level was below 6 m (for the practical reason that in that case the vacuum method used for sampling didn't work). Deep ground-

water levels occurred mainly in the central part of the Netherlands i.e. at the Veluwe. At the end 168 locations where found fit for sampling, containing 118 locations with forest stands where vitality characteristics (needle loss and needle colour) were determined either in 1988 (29) or 1989 (89).

Choice of the locations in this study
The 118 RIVM locations mentioned above formed the starting-point for our choice of locations. We tried to keep as many as possible locations common. However, 5 locations had to be dropped because corrected information about the forest stands showed that these stands were not included in the vitality survey. Whether they where to young (< 5 years) or they had turned into coppice or they where inaccessible. So 113 RIVM locations were left. However, only 100 locations included the seven tree species that we wanted to investigate. Furthermore, since we aimed at an optimal distribution of deposition levels and the vitality class for each tree species and an optimal distribution in soil type and ground water level, we dropped 11 RIVM locations of Scots pine and chose others instead. Finally 89 locations were left for sampling both soil and phreatic ground water. For choosing supplementary locations we used a forest vitality database with information on stand characteristics such as tree species, age and vitality class while adding site characteristics such as soil type and ground-water level by an overlay with a soil data base. Contrary to the RIVM the restriction that the location had to belong to the State Forestry Service was not used. Furthermore some extra locations on the Veluwe were chosen, their restriction in regard to the deep ground water didn't apply to the sampling for soil and soil solution.

Table 1 gives an overview of the train of thoughts concerning the distribution of tree species over our 150 locations.

Table 1   Distribution of seven major tree species over 150 locations

Tree specie	1[1]	2[2]	3[3]	4[4]	5[5]	6[6]	7[7]
Scots pine	44	66	34	66	66	45	(23 + 22)
Black pine	6	9	10	10	10	15	(10 + 5)
Douglas fir	6	9	10	10	10	15	(10 + 5)
Norway spruce	5	8	11	11	11	15	(11 + 4)
Japanese larch	6	9	11	11	11	15	(11 + 4)
remaining conifers	2	3	1	3			
Oak	17	25	22	25	25	30	(22 + 8)
Beech	3	5	2	5	5	15	(2 + 13)
remaining deciduous	11	16	11	16			
Total	100	150	113	157	138	150	(89 + 61)

[1]   Distribution (%) over the non-calcareous sandy soils in the Netherlands
[2]   Distribution of 150 locations according to the national percentages.
[3]   Distribution of the RIVM gridcells
[4]   Locations needed according to distribution RIVM gridcells and national distribution
[5]   Like 4 without remaining conifers and remaining deciduous trees.
[6]   Chosen distribution
[7]   (RIVM gridcells + supplementary chosen locations).

By overlaying data on tree species in 500 m x 500 m gridcells (CBS, 1985) with data on soil types in 100 m x 100 m gridcells (SC, soil map of the Netherlands

scale 1 : 50 000) we got information about the distribution of tree species over the non-calcareous sandy soils (Table 1). The idea was to divide the 150 locations as much as possible according to this distribution. Since we chose to include only seven major tree species, all other coniferous and deciduous trees were excluded. Comparison of the Columns 2 and 5 shows that the distribution of the locations over the tree species nearly matched the national distribution of tree species on non-calcareous sandy soils. However this resulted in only 5 locations with beech. To ensure a sufficiently large range in deposition level and vitality class within each tree species, this number is too few. For black pine, Douglas fir, Norway spruce and Japanese larch the same argument counts, the more because little is known about the response of these tree species on soil acidification. Consequently, we decided to divide the locations in the proportion 4:3:3 over three major groups of tree species i.e. fir-trees (Scots pine, black pine), more demanding conifers (Douglas fir, Norway spruce, Japanese larch) and deciduous trees (oak, beech) so that every tree species includes at least 15 locations.

2.2   Characterisation of the locations

At each site an indication of the position of the forest stands and of various stand and site characteristics, influencing the deposition level on a forest stand or the processes occurring in the forest soil (section 2.1), was made. Examples of relevant characteristics influencing atmospheric deposition are tree height (Stevens, 1987), canopy coverage (Draayers et al., 1992), distance of trees to the forest edge (Hasselrot and Grennfelt, 1987) and surrounding soil use (Boumans and Beltman, 1991). Examples of stand characteristics influencing buffer processes in the soil are soil type and ground water level classes (Leeters et al., 1994). More information on the characteristics that were assessed is given below.

Surrounding land use
The following aspects were assessed with respect to the position of the forest stand and surrounding soil use:
-   The presence of open spots or forest roads
-   The distance to the nearest forest edge i.e. 0 - 20 m, 20 - 40 m, 40 - 60 m, 60 - 80 m, 80 - 100 m, > 100 m
-   The position of the nearest forest edge with respect to the site
-   The land use at the nearest forest edge i.e. maize field, grassland, arable land, non-agricultural land

Stand characteristics
The following aspects were assessed with respect to stand characteristics:
-   The canopy coverage (the projection of the canopy on the soil), i.e. < 50%, 50 - 75%, > 75%. For the deciduous tree species (including Japanese larch) the canopy coverage may be less reliable because of the sampling period (February-May).
-   The estimated height of the stand, i.e. 0 - 5 m, 5 - 10 m, 10 - 15 m, 15 - 20 m, > 20 m

- The coverage of the soil by short vegetation, i.e. 0%, 0- 20%, 20 - 60%, 60 - 100%, 100%
- The character of the short vegetation, i.e. grasses, indicators of eutrophication, the rest (an indication of the present short vegetation with a score list was sometimes given but these results varied strongly, depending on the knowledge of the field worker).

Site characteristics
The following aspects were assessed with respect to site characteristics:
- Representative descriptions of the soil profile for the first 120 - 180 cm. The soil was characterised by the occurrence and thickness of A, B and C-horizons, by the estimated percentage organic matter, loam (texture) and the median value of the sand grains (granular). The horizon nomenclature according to De Bakker and Schelling (1989) was used. This nomenclature is a slight modification of the system of the International Society of Soil Science (FAO, 1988).
- The ground-water level classes, used for characteristic combinations of mean highest level in the winter and the mean lowest level in the summer (De Vries and Van Wallenburg, 1990).

2.3   Sampling of the soil

Sampling period
The soil was sampled in the period February the 15 to May the 16, 1990. This period was chosen based on results of intensive soil solution monitoring in Hackfort (Van Breemen et al., 1988). At these locations (sandy soils), the flux weighted concentrations of soil solutions components were calculated monthly by multiplying the flux of the unsaturated zone (simulation with the SWATRE model) with the measured concentrations in the soil solution. Analyses of the data of several intensively measured sites indicated that the concentration in early spring (March, April) is generally most representative for the annual flux weighted solute concentration (cf. section 1.1). The representativity of this period differed for each component of the soil solution depending on the yearly flux in concentration of that component. The pH and Fe concentration didn't change much during the seasons. Na and Cl had high concentrations in summer and fall. Ca, Mg, Al and NO_3 had higher concentrations in fall and winter. The concentration of K was lower in summer (uptake by vegetation) than in the rest of the year. The concentration of NH_4 differed strongly in time and space. Concentrations of SO_4 and H_2PO_4 were higher in summer whereas the concentration SO_4 was also high in winter but then mostly in the deeper soil (Van Breemen et al., 1988).

In order to have some idea about the variation in time during the sampling period we repeated sampling on several locations. Two locations (one in the province Overijsel and one in the province Brabant) where sampled three times. Eight locations spread over the country where each sampled twice.

Sampling depths

Samples were taken of the humus layer and three, mineral soil layers i.e. 0 - 30 cm (topsoil), 30 - 60 cm and 60 - 100 cm (subsoil). In the mineral topsoil (0 - 30 cm) the chemical composition of both solid phase and the soil solution was analysed. In the mineral soil layer 60 - 100 cm only the chemical composition of the soil solution was analysed. From the mineral soil layer 30 - 60 cm no analyses were performed, but the samples were stored in the soil archive of the Winand Staring Centre (the solid phase can eventually be analysed later). The chemical composition of the solid phase was limited to the mineral topsoil where most of the fine roots, responsible for nutrient uptake, do occur and soil acidification and N accumulation is likely to be most intensive. The soil solution was also measured in the subsoil below the root zone to assess input-output budgets for the forest sites and to derive a relationship with the ground-water quality measured at most of the sites.

Sampling number

At each site a composite sample of each layer was taken consisting of 20 sub-samples. This was done to minimise the influence of spatial variability. An evaluation of the Hackfort data showed that the spatial variability within the plots was the dominant source of error (Van Breemen et al., 1988). We chose the sample points within the forest stand according to a steady pattern. In the middle of the stand a square of 20 m x 20 m was delineated. Along the sites of this square, turning from the outside to the inside, 20 samples were taken at a mutual distance of 5 meters.

The number of sub-samples (20) for each composite soil sample was based on the results from a comparative study of three methods to extract soil solution (Verhagen and Diederen, 1991), i.e. by suction cups, as used in intensively monitored sites (e.g. Van Breemen et al., 1988), by centrifugation as used in this study (e.g. Kleijn et al., 1989; cf. section 2.3) and by aqueous extraction at a 1:3 soil solution ratio as used in correlative field studies (e.g. Houdijk, 1990). The three methods were compared at two forest stands, i.e. in Speuld and IJsselstein, at fifteen spots that were situated two meters apart, at two depths (topsoil and subsoil).

Results for the margin of error of the estimated mean concentration at each depth was nearly always between 10 and 30% (Table 2). The margin of error, D, was calculated according to (Hammond and McCullagh, 1978):

$$D = t_\alpha \cdot S / \sqrt{n} \tag{1}$$

where:
t_a = tabled Student t-factor for a given uncertainty a
S = standard deviation in percent of the mean value
n = number of observations

with t_a = 1.96 (a=0.05 i.e. 5% uncertainty) and N=15 (15 observations at each soil depth).

Table 2   The margin of error of the mean concentration of major elements at four soil depths

Depth (cm)	Location[1]	Margin of error (%)									
		H	Al	Ca	Mg	K	Na	NH$_4$	NO$_3$	SO$_4$	Cl
10	IJsselstein	26	13	11	20	17	17	31	13	19	16
20	Speuld	22	25	15	20	23	18	34	30	26	16
40	IJsselstein	23	29	21	18	17	10	31	14	16	11
60	Speuld	19	29	40	14	17	17	21	31	18	21

[1] N = 15 at each depth

The variability, and through that the margin of error, was relatively small for Na and Cl and relatively large for Al and NH$_4$. The error given in Table 2.2, i.e. approximately 20% for most elements, was considered acceptable, and consequently 20 sub-samples were taken. In order to reduce the uncertainty in the mean concentration of all elements below 20% or even 10%, the number of observations had to increase to approximately 100 and 700, respectively. This is due to the large variability in Ca concentration in the subsoil in Speuld. These numbers were considered unpractical.

During the sampling period the laboratory capacity for drying the samples of the humus layer appeared to be too small. This was a motive to reduce the sample material of the humus layer from 20 to 10 sub-samples on each location. Furthermore, Troedsson and Tamm (1969) showed that 10 samples are generally enough to reduce the uncertainty in the mean chemical composition of the humus layer to an acceptable value.

Sampling devices

The humus layer was sampled with a cylinder of steel with a diameter of 14.8 cm. For every sub-sample the thickness of the litter (L), fermented (F) and humus (H) horizon (Klinka et al., 1981) plus the total thickness was noted. Where the thickness of the humus horizon was more than 1 cm, the humus horizon was sampled apart. This was done since literature information indicated a clear difference in the chemical composition of this layer compared to the L and F layer and because the humus horizon gives information about the possibilities for appearance of certain plants. The L and F horizons were always sampled together. The green parts of the vegetation and the living roots were excluded from the sample. The material was weighed in the laboratory to derive information on the humus pool per ha for each stand

The mineral soil layers were sampled with a stabgimlet with a diameter of 2.5 cm. By taking 20 sub-samples this resulted in approximately 1 kg mineral soil, sufficient to do the aimed analyses. Practically it was difficult not to disturb the mineral soil when taking a sample of the humus layer. Therefore the samples of the mineral soil were taken nearby, but not in exactly the same spot as the sample of the humus layer.

2.4   Sampling of other forest ecosystem compartments

Foliage
At all 150 locations foliage (leaves or needles) was sampled by the Bosbureau Wageningen under supervision of the Dutch Forestry Research Institute (IBN-DLO). Sampling was done according to the guidelines of the Commission Advies Bosbemesting (Directie Bos en Landschapsbouw, 1990).

Nutrient contents in leaves and needles change during the seasons. To judge the nutrient supply the foliage was sampled in a period that the nutrient concentration is rather stable. At locations with the deciduous tree species oak and beech samples were taken of the fully matured foliage at long shoots (leaf + stalk) in August 1990. The sampled foliage of oak consisted of a mixture of spring shoots and Lammas shoots. At locations with the needle shedding conifer Japanese larch, samples were taken of the long shoots (no short shoots) in September 1990. At locations with the evergreen conifers Scots pine, black pine, Douglas fir and Norway spruce samples were taken of the half year old shoots during the period October 1990 till January 1991. The needles were removed after drying. No differentiation was made between spring shoots and Lammas shoots, but the complete annual shoots were sampled.

Nutrient contents in leaves and needles also depend on light exposition and the age of the leaf and needle. Therefore samples were taken from the upper and mid-third of the crown exposed to sunlight. Each composite sample consisted of 10 sub-samples of 10 different trees, not damaged by insects, pests, drought or late frost, neither polluted by birds and spread regularly in the forest stand. Results on the nutrient contents are given in the second report of this series (Hendriks et al., 1994).

Phreatic ground-water
The phreatic ground water was sampled by the RIVM per 500 m x 500 m gridcell. In each grid they took 10 samples every 50 meters along a transect in the biggest united area of forest and other non-agricultural lands (heather). When the transect was shorter than 450 meters, the remaining samples were taken along the middle of the transect. Every sample point lied at least 20 meters from the edge of a forest stand. In each of the 89 collective locations at least 3 ground water samples were taken in the forest stand where the vitality was observed, to compare the phreatic ground-water composition with the composition of the soil solution. Results on the chemical ground-water composition at these sites are given in the third report of this series (De Vries and Jansen, 1994).

2.5   Choice of chemical parameters and analysing methods

Parameter choice
The most important pool of nutrients in forest is the humus layer. Consequently, the contents of all major nutrients, i.e. C, N, P, K, Ca, Mg and S were measured for this layer. Contents of C, N and P were also measured for the mineral layer since the

C/N ratio is likely to increase due to the high N input (eutrophication) whereas P is an important nutrient whose availability might be limited due to acidification.

In order to gain insight in the buffer characteristics of the soil, the exchangeable cation contents (H, Al, Fe, Ca, Mg, K, Na and NH_4) and the CEC were measured both in the humus layer and the mineral topsoil. In the mineral layer the pools of readily dissolvable Al and Fe hydroxides were also measured, since it is likely that most forest soils are in the range of Al buffering (cf. section 1.1). Finally the content of important heavy metals, i.e. Pb, Cd, Zn, Cu, Cr and Ni were determined for the humus layer. This is done since heavy metal pollution, which is known to occur in forest soils (Kleijn et al., 1989), might also affect forest vitality.

In the soil solution, all the major cations and anions were measured, i.e. H, Al, Fe, Ca, Mg, K, Na, NH_4, NO_3, SO_4, Cl and $RCOO^-$.

Analysing methods
Total contents of C and N were determined by wet oxidation according to the methods of Kurmies (Kurmies, 1949) and Kjehldahl (Hesse, 1971), respectively. Total S contents were extracted in a concentrated mixture of nitric acid and hydrochloric acid and analysed by atomic absorption spectrometry (AAS). Total contents of P and of Ca, Mg, K, Zn, Cu, Cr and Ni in the humus layer were extracted in a concentrated mixture of sulphuric acid and nitric acid and analysed by inductively coupled plasma atomic emission spectrometry (ICP). Total contents of Pb and Cd were determined by an extraction with concentrated (9%) hydrochloric acid during three hours followed by ICP analyses of the extract.

Exchangeable contents of Al, Fe, Ca, Mg, K and Na were measured by extraction with a 0.01 M solution of silver thiourea during four hours (Chabra et al., 1975) followed by analyses with ICP (Al, Fe, Ca and Mg) and atomic absorption spectrometry (AAS). Exchangeable NH_4 contents were measured by extraction with 1.0 M KCl (Coleman et al., 1959) followed by analyses with a coulometric technique (flow injection analyser; FIA). The CEC was determined from the decrease in Ag concentration before and after the extraction (Ag is measured by ICP) and the exchangeable H content was calculated from the difference in CEC and exchangeable cation content.

The readily dissolvable contents of Al and Fe were measured by extracting the samples during four hours in the dark with an acid ammonium oxalate solution at pH 3 followed by ICP analyses of the extract (Schwertmann, 1964). In this extract the P content was also measured.

Dissolved concentrations of major ions were determined by centrifugation of a soil sample of 400 gr at 7500 rpm during 20 minutes. The centrifuge tube was made of polyoxymethylene (deldrin) and consisted of an upper soil-holding cup with a perforated base (holding ca 250 ml of soil) and a lower solution holding cup, fitting in a 500 ml hole rotor. Centrifugation generally took place within one day (18-30

hours) after collection of the soil samples. Immediately after centrifugation the pH was measured.

The soil solution samples were filtered over 0.45 µm. Concentrations of Al, Fe, Ca, Mg and SO_4 were analysed by ICP, K and Na by AAS and NH_4, NO_3, H_2PO_4 and Cl by FIA. The pH was measured by means of potentiometry. The concentration of organic anions was calculated from the DOC content (Oliver et al., 1983) that was measured by an organic carbon analyser.

2.6   Data processing

Basic statistical representation

Data about the chemical composition of the soil and soil solution were processed with the statistical program Genstat 5, release 3 (Payne et. al., 1993). Simple statistics on the variation of chemical data, i.e. measured element concentrations, element ratios and pools of elements are thus provided for the humus layer, mineral soil and soil solution. The variation is presented in tables by values for the minimum, 5, 50 and 95 percentiles and the maximum. Furthermore median values are presented for the soil chemical data as a function of horizon and tree species for the humus layer and as a function of soil type for the mineral topsoil. Median values for (a selection of) soil solution chemistry data are presented as a function of the environmental characteristics that are assumed to influence the soil solution composition (cf. Section 2.2).

Calculation of element pools

Element pools in the humus layer were calculated by multiplying the measured humus layer pool (cf. Section 2.3) with the element content in that layer. The pool of organic material in the humus layer was calculated by multiplying the humus layer pool with the organic matter content. This is indicated as the corrected pool of humus, since mineral soil in humus layer sample is mainly due to inaccurate sampling. Bulk densities of the humus layer were calculated by dividing the measured humus layer pool with the measured thickness in the field. Again, a difference is made between the bulk density of the whole humus layer and the organic material in that layer (corrected value). Element contents in the humus layer are given in percent of the organic matter content

Element pools in the mineral topsoil were calculated by multiplying an estimated bulk density of the soil with the soil thickness (always 30 cm) and the element content in the soil. Unlike the humus layer, the bulk density could not be estimated from the amount of soil sampled since the volume of soil was unknown. Bulk densities were therefore derived by a pedotransfer function with the organic matter content according to (Hoekstra and Poelman, 1982):

$$\rho = 1000/(a + b \cdot \text{Org Mat}(\%)) \tag{2}$$

Values used for a and b are 0.601 and 0.030 for poorly drained soils (GT ≤ V) and 0.646 and 0.025 for well-drained soils (GT ≥ VI; cf. Hoekstra and Poelman, 1982). The influence of the clay content on the bulk density was considered negligible in these sandy soils.

Assessment of element ratios and their interpretation
Element ratios in the humus layer and mineral soil are mainly limited to ratios of major nutrients, i.e. N, P and S, to carbon. C/N, C/P and N/P ratios give indications about the eutrophication status of the soil. In the mineral soil, the ratio of oxalate extractable P to Al and Fe is also given. This is an important parameter with respect to the degree of phosphate saturation of the soil (Schoumans, 1997).

Element ratios in the soil solution include the:
-   NH_4 and NO_3 to SO_4 ratio indicating the contribution of both compounds to soil acidification,
-   Al to SO_4 and NO_3 ratio, indicating the degree of Al mobilisation by acidic inputs,
-   NH_4/NO_3 ratio, indicating the degree of nitrification,
-   Al/RCOO ratio, indicating the Al speciation over non-toxic organic species and toxic free Al and
-   Ratios of Al or NH_4 to the nutrients Ca, Mg or K, which are supposed to affect root length and root uptake.

Assessment of relationships between element concentrations in the soil solution and soil solid phase
Relationships between element concentrations in the soil solution and the soil solid phase in the various soil layers (humus layer, mineral topsoil and mineral subsoil) were investigated by simple correlation coefficients between the various compounds. More specifically, the relationship between: (i) dissolved concentrations of acid cations (H+Al) and acid anions (SO_4+ NO_3) and (ii) dissolved NO_3 concentration in the mineral topsoil and subsoil in comparison to the C/N ratio of the humus layer.

According to Dise et al. (1998) and Gundersen et al. (1998) the forest floor C/N ratios may be used to assess risk for nitrate leaching. Gundersen et al. (1998) suggested threshold values of >30, 25 to 30, and <25 to separate low, moderate, and high nitrate leaching risk, respectively. This suggestion was based results obtained at 35 forest sites in Northwest and Central Europe. When deposition is accounted for, full N retention was found at C/N above 30 and almost no retention below C/N ratio 20. Input-output budgets from European forests presented Gundersen et al. (1998) also showed that above a threshold of approximately 10 $kgN.ha^{-1}.yr^{-1}$ in throughfall, sites start to have elevated nitrate-leaching rates, generally above 5 $kgN.ha^{-1}.yr^{-1}$. This information has been used in several model, such as SMART (De Vries et al., 1994a) and MAGIC (Cosby et al., 2001) to calculate nitrogen immobilisation as a fraction of the net N input, linearly depending on the C/N ratio. The validity of this approach was investigated by evaluating the measured NO_3 concentration data in view of measured C/N ratios and model calculated N deposition rates.

Assessment of aluminium dissolution parameters
In most soil acidification models, it is assumed that Al concentrations in the soil solution at the bottom of the root zone are in equilibrium with Gibbsite, thus leading to the following relationship between aluminium and protons:

$$\left(Al^{3+}\right) = K_{gibb} \cdot \left(H^+\right)^3 \tag{3}$$

Where $(H)_{crit}$ and $[Al]_{crit}$ are the H and Al activities (mol.l^{-1}) and K_{gibb} is the gibbsite equilibrium constant. Here, Al stands for the activity of free (uncomplexed) aluminium. This assumption is even the basis for the calculation of critical acid loads, using the so-called Simple Mass Balance (SMB) model (e.g. De Vries, 1993). Assuming a critical Al concentration, based on e.g. a critical Al/base cation ratio, the related critical H concentration is calculated with the Gibbsite equilibrium, according to:

$$[H^+]_{crit} = \left(\frac{\left[Al^{3+}\right]_{crit}}{K_{gibb}}\right)^{0.33} \tag{4}$$

where $[H]_{crit}$ and $[Al]_{crit}$ are the critical H and Al concentrations (mol.l^{-1}). The SMB model calculates H concentrations as a function of free (uncomplexed) Al concentrations instead of Al activities.

Data from a number of sites indicate that soil solutions at the bottom of the root zone are close to equilibrium with a gibbsite like phase (Johnson et. al., 1981; Dahlgren et al., 1989; Matzner and Prenzel, 1992). However, undersaturation with respect to gibbsite has been reported for a large number of sites, in particular in organic rich soils, at shallow depth or during episodes of high flow (Seip et. al., 1989; Matzner, 1992; Mulder and Stein, 1994). Moreover, experiments show that Al concentrations in the soil solution are strongly influenced by reactions with organic pools and by the kinetically constrained dissolution of Al hydroxides and silicates (Dahlgren and Walker, 1993; Berggren and Mulder, 1995; De Vries, 1994; Van der Salm and De Vries, 2001).

To incorporate this knowledge into soil acidification models, such as the SMB and SMART model, empirical based equilibrium relations between Al and H activities are an alternative for the gibbsite equilibrium, according to:

$$\left(Al^{3+}\right) = K_{Al} \cdot \left(H^+\right)^x \tag{5}$$

Where K_{Al} is the Al dissolution release constant and x is a dimensionless power constant, describing the reaction stoichiometry. For $x=3$, Eq. (3) is equal to Eq. (5). Empirical relations between Al and H activities, measured in the topsoil (0-30cm depth) and the subsoil (60-100cm depth) of the 150 forested sandy were based on a regression relationship between pAl (-log(Al) and pH assuming the relationship given in Eq. (5).

Actually, the measurements include only total Al concentrations (both free Al and Al complexed with dissolved organic carbon (DOC) and other complexes. Al^{3+} activities were thus calculated from the total concentration of Al and dissolved organic carbon (DOC) using the speciation program MINEQL+ (Schecher and McAvoy, 1994), combined with a triprotic organic acid model, in which complexation of Al by DOC is taken into account (Santore et al., 1995). In the latter model, the total concentration of organic acids is first calculated as a function of DOC according to:

$$A_T = M_D \cdot DOC \tag{6}$$

where A_T is the total concentration of organic functional groups (mol.l^{-1}), M_D is the site density of organic solutes (mol.mol^{-1}) and DOC is the DOC concentration (mol.l^{-1}). Santore et al. (1995) reported values for M_D between 0.014 for topsoil samples and 0.044 mol.mol^{-1}, for a B-horizon in the Hubbard Brook experimental forest in New Hampshire. In this study we used a value of 5.5 mol$_c$.kg^{-1}, or 0.066 mol.mol^{-1}, based on De Vries and Bakker (1998).

In the triprotic organic acid model, the various organic functional groups are represented as a triprotic organic acid. Al in solution can thus be complexed to A^{3-}, HA^{2-} and HA^{-}. The relevant reactions that were incorporated in the speciation model MINEQL+, including the associated equilibrium constants that were used to calculate complexation of Al with DOC, are given below, following (Santore et. al., 1995).

