

Chemical composition of the humus layer, mineral soil and soil solution of 200 forest stands in the Netherlands in 1995

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ABSTRACT

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A nation-wide assessment of the chemical composition of the soil solid phase and the soil solution in the humus layer and two mineral layers (0-10 cm and 10-30 cm) has been made for 200 forest stands in the year 1995. The stands were part of the national forest inventory on vitality, included seven tree species and were all located on non-calcareous sandy soils. The soils are nearly all characterised by high nitrogen and metal contents in the humus layer and low pH and base saturation values in the mineral layer, indicating the occurrence of eutrophication, acidification and heavy metal pollution. Of those stands, 124 were also sampled and analysed in 1990. Compared to 1990, results for the humus layer show: (i) a decrease (release) in N and metal contents and pools and (ii) a decrease in total and exchangeable pools of base cations, combined with increase in H saturation. This indicates a decrease in eutrophication but an ongoing acidification. In the soil solution, however, there is a decrease in Al/Ca and NH₄/K ratio's implying a slight recovery from acidification. For the mineral soil, the changes in element pools are too unreliable to make any distinct conclusion.

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

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Preface

To examine the impact of atmospheric deposition on (mainly) non-calcareous soils of Dutch forest, a survey of the chemical soil and soil solution composition below 200 forest stands, including seven major tree species, was carried out by the DLO Winand Staring Centre. This research is part of the national Forest Health Monitoring Network, which is coordinated by the National Reference Centre for Nature Management (IKC-N) and was financially supported by the Dutch Ministry of Agriculture, Nature Management and Fisheries

In this report the results are given of the chemical composition of the humus layer and the chemical composition of soil and soil solution on depths of 0-10 cm and 10-30 cm below surface. It forms a series with another report (424.1) in which the chemical soil and soil solution composition below 150 forest stands, partly coinciding with the 200 forest stands, is given in 1990. For various reasons, the latter report has been delayed extremely and consequently both reports are now published as a series. For a major part of the 200 forest stands, comparisons with the chemical compositions measured in 1990 (De Vries and Leeters, 2001) are made.

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Summary

Approach

Aim of the research

The condition of the Dutch forest has been observed nation wide on 3000 sites each year over the period 1984-1994 to gain insight in the development of the vitality of major tree species. The vitality was judged in terms of defoliation and discoloration. In 1995, an inventory of 200 forest stands, being the new Forest Health Monitoring Network, started to get a better insight in the effects of acidification, eutrophication and desiccation on the forest ecosystem. Within this Network, inventories are made of: (i) defoliation and discoloration (every year), (ii) decline by fungus or insects (every year), (iii) chemical composition of the soil and soil solution (every 5 year), (iv) chemical composition of needles and leaves (every 5 year), (v) species composition of the ground vegetation (every 5 year) and (vi) forest growth and atmospheric deposition (only for 14 forest stands).

The aim of this study is to give an overview of the chemical composition of humus layer, soil and soil solution in the 200 selected forest stands. Actually, 124 of the 200 forest stands selected for the new Monitoring Network were also investigated in 1990. At that time, the chemical composition of the foliage, humus layer, mineral soil and soil solution was investigated in 150 forest stands on non-calcareous sandy soils to gain insight in the impacts of atmospheric nitrogen and sulphur deposition. Another aim of this study is therefore to compare the chemical composition of humus layer, soil and soil solution between 1995 and 1990 for 124 of the 200 monitoring forest stands.

Site selection

The basis for the selection of the 200 locations of the new Forest Health Monitoring Network was their representativity for the total population of 3000 locations in which the forest health was measured since 1984. Furthermore, the selection was based as much as possible on the 150 locations measured in 1990. Eventually 124 forest stands were found fit to use and 76 were selected supplementary. The supplementary selection was mainly based on getting a good range over tree species, region, soil type, ground water level, area of the stand, age and presence of ground water level measurements. As in 1990, 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

The soil was sampled in the period March the 6 to May the 16 in 1995, since dissolved element concentrations in this period are most representative for the annual average concentration. At each site, composite samples were taken. This consisted of 10 sub-samples for the humus layer divided in an L & F horizon and an H horizon when the thickness was more than 1 cm. The humus layer was sampled with a cylinder of steel with a diameter of 14.8 cm. For every subsample the thickness of the litter (L), fermented (F) and humus (H) horizon plus the total thickness was noted. In the mineral soil 20 sub-samples were taken at depths of 0-10 cm and 10 – 30 cm. The sampling depths for the mineral soil was limited to 30 cm, 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 sample points were chosen according to a steady pattern related to 25 marked trees that are part of the vitality measurements.

An overview of the sampling and analyses program in 1995 is given in Table s1 in comparison to the program in 1990. The most important pool of nutrients in forest is the humus layer. Consequently the contents of the major nutrients, i.e. N, P, K, Ca and Mg were measured for this layer. Contents of N and P were also measured for the two mineral layers, since the N content is likely to be increased due to elevated N input, whereas P is an important nutrient whose availability might be limited due to acidification. In order to gain insight in the buffer characteristics and soil contamination of the soil, the pH, exchangeable cation contents and CEC and the contents of important heavy metals were measured in the humus layer and the mineral soil layer 0 - 10 cm. Dissolved concentrations of all the major cations and anions including pH were measured in the humus layer and both mineral layers.

Table s1 Comparison of the sampling and analyses program of the 200 forest stands investigated in this study in 1995 and the 150 forest stands investigated in 1990 (in total 124 forest stands were sampled in both years).

Analyses	1990			1995		
	Humus layer	0-30 cm	60-100 cm	Humus layer	0-10 cm	10-30 cm
pH-H ₂ O, pH-KCl	x	x	-	x	x	x
Total OM, N, P	x	x	-	x	x	x
Total Al, Fe, Ca, Mg, K	x	-	-	x	-	-
Total Pb, Cd, Cu, Zn, Ni, Cr	x	-	-	x	x	-
Exchangeable H, Fe, NH ₄ , Ca, Mg, K, Na	x	x	-	x	x	-
Dissolved H, Al, Fe, Ca, Mg, K, Na, NH ₄ , NO ₃ , SO ₄ , Cl, H ₂ PO ₄ , RCOO	-	x	x	x	x	x

The table shows that the following comparisons are possible:

- pH and concentrations and pools of (i) organic matter (OM) and major elements (N, P, Al, Fe, Ca, Mg, K), (ii) heavy metals (Pb, Cd, Cu, Zn, Ni, Cr) and (iii) exchangeable cations (H, Fe, NH₄, Ca, Mg, K, Na) in the humus layer.
- pH- H₂O and pH-KCl and concentrations and pools of (i) organic matter (OM) and major nutrients (N and P) and (iii) dissolved major ions (H, Al, Fe, Ca, Mg, K, Na, NH₄, NO₃, SO₄, Cl, H₂PO₄, RCOO) in the mineral topsoil (0-30 cm)

Chemical composition of the humus layer

Contents and pools of organic matter and nutrients

- The contents and pools of organic matter and nutrients varied largely following an almost normal distribution. Comparing nutrient pools with average annual growth uptakes shows that the pools in the humus layer can provide nutrients for a long period (> 30 years), except for K. In general, however, long-term nutrient supply comes from atmospheric deposition and long-term weathering, but the pools in the humus layer are an important buffer
- Median values of the nutrient contents in the humus layer hardly varied between tree species, except for oak and beech where relatively high Ca, Mg and K contents were found. Oak is mainly situated on relatively poorly drained soils with possible Ca input by seepage.
- Pools of organic matter and N were relatively low for black pine, Douglas fir and oak. Larger nutrient pools are partly correlated with larger pools of organic matter and partly with higher nutrient contents in the humus layer.

Soil acidity and exchangeable cations

- Results for the pH in a water extract and in a KCl extract generally varied between 3.5 and 6 and between 2.5 and 5.5, respectively. This is a slightly larger range than those encountered in the 150 forest stands in 1990
- As with the 150 forest stands in 1990, the cation exchange capacity (CEC) in the humus layer varied mostly 200 and 400 mmol_c.kg⁻¹, but the total range in the 200 stands (29-652 mmol_c.kg⁻¹) is larger than in the 150 stands (142-498 mmol_c.kg⁻¹).
- As with the 150 forest stands in 1990, exchangeable cations on the adsorption complex in the humus layer were generally dominated by protons (H) followed by Ca. The variation in exchangeable cation fractions was, however, larger than measured in the 150 forest stands in 1990.
- Both the exchangeable cation contents and cation pools decreased according to H > Ca followed by Mg, Al, Fe, NH₄, K and Na. Ranges in the cation pools were comparable to those of the 150 forest stands. Exchangeable base cation pools are generally larger under deciduous trees than under coniferous trees, reflecting the somewhat richer soil conditions for the former tree species.

Contents and pools of heavy metals

- The variation in heavy metal content in the humus layer is large. For all metals, the mean values are higher than the median values, since there are several forest stands with very high values.
- As in 1990, there is a relationship between regional patterns in heavy metal deposition and the heavy metal contents in the humus layer. For Pb, Cd, Cu and Zn, high values were found in the southern part of the Netherlands, more specifically in the strongly polluted Kempen area.
- The humus layers are in general most strongly polluted with Pb (approximately 50% of the plots exceeded the target value) followed by Zn and Cd.

Chemical composition of the mineral topsoil

Contents and pools of organic matter, nitrogen and phosphorus

- Compared to the humus layer, the contents of organic matter, nitrogen and phosphorus in the mineral soil are much lower. The N contents in organic matter, however, are the same in both layers with a median value of ca 2.2%.
- The organic matter pool in the mineral layer is higher than in the humus layer due to higher bulk densities in the mineral layers.
- In general, the contents and pools of organic matter and N decrease in the order Gleysols > Fimic Anthrosols > Podzols > Arenosols. A comparable order was found in 1990. The P contents and pools were highest in Fimic Anthrosols, reflecting the impact of long-term fertilisation in the past.

Soil acidity and exchangeable cations

- Results of the pH-H₂O and pH-KCl for the mineral top layer (0-10 cm) generally varied between 3.5 and 5.0 and between 3.0 and 4.5.
- As with the results obtained for a layer of 30 cm in 1990, the median CEC in the mineral layer of 10 cm was nearly ten times lower than in the humus layer (36 compared to 301 mmol_c.kg⁻¹). The average exchangeable cation pool (kmol_c.ha⁻¹) is, however, larger because of the much higher bulk density
- As in 1990, the proton saturation and base saturation is much lower and the Al saturation is much higher in the mineral topsoil compared to the humus layer. Al dominates the exchange complex in the mineral topsoil, reflecting that Al mobilisation is the dominant buffer mechanism in this layer.
- In accordance with the higher organic matter content, the CEC decreased from Gleysols > Podzols > Arenosols. Inversely the Al saturation was lower in the more Gleysols.

Contents and pools of heavy metals

- Contents of heavy metals in the mineral topsoil are nearly ten times lower (specifically Pb, Cd, Cu and Zn) than in the humus layer, reflecting the larger impact of atmospheric deposition on metal accumulation in the humus layer as compared to the mineral soil.
- There were only few stands where the target values for heavy metals were exceeded, implying that risks of elevated metal contents are mainly due to metal accumulation in the humus layer and not in the mineral topsoil.
- Despite the lower metal contents, the average heavy metal pools in the mineral layer were generally three (Pb, Cd, Cu and Zn) to five times (Ni, Cr) as large as in the humus layer, because of the much larger bulk density of the mineral topsoil.

Chemical composition of the soil solution

Element concentrations

- In the humus layer NO_3 concentrations are comparable to SO_4 concentrations due to the large release of N by mineralisation followed by nitrification. Inversely, as with the results in 1990, the SO_4 concentrations in the two mineral layers are generally higher than the NO_3 concentrations indicating the dominance of SO_4 in soil acidification.
- In the lowest mineral layer, the EU quality criterion for ground water of 50 mg.l^{-1} ($0.8 \text{ mol}_c.\text{m}^{-3}$) was exceeded at 26% of the plots, whereas Al concentrations were above a critical value of $0.2 \text{ mol}_c.\text{m}^{-3}$ at 69% of the plots.
- There is a consistent decrease in NH_4 with depth, reflecting the impact of preferential NH_4 uptake and nitrification, and a consistent increase in Al with depth, reflecting the impact of Al mobilisation.
- Ca concentrations are mostly higher than those of Mg and K, illustrating that Ca is the dominant base cation buffering the acid input.
- Unlike the results in 1990, the impacts of tree species are not so obvious. High concentrations in SO_4 and Cl occur below Douglas Fir and Norway Spruce, illustrating the impact of the high canopy coverage and Leaf Area Index of those trees on dry deposition and evapotranspiration.

Element ratios

- The average $(\text{NH}_4 + \text{NO}_3) / \text{SO}_4$ ratio, indicating the contribution of both compounds to soil acidification, decreases from 1.6 in the humus layer to 1.0 in the lowest mineral layer (10-30 cm depth). A similar trend is observed in the $\text{NH}_4 / \text{NO}_3$ ratio indicating the occurrence of nitrification and/or preferential NH_4 uptake. The $\text{Al} / (\text{SO}_4 + \text{NO}_3)$ ratio increases with depth, indicating that the increasing role of Al mobilisation in acid neutralisation with depth.
- As in 1990, both the Al/Ca ratio and the $\text{Al}/(\text{Ca}+\text{Mg}+\text{K})$ ratio can exceed an average critical value of 1.0. The ratio of NH_4 to K nearly always remains below a critical value of 5.
- Approximately 75 % 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 5% of the plots in the lowest mineral layer. In 1990, this percentage was 23 for a layer of 0-30 cm, indicating a decrease in Al concentrations in response to the lower S and N deposition. A more reliable comparison requires the use of similar plots as described

Differences in element contents and pools between 1995 and 1990

The chemical composition of the humus layer

The results that are obtained when considering all 124 plots together, that were sampled and analysed both in 1990 and 1995, show:

- A rather constant pool of organic matter, while the organic matter content decreased with nearly 17 g.kg^{-1} . The latter result implies that the contamination with mineral soil was slightly higher in 1995 than in 1990, leading to a larger pool of total mass in the organic layer in 1995
- An average decrease in all nutrient contents and nutrient pools in the humus layer, except for Mg. Changes in nutrient contents were significant for all nutrients except Mg, whereas changes in nutrient pools were only significant for Ca and K.
- An average significant increase in pH-H₂O by 0.1 over the 5 year-period, whereas the pH-KCl did hardly change.
- A rather constant pool of exchangeable cations (total CEC), whereas the contents and pools of exchangeable bases decreased significantly while the contents and pools of exchangeable protons increased significantly.
- A significant decrease in the average total contents of all heavy metals, except Cr, whereas a significant decrease in pools was only found for Ni.

In general, the results do indicate:

- A release in N from the humus layer in response to the decrease in N deposition in the period 1990-1995. The decrease in N content of approximately 0.68 g.kg^{-1} and in N pool of $11 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ ($53 \text{ kg N.ha}^{-1}.\text{yr}^{-1}$ in 5 year) seems likely, although the difference is not statistically significant with respect to pools.
- An ongoing acidification, considering the decrease in total pools of Ca and K and the decrease in base saturation, combined with increase in H saturation, despite the decrease in acid deposition between 1990 and 1995. The relatively constant pH-KCL and even the small increase in pH-H₂O is, however, not in line with these results. The decrease of approximately $5 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ for Ca seems possible but the decrease of nearly $3 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ for K is questionable, since K leaches very fast from the freshly fallen litter and the period in which the samples were taken might have influenced this result. The decrease in base cation pools and the increase in H pools of less than $1 \text{ kmol}_c.\text{ha}^{-1}$ in 5 years, being less than $200 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$, seems likely in view of the average acid input near $5 \text{ kmol}_c.\text{ha}^{-1}.\text{yr}^{-1}$ in this period.
- A release of heavy metals from the humus layer in response to the general decrease in metal deposition in the last decade, specifically with respect to Pb and Cd, although the results are not convincing when pool changes are considered.

Spatial variability and uncertainties in the measurements of the key parameters influence the differences. Therefore, results as a function of tree species, which are often based on approximately 10-15 stands, are not reliable in terms of temporal changes. In general a 5-year period seems, however, too small for definite conclusions, specifically when distinctions are made in tree species or soil types.

The chemical composition of the mineral topsoil

- The results for the differences in the total C, N and P contents and pools in the mineral topsoil (0-30cm) are not reliable because of the large amount of soil in a

- layer of 30 cm. For example, an increase of 0.01% (0.1 g.kg^{-1}), being the case for N, leads to an increase of several hundreds of kilograms, being unrealistic.
- These results indicate that monitoring a mineral layer of this thickness during a relatively short time period is not adequate.

The chemical composition of the soil solution in the mineral topsoil

A comparison of the average dissolved concentrations in the mineral topsoil (0-30 cm) in all 124 plots sampled and analysed both in 1990 and 1995, show:

- A strong decrease in the concentration of all major cations and anions. The concentrations of Cl decreased, however, most strongly and scaling the concentrations of all ions relative to Cl leads an increase in all major ions. Cl concentrations in 1990 were, however, extremely high in the forest topsoil because of very high Cl inputs in early spring in that period.
- A larger decrease in the average SO_4 concentration ($0.53 \text{ mol.}\cdot\text{m}^{-3}$) compared to the sum of the NH_4 and NO_3 concentration ($0.35 \text{ mol.}\cdot\text{m}^{-3}$), being a clear indication of the positive response to the larger decrease in S deposition compared to the decrease in N deposition in this period.

The decrease in the concentration of toxic Al and the increase in pH is not a proof of a recovery of the soil solution chemistry in response to the decreasing acid input because of possible differences in hydrology. Neither the original nor the scaled concentrations give a good indication of a possible recovery (original concentrations) or worsening (scaled concentrations) of the soil solution chemistry. The most important indication of a positive response of the soil solution chemistry to a decreased acid input between 1990 and 1995 is the decrease in the Al/Ca and NH_4/K ratio's, implying an improvement of the environmental circumstances in the root zone.

In summary, the results do indicate some recovery in soil and soil solution chemistry in terms of a release of N from the humus layer and a decrease in Al/Ca and NH_4/K ratio's in the soil solution. Nevertheless, the acidification, in terms of a decrease in total and exchangeable pools of base cations in the humus layer has still continued. For the mineral soil, the changes in element pools are too unreliable to make any distinct conclusion.

1 Introduction

1.1 Forest monitoring research in the Netherlands

Threats to the health of forest ecosystems by acidification, eutrophication and desiccation in response to atmospheric pollution, climate change and ground water table have triggered the monitoring of forest ecosystems in the Netherlands. Up to the 1990, research on the impact of elevated deposition levels of SO_x, NO_x and NH_x in the Netherlands has mainly been carried out within the Dutch Priority Programme on Acidification (1985-1991). Since that time, most research related to impacts on forest has been dedicated to monitoring, carried out within the context of the International Co-operative 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.

In the context of ICP forest, 11 so-called level I plots in the Netherlands are monitored on crown condition only since 1984. Actually, the condition of the Dutch forest was observed nation wide on 1500 sites each year over the period 1984-1994, specifically in view of the potential adverse effects of air pollution. The aim of this national inventory was to gain insight in the development of the vitality of major tree species in the Dutch forests. The vitality was judged in view of the crown condition, more specifically in terms of defoliation and discoloration (e.g. IKC, 1999). This information, however, can only be used to register changes in vitality and is not sufficient to show cause-effect relations between the threats and the forest condition.

Later on, also in the context of ICP forest, 14 Intensive Monitoring (so-called level II), forest stands in the Netherlands are monitored on a wider range of forest ecosystem aspects (De Vries et al., 1994; Leeters et al., 1998). These 14 stands are part of an inventory of 200 forest stands being the new Forest Health Monitoring Network that started in 1995 under the responsibility of the Ministry of Agriculture, Nature Management and Fisheries and executed by The National Reference Centre for Nature Management (IKC-N). This Forest Health Monitoring Network was initiated to get a better insight in the effects of acidification, eutrophication and desiccation on the forest ecosystem. The aim of the Forest Health Monitoring Network is to increase the insight in the:

- Development of the forest ecosystem quality, including the vitality of the major tree species;
- Causes of the changes in forest ecosystem.

Within this Forest Health Monitoring Network inventories are made of the:

- Defoliation and discoloration (every year),
- Decline by fungus or insects (every year),
- Chemical composition of the soil and soil solution (every 5 year),
- Chemical composition of needles and leaves (every 5 year),
- Species composition of the ground vegetation (every 5 year),

- Forest Growth and atmospheric deposition (only for 14 forest stands belonging to the ICP forest Intensive Monitoring plots that are monitored since 1992).

1.2 Aims of the present research

Within the Forest Health Monitoring Network the aim of this study is to give an overview of the chemical composition of humus layer, soil and soil solution in the 200 selected forest stands. A major part of the 200 forest stands selected for the new Monitoring Network (124, including 11 of the 14 level II stands) were also investigated in 1990. At that time, the chemical composition of the foliage, humus layer, mineral soil and soil solution was investigated in 150 forest stands on non-calcareous sandy soils to gain insight in the impacts of atmospheric nitrogen and sulphur deposition (De Vries and Leeters, 2001; Hendriks et al., 1994; De Vries and Jansen, 1994 and Leeters et al., 1994). Another aim of this study is therefore to compare the chemical composition of humus layer, soil and soil solution between 1995 and 1990 for 124 of the 200 monitoring forest stands (compare De Vries and Leeters, 2001).

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 the 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 location of the various forest stands with a description of the forest condition, deposition level, stand and site characteristics. Results for the humus layer are given in Chapter 4. This includes the variation in total contents and pools of major nutrients (N, P, Ca, Mg, K), exchangeable cations (H, Al, Fe, Ca, Mg, K, Na, NH₄) and important heavy metals (Pb, Cd, Cu, Zn, Ni, Cr). The results for the mineral layers are given in Chapter 5. This includes the variation in total contents and pools of organic matter, N and P for the layers 0-10 cm and 10-30 cm and the contents and pools of exchangeable cations and heavy metals (Pb, Cd, Cu, Zn, Ni, Cr) in the layer 0 - 10 cm.

The result of the composition of the soil solution are given in Chapter 6. This includes the variation in major element concentrations and element ratios for the humus layer and forest topsoil (0 - 10 cm and 10 - 30 cm). Chapter 7 gives an evaluation of the differences between 1990 and 1995. The results are presented as differences in organic matter for the humus layer and mineral layer (0-30 cm), separately as well as for the total of both layers. Differences in exchangeable cations and heavy metals could only be given for the humus layer, whereas the differences in soil solution composition could only be given for the layer 0-30 cm. Finally, major results and conclusions are presented in Chapter 8.

2 Methods

2.1 Choice of the locations

The 200 locations of the new Forest Health Monitoring Network were selected by the agency of Daamen, Schoonderwoerd, Miedema and de Klein ordered by The National Reference Centre for Nature Management (IKC-N). The basis for the selection was the representativity of the 200 locations for the total population of 3000 locations in which the forest health was measured since 1984. Furthermore the selection was based as much as possible on the same locations (150) as measured in 1990 by SC-DLO (De Vries and Leeters, 2001).

The 150 forest stands were checked on their representativity for the whole population of 3000 stands and on several pragmatic criteria concerning their utility for the new Forest Health Monitoring Network. Eventually 124 forest stands were found fit to use and 76 were selected supplementary. The supplementary selection was based on getting a good range over tree species, region, soil type, ground water level, total area of the stand, age, presence of ground water level measurements, ownership and correspondence with the ICP level I locations. A list of the separate locations, with their positions, tree species, sampling dates, soil types and ground water level classes, is given in Annex 2.

2.2 Characterisation of the locations

At each site an indication was made of the various stand characteristics, influencing the deposition level on a forest stand or the processes occurring in the forest soil. This included the position of the forest stands and the stand and site characteristics.

Surrounding soil use

- Distance to the nearest forest edge, i.e. 0-20 m, 20-40 m, 40-60 m, 60-80 m, 80-100 m and > 100 m.
- Position of the nearest forest edge with respect to the site.
- Land use at the nearest forest edge i.e. maize field, grassland, and arable or non-agricultural land.

Stand characteristics

- Canopy coverage, i.e. < 50%, 50-75% or >75%. For the deciduous tree species (including Japanese Larch) the canopy coverage may be less reliable because of the sampling period (March-May).
- Estimated height of the stand, i.e. 0-5 m, 5-10 m, 10-15 m, 15-20 m, or > 20 m.

Site characteristics

For every stand a representative description of the soil profile and ground water level class was made for the first 180 cm. The soil was characterised by the occurrence and thickness of A, B and C horizons, the estimated percentage organic matter, loam (texture) and 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 was characterised by the mean highest level in the winter and the mean lowest level in the summer period. Classes were used for characteristic combinations of mean highest and mean lowest ground water level (De Vries and Van Wallenburg, 1990). For part of the stands, a description was already made in 1990. These descriptions were checked.