$A^{3-} + H^+$	$\rightarrow$	HA^{2-}		$\log K = 6.48$
$A^{3-} + 2H^+$	$\rightarrow$	H_2A^-		$\log K = 11.69$
$A^{3-} + 3H^+$	$\rightarrow$	H_3A		$\log K = 13.71$
$Al^{3+} + A^{3-}$	$\rightarrow$	AlA		$\log K = 7.89$
$Al^{3+} + A^{3-} + H^+$	$\rightarrow$	$AlHA^+$		$\log K = 12.86$
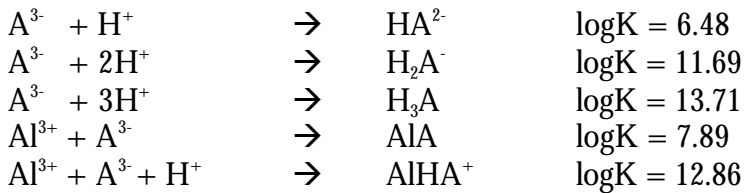
A test for soil solutions from a number of column experiments on Dutch sandy soils showed that the calculated concentrations of organically complexed Al were comparable ($<10\%$) to measured concentrations (Van der Salm, 1999). The relations between pAl (-log(Al)) and pH of the soil solution were calculated for both activities and concentrations, since the SMB model calculates H concentrations as a function of Al concentrations instead of Al activities.

For the topsoil, an alternative description of Al release was also tested, since Al activities, in particular in the topsoil, can be influenced by complexation of Al to organic matter (Cronan et al., 1986; Mulder and Stein, 1994). The binding of Al to organic sites can be described by the following equation (Mulder and Stein, 1994; Van der Salm and De Vries, 2001):

$$\left(Al^{3+}\right) = K \cdot \frac{(RAl^{3-x})}{(RH_x)} \cdot (H^+)^x \tag{7}$$

where K is the equilibrium Al release constant and (RAl^{3-x}) and (RH_x) the occupation of the complexation sites by Al and H. The occupation of the complexation sites with Al can be estimated from extractions with Na-pyrophosphate, and RH_x can be estimated from the organic matter content (Wesselink et al., 1996). Equation (7) can then be rewritten to calculate K according to:

$$\left(Al^{3+}\right) \cdot C / Al_p = K \cdot (H^+)^x \tag{8}$$

where C is the organic matter content and Al_p is the pyrophosphate extractable Al content of the samples. Unfortunately, data on Na-pyrophosphate extractable Al where not available for the examined sites. In A horizons the amount of inorganic Al is, however, often negligible and accordingly the amount of pyrophosphate extractable Al is comparable to the amount of Al that can be extracted by NH_4-oxalate. Data for oxalate extractable Al were available for the topsoil samples (0-30 cm) and were thus used to estimate the occupation of organic sites with Al. The values of K and x were derived for relations between $p(Al. C/Al_{ox})$ and pH of the soil solution, using both activities and concentrations of uncomplexed aluminium.

Assessment of cation exchange constants
Cation exchange is an important process in buffering soil acidification. In several soil acidification models, such as RESAM (De Vries et al., 1995a) and NUCSAM (Groenenberg et al., 1995), cation exchange is described by Gaines-Thomas equations with Ca as reference ion according to:

$$\frac{frX_{ac}^{2}}{frCa_{ac}^{z_x}} = KX_{ex} \cdot \frac{[X]^2}{[Ca]^{z_x}} \tag{9}$$

where frX_{ac} (-) is the fraction of cation X on the adsorption complex, [X] is the concentration of ion X in solution (mol.l^{-1}), z_x (-) is the valence of cation X, and KX_{ex} is the Gaines-Thomas selectivity constant for exchange of cation X against Ca $((mol.l^{-1})^z x^{-2})$. In these models X stands for H, Al, Fe, Mg, K, Na or NH_4 and frX_{ac} is calculated by:

$$frX_{ac} = \frac{X_{ac}}{CEC} \tag{10}$$

where CEC is the cation exchange capacity (mmol$_c$.kg^{-1}) and X_{ac} is the exchangeable content of cation X (mmol$_c$.kg^{-1}). The sum of all fractions is equal to 1.

Since data for both the adsorbed and dissolved concentrations of H, Al, Fe, Mg, K, Na or NH_4 are available for the 150 forest stands, the various exchange constants, KX_{ex} with X = H, Al, Fe, Mg, K, Na or NH_4, were calculated for use in the models RESAM and NUCSAM. In this approach, use was made of the measured actual (unbuffered) CEC. This implies that the cation exchange constants are only

applicable in the limited pH range of the acid sandy soils considered (mainly between pH 3 and 4.5).

The CEC is dependent on the clay and organic matter content and increases also with an increase in pH. This is mainly due to release of protons from carboxyl groups of organic matter. These protons are irreversibly adsorbed at lower pH but can be released at higher pH and exchanged by e.g. Ca. To allow the calculation of the pH up to higher values, e.g. in response to liming or to extremely reduced atmospheric deposition inputs, it is important to use the exchangeable cation contents related to a buffered CEC. Examples are a CEC buffered at pH 6.5 (NH_4 acetate buffered CEC) or 8.2 (Barium chloride triethanol amine buffered CEC). In this situation the exchangeable proton fraction increases, whereas the exchangeable fraction of all other cations decreases. This type of description is used in the model SMART (De Vries et al., 1989b, 1994a). Since a pH of 6.5 is a reasonable upper value for non-calcareous soils, we used this CEC and the exchange constants related to those exchangeable fractions in the model.

The buffered CEC at pH 6.5 was not measured at the 150 forest stands. One way to estimate this value is to derive the CEC as a function of the clay and organic carbon content, accounting for the impact of pH according to (Helling et al., 1964):

$$CEC = (3.0 + 0.44 \cdot pH - KCl) \cdot \%clay + (-5.9 + 5.1 \cdot pH - KCl) \cdot \%OC \qquad (11)$$

where OC stands for organic carbon. This relationship can also be used to derive CEC values at a buffered pH, implying that the CEC only depends on the clay and organic carbon content. Breeuwsma et al. (1986), for example, found a relationship between the CEC buffered at pH 6.5 (NH_4 acetate buffered CEC) and the clay and organic matter content, with a regression coefficient of 5.0 for clay and 30 for organic carbon, being in reasonable to good agreement with Eq. (11). The adequacy of Eq. (10) was assessed by comparing the CEC values thus estimated with those measured at the actual pH-KCl (measured unbuffered value). To allow for discrepancies between the measured and estimated values at the actual pH-KCl, we updated the calculated CEC at pH 6.5 according to:

$$CEC_{updated(pH6.5)} = CEC_{calculated(pH6.5)} \cdot (CEC_{measured(pHactual)} / CEC_{calculated(pHactual)}) \qquad (12)$$

In the SMART model, the divalent base cations Ca and Mg are lumped as BC^{2+}, the monovalent cations K and Na are lumped as BC^+ and NH_4 is neglected. We thus calculated the exchange constants for H^+, Al^{3+} and BC^+ against BC^{2+} according to Eq. (8) with BC^{2+} (Ca+Mg) replacing Ca both at the adsorption complex and in solution. At present the interaction between monovalent and divalent base cations at the exchange complex is neglected in SMART, implying that the exchange constant for BC^+ against BC^{2+} is taken equal to zero.

On a European scale, data are mostly only available for the CEC and the base saturation, being the sum of the base cations Ca, Mg, K and Na. To allow model calculations for this situation we also calculated the exchange constants KAl_{ex} and

KH_{ex}, by replacing $frCa_{ac}$ in Eq. (8) by $frBC_{ac}$, with BC is Ca+Mg+K+Na, and replacing $[Ca^{2+}]$ by $[BC^{2+}]$, with BC^{2+} is $Ca^{2+}+Mg^{2+}$. This is of course not allowing to the rules of cation exchange but is based on the implicit assumption that monovalent base cations hardly interact with the exchange complex.

Assessment of phosphate adsorption parameters

The reaction of inorganic P in soil is characterised by a fast reversible process and a slow, almost irreversible, process. The fast reaction is generally attributed to P adsorption on surface sites (Van der Zee, 1988), whereas the slow reaction is mostly viewed as a diffusion controlled precipitation reaction (Barrow, 1983; Van Riemsdijk et al., 1984). In forest soils with low dissolved P concentration, the concentration of inorganic P (mainly H_2PO_4) is mainly controlled by equilibrium adsorption. For non calcareous sandy soils, Van der Zee (1988) showed that the fast reversible reaction with inorganic P can be described adequately by a Langmuir equation, according to:

$$P_{ad} = \frac{kP_{ad} \cdot P_{ad,max} \cdot [P]}{1 + kP_{ad} \cdot [P]}$$
(13)

where P_{ad} is the reversibly sorbed amount of P (mmol.kg^{-1}), $P_{ad,max}$ is the maximum amount of reversibly sorbed P (mmol.kg^{-1}), [P] is the dissolved inorganic P (H_2PO_4) concentration (mol.m^{-3}) and kP_{ad} is the equilibrium constant for adsorption of inorganic P (m^3.mol^{-1}). Eq. (12) can be rewritten to

$$[P] = 1/kP_{ad} \cdot \frac{P_{ad}}{(P_{ad,max} - P_{ad})}$$
(14)

The oxalate extractable amount of P, P_{ox}, is a measure for the total amount of phosphate sorbed by both reversible adsorption and slow diffusion controlled precipitation. The phosphate sorption capacity (PSC), related to both processes, appears to be related to the amount of oxalate extractable Al and Fe in the soil (Van der Zee, 1988; Schoumans and Groenendijk, 2000). In situations with large manure/fertiliser applications and high P concentrations (up to 3 mol.m^{-3}), the PSC has been estimated as (Schoumans and Groenendijk, 2000):

$$PSC = 0.5 \cdot (Al_{ox} + Fe_{ox})$$
(15)

where PSC is the phosphate sorption capacity (mmol.kg^{-1}) and Al_{ox} and Fe_{ox} stand for oxalate extractable Al and Fe, respectively (mmol.kg^{-1}).

The amount of reversibly sorbed phosphate, P_{ad}, is generally determined by the iron oxide-impregnated paper method with desorption times up to 48 h (Menon et al., 1989). The maximum amount of reversibly sorbed phosphate, $P_{ad,max}$, appears to be a constant fraction of the PSC, according to (Van der Zee, 1988; Schoumans and Groenendijk, 2000):

$$P_{ad,max} = 1/3 \cdot PSC \tag{16}$$

Assuming that this ratio holds at all P levels, the amount of reversibly sorbed P can be approximated as;

$$P_{ad} = 1/3 \cdot P_{ox} \tag{17}$$

Combining Eq. (14), (16) and (17) leads to:

$$[P] = 1/kP_{ad} \cdot \frac{P_{ox}}{(PSC - P_{ox})} \tag{18}$$

For each site, an estimate of the KP_{ad} was made by calculating the ratio of the measured inorganic P (H_2PO_4) concentration and the degree of P saturation, expressed by the ratio $P_{ox}/(PSC-P_{ox})$, where PSC was derived from the $Al_{ox} + Fe_{ox}$ content according to Eq (15). An estimate of the average KP_{ad} for sandy soils was made by a regression of the measured inorganic P concentration against the ratio $P_{ox}/(PSC-P_{ox})$. We also investigated whether the explained variation decreased when we used the degree of P saturation expressed as P_{ox}/PSC. When this is not the case, it implies that equilibrium phosphate adsorption can equally well be described as:

$$[P] = 1/kP_{ad} \cdot \frac{P_{ad}}{P_{ad,max}} \tag{19}$$

In its inverse form, Eq (19), looks like a linear adsorption equation. We also investigated, whether two different Langmuir types of adsorption could more adequately describe P adsorption, according to:

$$\frac{P_{ox}}{(PSC - P_{ox})} = kP_{ad} \cdot [P]^n \tag{20}$$

$$\frac{P_{ox}}{PSC} = kP_{ad} \cdot [P]^n \tag{21}$$

3 Characteristics of the forest stands

In this chapter an overview of the various locations with their deposition level, surrounding land use, stand and site characteristics are given. From the 150 selected locations 147 were actually sampled. One location (oak) appeared not accessible. Consequently, another oak stand with similar deposition level and tree height was sampled instead. Furthermore, at two locations the expected tree species were not found. Therefore, the distribution over tree species became slightly different i.e. Scots pine 44, Black pine 15, Douglas fir 16, Norway spruce 15, Japanese larch 15, Oak 30 and Beech 15 (cf. Table 1).

3.1 Location and deposition level

Non-calcareous sandy soils represent 34% of the Dutch soils. However roughly 84% of the Dutch forest is situated on these non-calcareous sandy soils (De Vries, 1989). The distribution of the 150 locations, over the total area of forest located on non-calcareous sandy soils in the Netherlands, is shown in Figure 1. The greatest united forest complexes are situated in the province Gelderland (central part of the Netherlands) in an area called the Veluwe. Relatively few locations lie in this area, caused by using in the first place the RIVM selection, which excluded this area (section 2.1). Figure 1 also shows the distribution of the locations, which are common with the sampling of the phreatic ground water (RIVM). Furthermore, 12 of the 85 common locations are indicated where regular monitoring takes place. At these monitoring locations soil solution (SC), ground water (RIVM) and foliage (IBN) is sampled since 1992.

The distribution of the 150 locations over tree species and acid deposition levels is given in Figure 2, Table 3 and 4. Acid deposition stands for the atmospheric deposition of NO_x, NH_x and SO_x minus the sea-salt corrected bulk deposition of the base cations. As with the actual distribution of tree species on a national scale (cf. data in brackets in Table 3), locations with Scots pine and black pine occurred mainly in the central (Gelderland) and the Southern part of the Netherlands (Brabant; cf. Table 3) in areas with high acid deposition levels (Fig. 2 and Table 4). Unlike the national distribution, locations with Douglas fir occurred mainly in the Southern (Brabant) and Northern part of the Netherlands (Drenthe; cf. Table 3), with slightly lower acid deposition levels compared to the pine species (Fig. 2 and Table 4). Locations with Norway spruce and Japanese larch occurred more often in the provinces Drenthe and Brabant and less often in the central area compared to the national distribution (Table 3). Especially for Norway spruce this corresponds to lower acid deposition levels (Fig. 2 and Table 4). The occurrence of locations with oak is slightly more southerly compared to the national distribution (Table 3). Consequently the acid deposition levels were high (Fig. 2 and Table 4). The distribution of beech corresponds largely to the national distribution and the acid deposition levels were more or less the same as those on Douglas fir.

Titel:

Gemaakt door:
ArcView Version 2.1
Voorbeeld:
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Commentaar:
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Figure 1 Distribution of the 150 locations over the forest areas on non-calcareous sandy soils
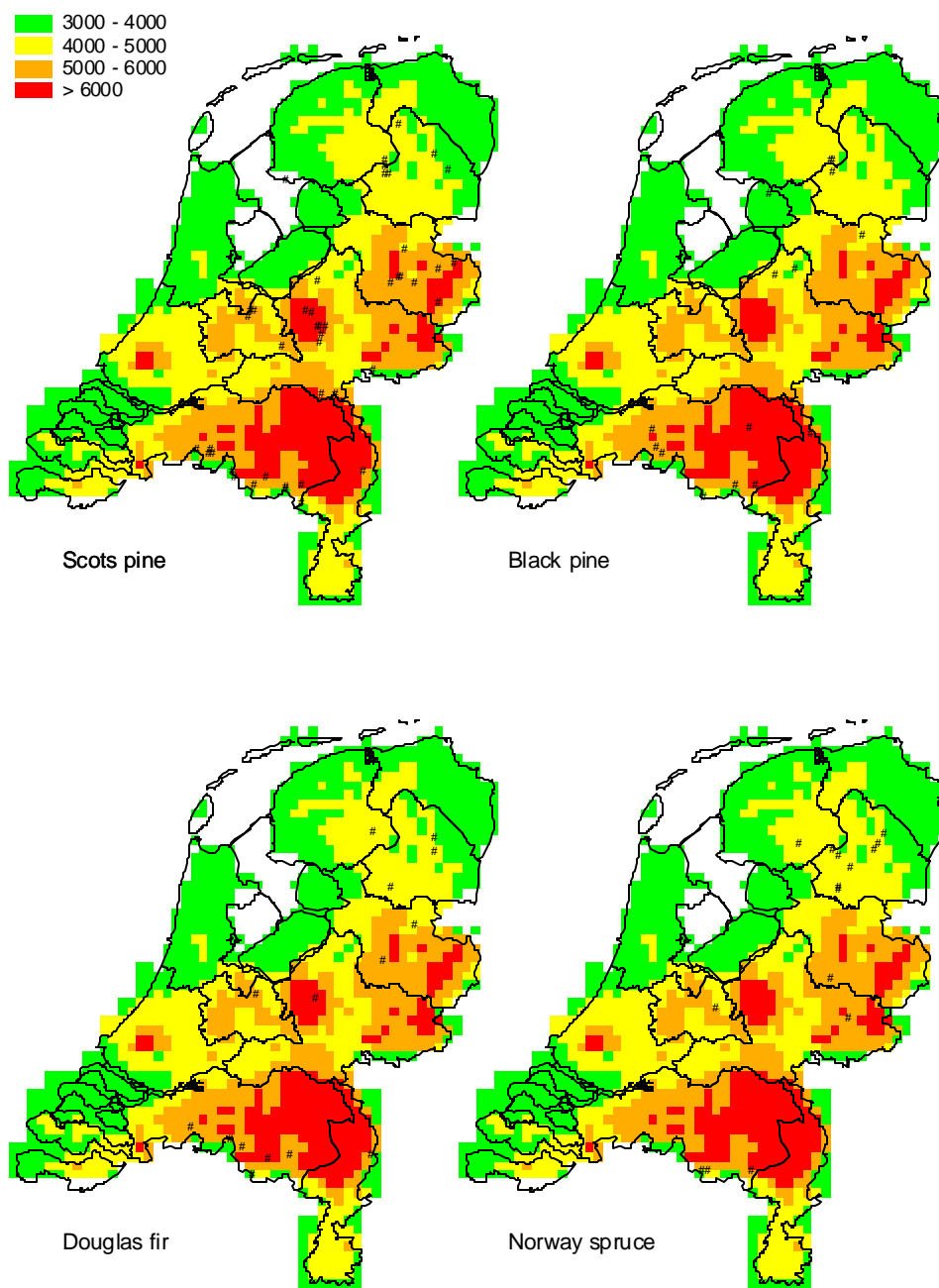
Legend:
- 3000 - 4000
- 4000 - 5000
- 5000 - 6000
- > 6000

Scots pine

Black pine

Douglas fir

Norway spruce

Figure 2 Distribution of tree species over acid deposition levels

Legend:
- 3000 - 4000 (green)
- 4000 - 5000 (yellow)
- 5000 - 6000 (orange)
- > 6000 (red)

Japanese larch

Groningen
Friesland
Drenthe
Flevoland
Overijssel
Utrecht
Gelderland
Noord-Brabant
Limburg

Oak

Beech
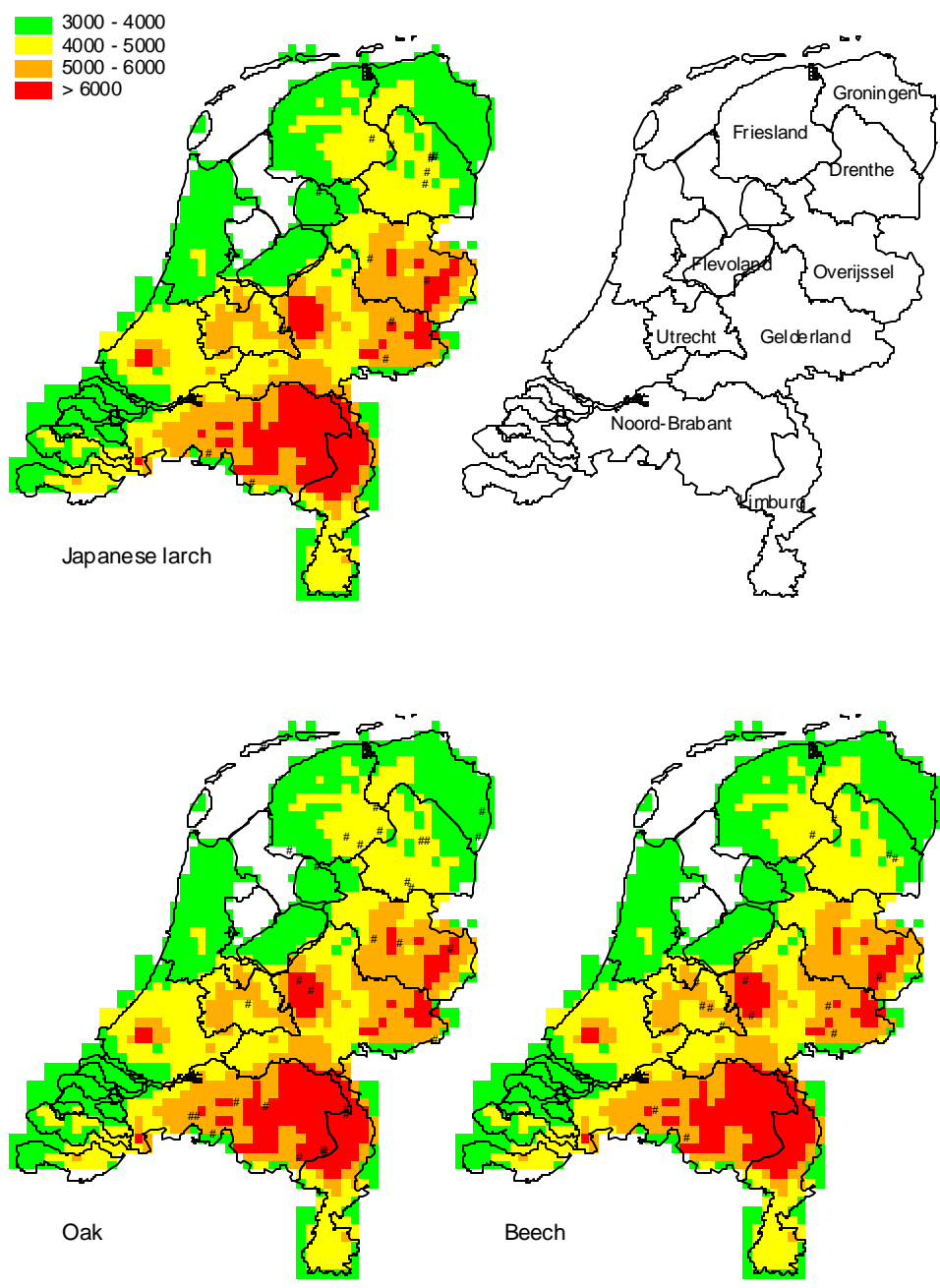
Figure 2 Distribution of tree species over acid deposition levels (continued)

Table 3   Distribution of the tree species of the 150 locations over Province and area

Province	Distribution (%)												
	Scots pine		Black pine		Douglas fir		Norway spruce		Japanese larch		Oak		Beech	
Groningen	0	(0)	0	(0)	0	(0)	0	(1)	0	(1)	7	(2)	0	(0)
Friesland	7	(1)	14	(1)	6	(2)	7	(5)	7	(4)	20	(7)	7	(2)
Flevoland	0	(-)	6	(-)	0	(-)	0	(-)	7	(-)	3	(-)	0	(-)
Drenthe	9	(5)	7	(1)	19	(11)	52	(26)	44	(27)	13	(11)	20	(7)
Overijssel	20	(11)	6	(3)	13	(12)	7	(16)	14	(14)	10	(14)	7	(7)
Gelderland	25	(38)	14	(12)	6	(44)	7	(20)	14	(31)	10	(23)	26	(49)
Utrecht	9	(6)	0	(6)	13	(10)	7	(5)	0	(7)	3	(6)	26	(12)
Brabant	25	(28)	47	(56)	37	(18)	20	(15)	14	(11)	27	(14)	14	(6)
Limburg	5	(11)	6	(12)	6	(2)	0	(8)	0	(3)	7	(10)	0	(4)
Area[**]													
North	16	(6)	27	(2)	25	(13)	59	(32)	58	(32)	43	(20)	27	(9)
Central	54	(55)	20	(21)	32	(66)	21	(41)	28	(52)	23	(43)	59	(68)
South	30	(39)	53	(68)	43	(20)	20	(23)	14	(14)	34	(24)	14	(10)

[*]   Between brackets the percentage of the total forest area in the Netherlands (CBS, 1985) is given.
[**] The areas North, Central and South contain respectively the first four, the second three and the last two provinces given above

Table 4   Distribution of the tree species of the 150 locations over acid deposition levels

Acid deposition ($mol_c.ha^{-1}.yr^{-1}$)	Distribution (%)							
	Scots pine	Black pine	Douglas fir	Norway spruce	Japanese larch	Oak	Beech	Total
< 3000	2	0	0	0	0	7	0	2
3000-4000	9	7	19	33	36	10	13	16
4000-5000	23	50	31	33	21	31	33	30
5000-6000	50	29	38	27	36	24	33	36
> 6000	16	14	13	7	7	28	20	16

More than 80% of the forest stands were located in areas with acid deposition levels above 4000 $mol_c.ha^{-1}.yr^{-1}$. Only 16% of them had very high deposition levels, above 6000 $mol_c.ha^{-1}.yr^{-1}$. These were mainly stands of oak and beech and seldom Norway spruce or Japanese larch (Table 4). Deposition levels of less than 3000 $mol_c.ha^{-1}.yr^{-1}$ were exceptional. Only two oak and one Scots pine stand were situated in such areas, respectively on the isle Terschelling and at the borders of the provinces Groningen and Friesland (Fig. 2).

3.2   Position of the forest stands

The land use in the surroundings of a forest, influences the atmospheric input. The degree to which this occurs is determined by the distance of the forest stand to the nearest forest edge, the land use at the nearest edge and the position of the nearest edge with respect to the site (section 2.2). These influences are supposed to interact. For example, the influence of maize fields on the atmospheric (N) deposition near a forest stand situated at the South, South-West area of the stand, is expected to be greater than the influence of e.g. non-agricultural land in the same position or

grassland at great distance from the forest stand or whatever land use situated in the Northern area of the forest stand.