2.3 Sampling of the soil

Sampling period

The soil was sampled in the period March the 6 to May the 16 in 1995. 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 solution 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. For more information see also De Vries and Leeters (2001).

Sampling depths

Samples were taken of the humus layer and two mineral soil layers i.e. 0 - 10 cm and 10 - 30 cm. When the thickness of the humus (H) horizon was more than 1 cm, the humus (H) horizon was sampled. Literature information indicates a clear difference in the chemical composition of this layer compared to the litter (L) and fermented (F) layer and the humus horizon gives information about the possibilities for appearance of certain plants. The L and F horizons were always sampled together. Furthermore the volume was measured to enable the calculation of the pools of elements. The sampling depths was limited to the mineral topsoil (layers 0 - 10 cm and 10 - 30 cm) where most of the fine roots, responsible for nutrient uptake, do occur and soil acidification and N accumulation is likely to be most intensive. For this layers also both the solid phase and soil solution were analysed (Section 2.4). All samples (solid phase) were stored and can eventually be used for extra analyses.

Sampling number and sampling method

At each site a composite sample was taken consisting of 10 sub samples for the humus layer and 25 sub samples for the mineral layers. This was done to minimise

the influence of spatial variability. For more information see also De Vries and Leeters (2001). The sample points in the forest stands were chosen according to a steady pattern related to marked trees. Within the framework of this Forest Health Monitoring Network 25 trees that are part of the vitality measurements were marked in groups of five within forest stands. In most forest stands these groups lie in a right line. The middle of a group is marked with a so called 'rocket' in the ground. This 'rocket' can be tracked with a metal detector for future samplings. The line connecting the middles of the groups forms the baseline. Sub samples were taken on certain points at a distance of 5 m on both sides of the baseline. Consequently, soil sampling did not disturb the area in which the vegetation had to be studied. For more details we refer to Annex 1.

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. The green parts of the vegetation and living roots were excluded from the sample. The material was weighed in the laboratory to derive information on the humus pool.

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 Choice of chemical parameters and analyses methods

Parameter choice

The most important pool of nutrients in forest is the humus layer. Consequently the contents of the major nutrients, i.e. N, P, K, Ca and Mg were measured for this layer. Contents of N and P were also measured for the two mineral layers, since the N content is likely to be increased due to elevated N input, 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 soil acidity, the exchangeable cation contents (H, Al, Fe, Ca, Mg, K, Na and NH_4) and the CEC were measured in the humus layer and the mineral soil layer 0 - 10 cm. In the mineral soil layer 10 - 30 cm only the soil acidity was determined. Finally the contents of important heavy metals (Pb, Cd, Zn, Cu, Cr and Ni) were determined for both the humus layer and the mineral layer 0- 10 cm. Dissolved concentrations of all the major cations and anions, i.e. H, Al, Fe, Ca, Mg, K, Na, NH_4 , NO_3 , SO_4 , Cl and RCOO^- , were measured in the humus layer and both mineral layers.

Analysing methods

Total contents of N were determined by wet oxidation according to the method of Kjeldahl (Hesse, 1971). Total contents of P and of Ca, Mg, K, Zn, Cu, Cr and Ni in the humus layer were extracted in a concentration 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 (AgTu) during four hours (Chabra et al., 1975) followed by analyses with ICP. Exchangeable NH₄ contents were measured by extraction with 1.0 M KCl (Coleman et al., 1959) followed by analyses with a colorimetric 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.

Dissolved concentrations of major ions were determined by centrifugation of a fresh soil sample of 400 gr in a POM (polyoxymethylene) container at 7500 rpm during 20 minutes. The soil solution samples were filtered over 0.45 µm. Centrifugation generally took place within one day (18-30 hours) after collection of the soil samples. Immediately after centrifugation the pH was measured. Concentrations of Al, Fe, Ca, Mg, K, Na and SO₄ were analysed by ICP, and NH₄, NO₃ and Cl by FIA. The pH was measured by means of potentiometry. The concentration of organic anions was calculated from the DOC content that was measured by an organic carbon analyser, according to Oliver et al. (1983).

2.5 Data processing

Basic statistical representation

The data have been processed with programs and special procedures within a Genstat 5 environment (Payne et al., 1993), which have been written for the processing of soil chemical data. 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 humus and soil solution. The data on site and stand characteristics have been processed in such way that they could be imported in the processing of the chemical data. The variation is presented in tables by values for the minimum, 5, 50 and 95 percentiles, the mean and the maximum. Furthermore mean values are presented for the humus layer as a function of tree species and for the mineral soil as a function of soil type.

Calculation of element pools

Element pools in the humus layer were calculated by multiplying the measured humus layer pool with the element content in that layer. Element pools in the mineral soil layers were calculated by multiplying an estimated bulk density of the soil with the soil thickness (10 or 20 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 as described in De Vries and Leeters (2001). In case of clay soils, which scarcely occurred in the 200 stands, the impact of the clay content was also accounted for in the assessment of the bulk density.

Assessment of element ratios and their interpretation

Element ratios in the soil solution include the ratios of NH_4 and NO_3 to SO_4 , indicating the contribution of N and S to soil acidification, ratios of Al to SO_4 and NO_3 indicating the degree of Al mobilisation by acidic inputs, NH_4/NO_3 ratio indicating the degree of nitrification. Furthermore, ratios of Al or NH_4 to the nutrients Ca, Mg or K give an indication about the effects on root length and root uptake. More information on the ratios and their relevance is given in De Vries and Leeters (2001).

Assessment of differences between contents and pools between 1990 and 1995

Repeated measurements of the concentration of an element X at times t1 and t2 give information on the change in that concentration. Similarly, repeated measurements of the amount of solid material (or of the bulk density) and the element concentration give information on the change in element pools. Differences between contents and pools in 1990 and 1995 were calculated, for approximately 124 forest stands, which were measured in both years. In a first assessment, the differences were calculated for each forest stand separately and the results were given as the mean of the differences per tree species or soil type. With the Student distribution ($\alpha = 0.05$), we checked whether the differences per tree species or soil type were significant.

Calculations made this way assume that changes between two measurements are only due to differences in time, as it does not take the spatial variability (in terms of the standard deviation of the measurements) into account. Whether the calculated differences, based on repeated measurements are significant, depends on (i) the standard deviation (s) of the concentration of the considered element (and the amount of solid material in case of pools) and (ii) the number of samples (n) that were taken at each survey. An estimate of the required changes in element concentrations and element pools to assess a statistically significant trend can be derived from results of the first survey by assuming that (De Vries et al., 2000):

- The standard deviation in element concentration and pools of solid material remain constant, which is reasonable when n is large. This assumption implies that one only needs a value of s at the first sampling period.

- The number of samples stays constant in the first and second survey.

Using these assumptions, one can derive that the difference between element concentrations \hat{X}_1 and \hat{X}_2 is significant when (see also Annex 3):

$$|\hat{X}_2 - \hat{X}_1| \geq t_a \cdot s_{x_1} \cdot \sqrt{2/n} \quad (1)$$

where:

t_a = tabled student t factor for a given uncertainty; for $\alpha = 0.05$, $t_a \sim 2$

Using these assumptions, one can derive that the measured difference in element pools between two time periods is only statistically significant when (see Annex 3):

$$|\hat{Z}| \geq t_a \cdot \sqrt{\frac{2}{n^2} \cdot S_X^2 \cdot S_Y^2 + \left(\frac{2\hat{Y}^2}{n}\right) \cdot S_X^2 + \left(\frac{2\hat{X}^2}{n}\right) \cdot S_Y^2} \quad (2)$$

For each location a comparison was made between the measured difference in the contents and pools and the required statistically significant difference, calculated with the equations (1) and (2), respectively. To analyse the result only those locations were taken into account where the measured difference was equal or greater than the required statistically significant difference. In other words only the results of significant differences were reported and discussed.

Since the standard deviations of the measurements were not known for each site separately, average estimates were made based on available data in the sites or in the literature. For the pools in the humus layer, the standard deviation was calculated from the measured variation in the thickness of each separate sub sample. On average the standard deviation compared to the mean was approximately 0.30, which means a coefficient of variation of 30%. For the pools in the mineral layer, a standard deviation compared to the mean of 0.1, coefficient of variation of 10%, was assumed because there is no great variation in the thickness of this layer. The standard variation of the contents in both the humus layer and the mineral layer was assumed in between, namely 0.20, coefficient of variation 20%. Standard deviations for the various element concentrations in the soil solution were derived from repeated measurement at fifteen spots, taken in Speuld and Ysselstein (De Vries and Leeters, 2001) as given in Table 1.

Table 1 Standard deviations relative to the mean (s) used to calculate significant differences for the element concentrations in the soil solution.

Standard deviations relative to the mean									
NH ₄	NO ₃	SO ₄	H	Al	K	Mg	Na	Cl	Ca
0.65	0.45	0.45	0.45	0.40	0.40	0.40	0.35	0.35	0.30

3 Characteristics of the forest stands

In this chapter an overview is given of the distribution of the various locations over deposition level, surrounding land use, stand and site characteristics. A list of the separate locations, with their positions, tree species, sampling dates, soil types and ground water level classes, is given in Annex 2.

3.1 Location, forest condition 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 et al., 1989). The greatest united forest complexes are situated in the central part of the Netherlands in an area called the Veluwe. The distribution of the 200 locations over tree species and the forest soils in the Netherlands is shown in Fig. 1. This figure shows also the 14 locations which are selected for the long term intensive monitoring in European context (ICP Forest level II plots).

The distribution of the 200 locations over five main forest regions, over the forest health condition class and over both nitrogen and acid deposition levels are given in Table 2, Table 3, Table 4 and Table 5, respectively.

Table 2 Distribution (%) of tree species over forest regions

Forest regions ¹⁾	Tree species							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
Northern	21	15	30	50	61	15	15	25
Eastern	21	0	11	10	15	20	18	15
Central	26	10	41	10	8	20	41	24
Southern	32	45	18	30	8	21	11	24
Coast	0	20	0	0	0	4	0	3
Rest	0	10	0	0	8	20	15	9
Number of plots	42	20	27	20	13	51	27	200

¹⁾ The Forest areas are divided into regions according to the Forest Health Monitoring Network based on the 4th bosstatistiek (Reuver, 1996)

Most tree species are distributed fairly over the Northern, Eastern, Central and Southern regions (Table 2). A few forest stands are situated in the Coast and rest regions. In order to be able to give statements about a region it is aimed to have about 10 forest stands. Limited by the total number of forest stands this could not be reached for all regions and species. Black pine clearly occurs mainly in the Southern region, Douglas Fir mainly in the Central and Northern region, Norway spruce and Japanese Larch mainly in the Northern region and beech mainly in the Central region.

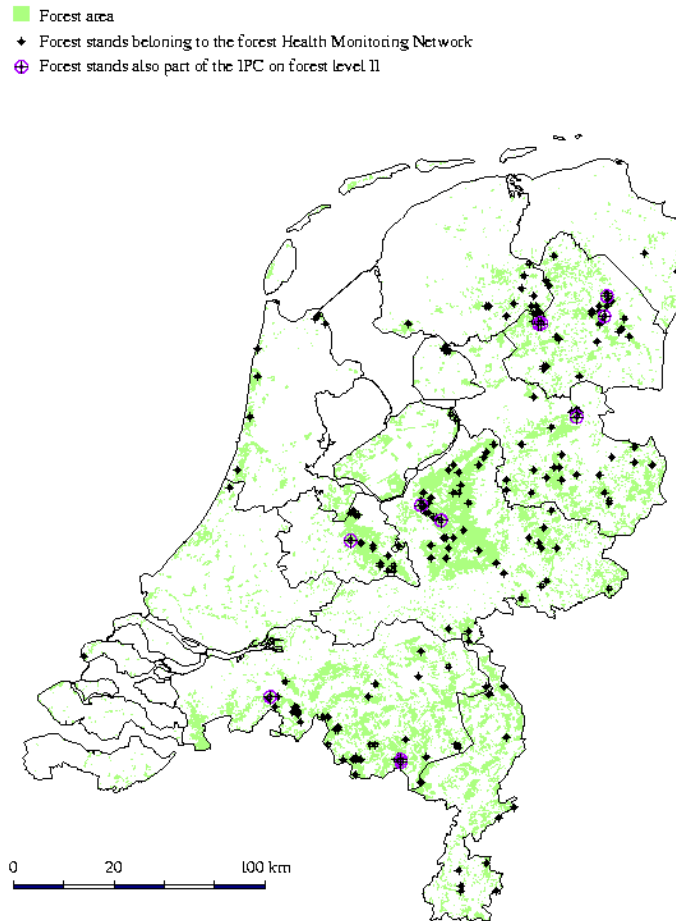


Figure 1 Distribution of the 200 locations over tree species and the forest soils

The most important indicators of the health condition of trees are defoliation and discoloration of the foliage of which defoliation is judged to be the most important aspect. The forest condition class as given in Table 2 is a combination of the defoliation class and the discoloration class for each individual measured tree. Scots pine, Japanese Larch, oak and beech have mainly good or satisfactory health, whereas poor to very poor health conditions are mainly found in stands of Douglas Fir, Black pine and Norway spruce. The health conditions for Douglas Fir, Black pine and Norway spruce seem to deteriorate every year. Douglas Fir even reached the worse health conditions ever since 1984 (Hilgen, 1995).

Table 3 Distribution (%) of tree species over the forest health condition class

Forest condition class	Tree species						
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech
Good health	70	15	3	22	49	58	48
satisfactory health	15	19	8	20	40	29	35
poor health	12	58	80	46	9	11	14
very poor health	3	8	9	12	2	2	3

Estimates of the acid deposition level, being equal to the sum of SO_x, NO_x, and NH_x deposition corrected for the input of base cations were based on calculated values for 1 x 1 km grids with the DEADM model (Erisman, 1991). More than 55% of the forest stands were located in areas with acid deposition levels less than 4000 mol_c.ha⁻¹.yr⁻¹. Especially forest stands of Norway spruce and Japanese Larch were situated in these areas. Deposition levels of less than 2000 mol_c.ha⁻¹.yr⁻¹ were exceptional. Only one beech stand was situated in such area. Compared to 1990, the deposition levels have decreased; in 1990 more than 80% of the forest stands was located in areas with acid deposition levels above 4000 mol_c.ha⁻¹.yr⁻¹. However these studies are not fully comparable because not all locations do overlap in both years.

Table 4 Distribution (%) of tree species over the calculated acid deposition for 1995

Acid deposition ¹⁾ (mol _c .ha ⁻¹ .yr ⁻¹)	Tree species							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
< 2000	-	-	-	-	-	-	4	1
2000 - 3000	10	30	15	30	31	24	15	20
3000 - 4000	43	25	33	40	54	37	26	37
4000 - 5000	33	35	37	15	15	27	44	31
> 5000	14	10	15	15	-	12	11	12

¹⁾ The acid deposition level is calculated as the atmospheric deposition of NO_x, NH_x and SO_x minus the seasalt corrected (bulk) deposition of base cations

Critical acid loads, related to an increased ratio of Al to the base cations Ca, Mg and K varied mostly between 1500 and 3500 mol_c.ha⁻¹.yr⁻¹, depending mainly on the buffer rate of the soil and the sensitivity of the tree species to elevated Al/(Ca+Mg+K) ratios (De Vries, 1996). At least 80% of the forest stands are located in area's exceeding these critical acid loads.

More than 80% of the forest stands were located in areas with total N depositions less than 3500 mol_c.ha⁻¹.yr⁻¹. Especially forest stands of Douglas Fir were situated in these areas. Total N deposition lower than 1500 mol_c.ha⁻¹.yr⁻¹ were exceptional, while total N depositions higher than 4500 mol_c.ha⁻¹.yr⁻¹ did not occur.

Table 5 Distribution (%) of tree species over the calculated total N deposition for 1995

Total N deposition (mol _c .ha ⁻¹ .yr ⁻¹)	Tree species							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
< 1500	0	5	0	0	0	0	4	1
1500 - 2500	21	40	37	40	70	41	37	38
2500 - 3500	69	45	63	50	15	49	52	52
3500 - 4500	10	10	0	10	15	10	7	9
> 4500	0	0	0	0	0	0	0	0

Critical N loads related to impacts on the species diversity of the ground vegetation of forests generally varied between 1000 and 1500 mol_c.ha⁻¹.yr⁻¹ (approximately 15-20 kg.ha⁻¹.yr⁻¹; Bobbink et al., 1996). Almost all forest stands exceed these critical loads, thus being in a state of risk with respect to impacts on ground vegetation. Critical loads related to impacts on tree health, such as nutrient imbalances and increased shoot-root ratios causing drought stress, varied mostly between 1500 and 3000 mol_c.ha⁻¹.yr⁻¹, depending amongst others on the relative contribution of NH₄ and NO₃ deposition, the nitrification rate and buffer rate of the soil and the tree species (De Vries, 1993; Bobbink et al., 1996). Present N loads do occur in that range, thus indicating the possibility of those adverse effects.

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 on a forest 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 of the forest stand or what ever land use situated in the Northern area of the forest stand.

The distribution of the tree species of the 200 locations over the distance to the nearest forest edge, the surrounding land use and the direction of the forest edge are given in Table 6, Table 7 and Table 8. In general it is assumed that the influence of atmospheric deposition decreases with an increasing distance to the forest edge and becomes steady at distances greater than approximately 5 times the tree height. Approximately half (48%) of the forest stands is located within 80 m from the forest edge, of which most are located on distances less than 40 m. Approximately 46% is located at a distance of more than 100 m from the forest edge, especially stands of Douglas Fir, Japanese Larch and Norway spruce. The influence of land use decreases from maize field > grassland > arable land and non-agricultural land. Most forest stand (53%) are located in the area of maize fields and grassland. Especially forest stands of oak, beech and Norway spruce are situated nearby these types of land use. Forest stands of Norway spruce are situated most of all nearby maize fields.

Table 6 Distribution (%) of tree species over the distance to the nearest forest edge

Distance to the nearest forest edge (m)	Tree species ¹⁾							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
< 20	14	11	8	16	-	18	16	13
20 - 40	16	16	8	11	31	18	16	16
40 - 60	19	5	8	5	8	6	24	11
60 - 80	5	5	8	5	-	16	4	8
80 - 100	5	11	-	5	-	6	12	6
> 100	41	52	68	58	61	36	28	46

¹⁾ For 12 plots (6%) the distance to the nearest forest edge is unknown

Table 7 Distribution (%) of tree species over the surrounding land use

Surrounding land use	Tree species ²⁾							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
Maize field	3	-	13	25	-	6	8	7
Grassland	43	33	38	31	31	63	50	46
Arable land	16	39	21	25	46	25	21	25
Non-agricultural ¹⁾	38	29	29	19	23	6	20	22

¹⁾ Non-agricultural contains heather (15%), clear felling area (2%), built-up area (4%) and remaining plots (1%)

²⁾ For 20 plots (10%) the surrounding land use is unknown

Table 8 Distribution (%) of tree species over the direction of the forest edge

Direction of the forest edge	Tree species ¹⁾							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
North	11	6	8	-	8	10	4	8
North-East	11	17	4	24	15	8	8	11
East	14	6	8	6	15	13	29	13
South-East	5	6	17	6	15	13	-	9
South	22	11	8	12	8	27	25	19
South-West	8	6	13	12	23	4	8	9
West	19	22	25	29	-	17	4	17
North-West	11	28	17	12	15	8	21	14

¹⁾ For 19 plots (10%) the direction of the forest edge is unknown

The influence of atmospheric deposition is supposed to be greater at sides exposed to common wind directions as there are south-east, south and south-west. 37% of the forest stands is exposed to these wind directions. The direction of the forest edge was for all tree species distributed more or less equally over all directions. Stands of Japanese Larch, oak and Douglas Fir had relatively more forest edges situated to the Southern areas while black pine and Norway spruce had relatively more forest edges situated towards Northern areas.

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

The distribution of the tree species of the 200 locations over canopy coverage and tree height are given in Table 9 and Table 10.

Table 9 Distribution(%) of tree species over canopy coverage

Canopy coverage (%)	Tree species ¹⁾							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
< 50	33	16	-	-	25	4	-	11
50 - 75	47	32	28	32	50	42	24	37
> 75	19	53	72	68	25	54	76	52

¹⁾ For 16 plots (8%) the Canopy coverage is unknown

Most forest stands (52%) had a canopy coverage of more than 75%. The canopy coverage is related to tree species. As expected, Table 9 shows that forest stands of beech, Douglas Fir and Norway spruce had mainly high canopy coverages, more than 68% with a canopy coverage over 75% and the rest with canopy coverages over 50%. Low canopy coverages mainly occurred in forest stands of Scots pine and Japanese Larch.

Table 10 Distribution (%) of tree species over tree height

Tree height (m)	Tree species							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
< 5	2	-	-	-	-	2	4	2
5 - 10	5	30	7	15	-	14	7	11
10 - 15	19	35	7	30	-	18	-	16
15 - 20	64	35	19	40	23	33	11	35
> 20	10	-	67	15	77	33	78	37

Tree height is mainly a result of tree species and age combined with the site conditions, such as soil type and ground water level. The distribution over tree height is for the pine and deciduous species more or less equal to the distribution over age. Most forest stands had tree heights over 15 m (Table 10), whereas forest stands of beech, Japanese Larch and Douglas Fir had mainly tree heights over 20 m. Beech had also mainly older forest stands (over 60 years), while the forest stands of Japanese Larch and Douglas Fir were mainly between 40 and 80 years. Mainly low trees were found in forest stands of black pine. 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.

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. According to the classification system of De Bakker and Schelling (1989) for Dutch soils, 21 soil types have been distinguished. These soil types were clustered into six groups, based on their expected vulnerability for acidification (De Vries et al., 1989). The clustering is corresponding to a decreasing vulnerability for acidification, similar to the clustering of the 150 forest soil measured in 1990 (De Vries and Leeters, 2001; Table 11).

Table 11 Six distinguished soil groups named according to two different classifications

Group	Classification system	
	(FAO, 1988)	(De Bakker and Schelling, 1989)
1	Haplic Arenosols ¹⁾	Duin- en Vlakvaaggronden
2	Gleyic Podzols ²⁾	Veld- en Haarpodzolgronden
3	Cambic Podzols	Holtpodzol- en Vorstvaaggronden
4	Fimic Anthrosols	Enkeerd- en Loopodzolgronden
5	Umbric Gleysols ³⁾	Beekeerden en moerige gronden
6	Dystric Gleysols	(Oude) Kleigronden en Brikgronden

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

Results on ground water levels were clustered into five groups. The first group with very poorly drained ground water levels, contained the classes II and III. The main highest groundwater level in the winter period for this group lied between 0 and 45 cm, and the mean lowest in the summer period between 65 and 115 cm below surface. In these soils the ground water level stays all seasons within the root zone. The second group with poorly drained soils contained only ground water levels class V. The mean highest groundwater level lied mainly between 0 and 35 cm, at two forest stands however it went to 40 and 70 cm and the mean lowest lied between 120 cm to 200 cm and deeper below surface. 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 groundwater level lied between 45 and 75 cm and the mean lowest between 115 and mainly 185 cm below surface at several forest stands it went deeper than 200 cm. 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 groundwater levels. For class VII this lied between 85 and 135 cm and for class VIII even deeper than 140 cm below surface. The mean lowest ground water levels were in both classes always deeper than 150 cm below surface. In very dry areas it was even below 5 to 8 m below surface.

Table 12 Distribution (%) of soil types over the ground water level classes

Soil type	Ground water level class						Total
	II + III	V	IV + VI	VII	VIII		
Haplic Arenosols ¹⁾	10	13	21	13	43	24	
Gleyic Podzols ²⁾	2	20	25	23	29	43	
Cambic Podzols	-	-	3	-	97	15	
Fimic Anthrosols	8	17	25	8	42	6	
Umbric Gleysols ³⁾	23	15	46	15	-	6	
Dystric Gleysols	-	42	8	8	42	6	
Total	6	16	22	15	41	100	

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

The distribution of soil types over groundwater level classes (Table 12) shows that the Cambic Podzols were all (with exception of only one forest stand) very well drained, whereas the Umbric Gleysols were mainly (very) poor or moderately drained. The drainage status of Haplic Arenosols, Fimic Anthrosols and Dystric Gleysols varies, but is generally quite well. The drainage status of Gleyic Podzols varies also but in is general lower. More information about the soil groups is given in De Vries and Leeters (2001).

3.4.2 Distribution of forest stands over soil types and groundwater tables

Distribution over soil types was also a criterion for selection of the forest stands (Section 2.1). According to the total distribution of forest over Dutch soil types, most of the forest stands are located on Podzols. The distribution of tree species over soil type and ground water level is related to the demands or tolerance of the tree species. They usually are planted as much as possible on soils according to their demands.