Most forest stands were situated more than 100 meters from the forest edge. This was especially true for black pine, Douglas fir and Scots pine (Table 5). The coniferous species appeared to be mainly located in larger forest complexes, while the deciduous species (including Japanese larch) were mainly located near the forest edge especially oak.

Table 5   Distribution of the tree species of the 150 locations over distance to the nearest forest edge

Distance to the nearest forest edge (m)	Distribution (%)							
	Scots pine	Black pine	Douglas fir	Norway spruce	Japanese larch	Oak	Beech	Total
< 20	5	8	6	7	0	33	0	10
20-40	12	8	13	14	7	26	14	14
40-60	17	8	0	14	36	7	29	15
60-80	10	0	6	0	14	11	0	7
80-100	0	0	13	21	14	7	21	9
> 100	57	77	63	43	29	15	36	45

Corresponding to the relative great number of stands in larger forest complexes, black pine and to a lesser extent Douglas fir and Scots pine had more stands with non-agricultural land use in the neighbourhood (Table 6). Grassland was the most occurring land use type in the surroundings, especially near stands of oak, Japanese larch and Norway spruce. The occurrence of maize fields was little and for some tree species even negligible.

Table 6   Distribution of the tree species of the 150 locations over surrounding land use

Surrounding land use	Distribution (%)							
	Scots pine	Black pine	Douglas fir	Norway spruce	Japanese larch	Oak	Beech	Total
Maize field	8	0	0	14	0	11	7	7
Grassland	28	20	33	43	46	50	33	36
Arable land	35	20	33	21	31	32	33	31
Non-agricultural	31	60	33	21	23	8	27	26

The directions of the forest edges were distributed more or less equally over the 150 locations. Stands of oak, black pine and Norway spruce had relatively more forest edges situated to the Northern areas, while stands of Japanese larch were mainly situated to the Southern areas (Table 7).

3.3   Stand characteristics

Stand characteristics such as canopy coverage, tree height and of course tree species influence the atmospheric input and throughfall water and therefore the chemical composition of the soil and soil solution (section 2.1).

Table 7   Distribution of the tree species of the 150 locations over the direction of forest edges

Direction of forest edge	Distribution (%)							
	Scots pine	Black pine	Douglas fir	Norway spruce	Japanese larch	Oak	Beech	Total
N	5	9	13	0	0	40	7	5
NE	20	18	20	29	29	7	7	18
E	8	18	13	21	7	19	13	13
SE	8	9	13	21	7	11	7	10
S	18	0	7	14	14	22	20	15
SW	13	9	7	14	29	7	7	12
W	10	0	27	0	14	15	7	11
NW	20	36	0	0	0	15	33	15

The coverage of the canopy amounted in most locations between 50% and 75% (Table 8). The canopy coverage is related to tree species. As expected, Table 8 shows that beech, Douglas fir, Norway spruce and less obvious also oak, had mainly high coverage's whereas low coverage's mainly occurred in stands of Scots pine.

Table 8   Distribution of the tree species of the 150 locations over canopy coverage

Canopy coverage (%)	Distribution (%)							
	Scots pine	Black pine	Douglas fir	Norway spruce	Japanese larch	Oak	Beech	Total
< 50	51	23	6	13	8	7	14	23
50-75	40	69	44	47	85	62	29	51
> 75	9	8	50	40	8	31	57	26

Tree height is mainly a result of tree species and age and also of site conditions, such as soil type and ground water level. Consequently the distribution over tree height is more or less equal to the distribution over age, especially for the pine and deciduous species. Most locations had a tree height between 10 m and 15 m or higher (Table 9). Heights less than 5 m occurred only twice in two relatively young (15 - 20 years) stands of oak and beech. Most evident differences between tree species were that beech, Japanese larch and Douglas fir had mostly high trees, while black pine had obvious mainly low trees. Since beech and Douglas fir also had high canopy coverage's, great impacts of atmospheric deposition on soil solution chemistry may be expected for these tree species.

Table 9   Distribution of the tree species of the 150 locations over tree height

Tree height (m)	Distribution (%)							
	Scots pine	Black pine	Douglas fir	Norway spruce	Japanese larch	Oak	Beech	Total
< 5	0	0	0	0	0	3	7	1
5-10	11	57	6	13	7	21	7	16
10-15	32	36	25	53	7	45	13	32
15-20	48	7	25	20	29	17	13	27
> 20	9	0	44	13	57	14	60	23

3.4 Site characteristics

3.4.1 Clustering of soil types and ground-water tables

Site characteristics, such as soil type and ground water level, determine the influence of atmospheric deposition by their base saturation and processes, such as weathering or nitrogen transformations (Section 2.1). According to the classification system of De Bakker and Schelling (1989) for Dutch soils, 19 different soil types have been distinguished. These soil types were clustered into six groups, based on their expected vulnerability for acidification (De Vries et al., 1989a). In order of decreasing vulnerability these groups are given in Table 10.

Table 10 Six distinguished soil groups named according to three different classifications

Group	Classification system		
	(FAO, 1988)	(USDA, 1975)	(De Bakker and Schelling, 1989)
1	Haplic Arenosols[1]	Typic Udipsamments	Duin- en Vlakvaaggronden
2	Gleyic Podzols[2]	Typic Haplohumods	Veld- en Haarpodzolen
3	Cambic Podzols	Entric Haplorthods	Holtpodzol- en Vorstvaaggronden
4	Fimic Athrosols	Plaggepts	Enkeerd- en Loopodzolgronden
5	Umbric Gleysols[3]	Haplumbrepts	Beekeerden en moerige gronden
6	Dystric Gleysols	Typic Haploquod	Oude Kleigronden

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

Results on ground-water levels were clustered into five groups (cf. Table 11). The first group with very poorly drained ground-water levels, contained the classes II and III. The mean highest ground-water level in the winter period for this group lied between 5 cm and 45 cm and the mean lowest in the summer period between 65 cm and 100 cm below surface. In these soils the ground-water level stays all seasons within the root-area. The second group with poorly drained ground-water levels, contained only class V. The mean highest ground-water level lied between 0 cm and 40 cm and the mean lowest fluctuated from 125 cm to 200 cm below surface and deeper. These soils were wet in the spring and dry in the summer. The third group with moderately drained ground-water levels, contained the classes IV and VI. The mean highest ground-water level lied between 45 cm and 70 cm and the mean lowest fluctuated from 115 cm to 250 cm below surface and deeper. The fourth and fifth group with respectively well and very well drained ground-water levels, contained the classes VII and VIII. The difference between these classes were the mean highest ground-water levels, for class VII this lied between 85 cm and 140 cm and for class VIII even deeper than 140 cm below surface.

The distribution of soil types over ground-water level classes (Table 11) shows that the Cambic Podzols and Fimic Anthrosols are mostly well drained, whereas the Umbric and Dystric Gleysols are mostly poorly drained. The drainage status of Haplic Arenosols and Gleyic Podzols varies greatly, but drainage is generally quite well. More information of the various soil groups is given below.

Table 11 Distribution (%) of the soil types of the 150 locations over the ground-water level classes

Soil type	Ground-water level class					Total[4]	
	II+III	V	IV+VI	VII	VIII		
Haplic Arenosol[1]	11	-	14	11	64	100	(28)
Gleyic Podzols[2]	3	11	25	28	33	100	(75)
Cambic Podzols	-	-	6	6	88	100	(17)
Fimic Anthrosol	-	-	27	18	55	100	(11)
Umbric Gleysol[3]	28	16	42	14		100	(14)
Dystric Gleysol	-	80	20	-	-	100	(5)

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils
[4] number of locations between brackets

Haplic and Gleyic Arenosols

Arenosols are characterised by the absence of soil formation, also have only A and C-horizons. However at several locations symptoms of soil formation (E and B-horizons) were found, actually at three locations within 60 cm and at six location within 100 cm below surface. The humus layer had an average thickness of 7.8 cm. The average measured percentage organic matter of the topsoil (0 - 30 cm below surface) was 1.6 (Table 5.1.2). Further consisted this layer mainly of slightly loamy (5% - 12%) very fine sand (140 - 170 μm), except at a few locations were extremely loamy (30% - 40%) sand was found. Due to the locations were B horizons were found, the estimated percentage organic matter in the subsoil (30 - 60 cm and 60 - 100 cm below surface) lay between 0.1 and 6.0. Otherwise the differences between horizons were small, the percentage loam and the coarseness of the sand remained more or less the same through the profile. These soils occurred mainly in combination with the ground-water level classes VII (well drained) and VIII (very well drained; Table 11).

Gleyic and Carbic Podzols

Gleyic and Carbic Podzols are characterised by obvious soil formation, i.e. the occurrence of a B and/or E horizons. Three fourth of this group were Gleyic Podzols, with an organic rich mineral layer (A horizon) followed by an illuvial B horizon in which the illuviated parts consists of amorphous humus and sesquioxides. Sometimes there was a small horizon with bleached sand grains above the B-horizon. These soils are known to have little iron, sesquioxides and base cations have leached from the topsoil. Only with Gleyic Podzols situated high in regard to the ground-water level, iron and aluminium is accumulated in the lower parts of the B horizon (De Bakker and Schelling, 1989). The humus layer had an average thickness of 8.6 cm. In the first 30 cm below surface A, E and B horizons were found, the average measured percentage organic matter was 4.7 (Table 5.1.2). Between 30 cm and 60 cm only B-horizons, and between 60 cm and 100 cm below surface mainly BC horizons were found. These layers had an average estimated percentage organic matter of respectively 2.7 and 1.0. Further consisted these soils of slightly loamy (8% - 16%), moderately fine sand (150 - 200 μm). The Gleyic Podzols mainly occurred in combination with ground-water level classes V (14%), VI (30%), VII (32%) and VIII (18%). One fourth of this group were Carbic Podzols. In contrast to the Gleyic Podzols they have always an E horizon. These soils developed in drier

environments than the Gleyic Podzols. Therefore the A and E horizons do have low contents of aluminium, iron and to a lesser extent base cations, these elements are illuviated in the lower parts of the B and in the BC horizons. The humus layer had an average thickness of 7.0 cm. In the first 30 cm below surface A and E horizons were found, the average measured percentage organic matter was a little less than with the Gleyic Podzols, i.e. 4.4 (Table 5.1.2). Between 30 cm and 60 cm only B-horizons and between 60 cm and 100 cm below surface B but mostly C horizons were found. Consequently the average estimated percentage organic matter were respectively slightly higher (2.9) and lower (0.7) than those of the Gleyic Podzols. The Carbic podzols occurred only in combination with the ground-water level classes VII (20%) and VIII (80%).

Cambic Podzols
Like Gleyic and Carbic Podzols, the Cambic Podzols are characterised by the presence of soil formation although this is less obvious, they are weak podzols. In contrast to the Gleyic and Carbic Podzols, the Cambic Podzols have no illuviation of amorphous humus in the B-horizon. However less than with Gleyic and Carbic Podzols they do have illuviation of iron and aluminium. The humus layer had an average thickness of 8.3 cm. In the first 30 cm below surface A and B horizons were found, the average measured percentage organic matter in the topsoil was 3.2 (Table 5.1.2). Between 30 and 60 cm B and C horizons and between 60 cm and 100 cm below surface mainly C horizons were found. These layers had an average estimated percentage organic matter of respectively 1.2 and 0.5. Further consisted these soils of slightly loamy to very loamy (10% - 20%), moderately fine to moderately coarse sand (180 - 260 µm). The Cambic Podzols occurred almost only in combination with ground water level class VIII (very well drained; Table 11).

Fimic Anthrosols
These soils arose from anthropogenic influence. Many years of manuring caused a non-reworked A horizons thicker than 50 cm, rich in organic matter. Under the A horizon, B horizons do sometimes occur. The humus layer had an average thickness of 8.3 cm. In the first 30 cm below surface, only A horizons were found. The average measured percentage organic matter was 3.8 (Table 5.1.2). Between 30 cm and 60 cm also mainly A horizons and between 60 cm and 100 cm below surface A, B and C horizons were found. These layers had an average estimated percentage organic matter of respectively 5.0 and 3.5. Further consisted these soils of mainly loam poor or slightly loamy (8% - 12%) moderately fine to moderately coarse sand (160 - 280 µm). These soils occurred mainly in combination with the ground-water level classes moderately (VI), well (VII) and very well (VIII) drained (Table 11).

Umbric Gleysols
This group is characterised by the presence of organic rich layers or peat layers within the first 80 cm below surface. Circa two third of the locations in this group were 'eerdgronden' with organic rich topsoils. In the first 30 cm below surface only A horizons were found, the average measured percentage organic matter was 4.0. Between 30 cm and 60 cm also A horizons, and sometimes weak B-horizons, and between 60 cm and 100 cm below surface only C-horizons were found. These layers

had an average estimated percentage organic matter of respectively 1.5 and 0.1. Further consisted these soils of slightly loamy (10% - 15%) moderately coarse sand (155 - 180 μm). Circa a third of the locations in this group consisted of peat soils. In the first 30 cm below surface of these soils also only A horizons were found, but the average measured percentage organic matter was much higher i.e. 24. Between 30 cm and 60 cm mainly B and C-horizons and between 60 cm and 100 cm below surface several B and mainly C-horizons were found. These layers had an average estimated percentage organic matter of respectively 16 and 1.0. Further consisted these soils of mainly very loamy (9% - 22%) moderately coarse sand (100 - 160 μm). The humus layers for this group had an average thickness of 11 cm. These soils occurred in combination of the ground-water level classes poorly drained (V) and moderately (IV+VI) drained (Table 11).

Dystric gleysols

This group consisted of residual soils, not meant to be sampled in the first place because they are not non-calcareous sandy but old clay soils. The sampling of these locations is a result of the impurity of the soil map. They occurred on places where according to the soil map scale 1 : 50 000 sandy soils were expected. This is also a reason why we didn't exclude them. When using GIS information like a soil map, these soils occur also within the non-calcareous sandy soils. The humus layers had an average thickness of 7 cm. In the first 30 cm below surface only A horizons were found, the average measured percentage organic matter was 4.0 (Table 5.1.2). Between 30 cm and 60 cm A and C horizons and between 60 cm and 100 cm below surface C and a single B horizon were found, the estimated average percentages organic matter were respectively 1.5 and 1.0. Further because the group consisted of residual soils, the percentage loam had a great range from 25 to 70. The sand fraction was moderately coarse (155 - 170 μm). These soils occurred mainly in combination with the ground-water level class poorly drained (V) (Table 11).

3.4.2 Distribution of forest stands over soil types and ground-water tables

In general the distribution of the soil types of the 150 locations corresponded to the national distribution of forest soils. However Umbric Gleysols, Dystric Gleysols and Gleyic Podzols were slightly over-distributed (Table 12; total distribution). The relations between tree species and soil type are connected with the demands or tolerance of the tree species. They where planted on the different soils as much as Possible, according to their demands. Most tree species were found on Gleyic and Carbic Podzols, especially Norway spruce and Japanese larch. Because they have little demands towards nutrients and moisture, Scots pine and black pine were almost solely found on Arenosols and Gleyic Podzols. Douglas fir and Norway spruce have greater needs. Consequently, these trees were also found on mineral soils with a larger content of clay and organic matter.

Table 12 Distribution of the tree species of the 150 locations over soil type

Soil type	Distribution (%)								
	Scots pine	Black pine	Douglas fir	Norway spruce	Japanese larch	Oak	Beech	Total	
Haplic Arenosol[1]	30	50	13	0	7	10	0	18	(17)
Gleyic Podzol[2]	48	50	44	73	79	34	47	50	(43)
Cambic Podzol	20	0	19	0	7	7	13	12	(13)
Fimic Anthrosol	2	0	19	7	7	10	13	7	(8)
Umbric Gleysol[3]	0	0	6	20	0	24	20	10	(7)
Dystric Gleysol	0	0	0	0	0	14	7	3	(1)

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils
[4] Values in brackets are the percentage of the total forest area on the considered soils (De Vries et al., 1989a)

The coniferous tree species mainly occurred on well-drained soils, even though they sometimes occurred on moderately drained soils, whereas oak and beech were found relatively often on poorly drained soils. Japanese larch occurred on well-drained soils only (Table 13).

Table 13 Distribution of the tree species of the 150 locations over ground-water level class

Ground-water level class	Distribution (%)							
	Scots pine	Black pine	Douglas fir	Norway spruce	Japanese larch	Oak	Beech	Total
II+III	2	0	6	7	0	14	13	6
V	11	7	0	7	0	17	13	10
IV+VI	7	14	25	40	21	38	13	21
VII	16	21	31	13	50	7	20	20
VIII	64	57	38	33	29	24	40	44

4 Chemical composition of the humus layer

In this chapter we give an overview of the characteristics of the humus layer, subdivided in contents and pools of (i) organic matter (also thickness and bulk densities), (ii) nutrients, (iii) pH and exchangeable cations and (iv) heavy metals. First the variation in the observed data is given and then the influence of humus layer horizon and tree species is discussed. Furthermore, interpretations are given in view of available literature.

4.1 Pools, thickness and bulk densities of organic matter

Overall variation

The variation in thickness, pools and bulk densities of the humus layer is quite large (Table 14). As stated before, results are given for both the total pool, based on the weights the sampled humus layer, including mineral parts, and for the organic material in the humus layer. This, so-called, corrected pool of humus was calculated by multiplying the humus layer pool with the organic matter content, since mineral soil in humus layer sample is mainly due to inaccurate sampling. Bulk densities of the humus layer were calculated by dividing the measured humus layer pool with the measured thickness in the field. Again, a difference is made between the bulk density of the whole humus layer and the organic material in that layer (corrected value).

Table 14 Minimum, maximum, 5, 50 and 95 percentiles of the thickness, pool and bulk density of the humus layer

Statistics	Thickness (cm)	Pool (ton.ha^{-1})		Bulk density (kg.m^{-3})	
		uncorrected	corrected[1]	uncorrected	corrected[1]
minimum	2.0	20	9.2	62	39
5 percentile	3.6	36	21	80	50
50 percentile	8.3	95	66	124	77
95 percentile	13	185	113	242	107
maximum	16	298	156	490	134

[1] Corrected by multiplying the humus layer pool, including mineral soil parts, with the organic matter content. Note that the correction increases with an increasing pool or bulk density due to a lower organic matter content in those layers (more contamination of mineral soil).

Pools of organic matter in the humus layer varied mostly between 20 - 110 ton.ha^{-1}. Comparison of the humus layer pools with literature data (e.g. Mc Fee and Stone, 1965; Youngberg, 1966 and Van den Burg and Schoenfeld, 1988) indicate that most forest stands are in the phase of organic matter accumulation in the humus layer. In most forest stands, humus accumulation stops when the humus layer pool approaches a value of ca. 80 - 100 ton.ha^{-1} (Van den Burg and Schoenfeld, 1988) unless the conditions for de composition are extremely unfavourable (e.g. very wet circumstances). More than 50% of the stands have pools in or above this range. The maximum thickness of 16 cm, coinciding with an organic matter pool of 298 ton.ha^{-1}

(see the uncorrected value in Table 14), compares very well with maximum values reported by Mc Fee and Stone (1965).

The median bulk density of the humus layer (124 kg.m^{-3}; see the uncorrected value in Table 14) is slightly lower than data reported in the literature (e.g. Youngberg, 1966; Van den Burg and Schoenfeld, 1988; Kleijn et al., 1989), which are generally about 140 - 150 kg.m^{-3}. This is most likely due to a relatively thick layer of loose fresh leaves or needless in the L (litter) layer. This can also be derived from values given by Emmer (1995), who reported an average (corrected) bulk density of 30, 80 and 170 kg.m^{-3} for the L, F and H layer below Scots pine stands, respectively.

Comparison of an assumed maximum organic matter pool (corrected value) of ca 50 - 100 ton.ha^{-1} (depending on the conditions for decomposition) and a litterfall rate of ca 2 - 4 ton.ha^{-1}.yr^{-1} (De Vries et al., 1990) indicates an average annual litter decomposition rate of ca 1.5 - 8%. Since ca 40% of the freshly fallen leaves and needles mineralises during the first year (Janssen, 1983), the long-term decomposition rates vary between ca 1 and 5%. This is in the range of organic matter decomposition in the topsoil of agricultural soils in the Netherlands, which equals on average ca 2% per year (Kortleven, 1963).

Median values as a function of humus layer horizon and tree species
The humus layer mainly consisted of an F horizon with overlying freshly fallen leaves or needles (L horizon) with a much lower bulk density than the compacted humified H horizon (Table 15). In the H horizon, however, contamination with mineral soil occurred more often. Consequently, differences between the corrected bulk densities of the different horizons are much less than for the uncorrected values. The difference is lower than values reported by Emmer (1995) for these horizons (see above).

Table 15 Median values of the thickness, pool and bulk density for humus layer horizons

Horizon	N[1]	Thickness (cm)	Pool (ton.ha^{-1})		Bulk density (kg.m^{-3})	
			uncorrected	corrected	uncorrected	corrected
LF	142	7.3[2]	82	56	108	74
H	60 [3]	1.2	36	16	275	126
LFH	8	8.6	83	63	98	74
Total	150	8.3	95	66	124	77

[1] N is the number of locations.
[2] The median thickness of the L layer was 1.2.cm.
[3] At 60 locations, H horizons thicker than circa 1 cm were found, which were sampled separately.

Median values for the pool and bulk density of organic matter in the humus layer varied little between tree species (corrected values in Table 16), even though median thickness of the humus layer varied largely. Thickest median humus layers combined with the lowest median bulk density were found under Japanese larch, whereas thinnest median humus layers combined with a low bulk density and pool were found under black pine (Table 16). The humus layer under Japanese larch mainly consisted of a thick LF layer (median thickness 11.5 cm), indicating a low rate of humification. High bulk densities, combined with an average thickness of the humus

layer, were found under Scots pine, Norway spruce, oak and beech. It appeared that the humus layers of Norway spruce and Scots pine consisted for a relatively great part of H horizons (median thickness of respectively 1.2 and 1.9 cm), indicating a higher humification rate or an older forest stand. In general, the thickness of the H horizon increased with an increase in stand age, which has also been reported in the literature (Emmer, 1995).

Table 16 Median values of the thickness, pool and bulk density of the humus layer under seven major tree species

Tree species	Thickness[1] (cm)		Pool (ton.ha-1)		Bulk density (kg.m -3)	
			uncorrected	corrected	uncorrected	corrected
Scots pine	8.5	(7.4 / 1.9)	101	66	130	83
Black pine	6.3	(6.3 / 1.0)	66	40	111	64
Douglas fir	7.4	(6.6 / 0.5)	81	61	111	80
Norway spruce	8.2	(7.1 / 1.2)	92	65	130	88
Japanese larch	12	(11.5 / 0.7)	98	72	85	62
Oak	7.9	(6.0 / 0.9)	102	60	131	71
Beech	9.6	(8.1 / 0.7)	108	68	153	80

[1] Values in brackets are the thickness of the LF and H horizon, respectively.

Variation in organic matter contents
The organic matter content in the H layer was generally ca. 20% lower than in the LF layer (Table 17). A similar difference was observed by Emmer (1995) for five stands of Scots pine. Values below 25% for the H layer indicate the large degree of mineral contamination during sampling. Highest organic matter contents were generally found in the LFH horizons.

Table 17 Minimum, maximum, 5, 50 and 95 percentiles of the organic matter content in humus layer horizons

Horizon	N	Organic matter content (g.kg-1)				
		minimum	5%	50%	95%	maximum
LF	142	335	437	688	861	901
H	60	134	244	473	640	688
LFH	8	671	665	786	875	873
Total	150	242	423	664	838	901

The organic matter content of the humus layer varied considerably between different coniferous and deciduous tree species (Table 18). In stands of oak and beech, the organic matter contents were generally lowest, whereas highest values were generally found in stands of Japanese larch.

Table 18 Minimum, maximum, 5, 50 and 95 percentiles of the organic matter content in the total humus layer horizons under seven major tree species

Tree species	N	Organic matter content (g.kg-1)				
		minimum	5%	50%	95%	maximum
Scots pine	44	393	469	673	839	850
Black pine	15	322	347	654	828	837
Douglas fir	15	242	304	653	853	859
Norway spruce	15	413	453	695	831	842
Japanese. larch	16	662	663	796	866	873
Oak	30	301	335	577	739	901
Beech	15	498	500	631	718	723

4.2 Organic carbon and nutrients

Carbon and nutrient contents

An overview of the nutrient contents in the humus layer, normalised to the organic matter content is given in Table 19. Comparison of the results with various literature compilations (e.g. Kimmins et al., 1985; De Vries et al., 1990) indicate elevated contents of N and S and relatively low contents for P and Ca, whereas the Mg and K contents are very low. Compared to nutrient contents in foliage (Hendriks et al., 1994), the N and Ca contents are comparable, P and Mg contents are ca twice as low, whereas K contents are more than five times as low in the humus layer. This indicates the large mobility of K, which is almost directly leached from the freshly fallen foliage. The median C content in organic matter is 58% (Table 18), a value that is often used in the literature. In general, the nutrient contents were almost normally distributed, except for Ca where high contents were found in three calcareous soils.

Table 19 Minimum, maximum, 5, 50 and 95 percentiles of total nutrient contents in organic matter in the humus layer

Statistics	Nutrient contents (g.kg^{-1})						
	C	N	P	S	Ca	Mg	K
minimum	458	15	0.51	1.9	1.1	0.28	0.61
5 percentile	516	18	0.62	2.1	1.7	0.41	0.76
50 percentile	579	22	0.81	2.8	3.0	0.61	1.1
95 percentile	629	28	1.3	3.9	6.9	1.3	2.4
maximum	658	30	2.1	5.0	1.5	2.3	7.4

No striking differences in nutrient contents were found between the humus layer horizons except for Ca and K, with respectively lower and higher contents in the H horizon than in the LF horizon (Table 20). This observation is opposite to Emmer et al. (1991) who found a decreasing K/Ca ratio going from the F to the H horizon in a primary succession range under Scots pine.

Table 20 Median values of total nutrient contents in organic matter in the humus layer horizons

Horizon	Nutrient contents (g.kg^{-1})						
	C	N	P	S	Ca	Mg	K
LF	576	22	0.81	2.8	3.0	0.61	1.0
H	602	23	0.93	3.3	2.3	0.66	1.5
LFH	568	19	0.71	2.9	2.2	0.44	0.98
Total	579	22	0.81	2.8	3.0	0.61	1.1

Median nutrient contents in the humus layer hardly varied between tree species except for oak, where relatively high Ca contents were found. For oak the N, Mg and K content was also higher than for the other species (Table 21). This is in accordance with the elevated foliar N, Ca and K contents in oak (Hendriks et al., 1994), which has a higher nutrient demand and stands on relatively poorly-drained rich soils with Ca input by seepage (cf. Table 12 and 13). Nutrient contents in the humus layer below stands of Douglas are comparable to those observed in eight Douglas stands in 1987 (Kleijn et al., 1989).

Table 21 Median values of the total nutrient contents in organic matter in the humus layer under seven major tree species

Tree species	Nutrient contents (g.kg^{-1})						
	C	N	P	S	Ca	Mg	K
Scots pine	577	20	0.74	2.7	2.3	0.51	1.0
Black pine	557	19	0.79	2.8	2.5	0.53	1.0
Douglas fir	580	24	0.92	3.1	3.1	0.57	1.1
Norway spruce	583	22	0.89	2.8	2.7	0.53	0.96
Japanese. larch	567	22	0.75	2.9	3.4	0.66	0.83
Oak	580	27	0.93	3.2	4.6	0.99	1.4
Beech	588	24	0.90	2.8	2.7	0.66	1.3

Carbon and nutrient ratios

Ratios of C to N give indications about the degree of net N mineralisation (mineralisation minus immobilisation) in the humus layer. According to various textbooks. (e.g. Waring and Schlesinger, 1985; Stevenson, 1986) the critical C/N ratio at which net mineralisation starts varies between 20 - 30. The variation is determined by various factors influencing the rate of C and N mineralisation such as pH, moisture content and temperature (Hendriks, 1992). In general, immobilisation dominates at C/N ratios above 30 (oligotrophic systems), whereas mineralisation dominates at C/N ratios below 20 (eutrophic systems) in Dutch fens (Kemmers, 1990). Succow (1988) suggested a similar range for peat soils, which can be considered comparable to humus layers.

The distribution of the nutrient ratios was quite normal (Table 22). In general the C/N ratios in the humus layer of mineral poor non-calcareous sandy soils are expected to be larger than 25 coinciding with mesotrophic to oligotrophic environments. However, only some 50% of the sites had C/N ratios above 25. The lower C/N values indicate the effect of elevated N deposition. The number of sites exceeding a critical C/N ratio of 30 was 16%. In these sites, all N is assumed to immobilise. However, since the composition of organic matter varies considerably, the C/N ratio of decomposed organic matter may deviate strongly from the average C/N ratio. Various authors, such as Dammen (1988) and Verhoeven et al. (1990) thus observed net N mineralisation at C/N ratios above 40 and even 60. Data on elevated NO_3 concentrations in the soil solution at sites where the C/N ratio of the humus layer exceeds 30 also indicate that N immobilisation is not complete in this situation (Chapter 7).

Table 22 Minimum, maximum, 5, 50 and 95 percentiles of nutrient ratios in the humus layer

Statistics	Nutrient ratios				
	C/N	C/P	C/S	N/P	N/S
minimum	17	284	116	13	5.0
5 percentile	21	429	146	18	6.0
50 percentile	26	714	206	26	7.8
95 percentile	34	928	271	34	10
maximum	39	1126	301	43	12

Even though C/N ratios are relatively low compared to areas with a low N deposition, such as Scandinavia, the values indicate that considerable N immobilisation may still take place in most of the sites. This is in accordance with

results from input - output budgets of the 150 sites, which indicate that on average ca 80% of the incoming N is retained in the forest ecosystem (De Vries and Jansen, 1994).

As with the C/N ratio, the C/P and C/S ratios do give some indication about the rate of net P and S mineralisation. Assuming that fungi dominate mineralisation and using a C/P and C/S ratio of both 67 in fungi (Janssen, 1983) leads to a critical C/P and C/S ratio of 200. Similar values are given by Stevenson (1986). The numbers of sites exceeding these critical values are 100% for P and 45% for S (cf. Table 22). In a summarising literature review on decomposition and mineralisation of peat soils, Hendriks (1992), however, concludes that the relationship between C and P mineralisation is much weaker than between C and N. Most likely this is also the case for C and S. The observed nutrient ratios do, however, indicate that net mineralisation of P is likely to be very small, whereas net S mineralisation is considerable. The latter result is in accordance with results from input-output budgets of the 150 sites, which indicate that on average all the incoming SO_4 is leached from the system (De Vries and Jansen, 1994). The high C/P ratios indicate P deficiencies in these forest soils. This is in accordance with the results of foliar P contents, which indicate an absolute P deficiency in 63% of the sites (Hendriks et al., 1994).

As with the nutrient contents, no striking differences were found between nutrient ratios in the LF and H horizons (Table 23). This is contrary to the expectations. After litterfall, the humus layer is subjected to a complicated process of decomposition, humification and mineralisation. During the decomposition process N, P and S are mineralised, whereas C disappears as CO_2 out of the system. During the humification process N, P and S are build into complex organic structures. Therefore the C/N, C/P and C/S ratios decrease during these processes. Recently fallen leaves or needles in the LF horizon are hardly decomposed and are thus expected to have higher C/N, C/P and C/S ratios than the H horizon. In the mineral layer, however, the C/N and C/P ratios were obviously lower, especially the C/P ratio (Table 43). Jansen et. al. (1994) found the same differences between layers for the country-seat 'De Wildenborch'.

Table 23 Median values of nutrient ratios in the humus layer horizons

Horizon	N	Nutrient ratios				
		C/N	C/P	C/S	N/P	N/S
LF	142	26	716	209	27	8.0
H	60	27	685	183	25	6.9
LFH	8	29	779	217	26	7.7
Total	150	26	714	206	26	7.8

The median nutrient ratios in the humus layer varied little between tree species (Table 24). Lowest C/N, C/P and C/S ratios were generally found in the humus layers under oak.

Table 24 Median values of the nutrient ratios in the humus layer under seven major tree species

Tree species	Nutrient ratios				
	C/N	C/P	C/S	N/P	N/S
Scots pine	29	777	213	26	7.4
Black pine	30	754	199	23	6.9
Douglas fir	24	635	182	26	7.7
Norway spruce	27	672	219	26	8.1
Japanese. larch	26	750	204	30	8.1
Oak	22	640	179	27	8.2
Beech	25	672	212	26	8.3

Carbon and nutrient pools

As with the nutrient contents, pools of nutrients varied according to a normal distribution, except for Ca (Table 25). Average annual nutrient demands in view of net growth uptake are approximately 5-10 kg.ha^{-1} for N, 2.5-5 kg.ha^{-1} for Ca, 0.5-1.0 kg.ha^{-1} for Mg and 2-4 kg.ha^{-1} for K (De Vries, 1993). This implies that the pools in the humus layer can provide the tree with nutrients during a long period, except for K. In general, long-term nutrient supply consists of atmospheric deposition and long-term weathering, but the pools in the humus layer are an important buffer.

Table 25 Minimum, maximum, 5, 50 and 95 percentiles of the carbon and nutrient pools in the humus layer

Statistics	Nutrient pool (kg.ha^{-1})						
	C	N	P	S	Ca	Mg	K
minimum	5459	247	15	30	32	7.6	13
5 percentile	11478	469	22	65	77	14	28
50 percentile	36833	1430	51	177	185	39	65
95 percentile	67112	2549	96	327	376	91	173
maximum	89835	3061	141	458	600	183	648

As with the pools of organic matter (Table 15), the median nutrient pools in the LF horizon were almost three times the median pools found in the H horizon (Table 26). The only exception is K, which is due to the relatively high K content in the H horizon (see Table 20).

Table 26 Median values of the carbon and nutrient pool in the humus layer horizons

Horizons	Nutrient pool (kg.ha^{-1})						
	C	N	P	S	Ca	Mg	K
LF	32850	1189	44	148	164	32	57
H	9986	346	14	55	40	11	27
LFH	36489	1273	47	170	148	27	58
Total	36833	1430	51	177	185	39	65

As with the pools of organic matter (Table 16), median nutrient pools varied little between tree species, except for the low pools in black pine stands. (Table 27). Another difference is the slightly larger Ca, Mg and K pools in stands of Japanese Larch and the deciduous trees, oak and beech, correlating with higher K contents in the humus layer (Table 21).

Table 27 Median values of the carbon and nutrient pools in the humus layer under seven major tree species

Tree species	Nutrient pool (kg.ha^{-1})						
	C	N	P	S	Ca	Mg	K
Scots pine	37984	1363	49	176	153	38	69
Black pine	22718	727	31	115	82	25	41
Douglas fir	34028	1351	49	165	185	36	58
Norway spruce	36207	1562	55	193	207	34	62
Japanese. larch	40359	1621	59	209	268	48	62
Oak	36122	1592	57	182	241	50	74
Beech	40829	1579	66	195	185	43	82

4.3   Soil acidity and exchangeable cations

Soil acidity

Results for the pH in a water extract and in a KCl extract generally varied between 3.5 and 5 and between 2.5 and 4, respectively, in the humus layer (Table 28). Such low values are generally observed in humus layers of non-calcareous sandy soils in the Netherlands (Kleijn et al., 1989; Van Breemen and Verstraten, 1991; Emmer, 1995). Differences between pH-H$_2$O and pH-KCl were constant approximately 1. These differences generally increase with an increase in CEC. The pH values measured in the H horizon were lower than those in the LF horizon (Table 28). According to Emmer et al. (1991) there is a clear relation between the decrease of the pH and the accumulated pool of the acid, humified organic matter in the (H horizon) of the humus layer.

Table 28 Minimum, maximum, 5, 50 and 95 percentiles the pH-H$_2$O and the pH-KCl in the humus layer horizons

Statistics	pH-H$_2$O of the horizons				pH-KCl of the horizons			
	LF	H	LFH	Total	LF	H	LFH	Total
minimum	3.6	3.3	3.8	3.5	2.5	2.4	2.7	2.5
5 percentile	3.6	3.4	3.8	3.6	2.6	2.4	2.7	2.6
50 percentile	3.8	3.5	4.0	3.8	2.9	2.6	2.9	2.8
95 percentile	4.3	3.9	4.1	4.2	3.5	2.9	3.0	3.5
maximum	5.1	4.1	4.1	5.1	4.2	3.1	3.0	4.2

Differences in the median measured pH between the separate tree species were generally negligible (Table 29).

Table 29 Median values of the pH-H$_2$O and the pH-KCl for the humus layer horizons under seven major tree species

Statistics	pH-H$_2$O of the horizons				pH-KCl of the horizons			
	LF	H	LFH	Total	LF	H	LFH	Total
Scots pine	3.8	3.5	4.0	3.8	2.8	2.5	2.9	2.8
Black pine	3.9	3.5		3.9	3.0	2.6		2.9
Douglas fir	3.8	3.7	4.1[*)]	3.9	2.8	2.6	2.9[*)]	2.9
Norway spruce	3.8	3.5		3.7	2.8	2.5		2.8
Japanese. larch	3.8	3.5	3.8[*)]	3.7	2.8	2.5	2.7[*)]	2.7
Oak	4.0	3.7	4.0[*)]	3.9	3.0	2.8	3.0[*)]	2.9
Beech	3.8	3.6		3.7	2.8	2.5		2.7

[*)]   Based on one sample only

Cation exchange capacity

The cation exchange capacity (CEC), which is mainly related to the organic matter content, especially in the humus layer, varied considerably over the various forest stands (Table 30). Even the CEC normalised to the organic matter content varied quite strongly indicating the effect of organic matter quality and pH on the CEC. In most stands the CEC varied between 200 and 400 $mmol_c.kg^{-1}$. Comparison with literature data shows that the CEC for these humus layers is low. Youngberg (1966), for example, reports CEC values for humus layers in nine Douglas-fir stands ranging between 540 and 670 $mmol_c.kg^{-1}$. Reported organic matter contents varied between 69 and 86%, indicating a CEC ranging between ca 6 - 10 $mmol_c.kg^{-1}$ for 1% of organic matter. Khanna et al. (1986) and Van Wesemael (1992) report average values of ca 8.0 and 9.7 $mmol_c.kg^{-1}$ per % organic matter for humus layers in sub-alpine and Mediterranean forests, respectively. The differences may partly be due to the lower pH values in the Dutch forest stands (ca pH - H_2O ca 3.5 - 5) compared to those forest stands (pH - H_2O ca 4 - 6). Kalisz and Stone (1980), for example, reported an increase of 3.0 $mmol_c.kg^{-1}$ per % organic matter per pH unit. The average value of 7.6 $mmol_c.kg^{-1}$ for 1% organic matter reported by Kleijn et al. (1989) for mineral topsoils of acid sandy soil is also clearly higher than the values observed in the 150 forest stands, which range between 2.4 and 8.0 $mmol_c.kg^{-1}$ per % organic matter. The reason for this difference is most likely the lower degree of humification in the humus layer (see also Chapter 5).

Table 30 Minimum, maximum, 5, 50 and 95 percentiles of the CEC of the humus layer

Statistics	CEC		CEC of 1% organic matter
	$mmol_c.kg^{-1}$	$kmol_c.ha^{-1}$	$mmol_c.kg^{-1}$
minimum	142	5.0	2.4
5 percentile	201	8.8	3.6
50 percentile	302	30	4.7
95 percentile	386	54	5.9
maximum	498	73	8.0

The median CEC varied only slightly between the various humus layer horizons and tree species (Table 31). As with the organic matter contents, the median CEC in the humus layer was highest under Japanese larch and under black pine lowest (Table 16). In general the CEC was slightly higher in the LF horizon than in the H horizon which is most probably due to the higher organic matter content and pH of the LF horizon.

Table 31 Median values of the CEC for of humus layer horizons under seven major tree species

Tree species	CEC ($mmol_c.kg^{-1}$)				CEC ($kmol_c.ha^{-1}$)			
	LF	H	LFH	Total	LF	H	LFH	Total
Scots pine	281	294	273	275	23	14	23	29
Black pine	254	268		254	16	5.3		16
Douglas fir	319	305	358[*]	320	25	5.4	25[*]	26
Norway spruce	315	286		310	27	7.8		30
Japanese. larch	362	337	404[*]	370	35	10	32[*]	35
Oak	331	239		321	26	9.3		31
Beech	323	281		318	26	20		31

[*] Based on one sample only

Exchangeable cation contents and pools

Exchangeable cations on the adsorption complex in the humus layer were generally dominated by protons (H) followed by Ca (Table 32). Exchangeable Al contents were relative low, since there is no mineral pool of Al in organic matter. The distributions of the exchangeable cations in the humus layer were all relatively normal. There were several locations with relatively high Ca and/or Al and/or Fe occupation and several locations with relatively low H occupation.

Table 32 Minimum, maximum, 5, 50 and 95 percentiles of the exchangeable cation content (in percentage of the CEC) of the humus layer

Statistics	Exchangeable cation content (%)							
	H	Al	Fe	Ca	Mg	K	Na	NH_4
minimum	5.4	1.5	1.0	14	2.3	1.7	0.4	1.4
5 percentile	23	3.1	1.8	16	4.1	2.4	0.9	2.2
50 percentile	45	6.3	3.7	24	6.9	4.0	1.9	4.2
95 percentile	56	13	8.5	46	11	7.3	3.8	7.3
maximum	63	21	16	61	17	10	6.8	12

Obvious differences in exchangeable cation contents were observed between the LF and H horizon. The LF horizon had almost twice as high Ca, Mg, K, Na and NH_4 contents as the H horizons, which had on the other hand almost twice as high Al and Fe contents (Table 33). The lower contents of base cations correspond to the lower pH of the H horizon, which is correlated to the stronger dissociation of protons from the humified organic matter pool.

Table 33 Median values of the exchangeable cation content (in percentage of the CEC) for the humus layer horizons

Horizon	Exchangeable cation content (%)							
	H	Al	Fe	Ca	Mg	K	Na	NH_4
LF	44	5.7	3.5	26	7.1	4.1	1.9	4.5
H	56	12	6.0	14	3.6	2.7	0.9	2.2
LFH	47	6.3	3.4	24	6.1	4.5	2.2	4.7
Total	45	6.3	3.7	24	6.9	4.0	1.9	4.2

Exchangeable cation contents in the humus layer hardly varied between various tree species, except that the exchangeable base cation (specifically calcium) content was higher under oak while the exchangeable H content was lower (Table 34). A comparison between exchangeable and total contents of the cations Ca, Mg and K in the humus layer showed that the exchangeable content is 77%, 58% and 66%, respectively.

Table 34 Median values of the exchangeable cation content (in percentage of the CEC) of the humus layer under seven major tree species.

Tree species	Exchangeable cation content (%)							
	H	Al	Fe	Ca	Mg	K	Na	NH_4
Scots pine	49	7.1	3.9	22	5.7	4.2	1.8	4.1
Black pine	46	7.2	4.1	21	7.5	4.9	2.2	5.0
Douglas fir	44	5.8	3.3	25	6.0	3.8	2.6	5.7
Norway spruce	46	6.1	3.2	23	6.1	4.2	2.4	5.0
Japanese. larch	45	5.8	2.5	28	7.8	3.2	2.7	4.3
Oak	38	4.9	3.6	33	8.4	4.4	1.7	3.8
Beech	46	7.8	5.8	22	5.6	3.7	1.7	3.6

As with the exchangeable cation contents, the exchangeable cation pools decreased according to H > Ca followed by Mg, K, Na, Al, NH_4 and Fe (Table 35). James and Riha (1986) claimed that pH buffering in humus layers of acid forest soils is extremely important because of the relatively large pool of base cations in this layer. Considering a net acid input of ca 5.0 $kmol_c.ha^{-1}.yr^{-1}$ on Dutch forests in 1990 (Erisman, 1992), however, it is clear that the exchangeable pool of base cations is generally quite limited. Furthermore, a constant supply of base cations by litterfall and mineralisation and in throughfall prevents a large proton buffering by base cation release from the adsorption complex. This can also be derived from the low pH values in the humus layer, although the base saturation is relatively large.

Table 33 Minimum, maximum, 5, 50 and 95 percentiles of the exchangeable cation pool in the humus layer

Statistics	Exchangeable cation pool ($kmol_c.ha^{-1}$)							
	H	Al	Fe	Ca	Mg	K	Na	NH_4
minimum	0.44	0.11	0.13	1.0	0.29	0.24	0.04	0.15
5 percentile	2.6	0.40	0.39	2.6	0.64	0.45	0.12	0.35
50 percentile	13	1.9	1.0	7.3	1.8	1.1	0.52	1.2
95 percentile	24	5.7	2.9	13	4.0	2.3	1.3	2.4
maximum	44	11	8.3	29	7.8	4.4	3.1	3.5

4.4 Heavy metals

Overall variation in heavy metal contents

The variation in heavy metal contents in the humus layer is large. The concentrations are clearly elevated compared to values observed for relatively unpolluted humus layers. Background concentrations, based on observations in humus layers in the northernmost part of Sweden, where the influence of long-distance dispersal of atmospheric pollution is low and outside the influence of local emission sources, are comparable to the 5 percentiles observed in the 150 forest stands (cf. Table 36 and 37).

Table 36 Minimum, maximum, 5, 50 and 95 percentiles of the heavy metal content in the humus layer (uncorrected samples of humus layer including mineral soil)

Statistics	Heavy metal content ($mg.kg^{-1}$)					
	Pb	Cd	Cu	Zn	Ni	Cr
minimum	17	0.14	4.3	29	4.4	4.0
5 percentile	40	0.34	7.1	39	5.9	7.6
50 percentile	113	0.68	16	72	12	13
95 percentile	282	2.1	45	219	22	27
maximum	745	4.9	268	852	111	46

In general, there was a clear relationship between the regional patterns in heavy metal deposition and the heavy metal contents in the humus layer (Leeters et al., 1994). The high to extremely high contents of Pb, Cd, Cu and Zn, above the critical value and intervention value respectively, were mainly located in the strongly polluted Kempen area in the southern part of the Netherlands. With respect to Cd and Zn, these high contents exclusively occur in this area, where a zinc smelter has emitted large amounts of both heavy metals. Metal contents with a similar order of magnitude as

the maximum values for Pb, Cd, Cu and Zn have been reported in humus layers in the Kempen area (Pedroli et al., 1990; Van Mourik, 1991; Wilkens, 1995).

Elevated metal contents in humus layers have been observed in all areas with an elevated atmospheric input of heavy metals, such as southern Norway (Steinnes et al., 1988), New Hampshire (Reiniers et al., 1975; Andresen et al., 1980; Siccama et al., 1980), Germany (Heinrichs and Mayer, 1986; Neite et al., 1992) and the Netherlands (Kleijn et al., 1989; Pedroli et al., 1990; Van Mourik, 1991). Except for Zn, which is extremely high due to the occurrence of a zinc smelter, similar high values have been reported for forests in Germany (Brümmer et al., 1986; Heinrichs and Mayer, 1986). In general, the range in reported Pb, Cd, Cu and Zn contents in ca 300 humus layers in North-Rhine-Westphalia is even ca twice as high for Pb and Cu, whereas it is comparable for Cd and Zn (Neite et al., 1992). The main cause of the elevated heavy metal contents in forest soils is the atmospheric deposition of these metals induced by emissions from industry and traffic. Some contamination might be due to the use of heavy metal containing fertilisers or sewage sludge in the past, but this influence is likely to be negligible.

The contents of Cd and Zn in the humus layers were highly correlated (Table 37). Reasonably high correlations were also found between contents of Pb and those of Ni, Cd and Zn. This indicates co-deposition of these metals. Similar correlations were observed in surface soils (top 3-5 cm of the Ah horizons) in Southern Norway (Steinnes et al., 1988). Metal concentrations in this top mineral layer are often quite comparable to the humus layer (Parker et al., 1978).

Table 37 Correlations between contents of heavy metals in the humus layer

Heavy metal	Correlation coefficient					
	Pb	Cd	Cu	Zn	Ni	Cr
Pb	-					
Cd	0.49	-				
Cu	0.28	0.25	-			
Zn	0.42	**0.90**	0.20	-		
Ni	0.50	0.01	-0.03	0.00	-	
Cr	0.35	0.34	0.19	0.31	0.20	-

Risks of elevated heavy metal contents in humus layers
In order to judge the risk associated with the elevated heavy metal contents, information is needed on critical levels, which are defined as the maximum metal contents which do not show an adverse effect on the terrestrial ecosystem. In this context, a distinction can be made in effects of elevated metal concentrations on (Tyler, 1992):
- (i) Soil microorganisms and macrofungi. Effects include reduced microbial biomass and/or species diversity, thus affecting microbial processes such as enzyme synthesis and activity, litter decomposition, associated with C and N mineralisation, and soil respiration. A review of these effects is given by Bååth (1989).

- (ii) Soil fauna, especially invertebrates such as nematodes and earth worms. Effects include a decrease in abundance, diversity and biomass. A review of these effects is given by Bengtsson and Tranvik (1989)
- (iii) Vascular plants including trees. Effects include reduced development and growth of roots and shoots (toxicity symptoms), elevated concentrations of starch and total sugar and decreased nutrient contents in foliar tissues (physiological symptoms) and decreased enzymatic activity (biochemical symptoms). A review of these phytotoxic effects is given by Balsberg-Påhlsson (1989).

Other effects are heavy metal accumulation in terrestrial fauna, such as birds, and humans but these are considered (relatively) unimportant with respect to forest ecosystems. Effects on vascular plants are primarily related to concentrations in the soil solution and foliar contents (Balsberg-Påhlsson, 1989), whereas effects on soil microbio and soil invertebrates are specially related to total metal contents, either in the humus layer or the mineral soil. (Bååth, 1989; Bengtsson and Tranvik, 1989; Witter, 1992; Tyler, 1992). A summarising overview of the critical contents in humus layers thus derived is given in Table 38 (After Tyler, 1992). Table 38 also contains information on critical concentration levels used in the Dutch legislation.

Table 38 Background values and different critical values of heavy metal contents in humus layers

Type of concentration level	Heavy metal content (mg.kg^{-1})					
	Pb	Cd	Cu	Zn	Ni	Cr
Background value[1]	15	0.35	5	35	10	2.5
Target value[2]	115	1.8	55	145	20	50
Critical value[3]						
- soil microbiota	500	3.5	20	300	50	30
- soil invertebrates	150	10	100	500	-	-
- both effects	150	3.5	20	300	50	30
Intervention value[4]	720	27	290	770	60	190

[1] Based on data in northern most Sweden (Andersson et al., 1991), except for Ni, which is based on observed Ni contents in unpolluted peat soils in the Netherlands (Edelman, 1983).
[2] Based on concentrations in topsoils of relatively unpolluted areas in the Netherlands (Edelman, 1983). The values are calculated from a given intercept and a relation with the organic matter content. For Ni the target value was arbitrarily set twice as high as the background value.
[3] Based on an overview by Tyler (1992) for humus layers or mor horizons, except for Ni, which is based on Witter (1992). The latter value refers to mineral soils and not to humus layers.
[4] Values used in the Dutch legislation.

The most important levels are the target value and the intervention value. The target value is simply based on heavy metal contents in the top 10 cm of agricultural soils and forest soils, which were assumed to represent background values (Edelman, 1983; Edelman and De Bruin, 1986). The values depend on the content of organic matter and clay (Annex 1). The values given in Table 37 are based on an assumed clay content of 0% and an organic matter content of 66%, namely the median value observed in the humus layers (Table 14). The so-called intervention values, above which sanitation actions are required, also depend on the clay and organic matter content (Annex 1). The values given in Table 38 are based on the same assumptions as those given for the target values.

Compared to background concentrations (cf. Table 36 and Table 38), pollution of heavy metals is mainly limited to Pb, Cd, Cu and Zn. In general, the humus layers are most strongly polluted with Pb, followed by Zn, Cd and Cu (Table 39). Extremely high values, exceeding the so called intervention value, above which sanitation actions are required, were only observed for Pb, Cu, and Zn (compare Table 36 and 38) at three locations.