Table 13 Distribution (%) of tree species over soil types

Soil type	Tree species							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
Haplic Arenosols ¹⁾	33	50	7	15	15	29	4	24
Gleyic Podzols ²⁾	43	50	52	80	77	24	22	43
Cambic Podzols	21	-	30	-	-	12	26	15
Fimic Anthrosols	2	-	11	-	8	8	11	6
Umbric Gleysols ³⁾	-	-	-	5	-	18	11	6
Dystric Gleysols	-	-	-	-	-	10	26	6

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

Coniferous species occurred mainly on Arenosols and Podzols, whereas the deciduous species occurred also on Fimic Anthrosols and Gleysols (Table 13). Japanese Larch black pine and Scots pine were almost solely located on Haplic Arenosols and Gleyic Podzols because they have little demands towards nutrients and moisture. Norway spruce however who has just like Douglas Fir greater needs

was also almost solely located on nutrient and moisture poor soils, whereas Douglas Fir also occurred on Fimic Anthrosols which are richer on nutrients (larger contents of organic matter).

Table 14 Distribution (%) of tree species over ground water level classes

Ground water level class	Tree species							Total
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech	
II + III	2	-	-	10	-	12	7	6
V	19	10	-	20	23	24	11	16
IV + VI	17	10	25	40	15	25	14	22
VII	12	30	11	10	38	12	11	15
VIII	50	50	63	20	23	27	56	42

According to them being located on mainly Haplic Arenosols, Gleyic and Cambic Podzols, forest stands of Japanese Larch, Scots pine, black pine and Douglas Fir were mostly well or very well drained (Table 12 and Table 14). Beech also occurred mainly on very well drained sites. Norway spruce with greater demands on moisture and oak with a greater tolerance on moisture occurred mainly on the moderately and poor drained sites.

4 Chemical composition of the humus layer in 1995

In this chapter an overview is given of the characteristics of the humus layer, subdivided in contents and pools of organic matter and nutrients (Section 4.1), acidity and exchangeable cations (Section 4.2) and heavy metals (Section 4.3). Results include the variation in the data of 1995 and the median values per tree species. The variation is presented by means of minimum, mean and maximum and by the 5, 50 and 95 percentile values.

Unlike, the inventory in 1990 (De Vries and Leeters, 2001), no distinction was made in the various humus layers. Furthermore, the C content was not measured, apart from the 11 forest stands, belonging to the monitoring programme of the ICP on forest level II, and information on e.g. C/N and C/P ratios, which give indications about the eutrophication status of the humus layer, is neither presented. All nutrient contents are expressed, however, in percent of the organic matter content. All results are presented with ample interpretation, since an in-depth interpretation of this kind of data is given in De Vries and Leeters (2001).

4.1 Organic matter and nutrients

The ranges in organic matter and the nutrient contents in organic matter in the humus layer are given in Table 15. The organic matter and nutrient contents were all distributed normally, except for Ca (Table 15). The median and mean values were comparable for organic matter, N and P, but median Ca, Mg and K contents were lower than the mean contents. When the results were not corrected for the organic matter content, the range in nutrient contents in the humus layer varied from 6-22 g.kg⁻¹ for N, 0.27-0.94 g.kg⁻¹ for P, 0.58-15 g.kg⁻¹ for Ca, 0.16-1.8 g.kg⁻¹ for Mg and 0.35-2.3 g.kg⁻¹ for K. For N and P contents, these variations are approximately the same as the range of the variations found on a European level (De Vries et al., 1998).

Table 15 Minimum, maximum, mean, 5, 50 and 95 percentiles of the organic matter content and the nutrient contents in organic matter in the humus layer.

Statistics	Organic matter and nutrient contents					
	OM (g.kg ⁻¹)	N (g.kg ⁻¹)	P (g.kg ⁻¹)	Ca (g.kg ⁻¹)	Mg (g.kg ⁻¹)	K (g.kg ⁻¹)
Minimum	269	13	0.45	0.82	0.35	0.45
5 percentile	408	17	0.63	1.5	0.42	0.59
50 percentile	648	22	0.84	2.8	0.66	0.94
Mean	644	22	0.88	3.8	0.80	1.15
95 percentile	851	26	1.3	9.1	1.7	2.5
Maximum	905	28	1.6	23	3.0	4.8

Several very high Ca contents (> 9 g.kg⁻¹) were found at three locations with calcareous soils (nr 207, 2013 and 2014 see Appendix 2) and at one location in the 'Kuinderbos' (2006). Soils in the 'Kuinderbos' are covered by very calcareous sand covers, which explains the high Ca values. One of these locations (207) was also measured in 1990. High Ca contents (6-9 g.kg⁻¹) were also measured at several other

locations, that were mainly located in the Northern part of the Netherlands. All plots with high Ca contents had deciduous species (see also Table 16).

The range of the Mg and K contents was much lower than the variation found on a European level (both 0.5-10 g.kg⁻¹). Since litterfall is the major source for basic cations in the humus layer, this comparison may partly be influenced by the variation of tree species involved. The range in nutrient contents in the humus layer and the median contents are comparable to the results of the study in 150 forest stands in 1990 (De Vries and Leeters, 2001). A strict comparison, however, requires that results of the same sites are used (See Section 7.1). As in 1990, the N contents are relatively high, the P and Ca contents were relatively low and the Mg and K contents were very low.

The relation between contents in the humus layer and tree species is shown in Table 16. Median values of the nutrient contents in the humus layer hardly varied between tree species, except for oak and beech where relatively high Ca, Mg and K contents were found. Oak is mainly situated on relatively poorly drained soils with possible Ca input by seepage. Furthermore, two of the three calcareous soils are located under oak. Because of their nutrient demand, oak and beech are located mostly on relatively mineral rich soil types. As with the contents in the humus layer, deciduous species have generally higher Ca, Mg and K contents in the foliage (Hendriks et. al., 1994).

Table 16 Median values of the organic matter contents and the nutrient contents in organic matter in the humus layer under seven major tree species

Tree species	Organic matter and nutrient contents					
	OM (g.kg ⁻¹)	N (g.kg ⁻¹)	P (g.kg ⁻¹)	Ca (g.kg ⁻¹)	Mg (g.kg ⁻¹)	K (g.kg ⁻¹)
Scots pine	678	20	0.74	2.23	0.56	0.86
Black pine	611	19	0.78	2.31	0.66	0.80
Douglas fir	665	22	0.86	2.50	0.62	0.76
Norway spruce	721	21	0.89	2.51	0.54	0.74
Japanese larch	779	21	0.73	2.61	0.65	0.71
Oak	599	24	0.98	4.21	1.00	1.25
Beech	642	22	0.88	3.20	0.65	1.09

As with the organic matter and nutrient contents, the pools of organic matter and nutrients varied largely, following an almost normal distribution, except for Ca and K (Table 17). Compared to the variation between the 5 and 95 percentile on a European level (De Vries et al., 2000), the N, P, Ca and Mg pools in this study are higher for the 5 and 50 percentiles and lower for the 95 percentiles. For the K pools the 5 and 50 percentiles are the same and the 95 percentile is also lower in this study. Comparing nutrient pools with average annual growth uptakes (De Vries and Leeters, 2001) shows that the pools in the humus layer can provide nutrients for a long period (> 30 years; N even > 100 years), except for K. In general, however, long-term nutrient supply comes from atmospheric deposition and long-term weathering, but the pools in the humus layer are an important buffer.

Table 17 Minimum, maximum, mean, 5, 50 and 95 percentiles of the organic matter pool and the nutrient pools in the humus layer

Statistics	Organic matter and nutrient pool					
	OM (ton.ha ⁻¹)	N (kg.ha ⁻¹)	P (kg.ha ⁻¹)	Ca (kg.ha ⁻¹)	Mg (kg.ha ⁻¹)	K (kg.ha ⁻¹)
Minimum	6	109	4.0	15	5.9	7.1
5 percentile	16	350	14	53	13	16
50 percentile	58	1233	48	156	39	52
Mean	57	1223	49	177	41	62
95 percentile	103	2241	86	331	85	144
Maximum	150	3110	133	730	129	328

Pools of organic matter were relatively low for black pine, Douglas Fir and oak (Table 18). Consequently the N pools were also relatively low for these species. Another difference between the tree species was the slightly larger Ca and Mg pools for Japanese Larch, beech and oak and also the slightly larger pools of K for Scots pine, oak and beech. Larger nutrient pools are partly correlated with larger pools of organic matter (N and K for Scots pine) and partly with higher nutrient contents in the humus layer (Ca, Mg, K for Japanese Larch, oak and beech; see also Table 16).

Table 18 Median values of the organic matter and the nutrient pool in the humus layer under seven major tree species

Tree species	Organic matter and nutrient pool					
	OM (ton.ha ⁻¹)	N (kg.ha ⁻¹)	P (kg.ha ⁻¹)	Ca (kg.ha ⁻¹)	Mg (kg.ha ⁻¹)	K (kg.ha ⁻¹)
Scots pine	65	1311	52	136	39	62
Black pine	54	979	44	130	34	48
Douglas fir	50	931	42	145	37	40
Norway spruce	67	1374	57	185	38	49
Japanese larch	72	1670	52	206	47	52
Oak	47	1056	41	205	40	55
Beech	63	1365	55	173	42	65

4.2 Soil acidity and exchangeable cations

The distributions of pH, CEC and exchangeable cations in the humus layer were all relatively normal. The mean and median values were quite comparable in most cases. Values of pH in water and in KCl extract in the humus layer varied between 3.5 and 6.0 and between 2.5 and 5.5 respectively (Table 19). This is a slightly larger range than those encountered in the 150 forest stands in 1990 (De Vries and Leeters, 2001). Again, however, a strict comparison requires the use of results from similar sites as presented in Section 7.2. The median and mean values of ca 4 and 3, respectively are values which 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). There are several forest stands with relatively high pH values, due to the occurrence of some clay soils that are part of this monitoring network. As with the results from the forest stands in 1990 (De Vries and Leeters, 2001), the differences between pH-H₂O and pH-KCl were constant approximately 1.

As with the 150 forest stands in 1990, the cation exchange capacity (CEC) in the humus layer varied mostly 200 and 400 mmol_c.kg⁻¹, but the total range in the 200 stands (29-652 mmol_c.kg⁻¹) is larger than in the 150 stands (142-498 mmol_c.kg⁻¹; De Vries and Leeters, 2001). Again, a strict comparison based on results from the same plots is given in Section 7.2. As reported in De Vries and Leeters (2001), the CEC for these humus layers is low compared to literature data. Reported organic matter contents varied between 27 and 90%, indicating a CEC ranging between ca 2 - 10 mmol_c.kg⁻¹ for 1 % organic matter, being lower than values reported for the mineral layer (see also De Vries and Leeters, 2001). The reason for this difference is most likely the lower degree of humification in the humus layer.

Table 19 Minimum, maximum, mean, 5, 50 and 95 percentiles of pH, CEC and exchangeable cation content (in percentage of the CEC) of the humus layer

Statistics	pH (-)		CEC (mmol _c .kg ⁻¹) and exchangeable cations (%)								
	pH-H ₂ O	pH-KCl	CEC	H	Al	Fe	Ca	Mg	K	Na	NH ₄
Minimum	3.5	2.5	29	0.0	0.0	0.01	0.01	0.01	0.01	0.0	0.06
5 percentile	3.6	2.6	195	14	0.23	1.1	11	4.1	0.21	0.03	1.3
50 percentile	3.9	2.8	301	47	5.3	4.6	25	6.9	2.4	1.2	3.7
Mean	4.0	3.0	306	43	5.7	6.2	28	7.9	2.4	1.5	4.3
95 percentile	4.7	3.8	433	66	11	18	57	15	4.5	3.3	8.7
Maximum	6.0	5.6	652	100	30	30	82	25	24	15	29

As with the 150 forest stands in 1990, exchangeable cations on the adsorption complex in the humus layer were generally dominated by protons (H) followed by Ca (Table 19). Exchangeable Al contents were relatively low, since there is no mineral pool of Al in organic matter. The variation in exchangeable contents in % of the CEC was, however, larger than measured in the 150 forest stands in 1990. There were several locations with a relatively high occupation of almost all cations and several locations with relatively low H occupation. Even the Mg, K, NH₄ and Na occupation was sometimes near or even over 20%. The base saturation has a wide range from 0.2 % to 96% (the latter being calcareous soils), with a median value of 35% and a 95 percentile of 61%, indicating that there are several locations with very high base saturation. Just as with the pH, these high base saturations are due to the occurrence of calcareous soils and clay soils.

Differences in the median pH between the tree species were generally negligible (Table 20). The median CEC varied only slightly between the various tree species. As with the organic matter content (Table 16), the median CEC was highest under Japanese larch and lowest under Scots pine and black pine. The same pattern was found in the 150 forest stands in 1990 (De Vries and Leeters, 2001). Exchangeable cation contents in the humus layer did not vary much between the tree species but base saturation was clearly highest under oak, followed by beech and black pine (Table 20). Comparable results were found for oak in 1990. A comparison between total and exchangeable contents of the cations Ca, Mg and K showed that the exchangeable contents were respectively 78%, 58% and 46% of the total contents, which is comparable to the data of the 150 forest stands in 1990.

Table 20 Median values of pH, CEC and exchangeable cation content (in percentage of the CEC) of the humus layer under seven major tree species

Tree species	pH (-)		CEC(mmol _c .kg ⁻¹) and exchangeable cations (%)								
	pH-H ₂ O	pH-KCl	CEC	H	Al	Fe	Ca	Mg	K	Na	NH ₄
Scots pine	3.9	2.8	267	50	5.9	5.8	20	6.3	2.4	1.1	3.6
Black pine	4.0	2.9	267	45	5.7	4.4	22	7.6	2.6	1.3	3.9
Douglas fir	3.8	2.8	302	46	6.6	4.9	25	6.4	2.2	1.5	3.6
Norway spruce	3.9	2.8	313	49	5.4	3.7	26	5.8	1.3	1.5	5.4
Japanese larch	3.8	2.7	363	51	4.1	3.3	26	8.6	0.6	2.0	3.3
Oak	4.0	2.9	321	35	3.3	4.1	34	9.7	3.0	1.0	3.4
Beech	3.9	2.9	339	45	5.2	5.2	25	6.4	2.4	1.1	3.5

As with the exchangeable cation contents, the cation pools decreased according to H > Ca followed by Mg, Al, Fe, NH₄, K and Na (Table 21). Ranges in the cation pools were comparable to those of the 150 forest stands (De Vries and Leeters, 2001). The median exchangeable base cation pool is comparable to the net acid input from the atmosphere, implying that proton buffering by base cation release from the adsorption complex in the humus layer is very limited. The relatively low pH values also indicate that pH buffering is not an important process in the humus layer, even though base saturation is relatively high. As mentioned by De Vries and Leeters (2001), the supply of base cations by throughfall and mineralisation leads to high dissolved base cation concentrations in the humus layer, thus preventing proton buffering by exchange with base cations from the adsorption complex.

Table 21 Minimum, maximum, 5, 50 and 95 percentiles of the exchangeable cation and CEC pool in the humus layer

Statistics	Exchangeable cation and CEC pool (kmol _c .ha ⁻¹)								
	H	Al	Fe	Ca	Mg	K	Na	NH ₄	CEC
Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	1.8
5 percentile	1.4	0.06	0.15	1.4	0.64	0.02	0.01	0.26	7.6
50 percentile	12	1.4	1.2	6.2	1.8	0.56	0.29	0.96	27
Mean	12	1.7	1.8	7.0	2.0	0.64	0.40	1.1	27
95 percentile	25	3.9	5.6	14	4.2	1.4	1.1	2.2	48
Maximum	53	15	12	24	7.0	12	4.0	3.9	80

The variation in median values of the exchangeable base cation pools is low between tree species (Table 22). Similar conclusions can be drawn when using mean values.

Table 22 Median values of the exchangeable cation and CEC pool in the humus layer under seven major tree species

Tree species	Exchangeable cation and CEC pool (kmol _c .ha ⁻¹)								
	H	Al	Fe	Ca	Mg	K	Na	NH ₄	CEC
Scots pine	14	1.7	1.7	5.5	1.7	0.27	0.62	1.1	28
Black pine	8.7	1.4	1.0	5.3	1.6	0.27	0.57	0.91	21
Douglas fir	10	1.7	1.1	6.4	1.7	0.38	0.55	0.87	26
Norway spruce	14	1.7	1.2	7.3	1.7	0.44	0.39	1.3	28
Japanese larch	18	1.5	1.2	9.0	2.8	0.58	0.21	0.99	36
Oak	8.7	0.89	0.88	6.8	2.2	0.23	0.62	0.86	21
Beech	14	1.3	1.6	7.3	1.5	0.24	0.48	0.98	33

Exchangeable base cation pools are generally larger under deciduous trees than under coniferous trees, reflecting the somewhat richer soil conditions for the former tree species.

4.3 Heavy metals

Overall variation in heavy metal contents

The main source of heavy metals in forest soils, specifically in humus layers, is the atmospheric deposition of these metals induced by emissions from industry and traffic. For lead and cadmium, it is most likely even almost the only source. 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. Because of their origin and their strong fixation to organic matter, the heavy metals mainly accumulate in the humus layer and the mineral topsoil (Kleijn et al., 1989; Siccama et al., 1980). An overview of the heavy metal contents in the humus layer is given in Table 23.

Table 23 Minimum, maximum, mean, 5, 50 and 95 percentiles of the heavy metal content in the humus layer

Statistics	Heavy metal content (mg.kg ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
minimum	13	0.0	5.3	29	1.7	3.6
5 percentile	22	0.21	8.3	36	3.1	8.3
50 percentile	90	0.52	14	62	7.0	14
mean	95	0.64	18	81	7.7	15
95 percentile	185	1.6	33	183	13	27
maximum	373	5.3	254	693	37	45

The variation in heavy metal content in the humus layer is large. For all metals, and particularly for Zn, the mean values are higher than the median values, indicating that there are several forest stands with high values. This is also shown by the difference between the 50 and the 95 percentile. For Cd and Zn the 95 percentile is even three times the median value. In general, there is a relationship between regional patterns in heavy metal deposition and the heavy metal contents in the humus layer (Leeters et al., 1994). For Pb, Cd, Cu and Zn, high values were found in the southern part of the Netherlands, more specifically in the strongly polluted Kempen area. Highest Cd and Zn values were found in forest stands in the area of Budel, known to be influenced by the zinc smelter at that place which emitted large amounts of both heavy metals. The ranges in heavy metals are comparable compared to those 1990, except for Pb. For this metal the 5%, 50% and 95% values were clearly higher in 1990, indicating a decrease in Pb content in response to decreased Pb deposition, due to e.g. unleaded gasoline since a decade. Again, a more specific comparison requires use of results from the same stands as presented in Section 7.3.

Risks of elevated heavy metal contents in humus layers

Information on background concentrations and critical levels of heavy metals is presented in Table 24 and a comparison of the results presented in table 23 with those background concentrations and critical levels is given in Table 25, respectively.

Background concentrations (Table 24) are based on values observed for relatively unpolluted humus layers in the most northern part of Sweden (Andersson et al., 1991). In this area the influence of long-distance dispersal of atmospheric pollution is low and there is no influence of local emission sources. Critical levels, defined as the maximum metal contents which do not show an adverse effect on the terrestrial ecosystem, are based on effects of elevated metal concentrations on soil micro organisms and macrofungi, soil fauna (especially invertebrates such as nematodes and earth worms) and vascular plants, including trees. A summarising overview of the critical contents in humus layers thus derived is given in Table 24 (After Tyler, 1992). More information on the derivation of those critical levels is given in De Vries and Leeters (2001).

Table 24 Background values and different critical values of heavy metal contents in the humus layer

Type of content 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⁾	114	1.8	54	147	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⁾	713	26	289	756	60	190

¹⁾ Based on data of the most northern part of 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 maximum concentrations in topsoils of relatively unpolluted areas in the Netherlands (Edelman, 1983; Edelman and De Bruin, 1986). 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 Dutch legislation.

Table 24 also contains information on critical concentration levels used in the Dutch legislation. The Dutch system used for the evaluation of the pollution of the soil with heavy metal contents recognises three critical levels for each pollutant:

- the Target Value (Dutch: *Streefwaarde*), i.e. the assumed maximum for the range of background values as measured in the top (10 cm) of agricultural and forest soils (Edelman, 1983; Edelman and De Bruin, 1986),
- the Intervention Value (Dutch: *Interventiewaarde*), i.e. the minimum value for serious pollution, indicating that sanitation actions are required,
- the Examination Value (Dutch: *Toetsingswaarde*), i.e. the value above which more research to the extent and the source of the pollution is necessary.

Both the target and intervention value depend on the organic matter and clay content of the soil (see Annex 4). The target and intervention values given in Table 24 are based on an assumed organic matter content of 64%, namely the mean value observed in the humus layer (see Table 15) and a clay content of 0%.

The 5 percentiles observed in the 200 forest stands (Table 23) are clearly higher than the background concentrations for Pb, Cu, and Cr as presented in Table 24. The 50 percentiles are even clearly elevated for all metals except Ni. Elevated metal contents

in humus layers have been observed in all areas with an elevated atmospheric input of heavy metals, mainly induced by emissions from industry and traffic. Such observations have been made earlier in southern Norway (Steinnes et al., 1988), Germany (Heinrichs and Mayer, 1986; Neite et al., 1992) and the Netherlands (Kleijn et al., 1989; Pedroli et al., 1990;) as discussed in more detail by De Vries and Leeters (2001).

The exceedance of target and intervention values as given in Table 44 is calculated using the organic matter content of the separate forest stands. The examination value was calculated as the mean of the target and intervention value. Target values were exceeded at part of the plots for all metals except Cr. The humus layers in the 200 forest stands were in general most strongly polluted with Pb (approximately 50% of the plots exceeded the target value) followed by Zn and Cd. Examination values, however, were only exceeded at two forest stands, one for Zn and one for Pb. Extremely high values, exceeding the intervention value, above which sanitation actions are required, were only observed at one location for Zn. At one location (82) the Cu concentration under a Douglas fir was extremely high and exceeded almost the intervention value (cf. Table 23 and Table 24). This location is part of the level 2 plots (see Section 1) and also measured in the study of the 150 forest stands (De Vries and Leeters, 2001). Values in this location were high over the years, namely 268 and 738 mg.kg⁻¹. Critical values for Cu related to the effects on soil microbiota were exceeded in far more forest sites than the target value for Cu (53%). When using the critical value for the effects on soil invertebrates, however, as applied by De Vries and Leeters (2001), the exceedance was only 1.5 % (3 plots), being lower than the exceedance of the target value (cf. Table 24). Target values and critical values were exceeded mostly in forest stands with Douglas fir, Black pine and Scots pine.

Table 25 Distribution of forest sides over different critical levels of heavy metal contents in the humus layer

Critical level	Distribution (number of forest sides)					
	Pb	Cd	Cu	Zn	Ni	Cr
> Target value	52	7	2	12	3	0
> Critical value	18	1	53 (1.5)	3	0	7
> Examination value	1	0	1	1	0	0
> Intervention value	0	0	0	1	0	0

Pb contents were highest under Scots pine, Douglas fir and beech and lowest under Black pine and Oak (cf. Table 26 and Table 23). For all species, the target values and even the critical Pb values were exceeded at some of the forest stands. Actually for Douglas fir, Scots pine and Beech they were exceeded respectively in 41%, 29% and 41% of the forest stands. For the other species the exceedance was less than 25%. The median Cd content was clearly highest below Scots pine, followed by Douglas fir and Norway spruce, and highly comparable between the other tree species. Target values were exceeded mostly in Black pine stands (20%). The critical Cd value was exceeded in one Scots pine stand. As with Pb, Cu contents were highest under Scots pine, Douglas fir and beech. Target values were only exceeded at two locations, one under Scotch pine and one under Beech. As with Cd, the Zn contents were highest under Scots pine, Douglas fir and Norway spruce and target values were exceeded most under these tree species. Critical values were also exceeded for Scots pine,

Black pine and Norway spruce. Even the intervention value was exceeded at one location under Scots pine. Ni contents hardly varied but were somewhat higher under Scots pine, Douglas fir and Beech. The average Cr content was slightly higher in the humus layer of deciduous forest stands than coniferous stands.

Table 26 Median values of the heavy metal content in the humus layer under seven major tree species

Tree species	Heavy metal content (mg.kg ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
Scots pine	100	0.69	16	77	7.5	14
Black pine	77	0.45	13	49	5.9	12
Douglas fir	108	0.54	17	63	8.8	15
Norway spruce	78	0.54	14	64	6.1	13
Japanese larch	82	0.43	12	57	6.1	11
Oak	64	0.43	13	55	6.1	13
Beech	105	0.49	17	63	8.6	16

The heavy metal pools in the humus layer were calculated by multiplying the humus layer pool with the heavy metal contents in this layer (Section 2.5; Table 23). The heavy metals pools in the humus layer are important indicators for the rate of heavy metal deposition, since the binding capacity of these layers is large enough to absorb the heavy metal deposition of many years. As with the metal contents, the variation in heavy metal pools is large (Table 27).

Table 27 Minimum, maximum, 5, 50 and 95 percentiles of the heavy metal pool in the humus layer

Statistics	Heavy metal pool (kg.ha ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
minimum	0.03	0.00	0.17	0.83	0.04	0.11
5 percentile	1.1	0.01	0.29	1.4	0.13	0.26
50 percentile	7.7	0.04	1.4	5.6	0.60	1.2
mean	9.4	0.06	1.7	7.5	0.75	1.4
95 percentile	22	0.16	3.8	18	1.9	3.2
maximum	64	0.91	30	118	7.5	5.5

The variation in metal pools below different tree species is relatively small. Highest values for all metals do occur below beech, with the exception of Cd (Table 28).

Table 28 Median values of the heavy metal pool in the humus layer under seven major tree species

Tree species	Heavy metal pool (kg.ha ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
Scots pine	11	0.08	1.7	7.3	0.90	1.6
Black pine	6.4	0.04	1.0	4.9	0.51	1.3
Douglas fir	8.4	0.05	1.3	5.1	0.67	1.2
Norway spruce	6.6	0.05	1.3	5.3	0.56	1.1
Japanese larch	7.9	0.04	1.4	5.9	0.64	1.3
Oak	4.6	0.03	1.1	4.5	0.45	1.1
Beech	13	0.04	1.6	6.5	0.97	1.5

5 Chemical composition of the soil in 1995

In this chapter an overview is given of the characteristics of the mineral topsoil, subdivided in contents and pools of the organic matter and the nutrients (Section 5.1), acidity and exchangeable cations (Section 5.2) and heavy metals (Section 5.3). Presented are the variation in the data of 1995 and the distribution over soil types for the mineral layers 0 - 10 cm and 10 - 30 cm. As with the humus layer, the results are presented with ample interpretation, since a more in-depth interpretation of this kind of data is given in De Vries and Leeters (2001).

5.1 Organic matter and nutrients

Compared to the humus layer, the organic matter contents in the mineral soil are much lower (cf. Table 15, Table 17, Table 29 and Table 30). Compared to the humus layer the N and P contents are also much lower in the mineral layers. This phenomenon can be explained by the fact that both nutrients are predominantly bound to organic carbon, which decreases strongly from the humus layer to the mineral layers. However, when comparing the values of the N content in organic matter, the values of N are rather the same in the humus and the mineral layers with a median value of ca 2.2%. With respect to N in forest soils, values in the humus layer in general are lower than in the mineral layer. This indicates that there is still an impact of atmospheric N deposition in the N content in the humus layer.

Table 29 Minimum, maximum, mean, 5, 50 and 95 percentiles of the organic matter and nutrient contents and pools for the mineral layer 0 - 10 cm

Statistics	Contents			Pools		
	OM (g.kg ⁻¹)	N (g.kg ⁻¹)	P (g.kg ⁻¹)	OM (ton.ha ⁻¹)	N (kg.ha ⁻¹)	P (kg.ha ⁻¹)
Minimum	8.0	0.18	0.02	12	268	26
5 percentile	17	0.39	0.05	25	524	71
50 percentile	50	1.1	0.12	64	1464	151
Mean	58	1.3	0.17	68	1485	209
95 percentile	102	2.2	0.45	112	2550	543
Maximum	840	18	1.0	269	5901	1122

Table 30 Minimum, maximum, mean, 5, 50 and 95 percentiles of the organic matter and nutrient contents and pools for the mineral layer 10 - 30 cm

Statistics	Contents			Pools		
	OM (g.kg ⁻¹)	N (g.kg ⁻¹)	P (g.kg ⁻¹)	OM (ton.ha ⁻¹)	N (kg.ha ⁻¹)	P (kg.ha ⁻¹)
Minimum	4.0	0.10	0.01	12	300	40
5 percentile	9.0	0.18	0.04	27	546	128
50 percentile	32	0.64	0.10	90	1764	267
Mean	43	0.83	0.14	101	1986	376
95 percentile	84	1.8	0.39	195	4239	1046
Maximum	867	19	1.1	541	11756	3212

Compared to the humus layer, the values of the P content in organic matter in the mineral layer are approximately three times higher. This is, however, slightly misleading since only part of the total P is organically bound.

The organic matter pool in the mineral layer is higher than in the humus layer due to higher bulk densities in the mineral layers. These bulk densities have been derived from pedotransfer functions with organic matter content as described in De Vries and Leeters (2001) (see also Section 2.5). Consequently, the N and P pools are also much higher in the mineral layers than in the humus layer, even up to 2 times for N and ca 6 times for P. The ranges in N pools for the layer 0 - 10 in this study were comparable to the variation on a European level (De Vries et al., 2000), showing that both low and high values do occur in the Netherlands. The ranges in pools in the mineral layer 10 - 30 cm are greater than in the mineral layer 0 - 30 cm. This is mainly due to the larger layer thickness.

The maximum value for the organic matter content (Table 29 and Table 30) is much higher than the 95 percentile. These high values were found in the Umbric Gleysols (see also Table 32), which contain several organic rich soils with high organic matter contents. Leaving this soil type out, the maximum values become 130 and 110 g.kg⁻¹ respectively. Because the N content is strongly correlated with the organic matter content, there are also several high N contents found in the Umbric Gleysols. Leaving this soil type out, the maximum values for the N contents in the layers 0 - 10 and 10 - 30 become 3 and 2 g.kg⁻¹ respectively. For the P contents in both layers there were also maximum values which were clearly higher than the 95 percentile. These high values were found in Fimic Anthrosols, soils with intensive human influence (see also Table 32 and Table 32). Leaving this soil type out, the maximum value for the P content becomes 0.82 and 0.66 g.kg⁻¹ for the layers 0 - 10 cm and 10 - 30 cm respectively

The relative impact of soil type is comparable for the organic matter content and N content, as illustrated by the median values per soil type (Table 32 and Table 32). In general, the contents decrease in the order Umbric Gleysols > Dystric Gleysols > Gleyic Podzol > Fimic Anthrosol > Cambic Podzol > Haplic Arenosol. A comparable order was found in De Vries and Leeters (2001). Unlike organic matter and N, the P contents and pools generally decrease in the order Fimic Anthrosol and Dystric Gleysols > Umbric Gleysols and > Cambic Podzols > Gleyic Podzols and Haplic Arenosols.

As with the contents, the pools of organic matter, N and P show considerable variation between the soil types, specifically the high organic matter and N pools found in the Umbric Gleysols, which contain also organic rich soils, and the high P pools found in the Fimic Anthrosols, due to former fertilisation (sod-application) in the past (De Vries and Leeters, 2001). Contents of organic matter and N are lower in the layer 10 - 30 cm, whereas the contents of P are lower in the layer 0 - 10cm. All pools are higher in the layer 10 - 30 cm than in the layer 0 - 10 cm, except for the N pool in Dystric Gleysols. This is due to the difference in layer thickness (20 cm in the second layer versus 10 cm in the first layer).

Table 31 Median value of the organic matter and nutrient contents and pools for the mineral layer 0 - 10 cm for six soil types.

Soil type	Contents			Pools		
	OM (g.kg ⁻¹)	N (g.kg ⁻¹)	P (g.kg ⁻¹)	OM (ton.ha ⁻¹)	N (kg.ha ⁻¹)	P (kg.ha ⁻¹)
Haplic Arenosols ¹⁾	35	0.8	0.092	48	1168	125
Gleyic Podzol ²⁾	59	1.2	0.11	74	1470	137
Cambic Podzol	47	1.1	0.14	62	1382	176
Fimic Anthrosol	49	1.3	0.25	64	1746	326
Umbric Gleysol ³⁾	71	1.6	0.14	86	2040	148
Dystric Gleysol	55	1.6	0.26	70	1981	331

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

Table 32 Median value of the organic matter and nutrient contents and pools for the mineral layer 10 - 30 cm for six soil types

Soil type	Contents			Pools		
	OM (g.kg ⁻¹)	N (g.kg ⁻¹)	P (g.kg ⁻¹)	OM (ton.ha ⁻¹)	N (kg.ha ⁻¹)	P (kg.ha ⁻¹)
Haplic Arenosols ¹⁾	18	0.43	0.079	54	1222	227
Gleyic Podzol ²⁾	46	0.77	0.092	121	2044	233
Cambic Podzol	29	0.58	0.12	81	1618	329
Fimic Anthrosol	35	0.97	0.22	96	2577	613
Umbric Gleysol ³⁾	51	1.1	0.14	135	2877	236
Dystric Gleysol	27	0.62	0.18	76	1745	533

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

5.2 Soil acidity and exchangeable cations

Because significant changes in buffer characteristics of the soil were expected to occur in the mineral topsoil only, exchangeable cations were only determined for the mineral layer 0 - 10 cm. Soil acidity was determined for both mineral soil layers. The results of the pH in a water extract and in a KCl extract for the mineral top layer (0-10 cm) generally varied between 3.5 and 5.0 and between 3.0 and 4.5, respectively (Table 33).

Table 33 Minimum, maximum, mean, 5, 50 and 95 percentiles of pH, CEC and exchangeable cation content (in percentage of the CEC) of the mineral layer 0 - 10 cm.

Statistics	pH (-),		CEC(mol.c.kg ⁻¹) and exchangeable cations (%)								
	pH- H ₂ O	pH- KCl	CEC	H	Al	Fe	Ca	Mg	K	Na	NH ₄
Minimum	2.9	2.7	7.3	0.0	0.0	0.0	0.12	0.01	0.07	0.0	0.0
5 percentile	3.6	2.9	16	0.0	0.37	0.19	1.2	0.85	0.57	0.0	0.50
50 percentile	3.8	3.1	36	28	45	9	5	2.0	2.3	0.63	1.2
Mean	4.0	3.3	41	29	44	9	10	2.5	3.6	0.86	1.5
95 percentile	5.1	4.7	77	63	75	19	32	6.1	11	2.1	3.5
Maximum	7.4	7.3	155	99	88	22	93	14	51	23	11

Differences between pH-H₂O and pH-KCl were approximately 0.7, being less than in the humus layer layers. The high maximum values (above pH 7) are due to the presence of calcareous soils. The pH values generally increased by depth. The 90% range (difference between the 5% and 95%) for pH-H₂O values in the humus layer was 3.6 - 4.7, in the mineral layer 0 - 10 cm 3.6 and 5.1 and in the mineral layer 10 - 30 cm mostly between 3.7 and 5.3. Similarly, the pH-KCL values varied mostly between 2.6 and 3.8 in the humus layer, between 2.9 and 4.7 in the mineral layer 0 - 10 cm and between 3.0 and 4.9 in the mineral layer 10 - 30cm. Very high values were found for several locations, three of them (207, 2013 and 2014, see **Appendix 2**) having calcareous soils and also high Ca contents in the humus layer (see Section 4.1) and two of them are located in the 'Kuinderbos' and are probably covered by very calcareous sand covers.

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 34 and Table 19). As with the results obtained for a layer of 30 cm in 1990 (De Vries and Leeters, 2001), the median value in the mineral layer of 10 cm was nearly ten times lower than in the humus layer (36 compared to 301 mmol_c.kg⁻¹). The proton saturation and base saturation was much lower and the Al saturation was much higher in the mineral topsoil compared to the humus layer (Compare Table 33 and Table 19). Al dominates the exchange complex in the mineral topsoil, reflecting that Al mobilisation is the dominant buffer mechanism in this layer. The median base saturation was, however, below 10%, illustrating the strong acidification of those acid sandy soils.

The pH-H₂O and pH-KCl both show not much variation between soil types (Table 34). Nevertheless, obvious differences in exchangeable cation contents were observed between the various soil types. In accordance with the higher organic matter content, the CEC was higher in both Gleysols than in the Podzolic soils and in the Haplic Arenosol.

Table 34 Median values of pH, CEC and exchangeable cation content (in percentage of the CEC) of the mineral layer 0 - 10cm for six soil types

Soil type	pH (-)		CEC(mol _c .kg ⁻¹) and exchangeable cations (%)								
	pH-H ₂ O	pH-KCl	CEC	H	Al	Fe	Ca	Mg	K	Na	NH ₄
Haplic Arenosols ¹⁾	4.0	3.3	28	22	49	8.9	4.9	2.5	0.69	2.7	1.3
Gleyic Podzol ²⁾	3.8	3.1	39	29	48	5.9	5.5	1.7	0.66	1.9	1.1
Cambic Podzol	3.8	3.2	34	31	46	14	3.9	1.8	0.63	2.0	1.2
Fimic Anthrosol	3.8	3.0	33	35	29	15	6.9	2.5	0.61	3.4	1.7
Umbric Gleysol ³⁾	3.7	2.9	58	38	31	7.4	7.2	3.4	0.56	2.6	0.97
Dystric Gleysol	3.9	3.2	59	12	44	13	7.6	2.8	0.43	2.7	0.87

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

The median Al saturation was considerably higher in the Haplic Arenosol and in the podzolic soils (near 50%) than in the Fimic Anthrosol and in the Umbric Gleysol (near 30%). This difference is mainly due to a higher proton saturation and in the

Fimic Anthrosol also by a higher Fe saturation. In the two gleysoils, the Ca saturation is clearly higher, reflecting the larger buffer capacity of those soils (Table 34).

Despite the lower CEC in the mineral topsoil compared to the humus layer, the average exchangeable cation pool ($\text{kmol}_c\text{ha}^{-1}$) is approximately twice as large because of the ten times higher bulk density (Compare Table 35 and Table 21). As with the exchangeable cation contents, the exchangeable cation pools generally decreased according to $\text{Al} > \text{H} > \text{Ca} > \text{Fe} > \text{Mg}$ and $\text{K} > \text{Na}$ and NH_4 (Table 35). Despite the much lower base saturation, the exchangeable base cation pools in the mineral topsoil are comparable (Compare Table 35 and Table 21).

Table 35 Minimum, maximum, 5, 50 and 95 percentiles of the exchangeable cation and CEC pool in the mineral layer 0 - 10 cm

Statistics	Exchangeable cation and CEC pool ($\text{kmol}_c\text{ha}^{-1}$)								
	H	Al	Fe	Ca	Mg	K	Na	NH_4	CEC
Minimum	0.0	0.0	0.0	0.09	0.01	0.05	0.0	0.0	11
5 percentile	0.0	0.23	0.11	0.28	0.30	0.27	0.0	0.22	23
50 percentile	13	19	3.5	2.5	0.87	1.2	0.29	0.54	46
Mean	16	20	4.2	6.6	1.4	1.5	0.37	0.65	51
95 percentile	37	40	10	20	4.5	4.1	0.99	1.3	87
Maximum	166	63	15	192	17	13	3.1	4.1	207

The CEC and the exchangeable cation 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 36 and 31).

Table 36 Median values of the exchangeable cation and CEC pool in the mineral layer 0 - 10cm for six soil types

Soil type	Exchangeable cation and CEC pool ($\text{kmol}_c\text{ha}^{-1}$)								
	H	Al	Fe	Ca	Mg	K	Na	NH_4	CEC
Haplic Arenosols ¹⁾	4.8	15	2.6	1.9	0.89	0.27	1.2	0.48	38
Gleyic Podzol ²⁾	14	23	2.7	2.7	0.79	0.33	1.1	0.55	50
Cambic Podzol	13	19	5.7	1.6	0.67	0.27	0.97	0.48	45
Fimic Anthrosol	15	14	6.0	3.0	1.1	0.22	1.5	0.82	43
Umbric Gleysol ³⁾	15	19	5.5	3.8	1.2	0.28	1.5	0.66	67
Dystric Gleysol	7.0	32	8.1	5.8	2.2	0.37	2.1	0.67	76

¹⁾ including Gleyic Arenosols

²⁾ including Cambic Podzols

³⁾ including organic rich soils

5.3 Heavy metals

The contents of heavy metals in the mineral topsoil are lower than in the humus layer (Compare Table 37 and Table 23). This reflects the larger impact of atmospheric deposition on the metal accumulation in the humus layer as compared to the mineral soil. On average, the contents of Pb, Cd, Cu and Zn are nearly ten times as large in the humus layer than in the mineral topsoil, whereas the difference is a factor of two to three for Ni and Cr. This illustrates the much larger input of the former four

metals compared to the latter two metals. As with the humus layer, the variation in heavy metal content in the mineral topsoil is large and for all metals the mean values are higher than the median values, indicating that there are several forest stands with high values. This is also shown by the difference between the 50 and the 95 percentile. Comparison of the results with the target values in Table 24, shows, that the metal contents never exceed those values. The target values given in Table 24 are, however, based on an organic matter content of 64%, being the mean value observed in the humus layer. However, even when using the actual organic matter content in the mineral topsoil, there were only few stands where the target values were exceeded, implying that risks of elevated metal contents are mainly due to metal accumulation in the humus layer.

Table 37 Minimum, maximum, mean, 5, 50 and 95 percentiles of the heavy metal content in the mineral layer 0 - 10 cm

Statistics	Heavy metal content (mg.kg ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
Minimum	4.0	0.0	0.0	1.5	0.76	0.63
5 percentile	6.1	0.0	0.53	3.2	1.1	1.8
50 percentile	13	0.11	2.7	7.8	2.4	4.6
Mean	17	0.17	4.1	12	2.9	5.5
95 percentile	45	0.56	11	30	6.9	12
Maximum	96	1.4	37	123	11	20

The impact of soil type on heavy metal content is related to the organic matter content of the soil and the clay content, which are the most important adsorbents of heavy metals in the soils. Consequently, highest metal contents were generally found in the Dystric Gleysols followed by Umbric Gleysols. Lowest contents were generally found in the Haplic Arenosols with a low organic matter content (Table 38).

Table 38 Median values of the heavy metal content in the mineral layer 0 -10 cm for six soil types

Soil type	Heavy metal content (mg.kg ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
Haplic Arenosols ¹⁾	12	0.060	1.3	7.8	2.4	4.4
Gleyic Podzol ²⁾	12	0.14	2.7	6.0	1.9	3.9
Cambic Podzol	17	0.060	2.6	9.7	3.0	5.9
Fimic Anthrosol	21	0.13	4.7	7.7	2.6	4.5
Umbric Gleysol ³⁾	18	0.10	3.0	12	3.2	6.4
Dystric Gleysol	35	0.080	7.2	23	5.7	13

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

As with the metal contents, the variation in heavy metal pools is large (Table 39). Despite the lower metal contents in the mineral topsoil compared to the humus layer, the average heavy metal pools in the mineral layer were generally three (Pb, Cd, Cu and Zn) to five times (Ni, Cr) as large. This illustrates the impact of the much larger bulk density of the mineral topsoil compared to the humus layer (Compare Table 39 and Table 27).

Table 39 Minimum, maximum, mean, 5, 50 and 95 percentiles of the heavy metal pool in the mineral layer 0 - 10 cm

Statistics	Heavy metal pool (kg.ha ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
Minimum	5.8	0.0	0.0	2.1	1.0	0.80
5 percentile	8.5	0.0	0.70	4.4	1.5	2.4
50 percentile	17	0.10	3.3	10	3.1	6.0
Mean	22	0.20	5.1	15	3.7	7.1
95 percentile	55	0.70	13	42	9.3	16
Maximum	105	1.8	49	162	15	26

The impact of soil type on heavy metal pools is comparable to metal contents. Highest metal pools were generally found in the Dystric Gleysols followed by Umbric Gleysols, whereas the pools in the Podzolic soils and the Haplic Arenosols were generally quite comparable (Table 40).

Table 40 Mean values of the heavy metal pool in the mineral layer 0 - 10 cm for six soil types

Soil type	Heavy metal pool (kg.ha ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
Haplic Arenosols ¹⁾	16	0.08	1.83	11	3.3	6.3
Gleyic Podzol ²⁾	15	0.17	3.25	7.6	2.4	4.8
Cambic Podzol	22	0.08	3.27	13	4.0	7.6
Fimic Anthrosol	27	0.16	6.35	9.8	3.0	5.8
Umbric Gleysol ³⁾	22	0.11	4.06	14	3.6	7.8
Dystric Gleysol	42	0.10	8.86	26	7.3	18

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

6 Chemical composition of the soil solution in 1995

In this chapter an overview is given of the chemical composition of the soil solution, subdivided in element concentrations (Section 6.1), element ratios (Section 6.2), a comparison of element concentrations and element ratios with critical limits (Section 6.3) and relationships between element concentrations and ratios with tree species (Section 6.4). Presented are the variation in the data of 1995 and the distribution over tree species for the humus layer and the mineral layers 0 - 10 cm and 10 - 30 cm. As with the solid phase chemistry a more in-depth interpretation of this kind of data is given in De Vries and Leeters (2001).

6.1 Element concentrations

In the soil solution of both the humus layer and the two mineral layers, all the major cations and anions were measured, i.e. H, Al, Fe, Ca, Mg, K, Na, NH₄, NO₃, SO₄, Cl and RCOO⁻. Important indicators for acidification and eutrophication of the forest ecosystem are the pH and the dissolved concentrations of Al, SO₄, NO₃ and NH₄. Results for the humus layer and the two mineral layers of the 200 forest stands are given in Table 41 and Table 42, respectively.

In the humus layer NO₃ concentrations are comparable to SO₄ concentrations due to the large release of N by mineralisation followed by nitrification (Table 41). The impact of both processes is also illustrated by the strong decrease in NH₄ with depth (compare Table 41 and table 42). As with the results in 1990, the SO₄ concentrations in the two mineral layers, however, are generally higher than the NO₃ concentrations (Table 42) indicating the dominance of SO₄ in soil acidification. The mean concentrations of nearly all elements are slightly higher in the humus layer than in both mineral layers. Differences between ion concentrations in the two mineral layers are small, except for the concentrations of H and NH₄, which are higher in the topsoil (lower pH values).

Table 41 Minimum, maximum, 5, 50 and 95 percentiles of element concentrations in the soil solution of the humus layer

Element	Element concentration in humus layer (mol _c .m ⁻³)					
	min	5%	50%	mean	95%	max
H	0.00	0.05	0.18	0.19	0.38	0.45
Al	0.03	0.05	0.13	0.14	0.25	0.45
Fe	0.00	0.00	0.01	0.02	0.03	0.10
NH ₄	0.01	0.08	0.27	0.43	1.2	3.5
Ca	0.10	0.16	0.44	0.70	2.0	12
Mg	0.06	0.10	0.25	0.39	1.0	5.3
K	0.00	0.08	0.24	0.26	0.55	0.89
Na	0.06	0.17	0.29	0.36	0.78	3.6
Cl	0.00	0.18	0.54	0.83	1.7	16
NO ₃	0.00	0.10	0.69	0.88	2.3	8.3
SO ₄	0.23	0.41	0.69	0.84	1.8	3.8
RCOO	0.03	0.12	0.24	0.36	0.70	11

Table 42 Minimum, maximum, 5, 50 and 95 percentiles of element concentrations in the soil solution of the mineral layers from 0 - 10cm and 10 - 30cm

Element	Concentration in layer 0-10 cm (mol _c .m ⁻³)						Concentration in layer 10-30 cm (mol _c .m ⁻³)					
	min	5%	50%	mean	95%	max	min	5%	50%	mean	95%	max
H	0.0	0.01	0.20	0.22	0.46	0.62	0.0	0.01	0.13	0.14	0.32	0.66
Al	0.01	0.08	0.26	0.29	0.54	1.2	0.01	0.08	0.32	0.39	1.0	1.8
Fe	0.0	0.0	0.04	0.04	0.10	0.42	0.0	0.0	0.02	0.03	0.08	0.63
NH ₄	0.0	0.02	0.11	0.21	0.75	1.8	0.0	0.02	0.06	0.12	0.45	1.4
Ca	0.07	0.12	0.32	0.46	1.5	4.8	0.02	0.12	0.29	0.48	1.8	6.1
Mg	0.03	0.07	0.16	0.21	0.43	2.5	0.02	0.07	0.16	0.20	0.44	2.6
K	0.0	0.0	0.15	0.16	0.43	0.62	0.0	0.0	0.06	0.09	0.28	0.96
Na	0.02	0.13	0.29	0.39	0.95	3.9	0.06	0.13	0.30	0.39	0.90	3.2
Cl	0.0	0.13	0.45	0.51	1.2	2.3	0.0	0.13	0.37	0.50	1.1	12
NO ₃	0.0	0.04	0.55	0.62	1.5	1.8	0.0	0.04	0.47	0.56	1.4	3.2
SO ₄	0.04	0.40	0.68	0.87	2.1	9.7	0.0	0.40	0.68	0.84	2.0	7.0
RCOO	0.11	0.12	0.22	0.25	0.49	1.0	0.07	0.12	0.24	0.27	0.52	1.4

In general there is a consistent decrease in NH₄ with depth, reflecting the impact of preferential NH₄ uptake and nitrification, and a consistent increase in Al with depth, reflecting the impact of Al mobilisation. Ca concentrations are mostly higher than those of Mg and K, illustrating that Ca is the dominant base cation buffering the acid input, most likely due to a high Ca input from the atmosphere. Observed high concentrations of Na and Cl are also an indication of high atmospheric inputs.