Table 39 Distribution of forested sites over different critical contents of heavy metals in humus layers, based on various sources and approaches

Type of concentration level	Distribution (%)					
	Pb	Cd	Cu	Zn	Ni	Cr
< Target value	55.3	94.7	98	89.3	98.7	100
Target-Critical value[1]	22.7	4.7	1.3	8.7	0.0	0
> Critical value	22.0	0.7	0.7	2.0	1.3	0

[1] The minimum value of effects on soil microbiota and soil invertebrates was used (Table 37), except for Cu.

Assuming that the critical values in Table 39 are correct, toxic effects of heavy metals on soil microbiota and soil invertebrates seems quite unlikely in Dutch forests, except for Pb. Elevated heavy metal concentrations in the soil solution and in the foliage (not measured) may, however, still affect the forest vitality. Furthermore, elevated metal contents in the litter layer may retard decomposition (Rühling and Tyler, 1973; Tyler, 1975; Tyler and Westman, 1979), thus lowering the availability of nutrients. Hendriks et al. (1994) thus found a relationship between the foliar P and Mg content in the 150 forest stands and the heavy metal contents in the humus layers. More research with respect to the possible role of heavy metals in novel forest decline thus seems warranted (cf. Nuorteva, 1990).

Median heavy metal contents as a function of humus layer and tree species
Differences between heavy metal contents in LF and H layers were relatively small (Table 40). Unlike data given by Van Mourik (1991), we did not observe a clear decrease in heavy metal content going from the LF to the H layer. Pedroli et al. (1990) observed a large difference in Pb, Cd, Cu and Zn contents in L and F layers but these humus layers horizons were not sampled separately in the present study.

Table 40 Median values of the heavy metal content in the humus layer horizons (uncorrected samples of humus layer including mineral soil)

Horizon	N	Heavy metal content ($mg.kg^{-1}$)					
		Pb	Cd	Cu	Zn	Ni	Cr
LF	142	105	0.68	16	73	11	12
H	60	149	0.73	19	61	13	19
LFH	8	132	1.0	23	93	11	12
Total	150	113	0.68	16	72	12	13

Contents of Pb, Cd, Cu and Zn, in humus layers generally decreased going from spruce forests to pine forests to deciduous forests (Table 41). Highest contents were mostly found below stands of Douglas fir and lowest below oak stands. This is most likely due to a decrease in leaf biomass, thus affecting the dry deposition of heavy metals. The influence of the forest canopy on dry deposition can also be derived

from the ratio between heavy metal contents in humus layers below forested sites and nearby non-forested sites, such as heathlands. Average ratios thus derived for five paired sites vary between 2.3 and 2.9 for Pb, Cd, Cu and Zn and between 1.1 and 1.7 for Ni and Cr (De Vries and Bakker, 1998). This illustrates that contents of Pb, Cd, Cu and Zn are clearly influenced by atmospheric inputs. The effect of elevated dry deposition of elements by forest canopies is also evident in the soil solution (Chapter 6).

Table 41 Median values of the heavy metal content in the humus layer under seven major tree species (uncorrected samples of humus layer including mineral soil)

Tree species	Heavy metal content (mg.kg^{-1})					
	Pb	Cd	Cu	Zn	Ni	Cr
Scots pine	127	0.87	17	76	12	13
Black pine	109	0.68	15	70	12	12
Douglas fir	146	0.85	24	80	13	14
Norway spruce	104	0.64	16	64	9.2	13
Japanese. larch	105	0.67	15	73	10	11
Oak	76	0.52	13	64	12	14
Beech	122	0.60	17	63	13	16

Heavy metal pools
By multiplying the humus layer pool (Table 14) with the heavy metal contents in this layer (Table 36), the heavy metal pools in the humus layer were calculated (Section 2.6). As with the metal contents, the variation in the heavy metal pools is large (Table 42). The heavy metal pools are relatively large compared to reported literature data, especially with respect to Pb, Cu and Zn. Andersson et al. (1991) reported 90% intervals (intervals between the 5 percentile and 95 percentile) of 0.59-10 for Pb, 0.0-0.41 for Cd, 0.13-1.4 for Cu and 1.1-9.4 for Zn in humus layers in Sweden, influenced by atmospheric deposition (cf. Table 42). Values reported by Van Hook et al. (1977) on Cd and Zn pools in humus layers below forests in Eastern Tenessee also approach the lower range reported for Dutch forests (Table 42). Pb pools reported for forested sites in central New Hampshire (9 kg.ha^{-1}; Siccama et. al., 198o) approach the median value reported for Dutch forest.

Table 42 Minimum, maximum 5.50 and 95 percentile of heavy metal pools in the humus layer

Statistics	Heavy metal pool (kg.ha^{-1})					
	Pb	Cd	Cu	Zn	Ni	Cr
minimum	0.47	0.01	0.12	0.81	0.20	0.20
5 percentile	2.5	0.02	0.41	2.5	0.43	0.43
50 percentile	11	0.06	1.6	7.1	1.0	1.3
95 percentile	29	0.19	4.8	22	2.4	2.9
maximum	63	0.67	32	90	6.5	8.2

Apart from critical contents, Tyler (1992) also gives maximum pools of heavy metals that can be added to forest humus layers without exceeding critical values. These pools (in kg.ha^{-1}) equal 7.0 for Pb, 0.2 for Cd, 1.0 for Cu, 16 for Zn and 2.25 for Cr. Comparison with the data in Table 42 shows a considerable number of sites exceeding the critical value for Pb and Cu (more than 50%). Unlike the heavy metal contents, the variation in heavy metal pools below tree species do not clearly indicate

a decrease in dry deposition going from spruce (fir) stands to pine stands to deciduous stands (Table 43).

Table 43 Median values of the heavy metal pool in the humus layer below seven major tree species

Tree species	Heavy metal pool (kg.ha-1)					
	Pb	Cd	Cu	Zn	Ni	Cr
Scots pine	14	0.10	1.9	8.6	1.2	1.4
Black pine	5.8	0.05	0.7	4.4	0.70	0.69
Douglas fir	12	0.06	2.1	7.2	1.0	1.1
Norway spruce	8.5	0.07	1.4	7.6	0.93	1.3
Japanese. larch	10	0.06	1.3	6.9	1.0	1.0
Oak	9.2	0.05	1.4	6.1	0.85	1.3
Beech	16	0.07	2.2	7.2	1.5	1.8

Assessment of average annual metal deposition rates

An indication of the average annual deposition rate of heavy metals has been derived by dividing the heavy metal pool in the humus layer with the age of the trees. This approach assumes that (i) heavy metal accumulation started in the humus layer at the time of tree planting and (ii) the humus layer behaves as a perfect sink for heavy metals. The first assumption is reasonable for first-generation forests where tree age, (which was known) equals stand age (which was not known), but may lead to an overestimation in second-generation forests. On the other hand, the second assumption will lead to an underestimation, since part of the heavy metals are accumulating in the uppermost mineral layer and/or leached to lower soil depths.

Results of the calculated deposition rate vary considerably (Table 44). The variation in reported Pb, Cd and Zn deposition rates over the Netherlands (Van Jaarsveld et al., 1991), based on model calculations with the deposition model TREND (Van Jaarsveld and Onderdelinden, 1993) compares quite well with those given in Table 44. A more specific comparison with deposition data for the 150 forest stands, based on an overlay procedure with TREND model results for a 10 km x 10 km gridcell using 1985 emission data, however, shows that the TREND deposition data tend to be lower than those reported in Table 44. The ranges (in g.ha-^{1}.yr^{-1}) equal 114-203 for Pb, 0.47-1.5 for Cd, 7.2-29 for Cu and 30-89 for Zn (Leeters et al., 1994).

Table 44 Minimum, maximum 5,50 and 95 percentile values of the calculated average deposition rates of heavy metals on the forests since the time of planting

Statistics	Heavy metal deposition rate (g.ha-1.yr-1)					
	Pb	Cd	Cu	Zn	Ni	Cr
Minimum	1.8	0.02	0.53	5.4	5.9	2.2
5 percentile	57	0.37	12	56	10	11
50 percentile	199	1.3	31	139	21	25
95 percentile	647	5.4	105	536	67	85
Maximum	1910	14	1879	1499	208	177

Nevertheless, it is likely that the estimated values, both in Table 44 (and by the TREND model) are an underestimate of the annual input, especially with respect to Cd and Zn that are relatively mobile, but also with respect to Pb and Cu.

Available literature information on the distribution Pb, Cd, Cu and Zn in forest soil profiles in the Netherlands indicate that accumulation of these heavy metals is not limited to the humus layer. It also occurs in the uppermost mineral soil horizons, up to ca 30 cm. (Breeuwsma, 1983; Pedroli et al., 1990; Van Mourik, 1991; De Vries et al., 1994b; Wilkens, 1995). Leaching to lower soil depths is very limited for Pb and Cu, which form strong complexes with organic matter (Bergkvist et al., 1989). Humus layers and uppermost mineral layers thus act as an important sink for these heavy metals, considering that metabolisation by soil fauna or uptake by trees is limited (Bergkvist et al., 1989).

Contents of Pb, Cd, Cu and Zn in the mineral topsoil are generally more than ten times as low, as the humus layer. Considering the much larger (often more than times) bulk density of mineral soils, however, the pool of these metals in the mineral topsoil can be larger as in the humus layer. Data for the heavy metal contents up to a depth of 100 cm in twelve of the 150 forest stands indicate metal accumulation up to a depth of 30 cm for Pb, Cd and Cu and to a lesser extent Zn. The accumulated pool generally equalled or even exceeded the pool in the humus layer. Accumulated metal pools (in $kg.ha^{-1}$) varied between 13 and 74 for Pb, 0.05-0.65 for Cd, 1.0-16 for Cu and 2.0-17 for Zn (cf. Table 42). Regarding Cd and Zn, it is furthermore likely that a considerable amount has been leached from the soil profile, since their mobility is large, especially in strongly acidified soils. This can also be derived from elevated concentrations of Cd and Zn in ground-water below forests, especially in the highly contaminated `Kempen area' in the southern part of the Netherlands (Pedroli et al., 1990; Wilkens, 1995; Boumans and Fraters, 1995).

Considering the above-mentioned aspects, it is likely that the calculated metal deposition rates in Table 43 are underestimated. Another indication for this is the fact that the modelled deposition rates by Van Jaarsveld et al. (1991) and the interpolated values for the forest stands given in Leeters et al. (1994) are averages for a large area, with an average surface roughness related to low vegetations, which is less than for forests. Consequently dry deposition rates are likely to be higher. Based on the ratio of Pb, Cd, Cu and Zn pools in forested and non-forested sites, the underestimation may vary between 2-3 (see before).

4.5 Conclusions

Results on the chemical composition of the humus layer, subdivided in contents and pools of (i) organic matter, including thickness and bulk densities, (ii) nutrients, (iii) pH and exchangeable cations and (iv) heavy metals, has been given before. Major conclusions with respect to these aspects, in view of available literature, are given below.

Pools, thickness and bulk densities of organic matter
- Pools of organic matter in the humus layer varied mostly between 20 - 110 $ton.ha^{-1}$. Comparison with literature data indicates that parts of the forest stands are in the phase of organic matter accumulation in the humus layer. The humus

layer mainly consisted of an F horizon with overlying freshly fallen leaves or needles (L horizon) with a much lower bulk density than the compacted humified H horizon.

- The influence of tree species on the pool and bulk density of organic matter in the humus layer was smaller than on the thickness of the humus layer. Thickest humus layers combined with the lowest median bulk density were found under Japanese larch, whereas thinnest median humus layers combined with a low bulk density and pool were found under black pine
- The median bulk density of the humus layer (124 kg.m^{-3}) is slightly lower than data reported in the literature, which are generally about 140 - 150 kg.m^{-3}. This is most likely due to a relatively thick layer of loose fresh leaves or needless in the litter layer.

Contents, ratios and pools of organic carbon and nutrients
- Elevated S and N deposition is reflected by the chemical composition of the humus layer. Comparison of the nutrient contents in the humus layer with various literature compilations indicate elevated contents of N and S, relatively low contents for P and Ca and very low contents for Mg and K.
- C/N ratios vary mostly between 20 and 30, which is relatively low compared to areas with a low N deposition, such as Scandinavia. Nevertheless, the values indicate that considerable N immobilisation may still take place in most of the sites. This is in accordance with results from input - output budgets of the 150 sites, which indicate that an average ca 80% of the incoming N is retained in the forest ecosystem.
- C/S ratios vary mostly between 150 and 250, indicating that net S mineralisation is likely to be considerable. This is in accordance with results from input-output budgets of the 150 sites, which indicate that on average all the incoming SO_4 is leached from the system.
- C/P ratios are very high and vary mostly between 450 and 950, indicating that net mineralisation of P is likely to be very small, and that P deficiencies in these forest soils are likely. This is in accordance with the results of foliar P contents, which indicate an absolute P deficiency in 63% of the sites.
- Nutrient pools in the humus layer are such that they can provide the tree with nutrients during a long period, except for K, in addition to the nutrient supply by atmospheric deposition and long-term weathering.
- The impact of humus layer horizon and tree species on nutrient contents and nutrient ratios was small. For oak the N, Ca, Mg and K contents were higher than for the other species, in accordance with the elevated foliar contents for those nutrients in oak. The median pools of carbon and nutrient in the LF horizon were, however almost three times the median pools found in the H horizon.

Soil acidity and exchangeable cations
- Results for the pH in a water extract and in a KCl extract generally varied between 3.5 and 5 and between 2.5 and 4, respectively, in the humus layer. The pH values measured in the H horizon were lower than those in the LF horizon, due to the stronger dissociation of protons from the humified organic matter pool. The impact of tree species on the pH was small.

- The cation exchange capacity (CEC) of the humus layer varied mostly between 200-400 $mmol_c.kg^{-1}$, being nearly twice as low as values reported in literature. The CEC normalised to the organic matter content ranged between 2.4 and 8.0 $mmol_c.kg^{-1}$ per % organic matter, which is also low compared to literature data. The low values may partly be due to the low pH values in the Dutch forest stands, whereas the variation is also strongly related to the pH variation. The median CEC varied only slightly between the various humus layer horizons and tree species
- Exchangeable cations on the adsorption complex were generally dominated by protons (on average approximately 50%) followed by Ca (on average approximately 25%). Exchangeable Al contents were relative low, since there is no mineral pool of Al in the organic layer. The H horizons had almost twice as low exchangeable Ca, Mg, K, Na and NH_4 contents as the LF horizons, corresponding to the lower pH of the H horizon. Tree species, however, hardly affected exchangeable cation contents.

Contents and pools of heavy metals
- Approximately 95% of the forest stands do have contents of Pb, Cd, Cu and Zn in the humus layer that are higher than those observed in unpolluted areas (the northernmost part of Sweden). High to extremely high contents were mainly located in the strongly polluted Kempen area in the southern part of the Netherlands. Contents of Cd and Zn in the humus layers were highly correlated indicating co-emission and co-deposition of these metals.
- In general, the humus layers are most strongly polluted with Pb, followed by Zn, Cd and Cu. Extremely high values, exceeding the so called intervention value, above which sanitation actions are required, were observed for Pb, Cu, and Zn at three locations.
- Differences between heavy metal contents in LF and H layers were relatively small. Contents of Pb, Cd, Cu and Zn, in humus layers generally decreased going from spruce forests to pine forests to deciduous forests, but such a trend was not found for the heavy metal pools
- Toxic effects of heavy metals on soil microbiota and soil invertebrates seems quite unlikely in Dutch forests, except for Pb. Elevated metal contents in the litter layer may, however, retard decomposition, thus lowering the availability of nutrients.
- Estimated average annual deposition rate of heavy metals, derived by dividing the heavy metal pool in the humus layer with the age of the trees, were generally higher than those simulated by atmospheric deposition models. This is likely due to the higher surface roughness of forests compared to low vegetation.

5 Chemical composition of the mineral topsoil

In this chapter we give an overview of characteristics of the mineral soil, subdivided in contents and pools of (i) organic matter (also bulk densities), (ii) nutrients and nutrient ratios, (iii) pH and exchangeable cations and (iv) oxalate-extractable Al, Fe and P. First the variation in the observed data is given and then the influence of soil type and soil layer is discussed.

5.1 Contents and pools of organic matter

Compared to the humus layer, the organic matter contents in the mineral soil are much lower, but the pool of organic matter is generally twice to thrice as large (cf. Table 14 corrected values and Table 45). This is due to the much (ca. ten times) higher bulk densities of the mineral soil, which have been derived from the pedotransfer functions with organic matter content as described in Section 2.6, Eq. (2). There are two mineral layers with an organic matter content above 30% (one even up to 79%; Table 45) which can be considered as peat soils.

Table 45 Minimum, maximum, 5, 50, and 95 percentiles of the organic matter content, bulk density and total pool of organic matter, carbon, nitrogen and phosphorus in the mineral topsoil

Statistics	Organic matter content ($g.kg^{-1}$)	Bulk density ($kg.m^{-3}$)	Organic matter pool ($ton.ha^{-1}$)
minimum	7	150	34
5 percentile	9	1199	43
50 percentile	38	1393	159
95 percentile	77	1592	277
maximum	790	1608	466

Both the content and pool of organic matter generally increased from Haplic Arenosols < Cambic Podzols < Fimic Anthrosols < Dystric Gleysols < Gleyic Podzols < Umbric Gleysols (Table 46).

Table 46 Median values of the organic matter content, bulk density and the total pool of organic matter in the mineral topsoil of six soil types

Soil type	N	Organic matter content ($g.kg^{-1}$)	Bulk density ($kg.m^{-3}$)	Organic matter pool ($ton.ha^{-1}$)
Haplic Arenosol[1]	26	16	1541	70
Gleyic Podzol[2]	74	45	1345	182
Cambic Podzol	17	29	1453	126
Fimic Anthrosol	11	35	1404	143
Umbric Gleysol[3]	14	56	1300	218
Dystric Gleysol	5	41	1336	164

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

It illustrates that the organic matter content increases when the circumstances for decomposition are less favourable; in this case too wet or too acid.

5.2   Organic carbon and nutrients

Carbon and nutrient contents and ratios

Compared to the humus layer, the C and N contents in organic matter were generally lower in the mineral soil. Median C and N contents were 425 and 20 g.kg^{-1}, respectively (Table 47), compared to 579 and 22 g.kg^{-1} in the humus layer (Table 19). With respect to N, this is contrary to what is generally found in forest soils and it again indicates the impact of atmospheric N deposition in the N contents in the humus layer. Moreover, N contents in the humus layer are much higher than in relatively unpolluted areas such as e.g. Scandinavia, suggesting N immobilisation due to high N deposition. The range in both C and N contents is, however, larger in the mineral topsoil compared to the humus layer. For example, N contents exceeding 30 g.kg^{-1} in the mineral topsoil do occur in approximately 5% of the plots, whereas this is the maximum value in the humus layer. The C/N ratio is also lower in the mineral soil, which is to be expected considering the stronger degree of humification.

The total P contents in organic matter are clearly higher in the mineral topsoil than in the humus layer, but this is a bit misleading since only part of the total P is organically bound (Compare Table 47 and Table 22). The C/P and N/P ratios are much lower in the mineral soil since P not only occurs in organic matter but also in mineral form.

Table 47 Minimum, maximum, 5, 50, and 95 percentiles of nutrient contents (in percentage of the organic matter) and nutrient ratios of the mineral topsoil

Statistics	Nutrient content (g.kg^{-1})			Nutrient ratio		
	C	N	P	C/N	C/P	N/P
minimum	257	13	0.7	10	13	0.76
5 percentile	311	15	1.2	14	45	2.8
50 percentile	425	20	2.8	20	154	7.6
95 percentile	519	29	9.0	28	365	16
maximum	596	41	33	34	537	21

Median nutrient contents in the mineral topsoil did not vary much between the six considered soil types (Table 48). N contents were, however, clearly higher in the relatively rich Anthrosols and Humic Gleysols than the relatively poor Arenosols and Podzols. Furthermore, the total P content is much larger in the Fimic Anthrosols, indicating the impact of long-term fertilisation (sod application) in the past centuries on these soils, which gave them their present appearance of an organically rich topsoil of more than 50 cm. Furthermore, the P content is comparatively low in the Umbric Gleysol. These anomalies are further reflected in a low C/P ratio and N/P ratio in the Fimic Anthrosols and Umbric Gleysols, respectively (Table 48).

Table 48 Median values of the nutrient contents (in percentage of the organic matter) and nutrient ratios of the mineral topsoil for six soil types

Soil type	Nutrient content (g.kg^{-1})			Nutrient ratio		
	C	N	P	C/N	C/P	N/P
Haplic Arenosol[1]	378	22	3.9	18	91	5.4
Gleyic Podzol[2]	431	19	2.6	24	228	9.8
Cambic Podzol	426	19	3.7	23	123	5.4
Fimic Anthrosol	483	27	7.5	17	64	3.6
Umbric Gleysol[3]	439	21	1.9	20	261	12.4
Dystric Gleysol	458	29	3.7	16	114	7.1

[1] including Gleyic Arenosols

[2] including Carbic Podzols

[3] including organic rich soils

Carbon and nutrient pools

Despite the fact that the N contents in organic matter in the mineral topsoil are slightly lower than in the humus layer, the N pools in the mineral topsoil are much higher than in the humus layer (Table 49). This is because the pool of organic matter in the mineral topsoil, and thereby also the C pool is generally twice to thrice as large as in the humus layer, due to the much higher bulk density of the mineral layer (Section 5.1). Considering this difference and the larger P content in the mineral topsoil than in the humus layer, it is clear that the P pools are much larger in the mineral layer (Compare Table 49 and 25).

Table 49 Minimum, maximum, 5, 50, and 95 percentiles of the total pools of C, N and P in the mineral topsoil

Statistics	C pool (kg.ha^{-1})	N pool (kg.ha^{-1})	P pool (kg.ha^{-1})
minimum	8683	576	100
5 percentile	15828	942	182
50 percentile	70625	3144	362
95 percentile	131374	6874	1530
maximum	246524	9486	4473

Median C, N and P pools in the mineral topsoil varied quite strongly between the six considered soil types (Table 50). C and N pools increased from Haplic Arenosol < Cambic Podzol < Gleyic Podzol < Fimic Anthrosol < Dystric Gleysol < Umbric Gleysol.

Table 50 Median values for the total pools of C, N and P in the mineral topsoil for six soil types

Soil type	C pool (kg.ha^{-1})	N pool (kg.ha^{-1})	P pool (kg.ha^{-1})
Haplic Arenosol[1]	26738	1648	252
Gleyic Podzol[2]	76483	3425	342
Cambic Podzol	57539	2728	545
Fimic Anthrosol	69104	3761	1222
Umbric Gleysol[3]	99048	5554	418
Dystric Gleysol	76152	4501	637

[1] including Gleyic Arenosols

[2] including Carbic Podzols

[3] including organic rich soils

This is mainly due to the increasing amount of organic matter in this direction of soils, which is clearly reflected in the C pools. The sensitivity of acid forest soils to N accumulation is likely to decrease in the same direction.

5.3   Soil acidity and exchangeable cations

Soil acidity

As with the humus layer, results for the pH in a water extract and in a KCl extract generally varied between 3.5 and 4.5 and between 2.5 and 4.0, respectively, in the mineral topsoil (Table 51). Differences in the measured pH between the soil types were generally small. Such low values are generally observed in mineral topsoils of non-calcareous sandy soils in the Netherlands (e.g. Kleijn et al., 1989; Van Breemen and Verstraten, 1991). Differences between pH-H_2O and pH-KCl were approximately 0.5, being less than in the humus layer. This can be expected considering the higher H adsorption in the humus layer and thus the higher impact of a KCl extract on exchanging protons from the exchange complex. As with the humus layer, the differences between pH-H_2O and pH-KCl generally increased with an increase in CEC.

Table 51 Minimum, maximum, 5, 50, and 95 percentiles of the pH-H_2O and the pH-KCl of the mineral topsoil for six soil types

Soil type	pH-H_2O					pH-KCl				
	min	5	50	95	max	min	5	50	95	max
Haplic Arenosol[1]	3.7	3.9	4.2	4.7	4.9	3.4	3.5	3.8	4.3	4.3
Gleyic Podzol[2]	3.7	3.8	4.0	4.5	5.4	2.9	3.1	3.5	3.9	4.2
Cambic Podzol	4.0	4.0	4.2	4.5	4.5	3.6	3.6	3.8	4.1	4.1
Fimic Anthrosol	3.7	3.7	3.9	4.3	4.3	3.1	3.1	3.2	3.7	3.7
Umbric Gleysol[3]	3.4	3.5	3.9	4.8	4.8	2.6	2.6	3.5	4.0	4.1
Dystric Gleysol	3.9	3.9	4.1	4.7	4.9	3.3	3.2	3.6	3.8	3.9

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

Cation exchange capacity

The CEC in the mineral topsoil was much lower than in the humus layer, in line with the much lower organic carbon content in the mineral soil. (Compare Table 52 and Table 30). The median value was even ten times lower (32 compared to 302 $mmol_c.kg^{-1}$). The CEC normalised to the percentage of organic matter, which is the main source of variation in CEC in sandy soils, was, however, clearly higher in the mineral topsoils than in the humus layer of the 150 forest stands (Compare Table 52 and Table 30). This is most likely due to the higher degree of humification in the mineral topsoil. The CEC normalised to the organic matter content also varied quite strongly. This effect is mainly cause by differences in organic matter quality and pH. Helling et al. (1964), for example, reported an increase of 5.1 $mmol_c.kg^{-1}$ per % organic carbon per pH unit (see Eq.), being equal to approximately 2.6 $mmol_c.kg^{-1}$ per % organic matter per pH unit. Kalisz and Stone (1980) have reported a comparable change. The median value of 8.3 $mmol_c.kg^{-1}$ for 1% organic matter is comparable to an average value of 7.6 $mmol_c.kg^{-1}$ for 1% organic matter, reported by

Kleijn et al. (1989) for eight sandy soil below Douglas stands. Despite the lower CEC in the mineral topsoil compared to the humus layer, the exchangeable cation pool ($kmol_c.ha^{-1}$) is larger because of the ten times higher bulk density (Compare Table 52 and Table 30).