6.2 Element ratios

Ranges in calculated relevant element ratios (see par. 2.5) in the soil solution in both the humus layer and the two mineral layers (0-10 cm and 10-30 cm) are given in Table 43, Table 44 and Table 45, respectively.

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. The results show a clear decrease in the (NH₄+ NO₃)/ SO₄ ratio with depth with mean values decreasing from 1.6 in the humus layer to 1.0 in the lowest mineral layer (10-30 cm depth).

Table 43 Minimum, maximum, 5, 50 and 95 percentiles of element ratios in the soil solution of the humus layer

Ratio	Element ratio in humus layer					
	min	5%	50%	mean	95%	max
Equivalent ratio						
NH ₄ /NO ₃	0.00	0.13	0.48	0.74	2.1	6.1
(NO ₃ + NH ₄)/SO ₄	0.11	0.37	1.5	1.6	3.0	13
Al/(SO ₄ + NO ₃)	0.01	0.04	0.09	0.10	0.20	0.28
Molar ratio						
Al/Ca	0.01	0.04	0.20	0.22	0.55	0.85
Al/(Ca + Mg + K)	0.01	0.02	0.07	0.08	0.19	0.25
NH ₄ /K	0.03	0.39	1.3	1.7	4.7	9.1

Table 44 Minimum, maximum, 5, 50 and 95 percentiles of element ratios in the soil solution of the mineral layer 0 - 10 cm

Ratio	Ratio in the mineral layer of 0-10 cm					
	min	5%	50%	mean	95%	max
Equivalent ratio						
NH ₄ /NO ₃	0.0	0.04	0.24	0.53	2.2	4.7
(NO ₃ + NH ₄)/SO ₄	0.05	0.20	1.0	1.2	2.7	7.9
Al/(SO ₄ + NO ₃)	0.0	0.08	0.20	0.24	0.57	1.1
Molar ratio						
Al/Ca	0.0	0.06	0.56	0.69	1.6	3.4
Al/(Ca + Mg + K)	0.0	0.04	0.23	0.28	0.65	1.0
NH ₄ /K	0.03	0.15	0.58	1.2	4.3	16

Table 45 Minimum, maximum, 5, 50 and 95 percentiles of element ratios in the soil solution of the mineral layer 10 - 30 cm

Ratio	Ratio in the mineral layer of 10-30 cm					
	min	5%	50%	mean	95%	max
Equivalent ratio						
NH ₄ /NO ₃	0.0	0.02	0.15	0.41	1.8	6.1
(NO ₃ + NH ₄)/SO ₄	0.01	0.11	0.83	1.0	2.1	4.9
Al/(SO ₄ + NO ₃)	0.0	0.03	0.31	0.38	0.85	2.5
Molar ratio						
Al/Ca	0.0	0.05	0.93	1.10	2.8	5.5
Al/(Ca + Mg + K)	0.00	0.03	0.40	0.48	1.1	3.3
NH ₄ /K	0.00	0.05	0.62	0.88	2.2	7

A similar trend is observed in the NH₄/NO₃ ratio indicating the occurrence of nitrification and/or preferential NH₄ uptake. The Al/ SO₄ + NO₃ ratio increases with depth, indicating that the increasing role of Al mobilisation in acid neutralisation with depth.

The molar element ratios are indicators for potential impacts on the forest ecosystem, specifically in view of root length and root uptake. In view of the above-mentioned processes, both the Al/Ca ratio and the Al/(Ca+Mg+K) ratio increase with depth, whereas the NH₄/K ratio decreases with depth. Results for the mineral layers show that both the Al/Ca ratio and the Al/(Ca+Mg+K) ratio can exceed an average critical value of 1.0. The ratio of NH₄ to K nearly always remains below a critical value of 5. Median NH₄/K ratios are even below 1.0 in both topsoil and subsoil.

6.3 Comparison of element concentrations and element ratios with critical limits

As with the results for the 150 forest stands in 1990 (De Vries and Leeters, 2001), the concentrations of NO₃ and Al and the molar ratios of Al/(Ca+Mg+K) and NH₄/Mg in soil solution were compared with critical chemical values to gain insight in possible negative impacts. Criteria thus used are given in Table 46. More information on the background of those values, including the relevant literature, is given in De Vries and Leeters (2001).

Table 46 Critical chemical values for the concentrations of NO₃ and Al and the molar ratios of Al/(Ca+Mg+K) and NH₄/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 ²⁾	<1 ³⁾	<0.5 ²⁾
2 (intermediate)	0.1 - 0.8	0.2 - 1.0	1 - 5	0.5 - 1.5
3 (high)	>0.8 ¹⁾	>1.0 ²⁾	>5 ³⁾	>1.5 ²⁾

- ¹⁾ The lower value is a clearly elevated NO₃ concentration that may be related to vegetation changes, whereas the lower value is the EU quality criterion for nitrate concentrations in ground water (50 mg.l⁻¹). The Dutch target value for NO₃ equals 25 mg.l⁻¹ (0.4 mol_c.m⁻³)
- ²⁾ Critical values reported in literature relation to effects on tree roots for more or less sensitive tree species
- ³⁾ The lower value is considered critical in view of decreased base cation uptake, whereas the upper value is simply five times as low.

Information on the percentage of plots exceeding the various critical limits is presented in the Tables 47 and 48. Results show that NO₃ concentrations are clearly elevated at nearly 90% 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 lowest mineral layer at 26% of the plots. Approximately 75 % 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 5% of the plots in the lowest mineral layer. In 1990, this percentage was 23 for a layer of 0-30 cm, indicating a decrease in Al concentrations in response to the lower S and N deposition. A more reliable comparison requires the use of similar plots as described in more detail in Chapter 7.

Table 47 The percentage of observations of NO₃ and Al concentrations in the mineral topsoil and subsoil between different class limits

NO ₃ concentrations exceeding limits (%)	Al concentrations exceeding limits (%)	
	Concentration class (mmol _c .m ⁻³)	Concentration class (mmol _c .m ⁻³)
< 100	9	13
100 - 800	61	60
> 800	31	26

Approximately 10-40% of the plots had an Al/(Ca+Mg+K) ratio above 0.5, depending on soil depth (Table 48) where impacts on root uptake may occur. Above a value of 1.5 those impacts are likely, but this hardly occurred. The NH₄/K ratio hardly ever exceeded the critical value of 5.

Table 48 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 (%)	NH ₄ /K ratio exceeding limits (%)	
	Ratio class (mol.mol ⁻¹)	Ratio class (mol.mol ⁻¹)
< 0.5	89	61
0.5 - 1.5	11	38
> 1.5	0	1

6.4 Relations with tree species

The concentrations of most ions in soil solution were especially influenced by tree species (Table 49). Unlike the results in 1990 (De Vries and Leeters, 2001), the impacts of tree species are not so obvious. High concentrations in SO₄ and Cl occur below Douglas Fir and Norway Spruce, illustrating the impact of the high canopy coverage and Leaf Area Index on dry deposition and evapotranspiration, since the concentration of these two elements is completely related to atmospheric inputs and water fluxes through the ecosystem.

Table 49 Median values of element concentrations and ratios for the humus layer under seven major tree species

Element/Ratio	Element concentration in humus layer (mol _c .m ⁻³)						
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech
H	0.23	0.18	0.21	0.17	0.16	0.13	0.19
Al	0.13	0.15	0.14	0.14	0.09	0.14	0.13
Ca	0.37	0.35	0.51	0.32	0.25	0.60	0.53
NH ₄	0.27	0.23	0.43	0.33	0.21	0.25	0.23
NO ₃	0.57	0.53	0.86	0.50	0.34	0.82	1.11
SO ₄	0.68	0.69	0.76	0.82	0.52	0.69	0.58
Cl	0.49	0.48	0.76	0.77	0.68	0.50	0.47
	Element ratio (mol.mol ⁻¹)						
Al/Ca	0.26	0.29	0.17	0.27	0.23	0.14	0.15
NH ₄ /K	1.3	1.2	2.5	2.0	1.9	0.90	0.93

Table 50 Median values of element concentrations and ratios for the mineral layer 0 -10cm under seven major tree species

Element/Ratio	Element concentration in mineral layer 0 -10cm (mol _c .m ⁻³)						
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech
H	0.22	0.16	0.26	0.18	0.21	0.17	0.21
Al	0.27	0.22	0.35	0.38	0.32	0.23	0.22
Ca	0.26	0.33	0.35	0.26	0.26	0.38	0.32
NH ₄	0.14	0.09	0.22	0.33	0.17	0.08	0.07
NO ₃	0.54	0.41	0.55	0.40	0.44	0.64	0.69
SO ₄	0.76	0.93	0.82	0.82	0.54	0.62	0.54
Cl	0.44	0.36	0.72	0.80	0.41	0.37	0.36
	Element ratio in mineral layer 0 -10cm (mol.mol ⁻¹)						
Al/Ca	0.67	0.67	0.55	1.20	0.80	0.46	0.49
NH ₄ /K	0.97	1.15	1.58	1.89	1.24	0.30	0.33

Table 51 Median values of element concentrations and ratios for the mineral layer 10 -30 cm under seven major tree species

Element/Ratio	Element concentration in mineral layer 10 - 30cm (mol _c .m ⁻³)						
	Scots pine	Black pine	Douglas Fir	Norway spruce	Japanese Larch	Oak	Beech
H	0.11	0.11	0.18	0.19	0.17	0.10	0.10
Al	0.30	0.23	0.47	0.55	0.45	0.31	0.28
Ca	0.22	0.28	0.34	0.22	0.27	0.33	0.27
NH ₄	0.07	0.05	0.14	0.16	0.05	0.05	0.05
NO ₃	0.49	0.37	0.58	0.48	0.40	0.54	0.41
SO ₄	0.77	1.00	0.86	0.86	0.50	0.56	0.59
Cl	0.34	0.30	0.58	0.44	0.53	0.34	0.34
	Element ratio in mineral layer 10 - 30cm (mol.mol ⁻¹)						
Al/Ca	1.10	0.58	0.98	1.56	1.42	0.53	0.88
NH ₄ /K	1.00	0.73	1.08	1.47	0.78	0.35	0.39

7 Evaluation of the differences in contents and pools of elements between 1995 and 1990

In this chapter a comparison is made between contents and pools of elements measured in 1990 and those measured in 1995 for 124 forest stands. A comparison of the sampling and analyses program in 1990 en 1995 is given in Table 52. The table shows that the following comparisons are possible:

- pH- H₂O and pH- KCl and concentrations and pools of (i) organic matter (OM) and major elements (N, P, Al, Fe, Ca, Mg, K), (ii) heavy metals (Pb, Cd, Cu, Zn, Ni, Cr) and (iii) exchangeable cations (H, Fe, NH₄, Ca, Mg, K, Na) in the humus layer.
- pH- H₂O and pH- KCl and concentrations and pools of (i) organic matter (OM) and major nutrients (N and P) and (iii) dissolved major ions (H, Al, Fe, Ca, Mg, K, Na, NH₄, NO₃, SO₄, Cl, H₂PO₄, RCOO) in the mineral topsoil (0-30 cm)

In 1990, the soil solution chemistry was measured in the subsoil (60-100 cm), but not in the humus layer, whereas the reverse is true for 1995. Consequently, a comparison was only possible for the forest topsoil. Furthermore, in 1990, the mineral topsoil was measured for the depth of 0 - 30 cm, but in 1995 the depths of 0 - 10 cm and 10 - 30 cm were sampled and analysed separately. To compare these layers, the results for the concentrations in the layers 0 - 10 cm and 10 - 30 cm in 1995 were averaged over 30 cm, while weighing them according to their thickness and density and then compared with the layer of 0 - 30 cm of 1990. Since the CEC and exchangeable cations were only measured in the layer of 0-10 cm in 1995, a comparison for those results could only be made for the humus layer.

Table 52 Comparison of the sampling and analyses program of the 200 forest stands investigated in this study in 1995 and the 150 forest stands investigated in 1990 (in total 124 forest stands were sampled in both years).

Analyses	1990			1995		
	Humus layer	0-30 cm	60-100 cm	Humus layer	0-10 cm	10-30 cm
pH- H ₂ O, pH- KCl	x	x	-	x	x	x
Total OM, N, P	x	x	-	x	x	x
Total Al, Fe, Ca, Mg, K	x	-	-	x	-	-
Total Pb, Cd, Cu, Zn, Ni, Cr	x	-	-	x	x	-
Exchangeable H, Fe, NH ₄ , Ca, Mg, K, Na	x	x	-	x	x	-
Dissolved H, Al, Fe, Ca, Mg, K, Na, NH ₄ , NO ₃ , SO ₄ , Cl, H ₂ PO ₄ , RCOO	-	x	x	x	x	x

First the results are given as the mean of the absolute differences compared to 1990 per tree species for the humus layer and per soil type for the mineral layer. Furthermore tables are given of the number of plots where the results were likely to be significant in view of the spatial variability (See section 2.5). Positive values mean higher contents and pools in 1995 and negative values mean lower contents and

pools in 1995. Furthermore, results are given in graphs of frequency distributions of differences based on all plots and based on the plots with statistically significant differences. Results are subdivided in contents and/or pools of organic matter and nutrients in the humus layer and mineral layer of 0-30 cm (Section 7.1), soil acidity and exchangeable cations in the humus layer (Section 7.2), heavy metals in the humus layer (Section 7.3) and in ion concentrations in soil solution in the mineral layer of 0-30 cm (Section 7.4).

7.1 Organic matter and nutrients in the humus layer and mineral layer

7.1.1 Mean differences in organic matter and nutrients

Humus layer

On average most nutrient contents in the humus layer decreased, except for Mg. For K the average change was significant for all tree species, but for the other nutrients, the average changes were only significant for one to three species (Table 53). Nevertheless, changes were calculated to be significant in view of the spatial variability (see Eq. 1 and 2 in Section 2.5) at approximately 50-80% of the plots (Table 54).

Table 53 Mean of the differences of the organic matter and the nutrient contents in organic matter in the humus layer under seven major tree species between 1995 and 1990 for all plots

Tree species	N	Mean difference (g.kg ⁻¹)					
		OM	N	P	Ca	Mg	K
Scots pine	35	-45.4	-1.070	-0.033	-0.428	-0.017	-0.144
Black pine	13	-93.0	-1.245	-0.067	-0.189	-0.032	-0.194
Douglas fir	13	-32.7	-0.929	-0.005	-0.363	-0.016	-0.165
Norway spruce	13	-1.6	0.126	0.003	-0.194	0.022	-0.123
Japanese larch	13	-20.8	-1.312	-0.052	-0.644	-0.021	-0.128
Oak	23	28.0	-0.086	-0.047	-0.516	0.024	-0.227
Beech	14	56.9	-0.058	-0.010	0.558	0.039	-0.141
Total	124	-16.7	-0.677	-0.032	-0.299	0.000	-0.163

A grey background indicates that the difference is significant ($t > 2.0$) or very significant ($t > 3.3$)

Table 54 Number of plots in which the differences in organic matter contents and nutrient contents in organic matter in the humus layer between 1995 and 1990 were significant for the different tree species

Tree species	Number of plots in which the changes were significant					
	OM	N	P	Ca	Mg	K
Scots pine	19	18	17	25	18	25
Black pine	9	9	8	9	6	10
Douglas fir	9	10	9	11	9	11
Norway spruce	6	4	8	8	7	10
Japanese larch	8	7	5	11	6	11
Oak	16	13	13	15	11	19
Beech	6	6	6	8	9	10
Total	73	67	66	87	66	96

For the N content the total average decrease was 0.677 g.kg^{-1} , being an average decrease of 3% compared to the contents in 1990. For Ca, the average decrease was 9% and for K it was even 19%. The latter value is questionable. It is known that K leaches very fast from the freshly fallen litter and it might be that there is an influence of the period in which the samples are taken on this result. There is no such clear cause-effect relationship between a decrease in acid deposition between 1990 and 1995 and K content to be expected. Limiting the results to the plots where the changes were significant lead to slightly higher average changes than those reported in Table 53.

Considering all forest stands, the average decrease in organic matter and nutrient pools is only significant for the Ca and K pools (Table 55). Nevertheless, as with nutrient contents, changes were calculated to be significant at approximately 50-80% of the plots (Table 56). Decreases are most significant for Japanese larch, especially the decrease of the N and Ca pool with nearly 30%. It is very questionable, however, whether those decreases are reliable. In case of nitrogen, it would imply a decrease of $50 \text{ kg.ha}^{-1}.\text{yr}^{-1}$, being comparable or higher than the annual average N deposition. Under black pine all pools, except for K, increase significantly, even up to 100%. It is unclear why this is the case. Here again, an increase of 266 kg.ha^{-1} in 5 years or $53 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ seems very unlikely as it exceeds the annual average N deposition. Furthermore, an increase in organic matter pool of nearly 12 ton.ha^{-1} in 5 years is very unlikely.

Considering all plots together, the results do indicate an average decrease of approximately $11 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ for N, which can be seen as a response to the decrease in N deposition. Nevertheless, there is still an ongoing acidification, as can be seen from the decrease of approximately $5 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ for Ca and nearly $3 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ for K (more questionable; see before) in response to the ongoing acid deposition. The decrease of Ca and K for both contents and pools is the most significant change, especially under Japanese larch.

Table 55 Mean of the differences of the organic matter and nutrient pools in the humus layer under seven major tree species between 1995 and 1990 for all plots

Tree species	N	Mean difference					
		OM (ton.ha ⁻¹)	N (kg.ha ⁻¹)	P (kg.ha ⁻¹)	Ca (kg.ha ⁻¹)	Mg (kg.ha ⁻¹)	K (kg.ha ⁻¹)
Scots pine	35	1.91	34	3.59	-22.6	3.51	-7.7
Black pine	13	11.62	266	10.43	33.1	9.57	9.2
Douglas fir	13	-5.62	-132	-0.57	-48.8	-3.21	-9.0
Norway spruce	13	-2.57	-55	-2.44	-32.2	0.56	-13.0
Japanese larch	13	-8.64	-269	-8.24	-76.0	-5.63	-13.9
Oak	23	-1.90	-117	-7.14	-33.1	-3.43	-34.3
Beech	14	-2.44	-183	-4.27	12.0	-0.53	-20.5
Total	124	-0.65	-53	-0.92	-24.7	0.30	-13.9

A grey background indicates that the difference is significant ($t > 2.0$)

or very significant ($t > 3.3$)

Table 56 Mean of the differences of the organic matter and nutrient pools in the humus layer under seven major tree species between 1995 and 1990 for the plots in which the differences were significant

Tree species	Number of plots in which the changes were significant					
	OM	N	P	Ca	Mg	K
Scots pine	16	16	19	26	24	20
Black pine	9	7	7	9	10	5
Douglas fir	8	6	6	13	10	10
Norway spruce	5	5	3	10	9	5
Japanese larch	3	4	4	12	10	6
Oak	12	14	11	20	17	13
Beech	8	6	6	11	11	7
Total	61	58	56	101	91	66

Mineral layer

On average the organic matter content and pool increased significantly in the layer 0 - 30 cm (Table 57), but the number of plots where the changes were significant was approximately 50%, irrespective of the nutrient considered (Table 58).

Table 57 Mean differences of the organic matter and nutrient contents (in percentage of the organic matter) and pools for the mineral layer 0-30 cm for six soil types between 1995 and 1990 for all plots

Soil type	Mean difference			Mean difference		
	OM	N	P	OM	N	P
	(g.kg ⁻¹)	(g.kg ⁻¹)	(g.kg ⁻¹)	(ton.ha ⁻¹)	(kg.ha ⁻¹)	(kg.ha ⁻¹)
Haplic Arenosols ¹⁾	4.5	0.078	-0.0083	14	224	-49
Gleyic Podzol ²⁾	6.6	0.105	0.0101	19	274	24
Cambic Podzol	5.3	0.091	0.0063	14	232	-3
Fimic Anthrosol	3.1	0.081	0.0148	7	183	9
Umbric Gleysol ³⁾	4.1	0.095	-0.1587	-35	-726	-288
Dystric Gleysol	-3.8	-0.148	-0.0204	-13	-567	-77
Total	5.1	0.085	-0.0072	11	145	-22

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

A grey background indicates that the difference is significant ($t > 2.0$)

or very significant ($t > 3.3$)

Table 58 Mean differences of the organic matter and nutrient contents (in percentage of the organic matter) and pools for the mineral layer 0-30 cm for six soil types between 1995 and 1990 for the plots in which the differences were significant

Soil type	Number of plots in which the changes in contents were significant			Number of plots in which the changes in pools were significant		
	OM	N	P	OM	N	P
	Haplic Arenosols ¹⁾	19	22	8	18	17
Gleyic Podzol ²⁾	39	34	33	29	25	26
Cambic Podzol	8	8	3	6	7	3
Fimic Anthrosol	3	5	6	2	5	5
Umbric Gleysol ³⁾	6	3	5	4	3	5
Dystric Gleysol	3	2	5	2	2	5
Total	78	74	60	61	59	51

¹⁾ including Gleyic Arenosols

²⁾ including Carbic Podzols

³⁾ including organic rich soils

This increase was on average 17%, but was mainly found in the Arenosols and Podzols, with increases up to 25%. The average N contents increased slightly, whereas the N pools did increase as a result of the increase of the organic matter. This effect was mainly found in the Gleyic Podzols. The average P contents and P pools decreased slightly. These results show that the repetition does not give reliable results in many situations. The average changes in N pools are absolutely impossible in the considered time period. Due to the large amount of soil in a layer of 30 cm, an increase of 0.01% N (0.1 g.kg⁻¹) leads to an increase of several hundreds of kilograms, being unreliable. These results indicate that monitoring a mineral layer of this thickness during a relatively short time period is not adequate (see also De Vries et al., 2000).

7.1.2 Frequency distributions of differences in organic matter and nutrients

Organic matter

The cumulative frequency distributions of the contents and pools of the organic matter in the humus layer (Figure 2A and B) for 1990 and 1995 do not differ very much. The ranges in values measured in 1995 are slightly larger than in 1990. The cumulative frequency distribution show that there are several locations with high organic matter contents in the mineral layer (Fig 2C). These high values were measured in the Umbric Gleysoils, which contain organic rich soils with high organic matter contents (see also Section 5.1). These soils have less influence on the organic matter pools (Figure 2D), because their bulk density is also lower. The pools of organic matter in the mineral layer seem to be a little higher in 1995 than in 1990. The cumulative frequency distributions of the contents and pools of the total of humus and mineral layer (Figure 2E, F) is very much influenced by the contents and pools in the mineral layer.

Differences in the organic matter content in the humus layer varied per plot between a decrease and increase of 500 g.kg^{-1} (Figure 3A). Statistically, differences smaller than approximately 75 g.kg^{-1} are not significant. On the other hand, as stated before, the high changes are likely unreliable. At the plots with significant changes, both decreases and increases were found in approximately 50% of the plots, indicating no clear direction in changes in the organic matter contents in the humus layer. In the mineral layer decreases in the organic matter content were lower (up to 35 g.kg^{-1}) than the increase (up to 80 g.kg^{-1} ; Figure 3C), indicating an increase of the organic matter contents in this layer between 1995 and 1990. Consequently, the decreases in the organic matter content in the total of humus and mineral layer were also lower (up to 40 g.kg^{-1}) than the increase (up to 70 g.kg^{-1} ; Figure 3E).

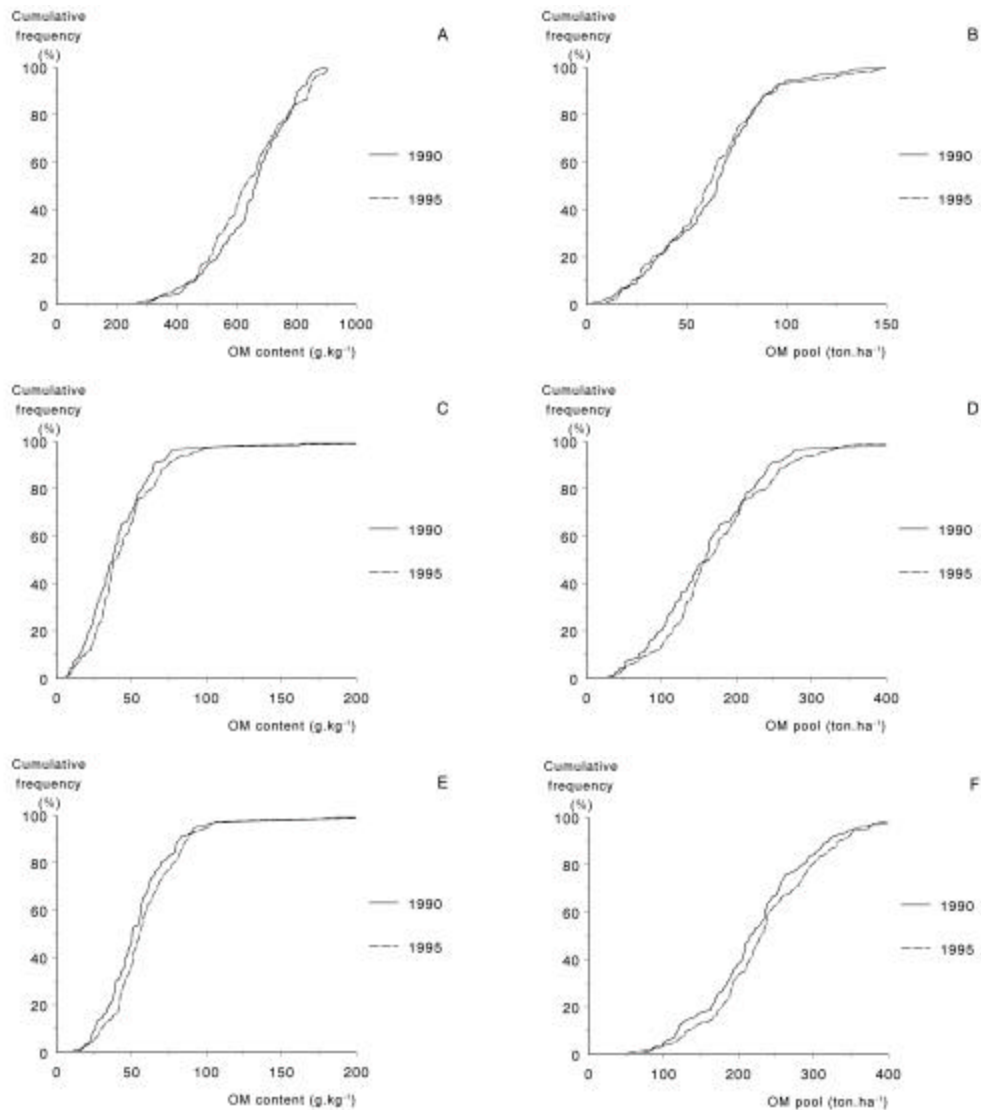


Figure 2 Cumulative frequency distributions for the organic matter contents en pools in the humus layer (A, B), the mineral layer 0-30 cm (C, D) and the total of humus and mineral layer (E, F) for the locations measured in both 1990 and 1995.

Differences in the pools of organic matter in the humus layer varied between a decrease or increase of 100 ton.ha⁻¹ (Figure 3B). Differences smaller than approximately 10 ton.ha⁻¹ for an increase and approximately 20 ton.ha⁻¹ for a decrease were not significant. At the plots with significant changes, decreases were found in approximately 40% of the plots and increases in approximately 60% of the plots, indicating an average increase of the organic matter pools in the humus layer in 1995 compared to 1990, as discussed before for Table 53. Differences in the pools of organic matter in the mineral layer varied between a decrease or an increase of approximately 100 ton.ha⁻¹ (Figure 3D). Differences smaller than approximately 20 ton.ha⁻¹ were not significant. At the plots with significant changes, decreases were found much less (approximately 20%) than increases (approximately 80%), indicating an increase of the organic matter pools in the mineral layer in 1995 compared to

1990. Consequently, an increase of the organic matter pools in the total of humus and mineral layer was also observed between 1995 and 1990. Differences in those pools varied between a decrease or an increase of $100 \text{ ton}\cdot\text{ha}^{-1}$ (Figure 3F). Differences smaller than approximately $25 \text{ ton}\cdot\text{ha}^{-1}$ for an increase and approximately $40 \text{ ton}\cdot\text{ha}^{-1}$ for a decrease were statistically not significant.

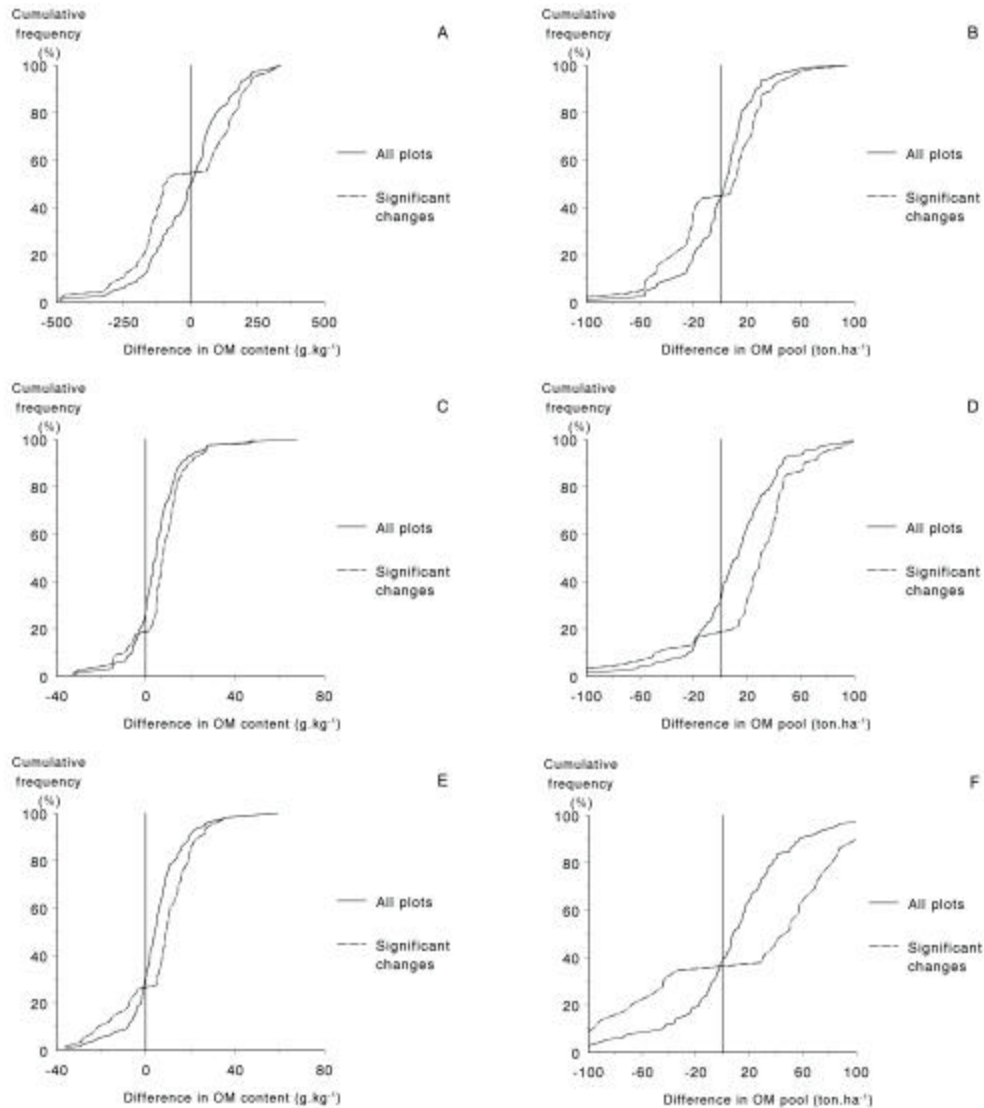


Figure 3 Cumulative frequency distributions of the measured differences in contents and pools of the organic matter per plot for the humus layer (A, B), the mineral layer 0-30 cm (C, D) and the total of humus and mineral layer (E, F) for all plots and for those plots where the differences were significant

Nitrogen

Because the content and pool of nitrogen is strongly correlated with the content and pool of the organic matter, the cumulative frequency distributions of Fig 4 are quite similar to those in Fig. 2. The nitrogen contents in the humus layer (Figure 4A) varied mostly between 6 and $20 \text{ g}\cdot\text{kg}^{-1}$, and the nitrogen pools (Figure 4B) between 100 and $3000 \text{ kg}\cdot\text{ha}^{-1}$. The contents and pools of nitrogen in the humus layer do not

differ much between 1990 and 1995, although the values in 1995 seem to be a little lower. As with the organic matter content, most plots have low nitrogen contents in the mineral layer, but several plots have very high nitrogen contents (Figure 4C). Due to the correlation between organic matter and nitrogen, these high nitrogen contents were also found in the Umbric Gleysoils (see also Section 5.1). The nitrogen contents in the mineral layer show no differences between 1990 and 1995, but the N pools seem to be somewhat higher in 1995 than in 1990. Nevertheless, those small changes lead to an average difference of $145 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ (Table 57), further supporting the statement that this kind of monitoring is unable to pick up reliable trends in N pools over a short time period.

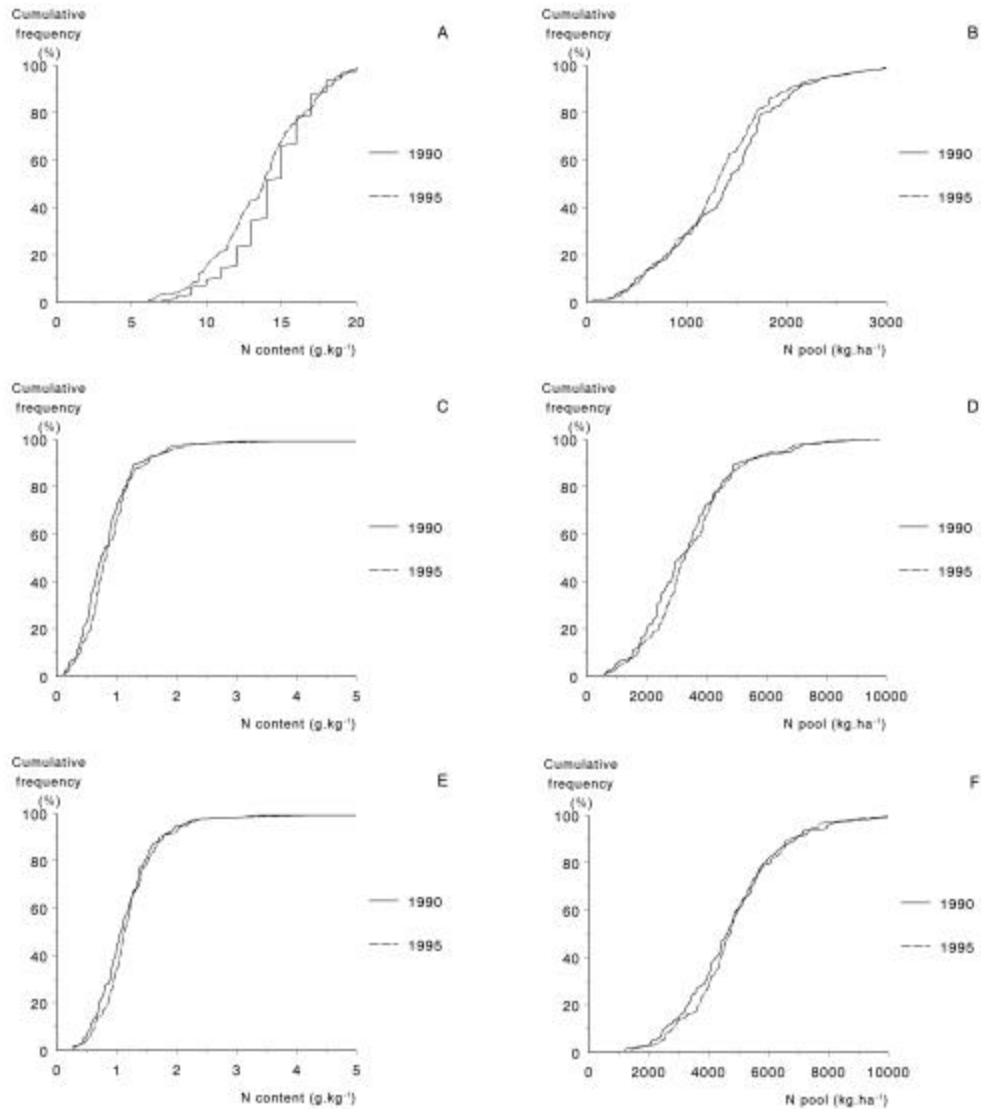


Figure 4 A cumulative frequency distribution for the nitrogen contents en pools in the humus layer (A, B), the mineral layer 0-30 cm (C, D) and the total of humus and mineral layer (E, F) for the locations measured in both 1990 and 1995.

The differences in nitrogen content in the humus layer varied per plot between a decrease and an increase of approximately 10 g.kg⁻¹ (Figure 5A). The significant changes varied between a decrease of 3 to 10 g.kg⁻¹ and an increase of 2 to 10 g.kg⁻¹. In those plots significant decreases were found in approximately 60% of the plots and increases in approximately 40% of the plots, indicating a small decrease of the nitrogen content in the humus layer in 1995 compared to 1990.

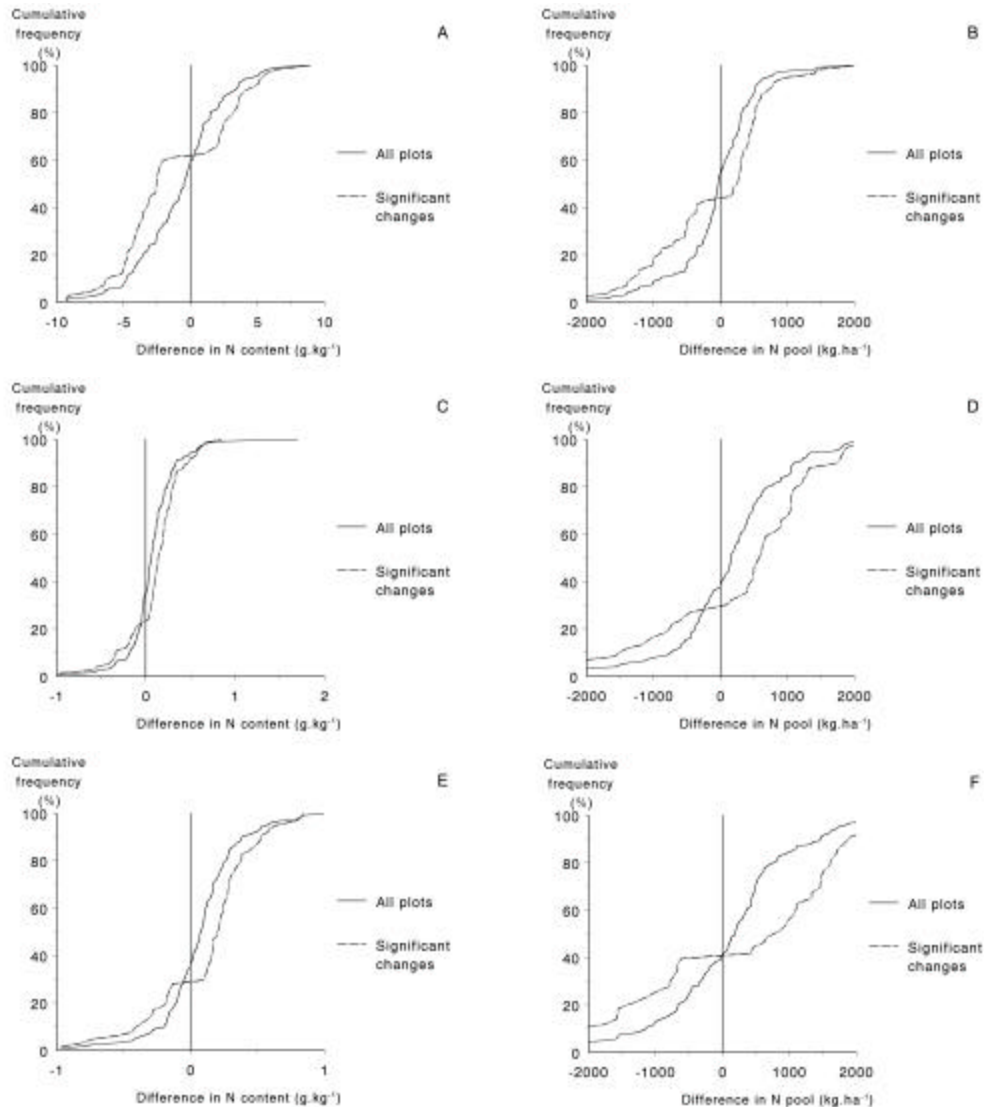


Figure 5 Cumulative frequency distributions of the measured differences in contents and pools of nitrogen per plot for the humus layer (A, B), the mineral layer 0-30 cm (C, D) and the total of humus and mineral layer (E, F) for all plots and for those plots where the differences were significant

The differences in nitrogen content in the mineral layer varied between an increase of approximately 1 g.kg⁻¹ and a decrease of approximately 2 g.kg⁻¹ (Figure 5C), indicating a decrease of the nitrogen content in the mineral layer. The differences in nitrogen content in the total of the humus and mineral layer varied between a decrease or increase of 1 g.kg⁻¹ (Figure 5E). Significant decreases were found in less

plots (approximately 30%) than significant increases (approximately 70%), indicating an increase of the nitrogen content in the total of humus and mineral layer in 1995 compared to 1990.

The differences of the nitrogen pools in the humus layer varied between a decrease or an increase of $2000 \text{ kg}\cdot\text{ha}^{-1}$ (Figure 5B). Significant decreases were found in approximately 40% of the plots and increases in approximately 60% of the plots. The differences in nitrogen pools in the mineral layer also varied between an increase or decrease of $2000 \text{ kg}\cdot\text{ha}^{-1}$ (Figure 5D). As with the humus layer, significant decreases were less than significant increases, indicating an increase of the nitrogen pools in the mineral layer between 1995 and 1990. Consequently the differences in nitrogen pools in the total of humus and mineral layer (Figure 5F) also indicate a small increase.

Phosphorus

The phosphorus contents in the humus layer (Figure 6A) varied between 0.30 and $1 \text{ g}\cdot\text{kg}^{-1}$, and the phosphorus pools (Figure 6B) between 0 and $150 \text{ kg}\cdot\text{ha}^{-1}$. The cumulative frequency distributions of the phosphorus contents and pools in the humus layer are almost the same in 1995 as in 1990, in line with the results presented in Table 57. Most phosphorus contents in the mineral layer varied between 0 and $0.25 \text{ g}\cdot\text{kg}^{-1}$, however a few plots have contents between 0.25 and $1 \text{ g}\cdot\text{kg}^{-1}$ (Figure 6C). These higher values are mainly found in the Fimic Anthrosols (see Section 5.1) and are due to the human influences on these soils. Plots with higher phosphorus contents also have higher phosphorus pools in the mineral layer (Figure 6D). Phosphorus pools in the mineral layer varied mostly between 100 and $2000 \text{ kg}\cdot\text{ha}^{-1}$. The cumulative frequency distributions of phosphorus contents and pools in the mineral layer are the same in 1995 as in 1990. The cumulative frequency distributions of phosphorus contents and pools in the total of humus and mineral layer (Figure 6E and F) are very much the same as those for the mineral layer, since the influence of the humus layer is very small.

Differences in phosphorus content in the humus layer varied per plot between a decrease of approximately $0.35 \text{ g}\cdot\text{kg}^{-1}$ and an increase of circa $0.25 \text{ g}\cdot\text{kg}^{-1}$ (Figure 7A). Differences smaller than approximately $0.10 \text{ g}\cdot\text{kg}^{-1}$ are not significant. Significant decreases were found in approximately 60% of the plots and increases in approximately 40% of the plots, indicating decrease of the phosphorus content in the humus layer in 1995 compared to 1990. Differences in the phosphorus pool in the humus layer varied per plot between a decrease and increase of approximately $90 \text{ kg}\cdot\text{ha}^{-1}$ (Figure 7B). The significant changes are greater than the changes in all plots. Significant decreases were found in approximately 40% of the plots and increases in approximately 60% of the plots, indicating a small increase of the phosphorus pools in the humus layer in 1995 compared to 1990.

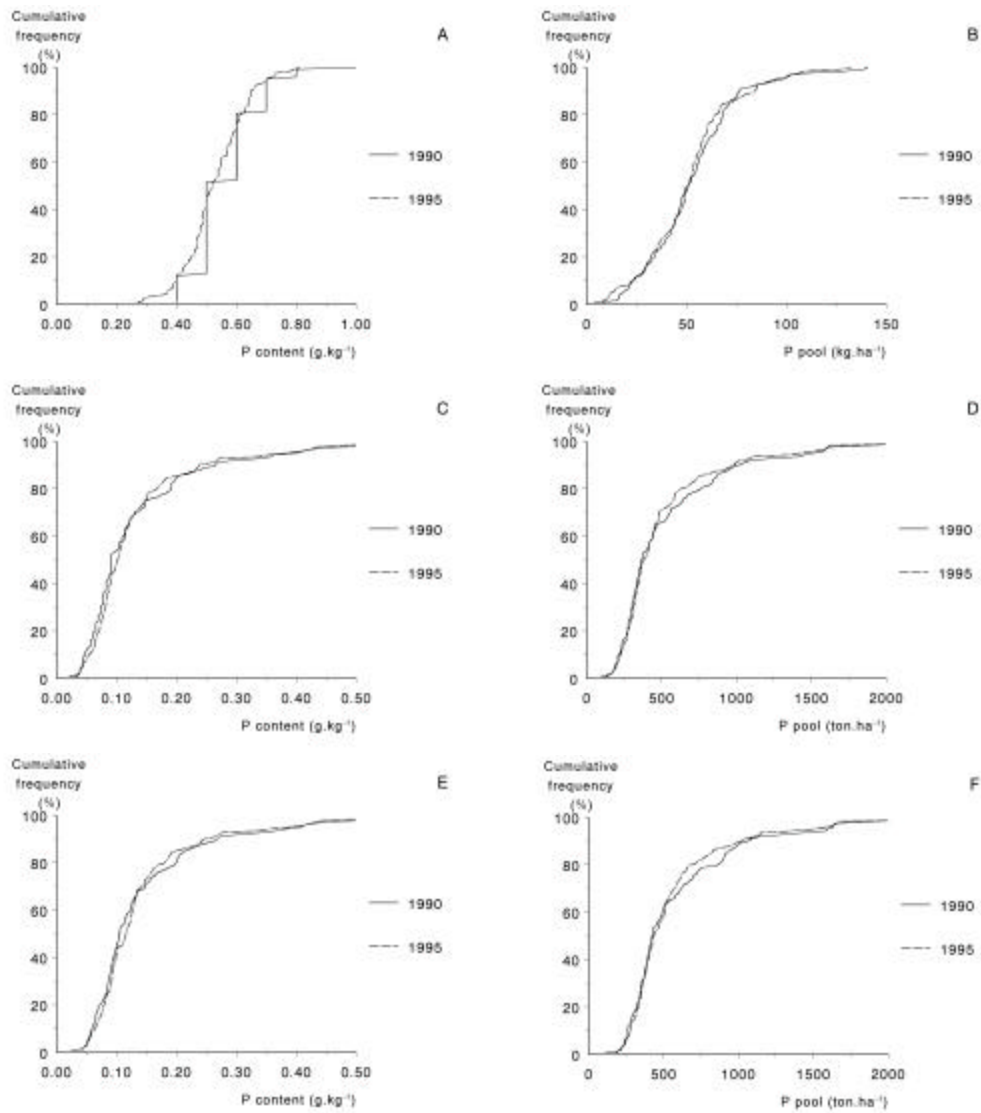


Figure 6 A cumulative frequency distribution for the phosphorus contents en pools per plots in the humus layer (A, B), the mineral layer 0-30 cm (C, D) and the total of humus and mineral layer (E, F) for the locations measured in both 1990 and 1995.

Differences in phosphorus content in the mineral layer varied per plot between a decrease of approximately 0.40 g.kg⁻¹ and an increase of circa 0.20 g.kg⁻¹ (Figure 7C). Significant decreases were found in approximately 35% of the plots and increases in approximately 65% of the plots, indicating an increase of the phosphorus content in the mineral layer in 1995 compared to 1990. Differences in the phosphorus pool in the mineral layer varied per plot between a decrease or increase of approximately 1000 ton.ha⁻¹. (Figure 7D). The significant changes do not differ much from the changes in all plots but they are a little greater. Significant decreases were found in approximately 50% of the plots and increases also in approximately 50% of the plots, indicating no changes of the phosphorus pools in the mineral layer in 1995 compared to 1990.