Table 52 Minimum, maximum, 5, 50, and 95 percentiles of the CEC of the mineral topsoil

Statistics	CEC		CEC of 1% organic matter
	$mmol_c.kg^{-1}$	$kmol_c.ha^{-1}$	$mmol_c.kg^{-1}$
minimum	5.8	29	3.6
5 percentile	10	48	5.7
50 percentile	32	134	8.3
95 percentile	73	261	14
maximum	287	359	28

The CEC and the exchangeable pools generally increased from Haplic Arenosols < Cambic Podzols < Fimic Anthrosols < Gleyic Podzols < Umbric Gleysols < Dystric Gleysols. This is quite comparable to the pools of organic matter, illustrating the relationship between these parameters (Compare Table 46 and 53). Per % organic matter, the CEC in the mineral topsoil is clearly higher in the Dystric Gleysol ($mmol_c.kg^{-1}$) than in all the other soils (between 6.5-10 $mmol_c.kg^{-1}$).

Table 53 Median values of the CEC of the mineral topsoil for six soil types

Statistics	CEC		CEC of 1% organic matter
	$mmol_c.kg^{-1}$	$kmol_c.ha^{-1}$	$mmol_c.kg^{-1}$
Haplic Arenosol[1]	15	67	9.8
Gleyic Podzol[2]	41	163	8.4
Cambic Podzol	21	88	6.9
Fimic Anthrosol	24	92	6.7
Umbric Gleysol[3]	50	176	8.2
Dystric Gleysol	71	291	14

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

Exchangeable cation contents and pools
The base saturation was much lower and the Al saturation was much higher in the mineral topsoil compared to the humus layer (Compare Table 54 and Table 32).

Table 54 Minimum, maximum, 5, 50, and 95 percentiles of the exchangeable cation content (in percentage of the CEC) of the mineral topsoil

Statistics	Exchangeable cation content (%)							
	H	Al	Fe	Ca	Mg	K	Na	NH_4
minimum	0.0	11	0.7	0.0	0.4	0.2	0.0	0.3
5 percentile	5.8	32	1.7	0.9	0.6	0.5	0.1	0.4
50 percentile	21	66	4.7	3.1	1.1	1.4	0.6	1.1
95 percentile	46	79	12	23	3.3	3.1	1.3	3.1
Maximum	57	87	22	87	10	6.4	6.5	5.3

This reflects that Al mobilisation in the humus layer is negligible but that it is the dominant buffer mechanism in the mineral topsoil. Unlike the humus layer, where the exchangeable cations on the adsorption complex were generally dominated by protons (H), exchangeable Al dominates the exchange complex in the mineral topsoil. Generally, Ca was the dominating base cation, being very high in the three calcareous soils (up to 87%). The median base saturation was, however, below 10%, illustrating the strong acidification of those acid sandy soils.

Obvious differences in exchangeable cation contents were observed between the various soil types (Table 55). The median Al saturation was considerably higher in the Haplic Arenosol and in the podzolic soils (approximately 65-75%) than in the Fimic Anthrosol and in the gleysoils (approximately 40-55%). Specifically in the Fimic Anthrosol, this difference is mainly due to a higher proton saturation and Fe saturation, suggesting that this soil type is even more acidified. In the two gleysoils, however, the Ca saturation is clearly higher (three to five times as high as in the podzols), reflecting the larger buffer capacity of those soils (Table 55).

Table 55 Median values of the occupation of the exchangeable cation content (in percentage of the CEC) of the mineral topsoil for six soil types

Soil type	Exchangeable cation content (%)							
	H	Al	Fe	Ca	Mg	K	Na	NH_4
Haplic Arenosol[1]	16	70	5.5	2.7	1.2	1.8	0.6	1.2
Gleyic Podzol[2]	24	66	3.8	2.9	0.9	0.9	0.5	0.9
Cambic Podzol	12	73	7.1	2.6	1.1	1.5	0.5	1.2
Fimic Anthrosol	32	42	11	4.1	1.5	2.0	0.8	1.9
Umbric Gleysol[3]	26	41	4.9	6.7	1.9	1.5	0.7	1.3
Dystric Gleysol	14	55	3.8	12	2.2	2.3	0.7	0.5

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

As with the exchangeable cation contents, the exchangeable cation pools generally decreased according to Al>H>Fe>Ca followed by Mg, K, Na and NH_4 (Table 56). Despite the much lower base saturation, the exchangeable base cation pools are only slightly lower in the mineral topsoil compared to the humus layer since the exchangeable total cation pool is much higher in the mineral soil (Compare Table 56 and Table 33). Again, considering a net acid input of ca 5.0 $kmol_c.ha^{-1}.yr^{-1}$ on Dutch forests in 1990 (Erisman, 1992), it is clear that the exchangeable pool of base cations in the mineral topsoil is very limited in most soils. At more than 50% of the soils he exchangeable base cation pool is comparable to this value.

Table 56 Minimum, maximum, 5, 50, and 95 percentiles of the exchangeable cation pool in the mineral topsoil

Statistics	Exchangeable cation pool ($kmol_c.ha^{-1}$)							
	H	Al	Fe	Ca	Mg	K	Na	NH_4
Minimum	0.0	12	1.0	0.0	0.33	0.43	0.0	0.33
5 percentile	3.3	30	1.6	0.61	0.56	0.65	0.16	0.57
50 percentile	29	71	5.5	4.1	1.2	1.5	0.66	1.4
95 percentile	100	150	15	45	5.8	4.8	2.1	3.5
Maximum	133	207	34	168	23	7.5	3.3	9.7

The differences in exchangeable cation pools between the various soil types are different from the exchangeable cation contents (Table 57). Unlike the Dystric Gleysoils, the median Al saturation was comparable among the soil types, but the exchangeable H, Fe and Ca pool is clearly higher in the two gleysoils compared to all other soil types.

Table 57 Median values of the exchangeable cation pool in the mineral topsoil for six soil types

Soil type	Exchangeable cation pool ($kmol_c.ha^{-1}$)							
	H	Al	Fe	Ca	Mg	K	Na	NH_4
Haplic Arenosol[1]	10	47	3.5	1.8	0.91	1.2	0.35	0.93
Gleyic Podzol[2]	34	96	5.2	4.7	1.2	1.2	0.79	1.5
Cambic Podzol	9.7	67	6.7	2.5	0.88	1.6	0.37	1.3
Fimic Anthrosol	31	41	11	4.1	1.3	2.0	0.75	1.7
Umbric Gleysol[3]	42	70	7.7	16	4.5	2.3	1.4	1.9
Dystric Gleysol	43	138	9.8	35	6.5	5.4	1.5	1.3

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

5.4 Oxalate extractable aluminium, iron and phosphorus

The contents and pools of oxalate extractable Al and Fe do give an indication of the buffer capacity of the soil in an acidified (Al buffer range) up to an extremely acidified (Fe buffer range) situation. Results show that the readily available Al pool varies mostly between 100- 1000 $kmol_c.ha^{-1}$ (Table 58). Considering a net acid input of ca 5.0 $kmol_c.ha^{-1}.yr^{-1}$ on Dutch forests in 1990, it is clear that this Al pool can be depleted at such extreme input within a period of approximately 20-200 years. De Vries et al. (1993) estimated Al depletion times of 10 –50 years in topsoils of 10 cm in response to various deposition scenarios, showing that Al depletion is a realistic danger at high acid inputs. The depletion of Al might induce an increase in Fe buffering, which in turn leads to a decrease in the availability of phosphate (De Vries, 1994). Furthermore, the decrease of those pools in podzolic sandy soils may cause a loss in the structure of those soils. In general Fe pools are clearly lower than those of Al (Table 58).

Table 58 Minimum, maximum, 5, 50, and 95 percentiles of the oxalate extractable aluminium and iron contents and pools in the mineral topsoil

Statistics	Al		Fe	
	$mmol_c.kg^{-1}$	$kmol_c.ha^{-1}$	$mmol_c.kg^{-1}$	$kmol_c.ha^{-1}$
minimum	7.7	37	2.1	7.8
5 percentile	42	171	8.3	35
50 percentile	110	451	31	130
95 percentile	215	766	121	492
maximum	289	1077	182	728

Both the content and pool of readily available Al generally were clearly lower for the Haplic Arenosols and Fimic Anthrosols compared to the other soils. The Fe pool was however highest in the Fimic Anthrosols, together with the Cambic Podzols and Dystric Gleysols (Table 59).

Table 59 Median values of the oxalate exchangeable aluminium and iron contents and pools in the mineral topsoil for six soil types

Soil type	Al		Fe	
	$mmol_c.kg^{-1}$	$kmol_c.ha^{-1}$	$mmol_c.kg^{-1}$	$kmol_c.ha^{-1}$
Haplic Arenosol[1]	63	292	23	106
Gleyic Podzol[2]	121	512	22	81
Cambic Podzol	133	571	77	336
Fimic Anthrosol	57	216	69	282
Umbric Gleysol[3]	103	343	30	99
Dystric Gleysol	118	502	51	202

[1] including Gleyic Arenosols

[2] including Carbic Podzols

[3] including organic rich soils

On average, the oxalate extractable content of P, which is a measure of the total amount of phosphate sorbed by both reversible adsorption and slow diffusion controlled precipitation (Section 2.6), is approximately half the total content of P (Table 60). The percentage of sorbed P varies from 14-100, which means that 0-86% of P is retained in minerals, which is only released by weathering. The ratio of oxalate extractable P to Al and Fe varies mostly from 0.02-0.18. Assuming a phosphate sorption capacity that is half the content of oxalate extractable Al and Fe (Eq. 14), the phosphate saturation of the sorption complex varies mostly from 4-36%. This is much lower than in agricultural soils where the input of P by animal manure has led to large areas of complete P saturation. Only 1 plot approached 80% saturation.

Table 60 Minimum, maximum, 5, 50, and 95 percentiles of phosphor parameters of the mineral topsoil

Statistics	P_{ox}	P_{ox}/P_{total}	$P_{ox}/(Al+Fe)_{ox}$
	$(mmol_c.kg^{-1})$	(%)	$(mol.mol^{-1})$
minimum	0.10	14	0.01
5 percentile	0.66	38	0.02
50 percentile	1.7	57	0.03
95 percentile	11	86	0.18
maximum	32	100	0.40

There is not much difference between the median P content and percentage of oxalate extractable P tot total P and oxalate extractable Al and Fe, with the exception of the Fimic Anthrosol (table 61).

Table 61 Medium values of phosphor parameters for the mineral topsoil of six soil types

Soil Type	P_{ox}	P_{ox}/P_{total}	$P_{ox}/(Al+Fe)_{ox}$
	$(mmol_c.kg^{-1})$	(%)	$(mol.mol^{-1})$
Haplic Arenosol[1]	0.93	51	0.03
Gleyic Podzol[2]	2.3	57	0.05
Cambric Podzol	2.3	61	0.04
Fimic Anthrosol	7.8	80	0.18
Umbric Gleysol[3]	1.8	52	0.03
Dystric Gleysol	1.9	41	0.03

[1] including Gleyic Arenosols

[2] including Carbic Podzols

[3] including organic rich soils

In this soil type, the all phosphorus parameters are much higher. Here, the median P saturation is even 36%. This illustrates the impact of previous sod application during centuries on those soils, as mentioned before.

5.5 Conclusions

Contents and pools of organic matter, carbon and nutrients
- Compared to the humus layer, the organic matter and carbon contents in the mineral soil are much lower, but the pools of both organic matter and carbon are generally twice to thrice as large, because of the much (ca. ten times) higher bulk densities of the mineral soil. The organic carbon content increases when the soils become more wet or acid, which are less favourable circumstances for decomposition.
- The N contents in organic matter were generally slightly lower in the mineral soil (median value of 20 $g.kg^{-1}$), than in the humus layer (median value of 22 $g.kg^{-1}$), indicating the impact of atmospheric N deposition on the N contents in the humus layer.
- Despite the high N contents in the humus layer, the C/N ratio was generally lower in the mineral soil, indicating the stronger degree of humification. C/P and N/P ratios were much lower in the mineral soil since P not only occurs in organic matter but also in mineral form.
- C and N contents and C and N pools generally increased in the direction Arenosols<Podzols<Anthrosols< Gleysols, reflecting partly the fertility of those soil types. Furthermore, the total P content and P pool was much larger in the Fimic Anthrosols, indicating the impact of long-term fertilisation in the past.

Soil acidity and exchangeable cations
- As with the humus layer, results for the pH in a water extract and in a KCl extract generally varied between 3.5 and 4.5 and between 2.5 and 4.0, respectively, in the mineral topsoil. Differences between pH-H_2O and pH-KCl were approximately 0.5, being less than in the humus layer.
- The CEC in the mineral topsoil (median of 32 $mmol_c.kg^{-1}$) was much lower than in the humus layer (median of 302 $mmol_c.kg^{-1}$) because of the much lower organic matter content in the mineral layer. The CEC, normalised to 1% of organic matter, was, however, higher in the mineral topsoil (median of 8.3 $mmol_c.kg^{-1}$) than in the humus layer (median of 4.7 $mmol_c.kg^{-1}$). This was also the case with the exchangeable cation pool because of the much higher bulk density of the mineral layer.
- The proton and base saturation was much lower and the Al saturation was much higher in the mineral topsoil compared to the humus layer. This indicates that Al mobilisation is the dominant buffer mechanism in the mineral topsoil, whereas exchange of protons with base cations dominates in the humus layer. The exchangeable cation pools generally decreased according to Al>H>Fe>Ca followed by Mg, K, Na and NH_4

- Al saturation was considerably higher in the more acidic Arenosols and Podzols (median of 65-75%) than in the more buffered Anthrosols and Gleysols (median of 40-55%).

Contents and pools of oxalate extractable aluminium, iron and phosphorus
- The readily available, oxalate extractable, Al pool varies mostly between 100- 1000 $kmol_c.ha^{-1}$. Considering the net acid input in 1990, this Al pool can be depleted within a period of within several decades to centuries.
- The ratio of oxalate extractable P to Al and Fe varies mostly from 0.02-0.18, implying phosphate saturation percentage between 4-36. This is much lower than in agricultural soils where the input of P by animal manure has increased this percentage.
- The content and pool of oxalate extractable Al was clearly lower in the Fimic Anthrosols compared to the other soils, whereas the oxalate extractable P content was much higher. Consequently, the degree of P saturation was much higher in those soils

6 Chemical composition of the soil solution

6.1 Trends in time

Soil sampling covered a period of 8 weeks from mid February to mid May. This can lead to fluctuations in element concentrations due to hydrological during this period. Therefore at 10 sites, sampled in February begin, we took a second sample in May. Results for the difference in the element concentration thus obtained is illustrated in Table 62.

Table 62 Median values of the difference in element concentrations of the soil solution between May and February 1990

Element	Difference in element concentration ($mol_c.m^{-3}$)		
	Topsoil	Subsoil	Total
pH	-0.04	-0.04	-0.04
Al	0.05	0.01	0.03
Fe	0.00	-0.01	0.00
NH_4	0.03	-0.04	-0.01
Ca	-0.01	-0.24	-0.11
Mg	0.02	0.00	0.02
K	0.10	0.03	0.03
Na	0.41	0.37	0.41
Cl	0.40	0.15	0.36
NO_3	-0.02	0.01	0.00
SO_4	0.16	-0.01	0.04
H_2PO_4 [1]	-0.17	0.00	0.00
RCOO	0.18	-0.02	0.09
Σ kat	0.44	0.06	0.33
Σ an	0.59	-0.05	0.41

[1] The concentration is given in mg $P.l^{-1}$

Results show that the concentrations of Na, Cl and SO_4 (behaving as tracers) differed most, especially in the topsoil. As expected, concentrations were higher in May as in February, especially in the topsoil, related to lower water fluxes in this period. For the other elements the median values of the differences were low. For the subsoil, the median Ca concentration was clearly higher in may than in February. At the individual sites, differences were large, but there was generally not such a systematic trend as for Na, Cl and SO_4. It should thus be kept in mind that specifically the differences in SO_4 concentrations between sites might not only be due to differences in SO4 input from the atmosphere and in stand and site characteristics influencing that input. It may also be due to differences in the time period in which the samples were taken. The results given in Table 61 do represent the median values. At individual sites these differences can be much larger.

6.2   General characterisation

Element concentrations

In the soil solution, all the major cations and anions were measured, i.e. H, Al, Fe, Ca, Mg, K, Na, NH_4, NO_3, SO_4, Cl and $RCOO^-$. Important indicators for acidification and eutrophication of the forest ecosystem are the dissolved Al and NO_3 concentration, respectively. In the forest topsoil, the dissolved concentration of NH_4 is also an important indicator for eutrophication. Regarding acidification, pH and SO_4 concentration are also interesting. Results for the mineral topsoil and subsoil of the 150 forest stands are given in Table 63.

Table 63 Minimum, maximum, 5, 50 and 95 percentiles of element concentrations in the soil solution of the mineral topsoil and the sub soil

Element	Concentration in the topsoil ($mol_c.m^{-3}$)					Concentrations in the subsoil ($mol_c.m^{-3}$)				
	min	5%	50%	95%	max	min	5%	50%	95%	max
H	0.04	0.07	0.25	0.56	1.6	0.00	0.02	0.13	0.28	0.46
Al	0.12	0.19	0.64	1.9	11	0.00	0.05	0.59	3.2	12
Fe	0.00	0.01	0.02	0.08	0.20	0.00	0.00	0.04	0.41	0.77
NH_4	0.04	0.06	0.19	1.1	3.2	0.02	0.04	0.09	0.12	1.4
Ca	0.06	0.13	0.44	1.8	3.5	0.06	0.09	0.38	3.1	18
Mg	0.06	0.11	0.25	0.75	1.6	0.04	0.07	0.23	0.85	4.3
K	0.03	0.08	0.20	0.61	1.2	0.02	0.04	0.10	0.31	1.9
Na	0.26	0.34	0.77	2.6	6.5	0.30	0.37	0.78	2.2	6.5
Cl	0.40	0.55	1.3	2.8	6.8	0.30	0.47	1.1	3.1	7.9
NO_3	0.00	0.03	0.53	1.8	5.6	0.00	0.03	0.48	2.4	17
SO_4	0.24	0.39	0.99	3.3	15	0.18	0.38	1.1	3.6	20
H_2PO_4[1]	0.00	0.00	0.00	0.69	3.3	0.00	0.00	0.06	2.08	3.73
RCOO	0.07	0.11	0.19	0.56	2.9	0.01	0.05	0.14	0.63	2.4
S kat	0.93	1.5	3.0	8.6	21	0.69	1.1	2.9	8.1	28
S an	0.94	1.5	3.0	8.1	20	0.78	1.1	3.1	8.4	34
S kat-an	-1.8	-0.62	-0.05	0.54	1.5	-6.5	-1.3	-0.11	0.27	0.80

[1] The concentration of this element is given in mg $P.l^{-1}$

The results show that the SO_4 concentrations are higher than the NO_3 concentrations indicating the dominance of SO_4 in soil acidification. NO_3 concentrations are generally higher than a target value of 0.4 $mol_c.m^{-3}$, used in the Netherlands with respect to drinking water quality. Al concentrations are generally above a critical value of 0.2 $mol_c.m^{-3}$, related to toxic effects on roots, based on literature information. Ca concentrations are mostly higher than those of Ng and K. This illustrates that Ca is the dominant base cation buffering the acid input. Most likely, the buffering is mainly due to a high base cation (mainly Ca) input from the atmosphere. Liming/fertilisation in the past may play a role as well. The high input from the atmosphere can be explained by strong filtering of base cations by the forest canopy. Total deposition on forests, especially near forest edges can be much higher (probably about 2.5 to 3.5 times higher) than wet deposition (Draayers et al., 1992).

Observed high concentrations of Na and Cl are also an indication of the forest filtering effect. Actually, the Na concentration is generally even higher than that of Ca, and certainly of Mg and K, but this correlated with an equally high Cl

concentration, illustrating the strong impact of sea salt input in the Netherlands. Differences between ion concentrations in the topsoil and subsoil are small, except for the concentrations of H and NH_4, which are higher in the topsoil (lower pH values).

Element ratios

Ranges in calculated relevant element ratios (see par. 2.6) in the soil solution in both the topsoil and subsoil are given in Table 64.

Table 64 Minimum, maximum, 5, 50 and 95 percentiles of element ratios in the soil solution of the mineral topsoil and the subsoil

Ratio	Ratio in topsoil					Ratio in subsoil				
	min	5%	50%	95%	max	min	5%	50%	95%	max
Equivalent ratio										
$(NO_3+NH_4)/SO_4$	0.04	0.26	0.80	1.7	2.5	0.00	0.06	0.57	1.5	2.5
NH_4/NO_3	0.04	0.10	0.49	2.8	6.8	0.01	0.04	0.21	2.1	9.8
$Al/(SO_4+NO_3)$	0.07	0.17	0.45	0.71	0.89	0.00	0.01	0.45	0.78	0.91
$Al/RCOO$	0.34	0.75	2.9	9.8	54	0.00	0.26	3.4	31	64
Molar ratio										
Al/Ca	0.06	0.19	1.1	2.5	9.0	0.00	0.01	1.4	5.1	6.1
$Al/(Ca+Mg+K)$	0.04	0.10	0.41	0.85	2.47	0.00	0.01	0.53	2.04	3.1
NH_4/K	0.12	0.33	1.1	4.7	18	0.06	0.20	0.98	2.4	6.7
NH_4/Mg	0.12	0.22	0.89	3.7	7.4	0.03	0.08	0.42	1.4	3.5

The equivalent element ratios do mainly give information on the fate on the buffering of the soil as it tells something on the N and S in the forest soil and the release of Al and base cations in response to the acid input. Focusing on in the mineral subsoil (60-100 cm depth), the results show that the $(NH_4+ NO_3)/ SO_4$ ratio is mostly below 1.0 (median value is 0.57). In 1990, the $(NH_4+ NO_3)/ SO_4$ ratio in the atmospheric input the Netherlands was larger than 1.0. Assuming that SO_4 behaves as a tracer, this implies that a considerable amount of nitrogen is retained as a result of uptake, immobilisation and/or denitrification. The NH_4/NO_3 ratio is mostly below 1.0 (median value is 0.21). This indicates a strong degree of nitrification and/or preferential NH_4 uptake, since the NH_4/NO_3 ratio in the atmospheric input in the Netherlands was (much) larger than 1.0 in 1990. The $Al/ SO_4 + NO_3$ ratio varies 0.01 and 0.8 (median value is 0.45), indicating that the role of Al mobilisation in acid neutralisation varies strongly. Most likely, the lower values for the $Al/ SO_4 + NO_3$ are due to a high input of base cations from the atmosphere in buffering the acid input, as discussed before. The equivalent $Al/RCOO$ ratio is much mostly much larger than 1.0 (median values in the topsoil and subsoil are 2.9 and 3.4, respectively) indicating that toxic free Al dominates the Al speciation compared to non-toxic organically complexed Al. Since non-toxic organically complexed Al is due to natural acidification, it implies that anthropogenic acidification due to atmospheric inputs of S and N is much higher than natural acidification. This result can be seen even clearer from the ratio of $(SO_4 + NO_3)/RCOO$, which was nearly always above 1.0 (not given in Table 64).

The molar element ratios are indicators for potential impacts on the forest ecosystem, specifically in view of root length and root uptake. Results for the mineral

topsoil (0-30 cm depth) and subsoil (60-100 cm depth) show that both the Al/Ca ratio and the Al/(Ca+Mg+K) ratio are mostly higher than 1.0, which are considered average critical values. Median values for the Al/Ca ratio are 1.1 in the topsoil and 1.4 in the subsoil, whereas the median Al/(Ca+Mg+K) ratios are 0.41 and 0.53 in the topsoil and subsoil, respectively. Due to the preferential uptake of NH_4 and the occurrence of nitrification, the ratio of NH_4 to K and of NH_4 to Mg nearly always remains below a critical value of 5. Because of the above-mentioned processes, the ratios are lower in the subsoil than in the topsoil. Median values are even near or below 1.0 for both ratios in topsoil and subsoil.

Comparison of element concentrations and element ratios with critical limits
In order to evaluate the results of the soil solution chemistry in terms of possible negative impacts, use was made of critical chemical values for the concentrations of NO3 and Al and the molar ratios of Al/(Ca+Mg+K) and NH4/Mg. Criteria thus used with an explanation of its background, are given in Table 65. In making the comparison, one has to be aware, however, that element concentrations measured at the sites in early spring may deviate from annual average values.

Table 65 Critical chemical values for the concentrations of NO_3 and Al and the molar ratios of Al/(Ca+Mg+K) and NH_4/K

Class	Concentration ($mol_c.m^{-3}$)		Molar ratio ($mol.mol^{-1}$)	
	NO_3	Al	NH_4/K	Al/(Ca+Mg+K)
1 (low)	<0.1[1]	<0.2[3]	<1	<0.5
2 (intermediate)	0.1 – 0.8	0.2 – 1.0	1 – 5	0.5 – 1.5[6]
3 (high)	>0.8[2]	>1.0[4]	>5[5]	>1.5

[1] Clearly elevated NO_3 concentration (Gundersen et al., 1998) that may be related to vegetation changes (Warfinge et al., 1992)

[2] EU quality criterion for nitrate concentrations in ground water

[3] Lowest critical value reported in relation to effects on tree roots of sensitive tree species (Cronan et al., 1989)

[4] Critical value reported in relation to effects on tree roots for less sensitive tree species (Cronan et al., 1989)

[5] Critical value related to decreased base cation uptake (Roelofs et al., 1985; Boxman et al., 1988)

[6] Most common range of critical values related to adverse impacts on roots, such as root growth and root uptake, depending upon tree species (Sverdrup and Warfinge, 1993).