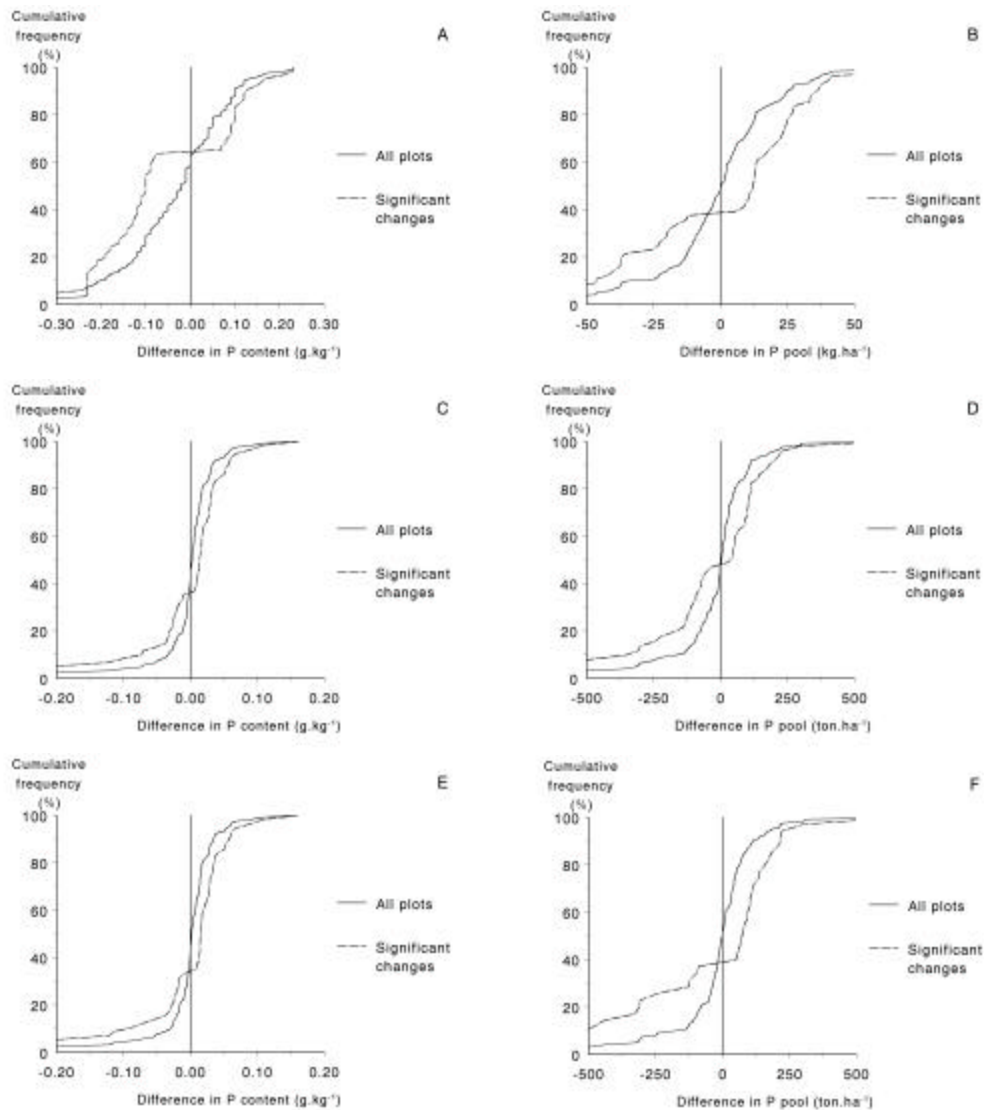


Figure 7 Cumulative frequency distributions of the measured differences in contents and pools of phosphorus per plot for the humus layer (A, B), the mineral layer 0-30 cm (C, D) and the total of humus and mineral layer (E, F) for all plots and for those plots where the differences were significant

Differences in phosphorus content in the total of humus and mineral layer varied per plot between a decrease of approximately 0.40 g.kg^{-1} and an increase of circa 0.20 g.kg^{-1} (Figure 7E). Significant decreases were found in approximately 35% of the plots and increases in approximately 65% of the plots, indicating an increase of the phosphorus content in the mineral layer in 1995 compared to 1990. Differences in the phosphorus pool in the total of humus and mineral layer varied per plot between a decrease or increase of approximately 1000 ton.ha^{-1} (Figure 7F). The significant decreases do not differ much from the changes in all plots but the significant decreases are clearly greater. Significant decreases were found in approximately 40% of the plots and increases also in approximately 60% of the plots, indicating a small increase of the phosphorus pools in the total of humus and mineral layer in 1995 compared to 1990.

Calcium, magnesium and potassium

Differences in contents and pools for the nutrient Ca, Mg and K between 1995 and 1990 can only be given for the humus layer as shown in Figure 8 and 9. In 1995 these nutrients were not measured in the mineral layer.

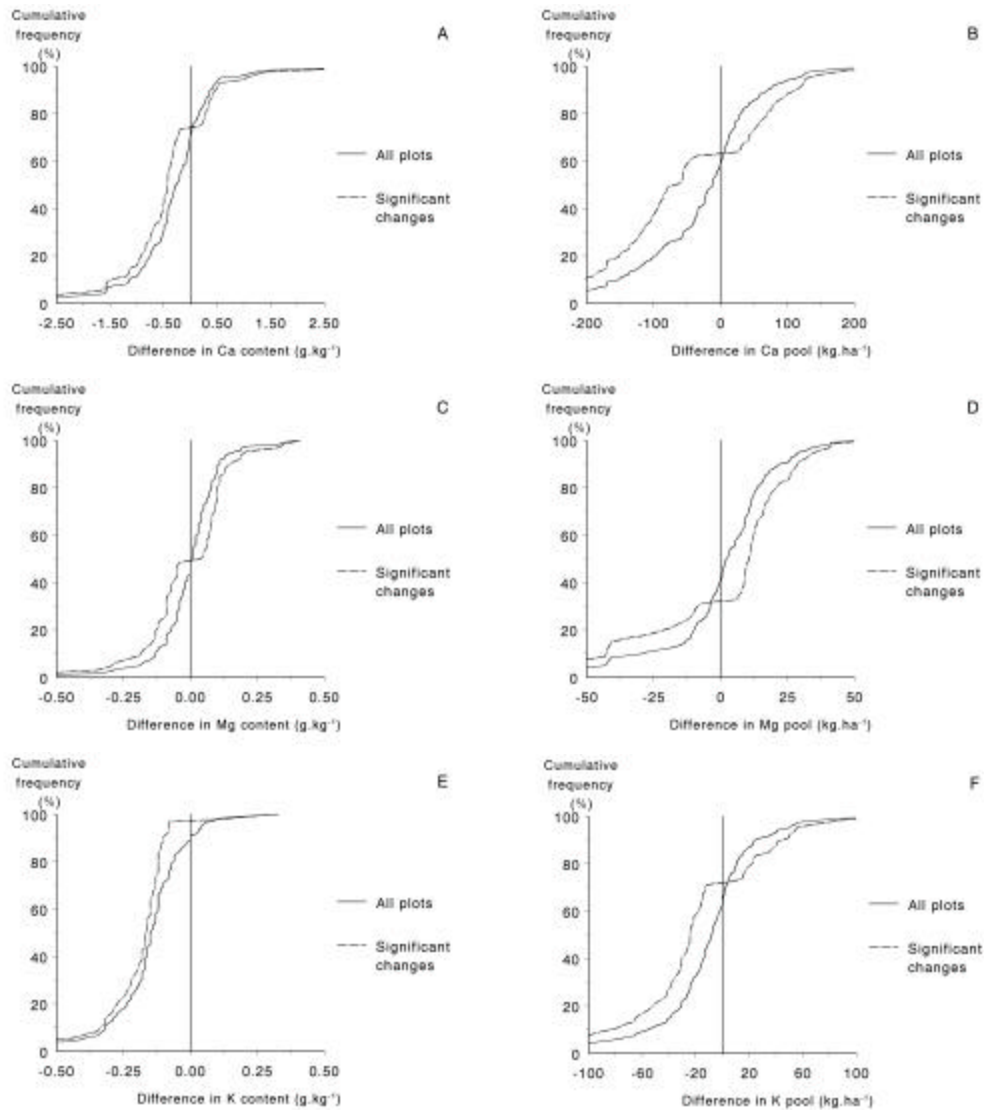


Figure 8 Cumulative frequency distributions of the measured differences in contents and pools of calcium (A, B), magnesium (C, D) and potassium (E, F) per plot, for all plots and for those plots where the differences were significant

Differences in the calcium content in the humus layer per plot varied between a decrease and an increase of approximately 5 g.kg^{-1} (Figure 8A). The significant changes are almost equal to the changes in all plots. Decreases were found in approximately 70% of the plots and increases in approximately 30% of the plots, indicating a decrease of the calcium contents in the humus layer in 1995 compared to 1990. Differences in the calcium pools in the humus layer varied per plot between a decrease or increase of approximately 400 kg.ha^{-1} (Figure 8B). Here the significant

changes are also almost equal to the changes in all plots. Decreases were found in approximately 60% of the plots and increases in approximately 40% of the plots, indicating a small decrease of the calcium pools in the humus layer in 1995 compared to 1990.

Differences in the magnesium content in the humus layer per plot varied between a decrease and an increase of approximately 0.5 g.kg^{-1} (Figure 8C). The significant changes are almost equal to the changes in all plots. Decreases were found in approximately 45% of the plots and increases also in approximately 55% of the plots, indicating a very small increase of the magnesium contents in the humus layer in 1995 compared to 1990. Differences in the magnesium pools in the humus layer varied per plot between a decrease of 100 kg.ha^{-1} or and increase of 60 kg.ha^{-1} (Figure 8D). Here the significant changes are also almost equal to the changes in all plots. Decreases were found in approximately 40% of the plots and increases in approximately 60% of the plots, indicating a small increase of the magnesium pools in the humus layer in 1995 compared to 1990.

Differences in the potassium content in the humus layer per plot varied between a decrease or an increase of approximately 0.5 g.kg^{-1} (Figure 8E). The significant changes are greater than the changes in all plots. Decreases were found in almost 100% of the plots. Differences in the potassium pools in the humus layer varied per plot between a decrease or an increase of approximately 100 kg.ha^{-1} (Figure 8F). Here the significant changes are also greater than the changes in all plots. Decreases were found in approximately 75% of the plots and increases in approximately 25% of the plots, indicating a clear increase of the potassium pools in the humus layer in 1995 compared to 1990.

7.2 Soil acidity and exchangeable cations in the humus layer

7.2.1 Mean differences in soil acidity and exchangeable cations

According to Table 59 the average pH-H₂O increased significantly by 0.1 over the 5 years and the pH-KCl did not change. One would expect the same effect for both pH measurements. This illustrates that unknown measurement errors and standard deviations do influence the results. It is difficult to draw a distinction between the real change and the change caused by natural deviation and measurement errors. Therefore one has to be careful with the conclusions that can be taken from this results. The relative pH changes on average are zero. Nevertheless, changes in pH-H₂O and pH-KCl were calculated to be significant (see Eq. 1 and 2 in Section 2.5) at approximately 50% of the plots (Table 60). The results show a decrease of the CEC, although not significant, being in line with the decrease in organic matter content (Table 53).

Table 59 Mean of the differences of the pH, CEC and exchangeable cation content (in percentage of the CEC) of the humus layer under seven major tree species between 1995 and 1990 at all plots

Tree species	Mean difference										
	pH- H ₂ O	pH- KCl	CEC (mol.c.kg ⁻¹)	H (%)	Al (%)	Fe (%)	Ca (%)	Mg (%)	K (%)	Na (%)	NH ₄ (%)
Scots pine	0.1	0.0	-34	3.2	-0.33	3.4	-2.8	0.22	-2.5	-0.64	0.41
Black pine	0.1	-0.1	-3.9	0.38	0.97	4.2	0.0	-0.33	-2.8	-1.1	-1.1
Douglas fir	-0.0	0.0	-16	0.91	0.0	2.9	-0.39	0.28	0.12	-1.2	-1.5
Norway spruce	0.2	0.0	4.6	5.6	-1.2	0.63	-1.6	0.34	-3.2	-1.0	0.51
Japanese larch	0.0	0.0	-1.2	6.7	-0.93	1.3	-3.3	0.24	-2.1	-1.0	-0.77
Oak	0.1	0.0	9.3	1.8	-1.3	1.1	-0.50	1.4	-2.4	-0.14	0.02
Beech	0.3	0.2	50	1.8	-2.7	1.6	2.5	0.30	-2.7	-0.96	0.05
Total	0.1	0.0	-4.3	2.9	-0.76	2.3	-1.2	0.40	-2.3	-0.78	-0.14

A grey background indicates that the difference is significant ($t > 2.0$) or very significant ($t > 3.3$)

Table 60 Number of plots in which the differences of the pH, CEC and exchangeable cation content of the humus layer between 1995 and 1990 were significant for the different tree species.

Tree species	Number of plots in which the changes were significant										
	pH- H ₂ O	pH- KCl	CEC	H	Al	Fe	Ca	Mg	K	Na	NH ₄
Scots pine	1	1	20	20	30	31	23	27	33	29	23
Black pine	0	2	6	10	9	10	9	10	12	9	10
Douglas fir	1	1	7	9	10	10	8	11	11	12	8
Norway spruce	1	1	3	9	9	11	7	10	13	12	13
Japanese larch	0	0	4	10	5	10	8	7	13	12	10
Oak	1	1	11	16	15	18	18	15	18	17	15
Beech	1	2	9	13	11	13	11	11	14	13	13
Total	5	8	60	87	89	103	84	91	114	104	92

The significant increase of exchangeable H is in contradiction with the observation that the pH has risen. The overall conclusion is thus that there is no clear evidence to say that the pH has increased due to the decrease in acid deposition in the period 1990-1995.

As with the total contents, the exchangeable contents of Ca and K decreased and for K this was on average significant. The same was found for Na. Inversely, the average Fe content increased significantly (Table 59). The decrease in base saturation, combined with increase in H and Fe saturation (at the expense of a decrease in Al) would imply an ongoing acidification of the soils. This is, however, not in line with the relatively constant pH. In relative terms, the changes in Fe, K and Na are very high. For Fe, the average relative increase is 69% and for K and Na the average relative decreases are 46% and 31%, respectively. For the exchangeable cations, the numbers of plots for which the changes are significant vary generally between 70 and 80% (Table 60).

As with the contents, the average pool of Fe did increase significantly, whereas the average pools of K and Na decreased significantly (Table 61). The decrease in base cation pools and the (not significant) increase in H pools is on average less than 1

kmol_c.ha⁻¹ in 5 years being less than 200 mol_c.ha⁻¹.yr⁻¹. Considering the average acid input of near 5 kmol_c.ha⁻¹.yr⁻¹ in this period, such a change is not unlikely. The average increase in Fe pools seems large, however. Specifically under black pine the increase was unlikely with pools in 1995 being four times higher as in 1990. In general the results for this tree species are deviating from all other tree species. As with the CEC and exchangeable cation contents the changes in CEC pools were significant at approximately 50% of the plots and for the exchangeable cation pools it varied mostly between 60 and 80 % (Table 62). The average changes for those plots were slightly higher than those at all plots.

Table 61 Mean of the differences of the exchangeable cation and CEC pool in the humus layer under seven major tree species between 1995 and 1990 for all plots

Tree species	Mean difference (kmol _c .ha ⁻¹)									
	H	Al	Fe	Ca	Mg	K	Na	NH ₄	CEC	
Scots pine	0.66	-0.27	0.61	-0.80	0.06	-0.73	-0.20	-0.07	-1.0	
Black pine	3.3	0.69	1.3	1.9	0.45	-0.10	-0.08	0.13	7.6	
Douglas fir	-0.80	0.21	1.3	-1.2	-0.22	0.46	-0.33	-0.54	-1.5	
Norway spruce	1.3	-0.37	0.19	-0.64	0.07	-0.91	-0.28	-0.02	-0.70	
Japanese larch	0.74	-0.43	0.48	-1.8	-0.20	-0.72	-0.45	-0.45	-2.9	
Oak	-0.95	-0.56	0.22	-0.29	0.24	-0.68	-0.09	-0.17	-2.2	
Beech	1.3	-0.47	1.3	0.64	0.20	-0.81	-0.33	-0.03	1.8	
Total	0.66	-0.23	0.71	-0.41	0.09	-0.56	-0.23	-0.13	-0.20	

A grey background indicates that the difference is significant ($t > 2.0$) or very significant ($t > 3.3$)

Table 62 Number of plots in which the differences of the exchangeable cation and CEC pool in the humus layer between 1995 and 1990 were significant for the different tree species.

Tree species	Number of plots in which the changes were significant									
	H	Al	Fe	Ca	Mg	K	Na	NH ₄	CEC	
Scots pine	22	22	29	19	21	26	24	20	19	
Black pine	7	5	10	8	7	9	9	12	8	
Douglas fir	4	11	9	5	7	11	8	6	6	
Norway spruce	7	6	10	6	5	13	9	10	4	
Japanese larch	7	8	10	5	8	13	10	11	7	
Oak	15	17	15	13	14	16	16	15	15	
Beech	11	10	12	8	8	12	12	10	9	
Total	73	79	95	64	70	100	88	84	68	

7.2.2 Frequency distributions of differences in exchangeable cations

Differences of CEC in the humus layer per plot varied between a decrease of 250 mmol_c.kg⁻¹ and an increase of approximately 200 mmol_c.kg⁻¹ (Figure 9A). The significant changes are greater than the changes in all plots. Differences smaller than approximately 65 mmol_c.kg⁻¹ were not significant. Significant decreases were found in approximately 50% of the plots and increases also in approximately 50% of the plots, indicating no significant differences in the CEC in the humus layer in 1995 compared to 1990, in line with the results presented earlier.

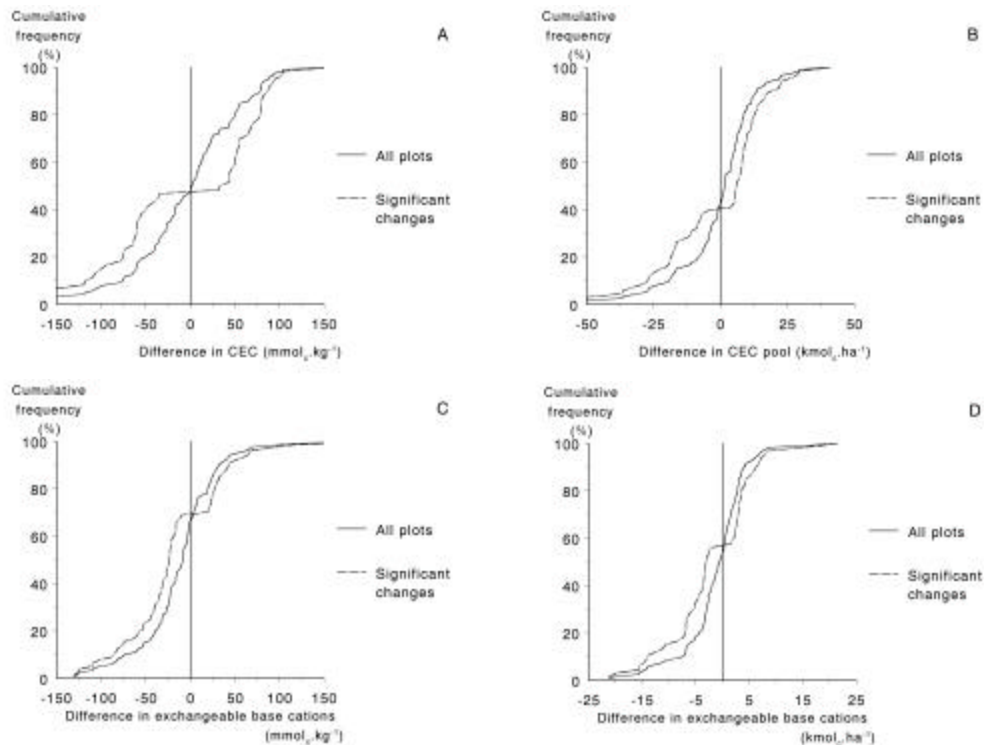


Figure 9 Cumulative frequency distributions of the measured differences in contents and pools of the CEC (A, B) and exchangeable base cations (C, D) per plot, for all plots and for those plots where the differences were significant

Differences in the pool of CEC in the humus layer per plot varied between a decrease and an increase of approximately $50 \text{ kmol}_c.\text{ha}^{-1}$ (Figure 9B). Significant decreases were found in approximately 40% of the plots and increases in approximately 60% of the plots. Nevertheless, the average CEC pool in the humus layer in 1995 did not increase compared to 1990 (see Table 61).

Differences of the exchangeable base cations in the humus layer per plot varied between a decrease of $125 \text{ mmol}_c.\text{kg}^{-1}$ and an increase of $250 \text{ mmol}_c.\text{kg}^{-1}$ (Figure 9C). Significant decreases were found in approximately 70% of the plots and increases in approximately 30% of the plots, indicating a decrease of the exchangeable base cations in the humus layer in 1995 compared to 1990, in line with the results in Table 59. Differences in the pool of the exchangeable base cations in the humus layer per plot varied between a decrease of $20 \text{ kmol}_c.\text{ha}^{-1}$ and an increase of $25 \text{ kmol}_c.\text{ha}^{-1}$ (Figure 9D). Significant decreases were found in approximately 55% of the plots and increases in approximately 45% of the plots, indicating a small decrease in the pools of exchangeable base cations in the humus layer in 1995 compared to 1990, in line with the results in Table 61.

7.3 Heavy metals in the humus layer

7.3.1 Mean differences in heavy metals

On average the average total contents of the heavy metals have decreased significantly with exception of Cr. (Table 63). Those decreases were relatively the highest for Ni (35%), followed by Cd and Pb (13 and 11%) and Zn and Cu (5 and 3%). The decreases of Pb, Cd and Ni were significant for almost all tree species, with hardly any variation between the species. The decrease in metal contents is in line with general decrease in metal deposition in the last decade, specifically with respect to Pb and Cd. The number of plots for which the changes were significant differed between approximately 80 and 95% (Table 64).

Table 63 Mean of the differences of the heavy metal content in the humus layer under seven major tree species between 1995 and 1990 for all plots

Tree species	Mean difference (mg.kg ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
Scots pine	-15	-0.16	-1.3	-16	-4.3	1.2
Black pine	-18	-0.03	-0.14	-9.5	-7.7	1.8
Douglas fir	-23	-0.13	-4.6	-4.0	-11	2.0
Norway spruce	-26	-0.18	-3.9	-9.2	-4.0	0.76
Japanese larch	-16	-0.19	-0.77	-4.7	-2.9	1.3
Oak	-17	-0.10	0.65	-5.8	-8.6	-0.41
Beech	-44	-0.10	-1.9	2.1	-6.0	-1.3
Total	-21	-0.13	-1.5	-8.3	-6.1	0.71

A grey background indicates that the difference is significant ($t > 2.0$) or very significant ($t > 3.3$)

Table 64 Number of plots in which the differences of the heavy metal content in the humus layer between 1995 and 1990 were significant for the different tree species.

Tree species	Number of plots in which the changes were significant					
	Pb	Cd	Cu	Zn	Ni	Cr
Scots pine	23	27	20	22	34	17
Black pine	11	7	10	6	12	10
Douglas fir	11	8	6	9	12	12
Norway spruce	11	11	9	8	13	8
Japanese larch	8	10	10	9	9	8
Oak	17	19	19	17	22	16
Beech	9	12	7	9	13	8
Total	90	94	81	80	115	79

As with the contents, the pools of Ni decreased significantly, and relatively almost as much as the contents (Table 65). For the other heavy metals there was no significant change for the average of the total pools. Even as with the contents, the Cd pools seem to decrease significantly under Norway spruce and Japanese larch and the Pb pools under Norway spruce and beech. Other than with the contents there is a significant increase of more than 100% of the Cu pools under black pine. This is, however, a result that is unlikely due to the unreliable increase in organic matter pool below this tree species (Table 55).

Table 65 Mean of the differences of the heavy metal pool in the humus layer under seven major tree species between 1995 and 1990 for all plots

Tree species	Mean difference (kg.ha ⁻¹)					
	Pb	Cd	Cu	Zn	Ni	Cr
Scots pine	0.43	0.00	0.17	0.67	-0.36	0.33
Black pine	2.6	0.04	0.59	2.9	-0.14	0.73
Douglas fir	-1.3	-0.01	-0.48	-0.87	-0.53	0.29
Norway spruce	-2.9	-0.02	-0.49	-1.4	-0.38	0.07
Japanese larch	-1.6	-0.02	-0.05	-0.35	-0.32	0.12
Oak	-2.0	-0.01	-0.09	-0.33	-0.30	-0.15
Beech	-4.7	-0.01	-0.25	-0.33	-0.58	-0.15
Total	-1.1	0.00	-0.05	0.09	-0.37	0.17

A grey background indicates that the difference is significant ($t > 2.0$) or very significant ($t > 3.3$)

Table 66 Number of plots in which the differences of the heavy metal pool in the humus layer between 1995 and 1990 were significant for the different tree species.

Tree species	Number of plots in which the changes were significant					
	Pb	Cd	Cu	Zn	Ni	Cr
Scots pine	28	33	25	26	33	24
Black pine	12	10	11	11	12	11
Douglas fir	13	11	10	10	13	13
Norway spruce	12	12	11	8	13	10
Japanese larch	12	11	12	12	11	10
Oak	19	22	21	20	22	22
Beech	12	14	10	11	13	11
Total	108	113	100	98	117	101

7.3.2 Frequency distributions of differences in heavy metals

Fig 10 shows frequency distributions of the differences in metal contents for all plots and for those plots where the differences were significant. Results hardly showed any difference.