Frequency distributions of the Al and NO_3 concentration and of the Al/(Ca+Mg+K) and NH_4/K ratio in both the mineral topsoil (0-30 cm) and subsoil (60-100 cm) show that those critical limits are frequently violated (Fig. 3).
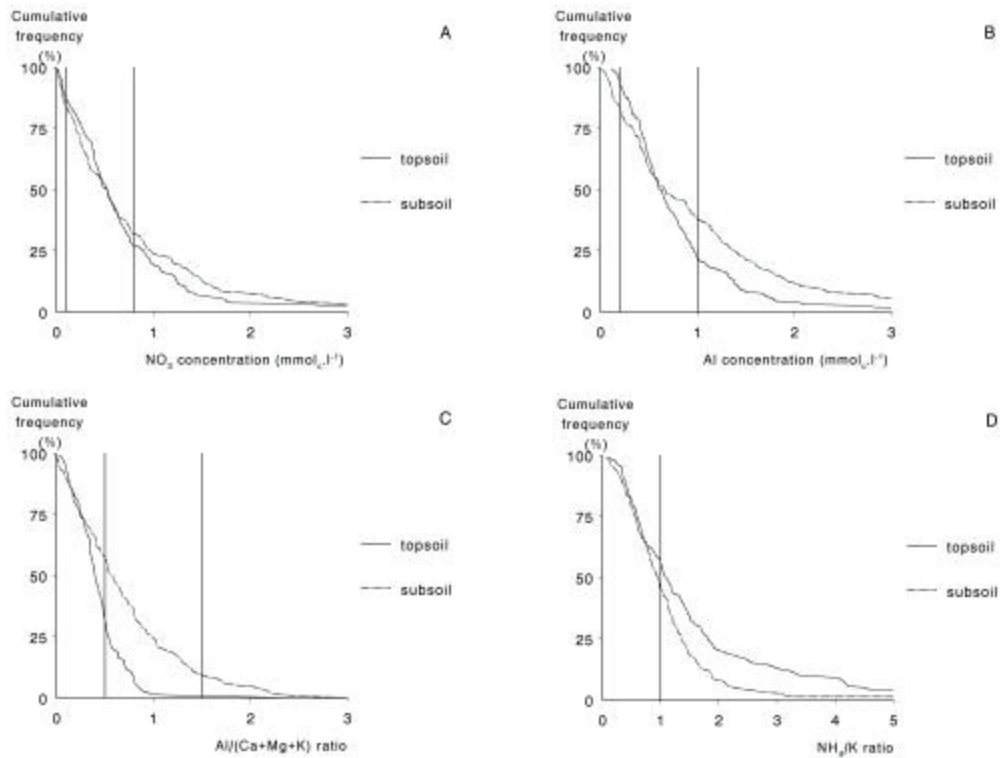
Fig 3 Frequency distributions of the NO_3 and Al concentration (A, B) and of the Al/(Ca+Mg+K) and NH_4/K ratio (C, D) in both the mineral topsoil (0-30 cm) and subsoil (60-100 cm)

Information on the percentage of plots exceeding the various critical limits is presented in the Tables 66 and 67. Results show that NO3 concentrations are clearly elevated at more than 80% of the plots. The EU quality criterion for ground water of 50 mg.l^{-1} (0.8 mol$_c$.m^{-3}) was exceeded in the subsoil at 32% of the plots, , whereas 55% of the sites exceeded the Dutch target value of 25 mg.l^{-1} (0.4 mol$_c$.m^{-3}) for NO_3. Approximately 80-90 % of the plots exceeded the most stringent limit found in literature for Al concentration, but even a criterion that was five times as large was exceeded at 23-35% of the plots, depending on depth. The drinking water standard of 0.2 mg.l^{-1} for Al was exceeded in the subsoil of all non calcareous soils (147 of the 150 plots).

Table 66 The percentage of observations of NO_3 and Al concentrations in the mineral topsoil and subsoil between different class limits

NO3 concentrations exceeding limits (%)			Al concentrations exceeding limits (%)		
Concentration class (mmol$_c$.m^{-3})	Topsoil	Subsoil	concentration class (mmol$_c$.m^{-3})	Topsoil	Subsoil
< 100	13	16	< 200	8	22
100 – 800	58	52	200 – 1000	69	43
> 800	29	32	> 1000	23	35

Approximately 50-60% of the plots had an Al/(Ca+Mg+K) ratio below 0.5, indicating that the impact on root uptake is likely to be small at those plots. The remaining plots had Al concentrations where such impacts are possible or even

likely. As mentioned before, the ratio of NH_4 to K nearly always remained below the critical value of 5.

Table 67 The percentage of observations of Al/(Ca+Mg+K) and NH₄/Mg ratios in the mineral topsoil and subsoil between different class limits

Al/(Ca+Mg+K) ratio exceeding limits (%)			NH₄/K ratio exceeding limits (%)		
Ratio class (mol.mol⁻¹)	Topsoil	Subsoil	Ratio class (mol.mol⁻¹)	Topsoil	Subsoil
< 0.5	67	46	<1	43	51
0.5 – 1.5	32	44	1-5	53	47
> 1.5	1	10	>5	5	1

6.3 Relations with deposition level, stand and site characteristics

Relations with deposition level and region

The results showed a relationship between the estimated average deposition level in grids where the forest were located and the concentrations in NO_3 and SO_4 in both topsoil and subsoil. In Table 68, this is illustrated for the topsoil. The impact on the concentrations of other major cations (specifically Ca and Al) appeared to quite small.

Table 68 Median values of the pH and the concentrations of major ions in the soil solution of the mineral topsoil for different acid deposition levels

Element	Element concentration (mol$_c$.m⁻³)			
	< 4000	4000-5000	5000-6000	> 6000
		(mol$_c$.ha⁻¹.yr⁻¹)		
pH	3.6	3.7	3.6	3.7
Al	0.63	0.57	0.69	0.62
NH₄	0.16	0.16	0.23	0.18
Ca	0.35	0.40	0.46	0.54
NO₃	0.37	0.39	0.55	0.70
SO₄	0.69	0.91	1.11	1.11

A more clear relationship was found between the element concentration and the region as illustrated in Table 69.

Table 69 Median values of pH and the concentrations of major ions in the soil solution of the mineral topsoil and subsoil for three regions

Element	Element concentration in the topsoil (mol$_c$.m⁻³)			Element concentration in the subsoil (mol$_c$.m⁻³)		
	North	Central	South	North	Central	South
pH	3.6	3.7	3.5	3.9	4.0	3.8
Al	0.54	0.59	0.80	0.48	0.42	1.2
NH₄	0.15	0.16	0.30	0.09	0.09	0.10
Ca	0.35	0.37	0.59	0.33	0.28	0.50
NO₃	0.38	0.45	0.64	0.33	0.44	0.88
SO₄	0.79	0.84	1.38	0.91	1.0	1.8

In general one expects an increase in acid deposition going from the north to the south and this is reflected in an increase in the concentrations of NH_4, NO_3 and SO_4

and in response to that also in the concentrations of Al and Ca. It should be remembered, however, that the effect of region also includes differences in the occurrence of tree species and other stand characteristics that do influence the soil solution chemistry, as discussed below.

Relations with stand characteristics

The concentrations of most ions in soil solution were especially influenced by tree species (Table 70). The impact of tree species on concentrations in NO_3, SO_4 and Al appeared to be even larger than the impact of the estimated average deposition level in grids where the forest were located. Lowest pH values and highest concentrations in NO_3, SO_4 and Al occur below Norway Spruce and Douglas Fir. The reverse is true for Oak and Beech, whereas Japanese Larch, Scots Pine and Black Pine occupy an intermediate position. Differences between tree species are probably caused by increased dry deposition and evapotranspiration, going from deciduous forest to pine forests to spruce forests.

Table 70 Median values of pH and the concentrations and ratios of major elements in the soil solution of the mineral topsoil under forest stands of seven major tree species

Element	Element concentration ($mol_c.m^{-3}$)						
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese larch	Oak	Beech
pH	3.6	3.7	3.4	3.6	3.7	3.8	?
Al	0.70	0.62	1.6	1.1	0.74	0.41	0.44
NH_4	0.18	0.20	0.63	0.49	0.23	0.13	0.14
Ca	0.38	0.36	0.93	0.58	0.45	0.51	0.27
NO_3	0.47	0.27	1.1	0.49	0.62	0.57	0.20
SO_4	0.97	0.80	2.2	2.0	1.0	0.85	0.63
	Element ratio ($mol.mol^{-1}$)						
Al/Ca	1.1	1.3	1.3	1.4	1.2	0.63	1.2
NH_4/K	1.0	1.2	2.6	2.5	1.7	0.53	0.64

Other stand characteristics that did influence the concentrations in soil solution were tree height, canopy coverage (Table 71). For most ions, concentrations increased with an increase in tree height and canopy coverage, most likely due to an increase in dry deposition and evapotranspiration. The impact of the distance to the nearest forest edge appeared to be small (not shown in Table 71).

In the Tables 70 and 71, the relation between soil solution chemistry and stand and site characteristics is assessed for each characteristic separately, whereas there is an interaction between those characteristics. Relationships between soil solution parameters and site characteristics were derived by multiple linear regression analysis (Leeters et al., 1994). Relative good relationships (explanation of more than 50% of the variance encountered) were found between the SO_4 and Al concentration and the tree species, tree height and acid atmospheric deposition. The influence of canopy coverage and distance of trees to the forest edge appeared to be less important. However, it should be noted that there is a relationship between these characteristics and the tree species. For example, the canopy coverage of Douglas Fir and Norway

Spruce is larger than for the other coniferous trees, and the distance to the forest edge is larger for coniferous than for deciduous trees.

Table 71 Median values of pH and the concentrations of major elements in the soil solution of the topsoil for important stand characteristics

Stand characteristic	pH	Element concentrations (mol_c/m^3)					
		Al	NH_4	Ca	Na	NO_3	SO_4
Canopy coverage (%)							
< 50	3.6	0.52	0.15	0.39	0.66	0.44	0.83
50-75	3.6	0.63	0.23	0.45	0.77	0.54	1.01
> 75	3.6	0.72	0.17	0.46	1.00	0.63	1.25
Tree height (m)							
< 5	3.8	0.19	0.08	0.15	0.33	0.21	0.35
5-10	3.7	0.40	0.14	0.36	0.56	0.31	0.73
10-15	3.6	0.67	0.23	0.44	0.80	0.54	1.03
15-20	3.6	0.73	0.23	0.45	0.78	0.58	1.02
> 20	3.6	0.78	0.18	0.46	0.89	0.53	1.08

Relations with site characteristics

Site characteristics that may influence the concentrations in soil solution are soil type and ground water level. For most ions, there were no clear relations between soil type and ion concentrations (Table 72). This is to be expected since all considered soil types are acid sandy soils, with relatively small differences in acid buffering.

Table 72 Median values of pH and the concentrations and ratios of major elements in the soil solution of the topsoil for six soil types

Element	Element concentration ($mol_c.m^{-3}$)					
	Haplic[1] Arenosol	Gleyic[2] Podzol	Cambic Podzol	Fimic Anthrosol	Umbric[3] Gleysol	Dystric Gleysol
pH	3.8	3.5	3.7	3.4	3.4	3.7
Al	0.62	0.66	0.80	0.61	0.55	0.48
NH_4	0.16	0.22	0.23	0.21	0.15	0.06
Ca	0.41	0.40	0.33	0.53	0.60	0.73
NO_3	0.56	0.45	0.58	0.64	0.58	0.39
SO_4	0.89	1.0	0.79	1.0	0.97	1.3
	Element ratio ($mol.mol^{-1}$)					
Al/Ca	1.1	1.2	1.4	0.19	0.74	0.44
NH_4/K	1.0	1.5	1.0	1.0	0.71	0.57

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

6.4   Conclusions

Element concentrations

- SO_4 concentrations were higher than the NO_3 concentrations indicating the dominance of SO_4 in soil acidification.
- NO_3 concentrations were generally higher than a target value of 0.4 $mol_c.m^{-3}$, used in the Netherlands with respect to drinking water quality.

- Al concentrations were mostly above a critical value of 0.2 $mol_c.m^{-3}$, related to toxic effects on roots.
- Differences between ion concentrations in the topsoil and subsoil were small, except for the pH, which is lower in the topsoil.

Element ratios
- The $(NH_4 + NO_3)/SO_4$, indicating the contribution of both compounds to soil acidification, is mostly below 1.0 (median value was 0.57), whereas this ratio was larger than 1.0 in the atmospheric input in the Netherlands in 1990. Assuming that SO_4 behaves as a tracer, this implies that a considerable amount of nitrogen is retained as a result of uptake, immobilisation and/or denitrification.
- The NH_4/NO_3 ratio, indicating the degree of nitrification, was mostly below 1.0 (median value was 0.21). This indicates a strong degree of nitrification and/or preferential NH_4 uptake, since the NH_4/NO_3 ratio in the atmospheric input in the Netherlands was (much) larger than 1.0 in 1990.
- The $Al/(SO_4 + NO_3)$ ratio, indicating the degree of Al mobilisation by acidic inputs, varied from strongly (from 0.01-0.8 with a median value of 0.45). Most likely, the lower values for the $Al/(SO_4 + NO_3)$ ratio are the result of a high base cation (mainly Ca) input from the atmosphere, due to strong filtering of base cations by the forest canopy. Liming/fertilisation in the past may also play a role.
- The median Al/RCOO ratio was 3.4, indicating that toxic free Al dominates the Al speciation compared to non-toxic organically complexed Al.
- Both the Al/Ca ratio and the Al/(Ca+Mg+K) ratio are mostly higher than 1.0, which are considered average critical values. Median values for the Al/Ca ratio are 1.1 in the topsoil and 1.4 in the subsoil, whereas the median Al/(Ca+Mg+K) ratios are .. and.. in the topsoil and subsoil, respectively. This implies that adverse effects of Al on roots are likely.
- The ratio of NH_4 to K and of NH_4 to Mg nearly always remained below a critical value of 5. Median values are even near or below 1.0 for both ratios in topsoil and subsoil. This is likely due to preferential NH_4 uptake and nitrification.

Relationships between soil solution chemistry and environmental factors
- The concentrations of most ions in soil solution were especially influenced by tree species. Lowest pH values and highest concentrations in NO_3, SO_4 and Al occur below Norway Spruce and Douglas Fir. The reverse is true for Oak and Beech, whereas Japanese Larch, Scots Pine and Black Pine occupy an intermediate position. Differences between tree species are probably caused by increased dry deposition and evapotranspiration.
- There was a clear impact of the estimated average deposition level in grids where the forest were located on concentrations in NO_3, SO_4 and Al, but it appeared to be smaller than the impact of tree species.
- Other stand characteristics that did influence the concentrations in soil solution were tree height, canopy coverage and to some extent the distance to the nearest forest edge. For most ions, concentrations increased with an increase in tree height and canopy coverage, most likely due to an increase in dry deposition and evapotranspiration.

7 Relations between ion concentrations in soil and soil solution and the assessment of model parameters

7.1 Introduction

Information on relationships between chemical parameters in soil and soil solution is crucial in models that simulate the response of soil to element inputs from the atmosphere. Most relevant are relationships or more precisely model parameters describing the major buffering processes in soils, which include N retention, Al release and cation exchange. Furthermore, the role of P adsorption is relevant to gain insight in the behaviour of this element that may be limiting in forest soils. Here we describe results of simple assessments (Section 7.2) and of derived model parameters, applying the theories described in section 2.6 (Section 7.3).

7.2 Relations between the chemical composition of the soil solution and solid phase

Correlation between ion concentrations in soil solution

In acidified soils, with a pH below 5, it is likely that the net acidic input by S and N compounds is mainly neutralised by Al release, while the remaining part is leached as protons. This hypothesis was tested by relating the sum of H plus Al concentration to the sum of the SO_4 and NO_3 concentration in both the mineral topsoil and subsoil. Results thus obtained showed a clear linear relationship between the H+Al concentration and the concentration of SO_4+NO_3 (Fig. 4).
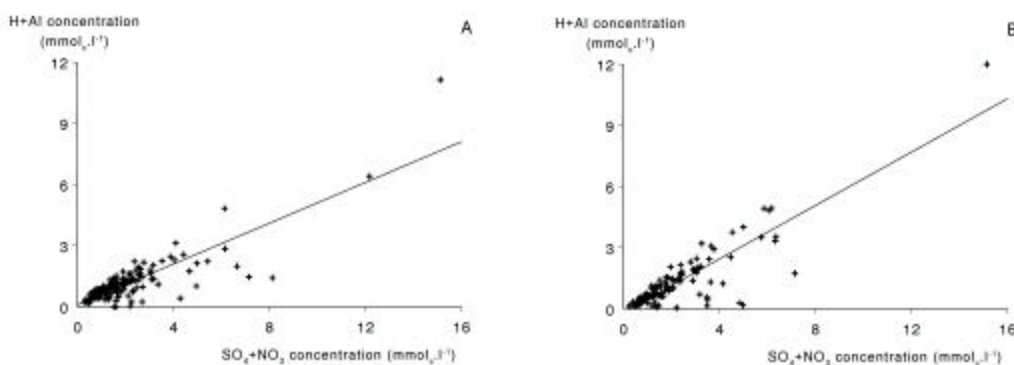
Figure 4 Relationships between the sum of the H plus Al concentration and the sum of the SO_4 and NO_3 concentration in the mineral topsoil (A) and the mineral subsoil (B) in stands with a pH below 5.

Both Fig. 4 and results of linear regression analyses for both depths (Table 73), showed that the concentration of H+Al got closer to the concentration of SO_4+NO_3 (a1 closer to 1) with increasing depth. A 1:1 relationship between [H+Al] and [SO_4+NO_3] in the soil layers below the root zone, indicates that external inputs of N and S to the soil (corrected for N and S retention in the soil), will cause mobilisation

and leaching of equivalent amounts of H and Al. Compared to results obtained for intensively monitored sites (e.g. De Vries et al., 1995b), the value of a1 in the subsoil was much less than one (0.66) and R^2_{adj} was also relatively low (0.75; cf. Table 73). The linearity of the relationship did not increase with increasing depth, as shown by a similar adjusted coefficient of determination (R^2_{adj}). Generally, lower values of a1 and of R^2_{adj} in the upper soil layers are mainly caused by a variable production of base cations (BC) and NO_3, induced by mineralisation and nitrification of plant litter. In the 150 forest stands, BC concentrations were generally quite high, also in the subsoil, which may partly be due to the fact that BC concentrations are slightly overestimated in centrifugates compared to lysimeters (De Vries et al., 1995b).

Table 73 Linear regression parameters in the relationship: '[H+Al]= a0+a1 [SO$_4$+NO$_3$]' for the mineral topsoil and subsoil, using plots with a pH below 5 and reliable soil solution chemistry data.

Nr plots	Depth (cm)	a_0 (mol$_c$.m^{-3})	a1 (-)	R^2_{adj} (%)
129	0-30	0.08	0.54	77
113	60-100	-0.17	0.66	76

Correlation between ion concentrations in soil solution and soil solid phase
The chemical composition of both soil and soil solution has only been measured in the mineral topsoil (0-30cm depth). Furthermore, the chemical soil composition has been assessed in the humus layer, whereas the soil solution has also been measured in the mineral subsoil (60-100cm depth). Results of correlations between the soil solid phase in both layers have been investigated for the exchangeable cation fractions and contents (Table 74). Correlation coefficients between element contents at the adsorption complex in the humus layer and mineral topsoil appeared to be larger for exchangeable fractions than for exchangeable contents (the latter value is strongly influenced by the CEC, of the mineral soil). Values were highest for the divalent base cations Ca and Mg (Table 74).

Table 74 Correlation coefficients for element contents at the adsorption complex between the humus layer and the mineral topsoil

Element	Correlation coefficients (-)	
	Exchangeable contents	Exchangeable fractions
H	0.09	0.22
Al	0.09	0.21
NH_4	0.20	0.38
Ca	0.48	0.51
Mg	0.31	0.57
K	0.32	0.31
Na	0.28	0.58

Dissolved concentrations of cations in the mineral topsoil were clearly correlated with the exchangeable fraction in that layer, although the correlation was very weak for Al (Table 75). As expected, the correlations strongly decreased with exchangeable cation contents. With the exception of NH_4, the relationships were also less clear with the exchangeable and total concentrations in the humus layer (Table75).

Table 75 Correlation coefficients between dissolved cation concentrations in the mineral topsoil, and the total and exchangeable cation concentrations in the humus layer and the mineral topsoil

Element	Correlation coefficient of the topsoil solution with ...				
	Mineral layer exchangeable fraction[1]		Humus layer total	Humus layer exchangeable fraction[1]	
H	0.41	(0.27)	-	-0.04	(-0.02)
Al	0.21	(0.01)	-0.02	0.03	(-0.03)
NH$_4$	0.64	(0.26)	0.29[2]	0.65	(0.63)
Ca	0.73	(0.64)	0.51	0.56	(0.55)
Mg	0.41	(0.10)	0.28	0.20	(0.21)
K	0.51	(0.16)	0.22	0.19	(0.30)
Na	0.63	(0.12)	0.34	0.50	(0.47)

[1] exchangeable content in brackets

[2] refers to total N

The relationship between dissolved nitrate concentration and C/N ratio

There was no clear relationship between the dissolved nitrate concentration in the subsoil and the C/N ratio of the forest floor (humus layer) as shown in Fig. 5A, being contrary to the results by Dise et al. (1998) and Gundersen et al. (1998). Gundersen et al. (1998) suggested that forest floor C/N ratios may be used to assess risk for nitrate leaching, distinguishing threshold values of >30, 25 to 30, and <25 to separate low, moderate, and high nitrate leaching risk, respectively. Actually, their data were limited to well-drained coniferous forests, and we thus limited our results also to such forest stands, requiring also the availability of a forest floor of at least 2 cm thickness. Nevertheless, the relationship was weak and did not really improve when scaling the NO$_3$ concentration to the estimated N input from the atmosphere. One might say that the quality of the data in the 150 forest stands (just one measurement of soil solution chemistry in the year and not a year round leaching flux) is lower than those presented by Gundersen et. al (1998), but the results do indicate that the C/N ratio of the forest floor does not seem to be the distinguishing indicator for the risk of N leaching. A similar conclusion can be derived form the (non-existing) relationship between the calculated N retention fraction and the C/N ratio of the forest floor and mineral topsoil (Fig. 6).
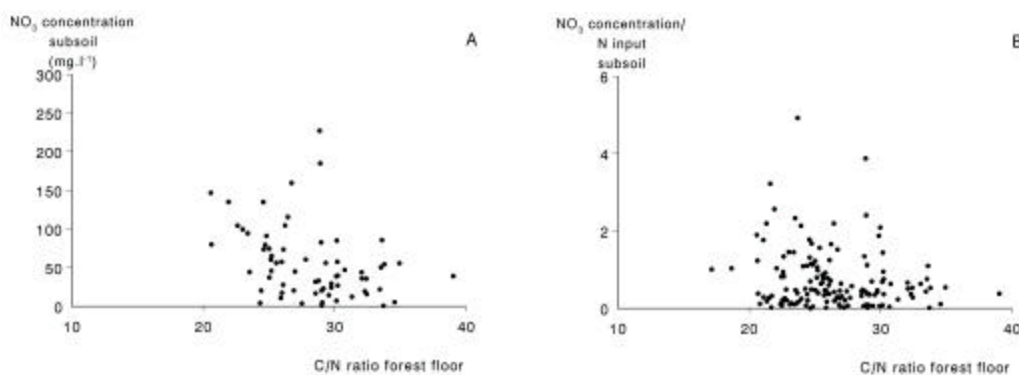

Figure 5 Relationships between the NO$_3$ concentration (A) and the ratio of the NO$_3$ concentration to the N input (B) and the C/N ratio of the humus layer (forest floor)
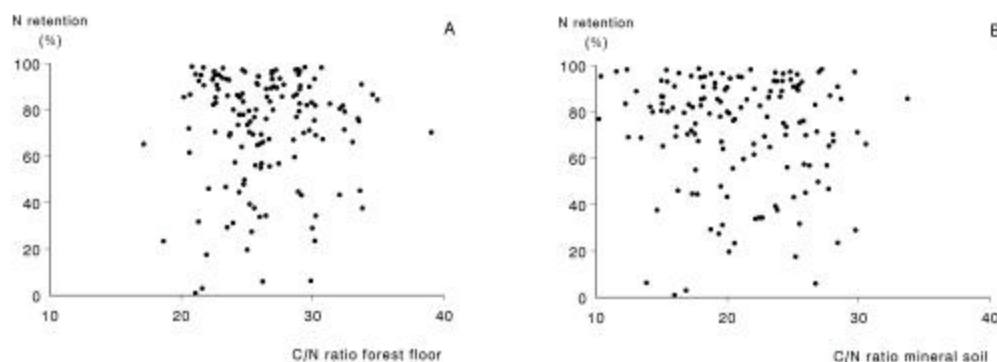
Figure 6 Relationships between the calculated N retention and the C/N ratio of the humus layer or forest floor (A) and the mineral topsoil (B).

7.3 Parameters describing the interaction between the soil solid phase and soil solution

Aluminium dissolution

In most soil acidification models, it is assumed that Al concentrations in the soil solution at the bottom of the root zone are in equilibrium with Gibbsite, as described in Eq. (3). The average Gibbsite equilibrium constant used in most models, e.g. those calculating critical loads is 8.0, assuming that this is the average value at the bottom of the root zone. The Gibbsite equilibrium constant does in principle refer to the relation between the free (uncomplexed) Al activity in solution and the pH, but several models do use the free or even total concentration Al in solution. Therefore, we calculated Gibbsite equilibrium constants for those three options, although the use of total concentrations is principally wrong. Results for the subsoil showed that a value of 8.0 is reasonable when considering the total concentrations (median value is 8.1 with a 90% percentile range of 7.2-8.8), but for the free Al concentration or activity, this value is clearly too high (Table 76). In the mineral topsoil, the Gibbsite equilibrium constants are lower (median value is 6.5-6.7 when using free Al concentration or activity, respectively) reflecting the much lower solubility of complexed Al or the limited rate of Al dissolution in that layer Table 76).

Table 76 Minimum, maximum, 5, 50 and 95 percentiles of the Gibbsite constant of the topsoil and subsoil

Statistic	Total Al concentration		Free Al concentration.		Free Al activity	
	Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil
Minimum	4.41	6.66	4.20	4.73	4.03	4.62
5 percentile	6.10	7.24	5.39	6.13	5.23	5.90
50 percentile	7.19	8.10	6.74	7.41	6.52	7.24
95 percentile	8.84	8.83	8.23	8.40	8.07	8.22
Maximum	14.65	17.38	10.72	10.93	10.58	10.79

The solubility of Al is comparable in the Arenosols and Podzolic soils, but clearly lower in the Fimic Anthrosol and to a lesser extent the Umbric Gleysol. This is most likely related to the different type of organic matter in the Fimic Anthrosols that have been organically manured during centuries in the past.

Table 77 Median values of the Gibbsite constant of the topsoil and subsoil solution for six soil types

Soil type	Total Al concentration		Free Al concentration.		Free Al activity	
	Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil
Haplic Arenosol[1]	7.62	8.20	7.19	7.40	7.00	7.22
Gleyic Podzol[2]	6.96	8.07	6.60	7.48	6.35	7.25
Cambic podzol	7.59	8.17	7.09	7.40	6.91	7.21
Fimic Anthrosol	6.66	7.64	6.14	6.66	5.93	6.52
Umbric Gleysol[3]	6.77	7.78	6.39	7.17	6.21	7.01
Dystric Gleysol	7.37	8.14	6.92	7.84	6.74	7.59

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

In general, the results are in line with the literature information that undersaturation with respect to gibbsite does occur in particular in organic rich soils and at shallow depth (Matzner, 1992; Mulder and Stein, 1994). Therefore, we investigated whether an empirically based equilibrium relation between Al and H activities is a good alternative for the gibbsite equilibrium, according to Eq. (5). Results thus obtained for total and free concentration of Al and the free Al activity in solution (Fig. 8) show that the slopes in the relationship strongly deviate from 3.0 in the topsoil, specifically when using total Al concentrations. A similar conclusion can be drawn when limiting the results to non-calcareous soils with a pH less or equal than 6.5. It is also true when using an alternative description of Al release by including the complexation of Al to organic matter in the description, according to Eq. (8), for which results are shown in Fig. 10.

The much lower slope in the topsoil follows also clearly from the results of regression analyses, presented in Table 78. The slope of the pAl-pH relationship in the mineral topsoil increased from ranged from 0.47 using total Al concentrations (which is not allowed) to 0.92 using free Al activities, when limiting the results to non-calcareous soils.

Table 78 Relationship between pAl and pH in the soil solution of Dutch soils based on total and free Al concentrations and free Al activities

Depth (cm)	pH range	Relationships								
		based on total Al concentrations			based on free Al concentrations			Based on free Al activities		
		Constant	slope	R^2_{adj}	Constant	slope	R^2_{adj}	Constant	slope	R^2_{adj}
0-30	2.5-7.5	1.98	0.47	27	-2.42	1.83	75	-2.14	1.80	76
	2.5-6.5	1.98	0.47	18	0.86	0.92	23	1.24	0.87	22
60-100	3.0-7.5	0.30	0.86	44	-5.47	2.54	87	-5.16	2.51	88
	3.0-6.5	-1.99	1.45	60	-7.09	2.96	77	-6.64	2.89	77
0-30[1]	2.5-7.5	-1.55	0.73	42	-5.30	1.91	81	-5.00	1.89	82
	2.5-6.5	-2.17	0.90	41	-3.28	1.35	43	-2.90	1.30	43

[1] Relation between $p(Al*C/Al_{org})$ and pH

A non-integer value between 1 and 2 implies that Al release in the mineral topsoil is most likely dominated by equilibrium complexation reactions with organic matter (Wesselink et al., 1996). Similar results were obtained on a European wide scale (De Vries et al., 1999). Differences in correlation coefficients between relationships based on activities and concentrations were negligible (Table 78). In the subsoil the slope

was close to 3.0 when limiting the results to non-calcareous soils, but the equilibrium constant was clearly lower than that of gibbsite (pK 8.1; May et al., 1979).
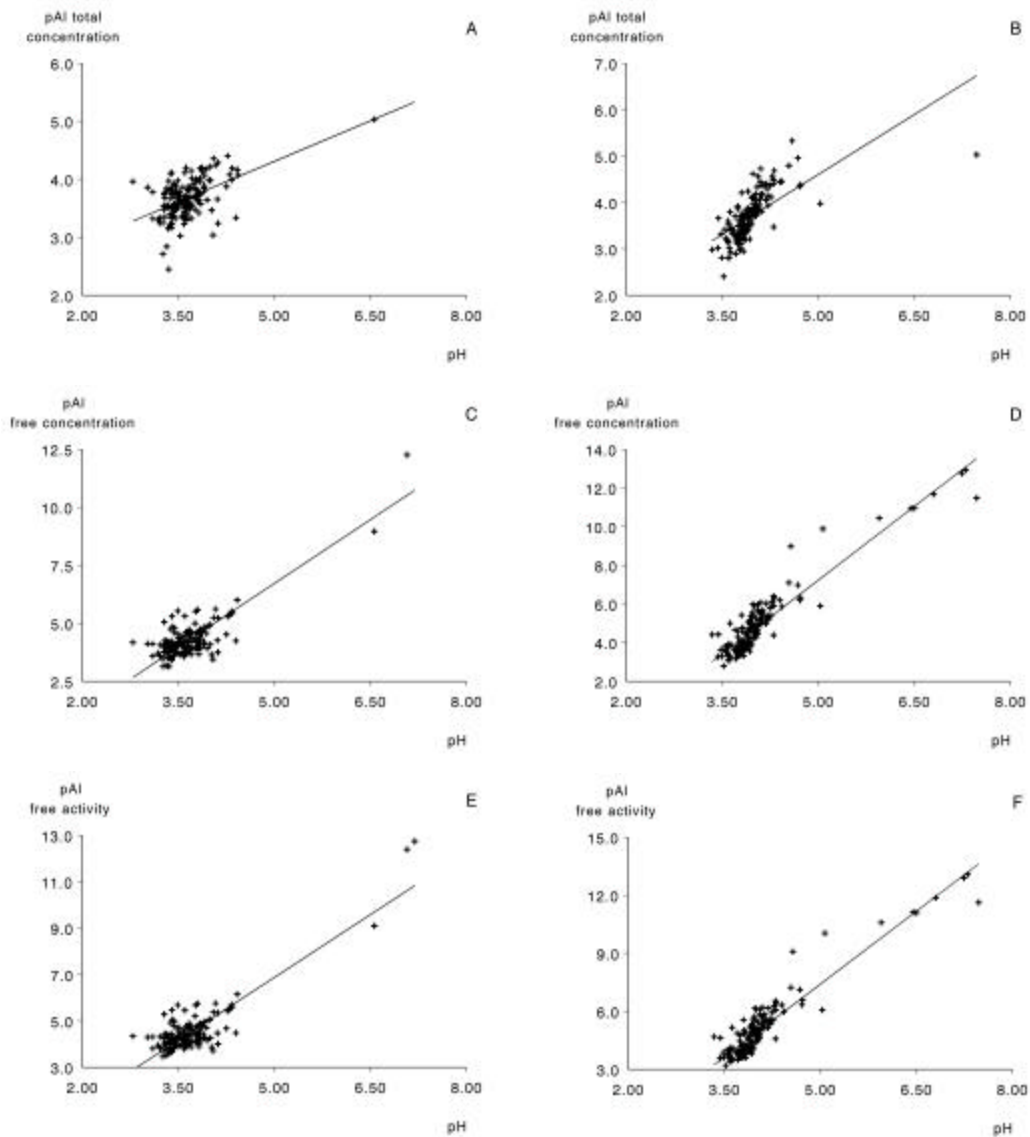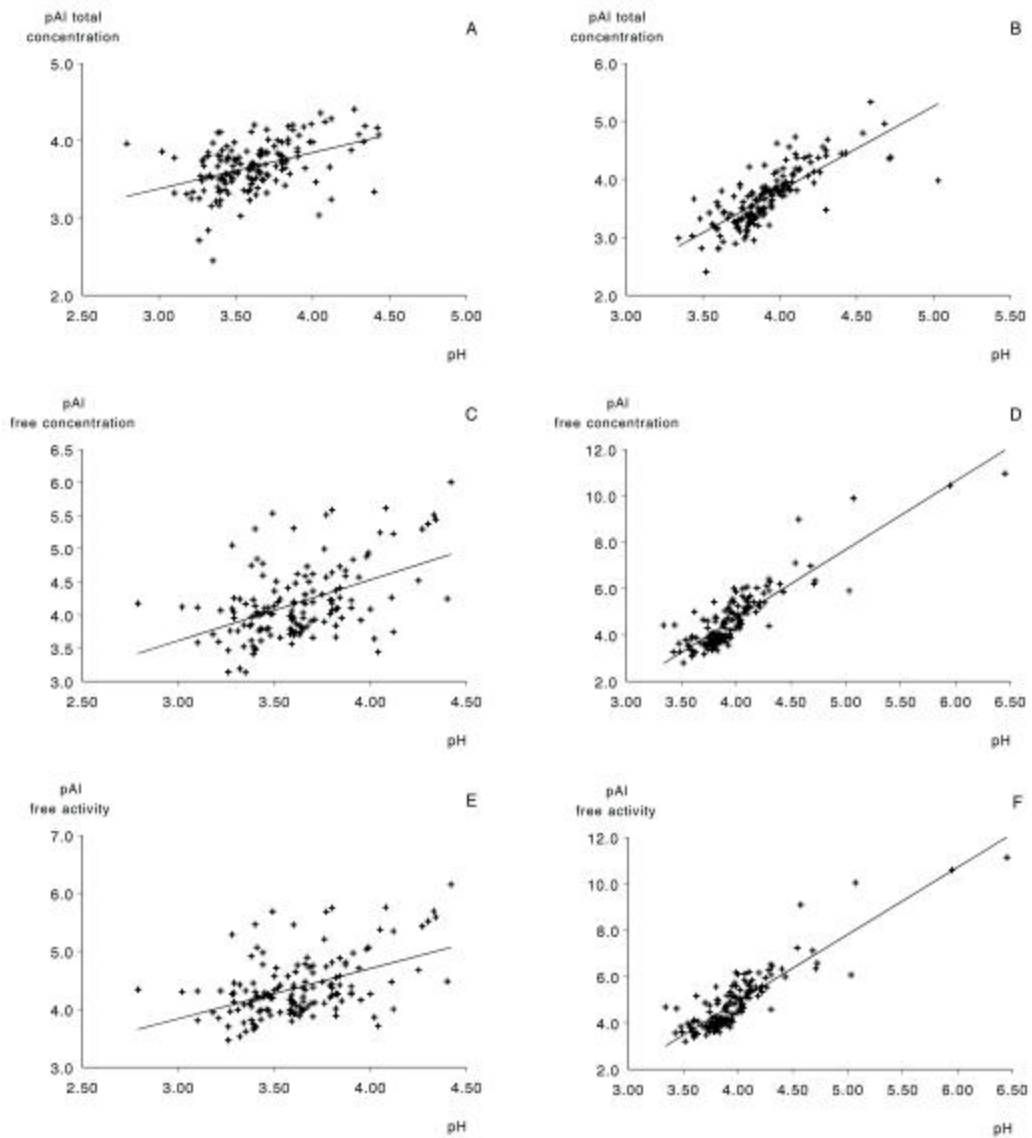

Figure 8. Relationships between the pAl (the negative logarhitm of the Al concentration in mol.l[1]) and pH for the topsoil (A, C, E) and subsoil (B, D, F), distinguishing between total Al concentration, concentration of free (uncomplexed Al) and the free Al activity, using all data..

Results showed that the relationship between pAl and pH in the topsoil (30 cm) of the sandy soils hardly changed by taking into account the occupation of the organic matter with Al. The slope of the pAl-pH relationship and R^2_{adj} were almost the same and also the solubility was comparable.

Figure 9. Relationships between the pAl (the negative logarhitm of the Al concentration in mol.l⁻¹) and pH for the topsoil (A, C, E) and subsoil (B, D, F), distinguishing between total Al concentration, concentration of free (uncomplexed Al) and the free Al activity, using the data for non-calcareous soils only..
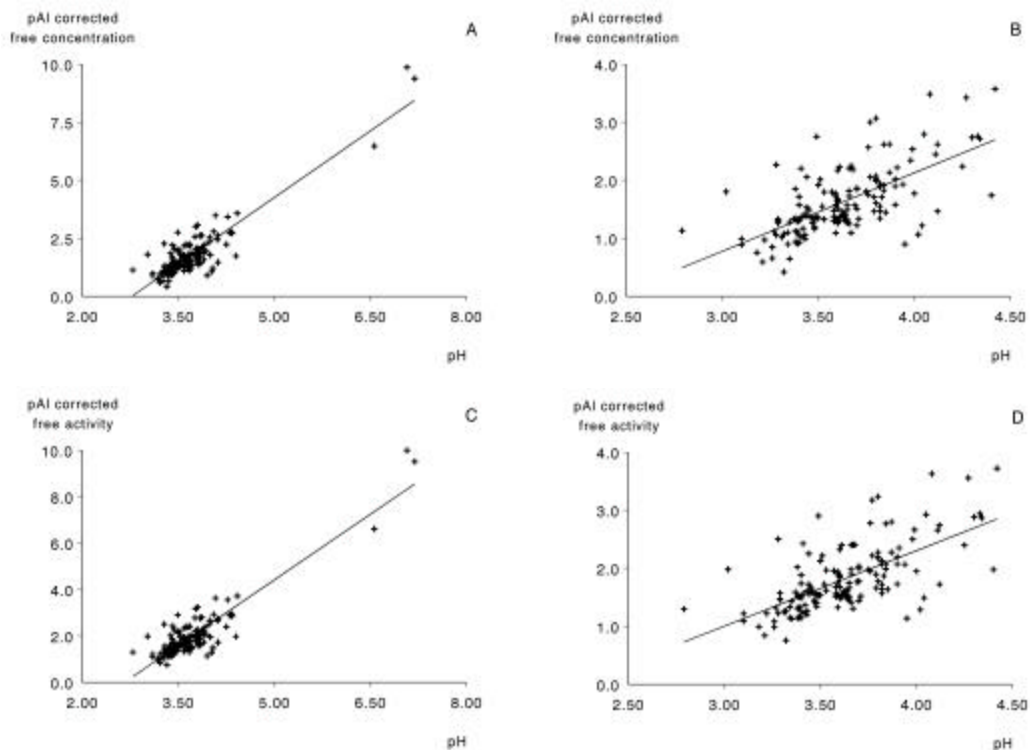
Figure 10. Relationships between the corrected pAl (the negative logarhitm of the Al concentration in mol.l^{-1}, multiplied by the ratio of the total C content and the oxalate extractable Al content) and the pH for the topsoil using all data (A, C) and the data for non-calcareous soils (B, D), distinguishing between, concentration of free (uncomplexed Al) and the free Al activity.

Cation exchange

Results of the calculated cation exchange constants, using the actual CEC are given in Table 79. Results showed a large variation in exchange constants, specifically for H and Al. The affinity of the exchange complex is clearly much higher for protons than for the other monovalent cations, for which the affinity decreases in the order NH_4 > K > Na. The affinity of trivalent Al and Fe for the exchange complex appeared to be comparable.

Table 79 Minimum, maximum, 5, 50 and 95 percentiles of exchange constants related to Ca in the mineral topsoil

Statistics	log Exchange constant (mol.l^{-1})^{z}x^{-2}						
	H	free Al	Fe	Mg	K	Na	NH$_4$
minimum	1.077	-1.002	-2.619	-1.436	0.101	-2.565	-0.322
5 percentile	2.441	0.021	-0.855	-0.949	0.609	-1.453	0.232
50 percentile	3.533	1.115	1.192	-0.581	1.332	-0.623	1.116
95 percentile	4.370	3.263	2.590	0.110	2.134	0.100	2.101
maximum	5.942	4.705	4.443	0.712	2.549	0.486	2.816

The influence of soil type appeared to be small with respect to the affinity for monovalent and divalent cations, but the affinity for Al and Fe was clearly lower in the two Gleysoils than in all other soils (Table 80).

Table 80 Median values of exchange constants related to Ca in the mineral topsoil for six soil types

Soil type	log Exchange constant $(mol.l^{-1})^z x^{-2}$						
	H	free Al	Fe	Mg	K	Na	NH$_4$
Haplic Arenosol[1]	3.692	1.468	1.341	-0.419	1.702	-0.493	1.444
Gleyic Podzol[2]	3.623	1.086	1.222	-0.615	1.148	-0.657	0.905
Cambic podzol	3.420	1.555	1.449	-0.441	1.690	-0.565	1.315
Fimic Anthrosol	3.601	1.083	1.027	-0.654	1.555	-0.653	1.329
Umbric Gleysol[3]	3.253	0.376	-0.042	-0.729	1.093	-0.576	1.136
Dystric Gleysol	3.607	0.730	-0.126	-0.520	1.637	-0.657	0.969

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

Results of the exchange constants that were calculated while using a potential CEC at pH 6.5, show clearly higher exchange constants for H, whereas the affinity for Al remains comparable (Table 81).

Table 81 Minimum, maximum, 5, 50 and 95 percentiles of exchange constants related to divalent base cations (Ca+Mg) and related to the total base saturation (Ca+Mg+K+Na) in the mineral topsoil

Statistics	log Exchange constant (Ca+Mg) $(mol.l^{-1})^z x^{-2}$			log Exchange constant (Ca+Mg+K+Na) $((mol.l^{-1})^z x^{-2}$	
	H	Free Al	K+Na	H	free Al
minimum	1.995	-0.759	-0.850	1.823	-0.866
5 percentile	3.333	0.260	-0.358	3.094	-0.050
50 percentile	3.895	1.392	0.331	3.703	0.882
95 percentile	4.797	3.428	1.019	4.571	2.707
maximum	6.246	4.759	1.358	6.108	3.905

As with the exchange constants calculated with the unbuffered CEC values, the influence of soil type appeared to be small with respect to the affinity for protons, but the affinity for Al and Fe was clearly lower in the two Gleysoils than in all other soils (Table 82).

Table 82 Median values of exchange constants related to divalent base cations (Ca+Mg) and related to the total base saturation (Ca+Mg+K+Na) in the mineral topsoil for six soil types.

Soil type	log Exchange constant (Ca+Mg)			log Exchange constant (Ca+Mg+K+Na)	
	H	Free Al	K+Na	H	free Al
Haplic Arenosol[1]	4.019	1.710	0.530	3.884	1.033
Gleyic Podzol[2]	3.850	1.422	0.229	3.697	0.998
Cambic podzol	4.038	1.757	0.516	3.797	0.833
Fimic Anthrosol	3.964	1.350	0.374	3.776	0.827
Umbric Gleysol[3]	3.599	0.582	0.184	3.439	0.428
Dystric Gleysol	3.905	0.918	0.502	3.831	0.541

[1] including Gleyic Arenosols
[2] including Carbic Podzols
[3] including organic rich soils

Phosphate adsorption
Relationships between the inorganic P concentration and two different expressions for the degree of phosphate saturation, i.e. the ratio $P_{ox}/(PSC-P_{ox})$ and the P_{ox}/PSC ratio, showed a comparable relation with the P_{ox}/PSC ratio (Fig. 11). This implies

that in forest soils, with low inorganic P concentrations, a linear adsorption description just as good as empirical approximation as a Langmuir description (Compare Section 2.6).
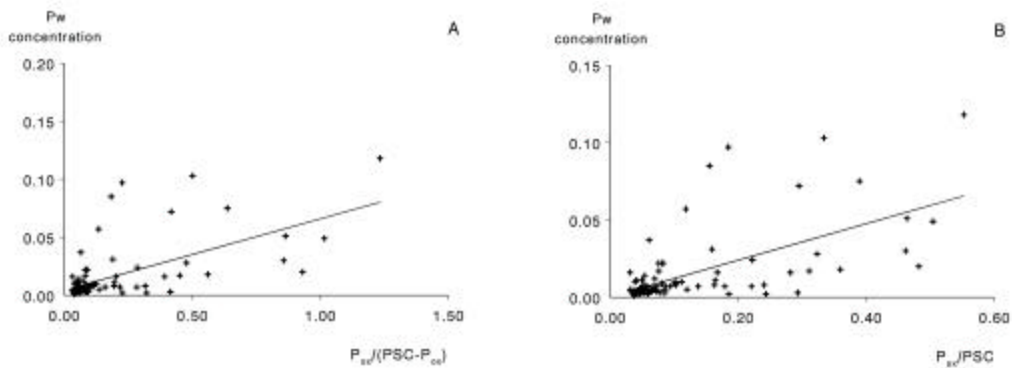

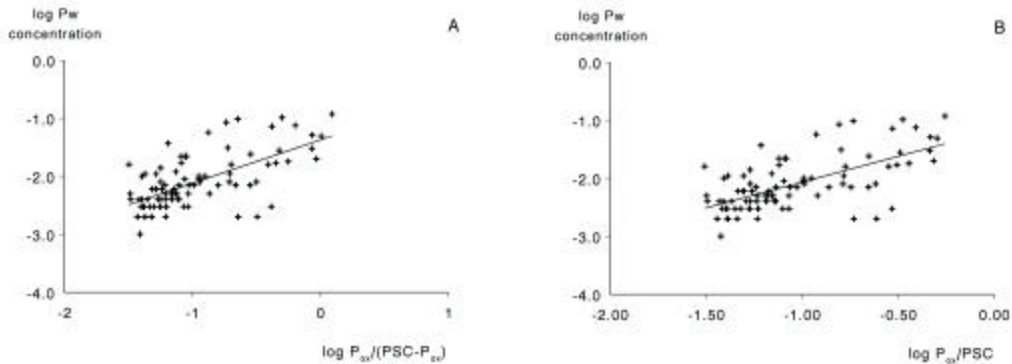*Figure 11. Relationships between the inorganic P concentration (in mmol.l^{-1}) and two different expressions for the degree of phosphate saturation (A, B).*

We also investigated, whether two different Langmuir types of adsorption could more adequately describe P adsorption, according to Eq (20) and (21), by relating the logarithmic inorganic P concentration with the two different expressions for the logarithmic degree of phosphate saturation. Results thus obtained gave similar relationships (Fig. 12).

Figure 12. Relationships between the logarithmic inorganic P concentration (in mmol.l^{-1}) and two different expressions for the logarithmic degree of phosphate saturation (A, B).

Results of regression analyses based on 92 observations (in many soils the dissolved inorganic P concentrations were below the detection limit) are presented in Table 83. The results show that the slope exponent do significantly deviate from 1.0, implying that a Freundlich description of the P adsorption behaviour seems most appropriate in acid sandy fort soils. Ranges in P adsorption constants using a Langmuir description and a linear description of P adsorption behaviour saturation are presented in Table 84. Using the Langmuir description, most values range between 3 and 40 $m^3.mol^{-1}$, with a median value of 14 $m^3.mol^{-1}$. This is clearly lower than values reported by Van der Zee (1988) for agricultural soils, who suggested a mean value of 35 $m^3.mol^{-1}$ with a range between 11 and 46 $m^3.mol^{-1}$.

Table 83 Relationships between original and logarithmic concentrations of inorganic P in solution and different descriptions for the degree of P saturation based on 92 observations.

Response variable (y)	Predictor variable (x)	intercept	slope	R^2_{adj}
[P]	$P_{ox}/(PSC-P_{ox})$	(0.00455)	0.06147	37.8
[P]	P_{ox}/PSC	(0.00052)	0.1180	37.8
log [P]	log $P_{ox}/(PSC-P_{ox})$	-1.3697	0.7471	41.9
log [P]	P_{ox}/PSC	-1.173	0.889	41.3

This implies that P adsorption is lower in acidic forest soils than in slightly acid agricultural soils. There was, however, no relationship between the range in adsorption constants and the pH or organic matter content.

Table 84 Ranges in P adsorption constants ($m^3.mol^{-1}$) using a Langmuir description and a linear description of P adsorption behaviour saturation based on 92 observations.

P adsorption constant	Mean	%SD	Min	5%	50%	95%	Max
$P_{ox}/([P]*(PSC-P_{ox})$	19.5	123	1.8	2.5	14.1	40.3	160
$P_{ox}/([P]*PSC)$	16.0	113	1.6	2.2	12.8	31.4	122

7.4   Conclusions

Correlation between ion concentrations in soil and soil solution
- In the considered acidic sandy soils, there is a clear linear relationship between the H+Al concentration and the concentration of SO_4+NO_3, indicating that the net acidic input by S and N compounds is mainly neutralised by Al release, while the remaining part is leached as protons.
- In the mineral topsoils, there was a clear correlation between dissolved cation (H, Al, NH_4, Ca, Mg, K, Na) concentrations and exchangeable cation fractions at the adsorption complex (r= 0.4-0.7), with the exception of Al, where the correlation is weak.
- There was no clear relationship between the dissolved nitrate concentration in the subsoil and the C/N ratio of the forest floor (humus layer), which is contrary to results published in the literature.

Aluminium dissolution and cation exchange
- In the mineral topsoil, Al concentrations in the soil solution can not be described with the Gibbsite equilibrium equation, that is generally used in soil acidification models. The slope of the pAl-pH relationship is near 1, which implies that Al release in the mineral topsoil is most likely dominated by equilibrium complexation reactions with organic matter.
- In the mineral subsoil, the slope of the pAl-pH relationship was close to 3.0, which would indicate equilibrium with Gibbsite, but the equilibrium constant was clearly lower than that of gibbsite (undersaturation).
- There is a large variation in exchange constants, specifically for H and Al. The affinity of the exchange complex is clearly much higher for protons than for the other monovalent cations. The influence of soil type appeared to be small with respect to the affinity for monovalent and divalent cations, but the affinity for Al and Fe was clearly lower in the two Gleysoils than in all other soils.

Phosphate adsorption
- In forest soils, with low dissolved inorganic P concentrations (up to 2 mg.l^{-1}), the interaction between soil solid phase and soil description can best be described with a non-linear Freundlich equation. This gives a better prediction of the dissolved inorganic P concentration than the Langmuir description used in agricultural soils.
- P adsorption is lower in acidic forest soils than in slightly acid agricultural soils. There was, however, no relationship between the range in adsorption constants and the pH or organic matter content.

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