Differences in the Pb content in the humus layer per plot varied mostly between a decrease and an increase of 100 mg.kg⁻¹ (Figure 10A). For Cd it varied mostly between a decrease and increase of approximately 0.75 mg.kg⁻¹ (Figure 10B). The significant changes were almost equal to the changes in all plots. For both metals, decreases were found in approximately 80% of the plots and increases in approximately 20% of the plots, indicating a decrease of the Pb and Cd content in the humus layer in 1995 compared to 1990, in line with the results presented in Table 63.

Differences in the Cu content in the humus layer per plot varied mostly between a decrease and an increase of 15 mg.kg⁻¹ (Figure 10C). For Zn it varied mostly between a decrease and increase of approximately 100 mg.kg⁻¹ (Figure 10D). Decreases were found in approximately 60% of the plots and increases in approximately 40% of the plots, indicating a small decrease of the Cu and Zn content in the humus layer in 1995 compared to 1990, in line with the results presented in Table 63.

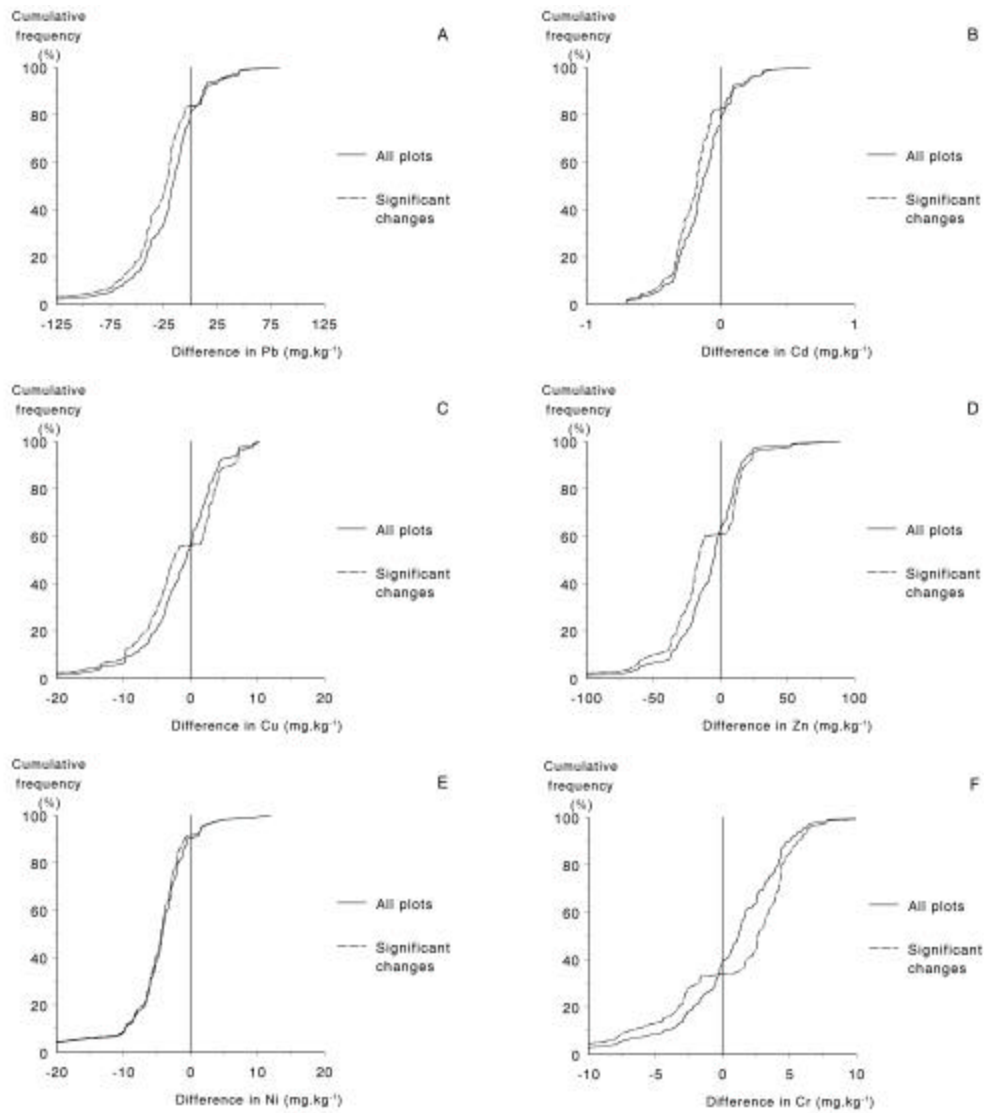


Figure 10 Cumulative frequency distributions of the measured differences in the contents of lead (A), cadmium (B), copper (C), zinc (D), nickel (E) and chrome (F) in the humus layer per plot, for all plots and for those plots where the differences were significant

Differences in the Ni content in the humus layer per plot varied mostly between a decrease and an increase of 20 mg.kg⁻¹ (Figure 10E). Decreases were found in approximately 90% of the plots, where most plots had a decrease between 0 and 20 mg.kg⁻¹. Several plots however show extremely high decreases up to 100 mg.kg⁻¹. Increases were found in approximately 20% of the plots. This indicates a major decrease of the nickel content in the humus layer in 1995 compared to 1990, in line with the results presented in Table 63. Differences in the Cr content in the humus layer per plot varied between mostly between a decrease and increase of approximately 10 mg.kg⁻¹ (Figure 10F). Decreases were found in approximately 40% of the plots and increases in approximately 60% of the plots, indicating a small increase of the chrome content in the humus layer in 1995 compared to 1990 (compare Table 63).

Frequency distributions of the differences in metal contents for all plots and for those plots where the differences were significant are presented in Fig 11. Results hardly showed any difference.

The Pb pools in the humus layer per plot varied mostly between a decrease and an increase of 20 kg.ha⁻¹ (Figure 11A), but several plots had a large decrease or increase up to 30 kg.ha⁻¹. For Cd it varied mostly between a decrease and increase of approximately 0.12 kg.ha⁻¹ (Figure 11B), but several plots had a large increase of 20 kg.ha⁻¹. Decreases were found in approximately 60% of the plots and increases in approximately 40% of the plots.

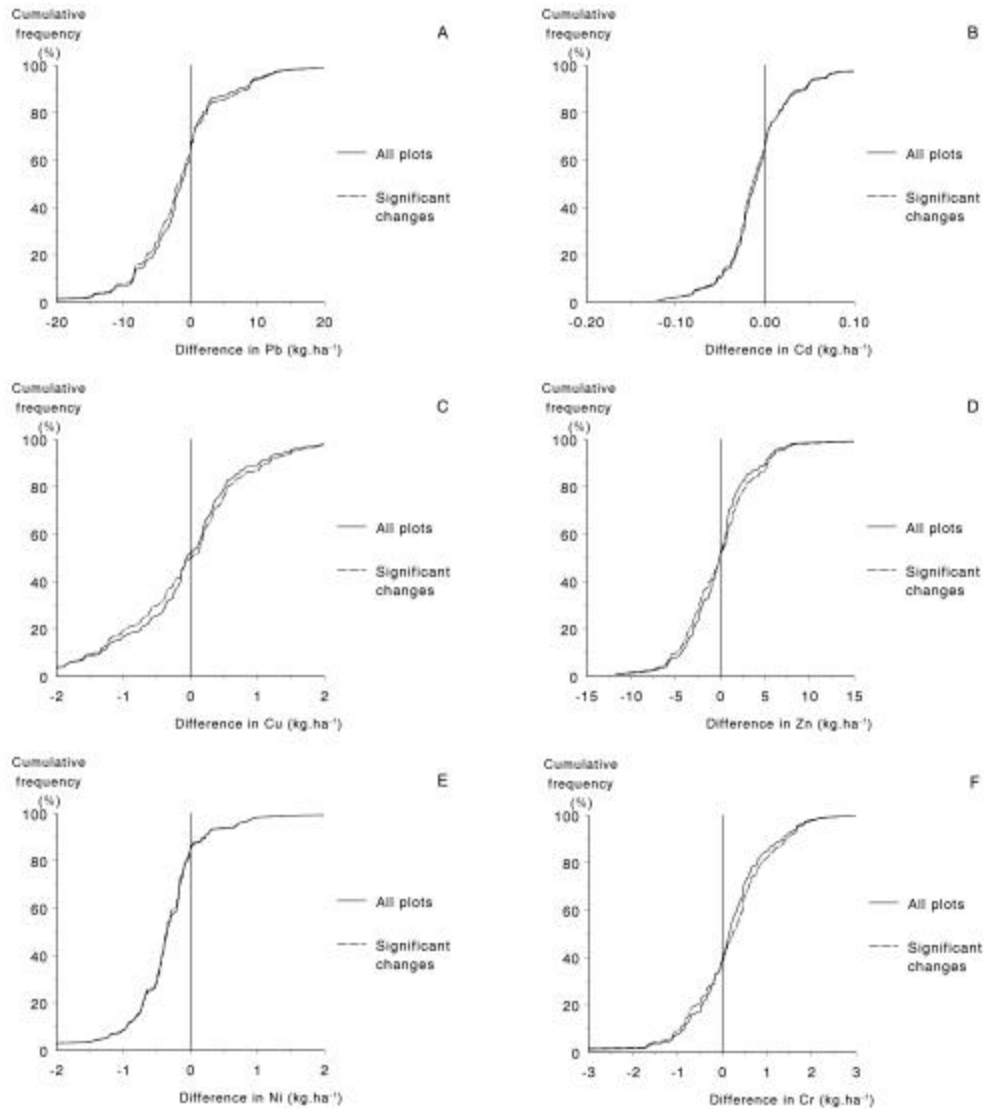


Figure 11 Cumulative frequency distributions of the measured differences in the pools of lead (A), cadmium (B), copper (C), zinc (D), nickel (E) and chrome (F) in the humus layer per plot, for all plots and for those plots where the differences were significant

As shown before, there is indeed a small average decrease in the Pb pool in the humus layer in 1995 compared to 1990 (Table 65), but this is not the case for the Cd pool.

Differences in the copper pools in the humus layer per plot varied mostly between a decrease and an increase of $2 \text{ kg}\cdot\text{ha}^{-1}$ (Figure 11C) but several plots had large increases up to $5.5 \text{ kg}\cdot\text{ha}^{-1}$. Differences in the zinc pools in the humus layer per plot varied mostly between a decrease and an increase of $15 \text{ kg}\cdot\text{ha}^{-1}$ (Figure 11D) but several plots had large decreases up to $30 \text{ kg}\cdot\text{ha}^{-1}$ while most plots had decreases between 0 and $10 \text{ kg}\cdot\text{ha}^{-1}$. Decreases were found in approximately 50% of the plots and increases also in approximately 50% of the plots, indicating no changes in the Cu and Zn pools in the humus layer in 1995 compared to 1990 (compare Table 65).

Differences in the Ni pools in the humus layer per plot varied mostly between a decrease and an increase of $2 \text{ kg}\cdot\text{ha}^{-1}$ (Figure 11E), but some plots had decreases up to $5.5 \text{ kg}\cdot\text{ha}^{-1}$ and increases up to $4.5 \text{ kg}\cdot\text{ha}^{-1}$. Decreases were found in approximately 90% of the plots and increases also in approximately 10% of the plots, indicating a clear decrease of the nickel pools in the humus layer in 1995 compared to 1990.

Differences in the Cr pools in the humus layer per plot varied mostly between a decrease and an increase of $3 \text{ kg}\cdot\text{ha}^{-1}$ (Figure 11F), but several plots had large decreases up to $5 \text{ kg}\cdot\text{ha}^{-1}$. Decreases were found in approximately 40% of the plots and increases in approximately 60% of the plots, indicating a small increase in the Cr pools in the humus layer in 1995 compared to 1990 (compare Table 65).

7.4 Soil solution chemistry in the mineral layer

7.4.1 Mean differences in soil solution chemistry

Results of the differences in soil solution chemistry showed that the average pH increased significantly under all tree species, whereas the average concentrations of all major cations and anions decreased significantly, when considering all plots (Table 67). The number of plots where the changes were significant varied from approximately 55-85%, depending on the ion considered (Table 68).

The Al, Ca and NH_4 concentration decreased significantly under almost all tree species with an average of 38%, 29% and 43% respectively. The change in NO_3 and SO_4 concentrations was not significant for all tree species. The decrease was also less, namely 3% and 7%. Very clearly is the overall decrease of Cl with percentages up to 75. This is most likely a more important reason for the decrease in ion concentrations than the decrease in acid deposition over this period.

For a good comparison of the differences the concentrations should be corrected for the impact of hydrology (humidity). One possibility for correcting the impact of humidity is to calculate the amount of elements in the root zone by multiplying the concentrations with the moisture content. Unfortunately, the moisture content was

not measured in 1990 and such a comparison could thus not be made. A possibility for correcting the impact of hydrological differences is to scale all ions to the Cl concentration. Applying this approach on the available data lead to the conclusion that relative to Cl all major ions have increased. This is, however, due to the fact that Cl concentrations in 1990 were extremely high in the forest topsoil due to extremely high Cl inputs in early spring (De Vries and Jansen, 1994). The differences are thus not a clear indication of a much dryer situation in 1990 than in 1995. Correcting for or scaling to chloride concentrations is therefore only an acceptable approach in an intensive monitoring approach (e.g. biweekly measurements) over a long-term period (several years) in which the Cl budget can be assumed to be zero (input equals output). With one single measurement in 1990 and 1995 one would come to wrong interpretations.

The most important indication of a positive response of the soil solution chemistry to a decrease in S and N deposition in the period between 1990 and 1995 is the decrease in the ratio's of aluminium to calcium and of ammonium to potassium. This is a clear indication for an improvement of the environmental circumstances in the root zone. Furthermore, the larger decrease in the average SO_4 concentration ($0.53 \text{ mol}_c.\text{m}^{-3}$) compared to the sum of the NH_4 and NO_3 concentration ($0.35 \text{ mol}_c.\text{m}^{-3}$) is a clear indication of the positive response to the larger decrease in S deposition compared to the decrease in N deposition in this period.

Table 67 Mean of the differences of de element concentrations and ratios for the mineral layer 0 -30 cm under seven major tree species between 1995 and 1990 for all plots

Tree species	Concentration ($\text{mol}_c.\text{m}^{-3}$)							Ratio ($\text{mol}.\text{mol}^{-1}$)	
	pH	Al	Ca	NH_4	NO_3	SO_4	Cl	Al/Ca	NH_4/K
Scots pine	0.2	-0.37	-0.13	-0.14	-0.08	-0.06	-0.85	-0.26	-0.53
Black pine	0.2	-0.35	-0.16	-0.18	-0.13	0.07	-0.7	-0.47	-0.21
Douglas fir	0.2	-1.32	-0.53	-0.42	-0.13	-1.67	-1.75	-0.41	-0.08
Norway spruce	0.2	-1.49	-0.4	-0.31	-0.34	-2.15	-1.52	-0.45	-1.07
Japanese larch	0.2	-0.38	-0.27	-0.2	-0.29	-0.42	-1.13	-0.07	-0.19
Oak	0.2	-0.09	-0.53	-0.1	-0.19	-0.41	-0.7	0.06	-0.26
Beech	0.2	-0.21	-0.06	-0.09	-0.11	-0.04	-0.8	-0.35	-0.21
Total	0.2	-0.52	-0.29	-0.18	-0.17	-0.53	-0.99	-0.25	-0.39

A grey background indicates that the difference is significant ($t > 2.0$)

or very significant ($t > 3.3$)

Table 68 Number of plots in which the differences of de element concentrations for the mineral layer 0 -30 cm between 1995 and 1990 were significant for the different tree species.

Tree species	Number of plots in which the changes were significant						
	H	Al	Ca	NH_4	NO_3	SO_4	Cl
Scots pine	29	32	29	18	21	23	28
Black pine	7	11	10	8	7	9	9
Douglas fir	11	13	12	7	4	13	11
Norway spruce	7	10	12	10	8	10	12
Japanese larch	9	12	13	11	7	10	12
Oak	18	17	18	14	14	13	22
Beech	12	10	9	11	9	8	13
Total	93	105	103	79	70	86	107

7.4.2 Frequency distributions of differences in soil solution chemistry

Frequency distributions of the concentrations of major cation and anions in the mineral layer (0-30 cm) in 1995 and 1990 for all plots and for those plots where the changes were significant are presented in Figure 12. Concentrations of SO_4 in the mineral layer (0-30 cm) varied between mostly between 0.5 and 5 $\text{mol}_c\text{.m}^{-3}$ with extremes up to 10 $\text{mol}_c\text{.m}^{-3}$. Approximately 90% of the plots had concentrations below 2.5 $\text{mol}_c\text{.m}^{-3}$ in 1990 and below 1 $\text{mol}_c\text{.m}^{-3}$ in 1995 (Figure 12A), indicating that the concentrations of SO_4 in the mineral layer were lower in 1995 than in 1990.

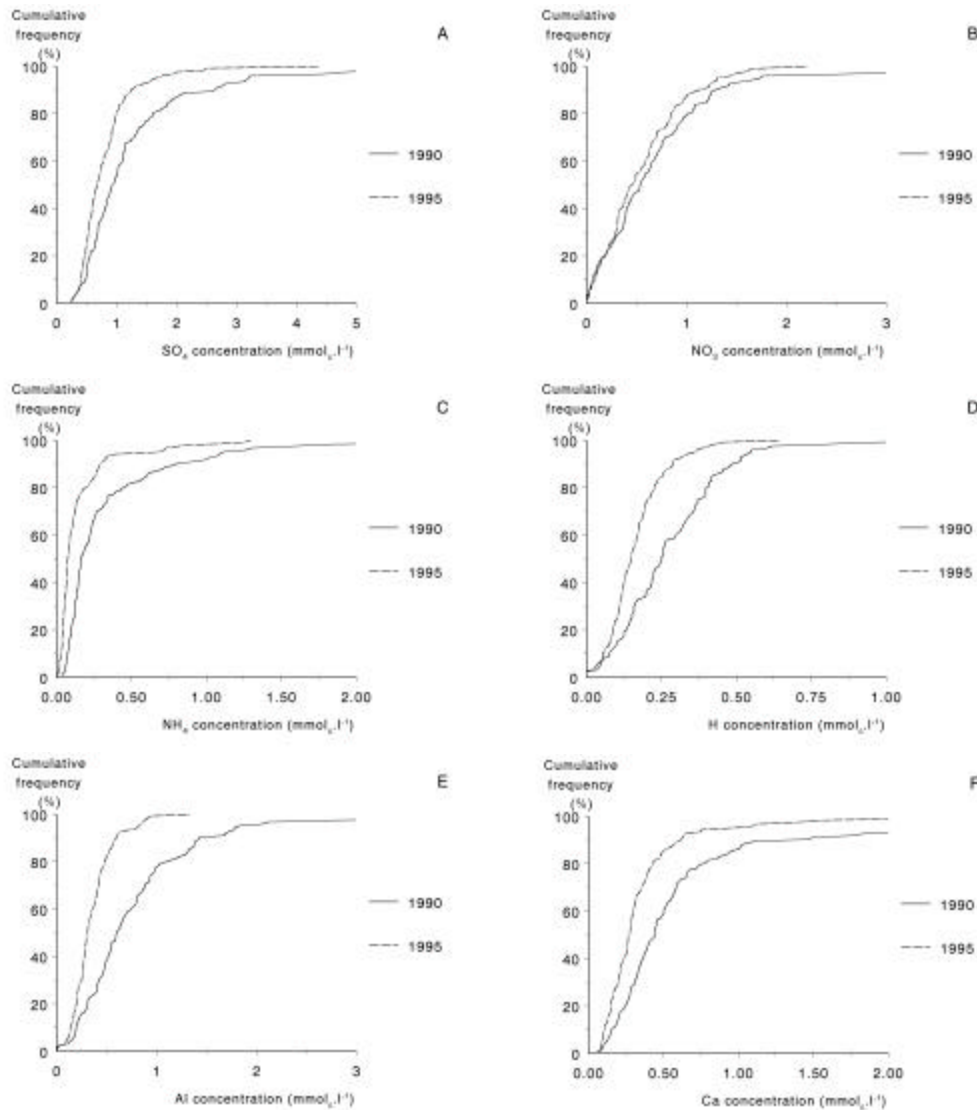


Figure 12 Cumulative frequency distributions for the concentrations of SO_4 (A), NO_3 (B), NH_4 (C), H (D), Al (E) and Ca (F) in the mineral layer (0-30 cm) for the locations measured in both 1990 and 1995

Concentrations of NO_3 in the mineral layer varied mostly between 0 and 3 $\text{mol}_c\text{.m}^{-3}$ (Figure 12B). Here also approximately 90% of the plots had concentrations below 1.5 $\text{mol}_c\text{.m}^{-3}$, while approximately 10% had values up to 6 $\text{mol}_c\text{.m}^{-3}$, especially in

1990. Concentrations of NO_3 in the mineral layer were generally slightly lower in 1995 than in 1990. Concentrations of NH_4 in the mineral layer varied mostly between 0 and $2 \text{ mol}_c.\text{m}^{-3}$ (Figure 12C). Approximately 90% of the plots varied between 0 and $0.25 \text{ mol}_c.\text{m}^{-3}$ in 1995 and between 0 and $1 \text{ mol}_c.\text{m}^{-3}$ for 1990. Approximately 10% of the plots had high values up to $3.5 \text{ mol}_c.\text{m}^{-3}$, especially in 1990. Concentrations of NH_4 in the mineral layer were lower in 1995 than in 1990.

Concentrations of H in the mineral layer varied mostly between 0 and $1 \text{ mol}_c.\text{m}^{-3}$ (Figure 12D). Almost all plots had values between 0 and $0.5 \text{ mol}_c.\text{m}^{-3}$. Several plots however, especially in 1990, had high values up to $1.7 \text{ mol}_c.\text{m}^{-3}$. Concentrations of H in the mineral layer were lower in 1995 than in 1990. Concentrations of Al in the mineral layer varied mostly between 0 and $3 \text{ mol}_c.\text{m}^{-3}$ (Figure 12E), but several plots, especially in 1990, had high values up to $5 \text{ mol}_c.\text{m}^{-3}$. Concentrations of Al in the mineral layer were lower in 1995 than in 1990. Concentrations of Ca in the mineral layer varied between 0 and $2 \text{ mol}_c.\text{m}^{-3}$ (Figure 12F), but extreme values up to $4 \text{ mol}_c.\text{m}^{-3}$ were observed. Concentrations of Ca in 1995 were lower than in 1990.

Frequency distributions of the differences in concentrations of major cation and anions in the mineral layer (0-30 cm) in 1995 and 1990 for all plots and for those plots where the changes were significant are presented in Figure 13. The significant changes were a little bit higher than the changes in all plots.

Differences in SO_4 concentrations in the mineral layer (0-30 cm) per plot varied between a decrease and an increase of $3 \text{ mol}_c.\text{m}^{-3}$ (Figure 13A). Significant decreases were found in approximately 80% of the plots and increases in approximately 20% of the plots, indicating a decrease of the SO_4 concentration in the mineral layer in 1995 compared to 1990.

Differences in NO_3 concentrations in the mineral layer per plots varied mostly between a decrease or increase of approximately $2.5 \text{ mol}_c.\text{m}^{-3}$ (Figure 13B). Significant decreases were found in approximately 60% of the plots and increases in approximately 40% of the plots, indicating a small decrease of the NO_3 concentration in the mineral layer in 1995 compared to 1990. Differences in NH_4 concentrations in the mineral layer per plots varied between a decrease of $2.0 \text{ mol}_c.\text{m}^{-3}$ and an increase of $0.5 \text{ mol}_c.\text{m}^{-3}$ (Figure 13C). Significant decreases were found in approximately 90% of the plots and increases in approximately 10% of the plots, indicating a clear decrease of the NH_4 concentration in the mineral layer in 1995 compared to 1990.

Differences in H concentrations in the mineral layer per plots varied between a decrease of $1.5 \text{ mol}_c.\text{m}^{-3}$ and an increase of $0.2 \text{ mol}_c.\text{m}^{-3}$ (Figure 13D). Significant decreases were found in approximately 90% of the plots and increases in approximately 10% of the plots, indicating a clear decrease of the H concentration in the mineral layer in 1995 compared to 1990. Differences in Al concentrations in the mineral layer per plots varied mostly between a decrease of $2 \text{ mol}_c.\text{m}^{-3}$ and an increase of $0.1 \text{ mol}_c.\text{m}^{-3}$ (Figure 13E). Significant decreases were found in approximately 99% of the plots and increases in approximately 1% of the plots,

indicating a clear decrease of the Al concentration in the mineral layer in 1995 compared to 1990. Differences in Ca concentrations in the mineral layer per plots varied mostly between a decrease of $1.0 \text{ mol}_c \cdot \text{m}^{-3}$ and an increase of $0.5 \text{ mol}_c \cdot \text{m}^{-3}$ (Figure 13F). Significant decreases were found in approximately 90% of the plots and increases in approximately 10% of the plots, indicating a clear decrease of the Ca concentration in the mineral layer in 1995 compared to 1990.

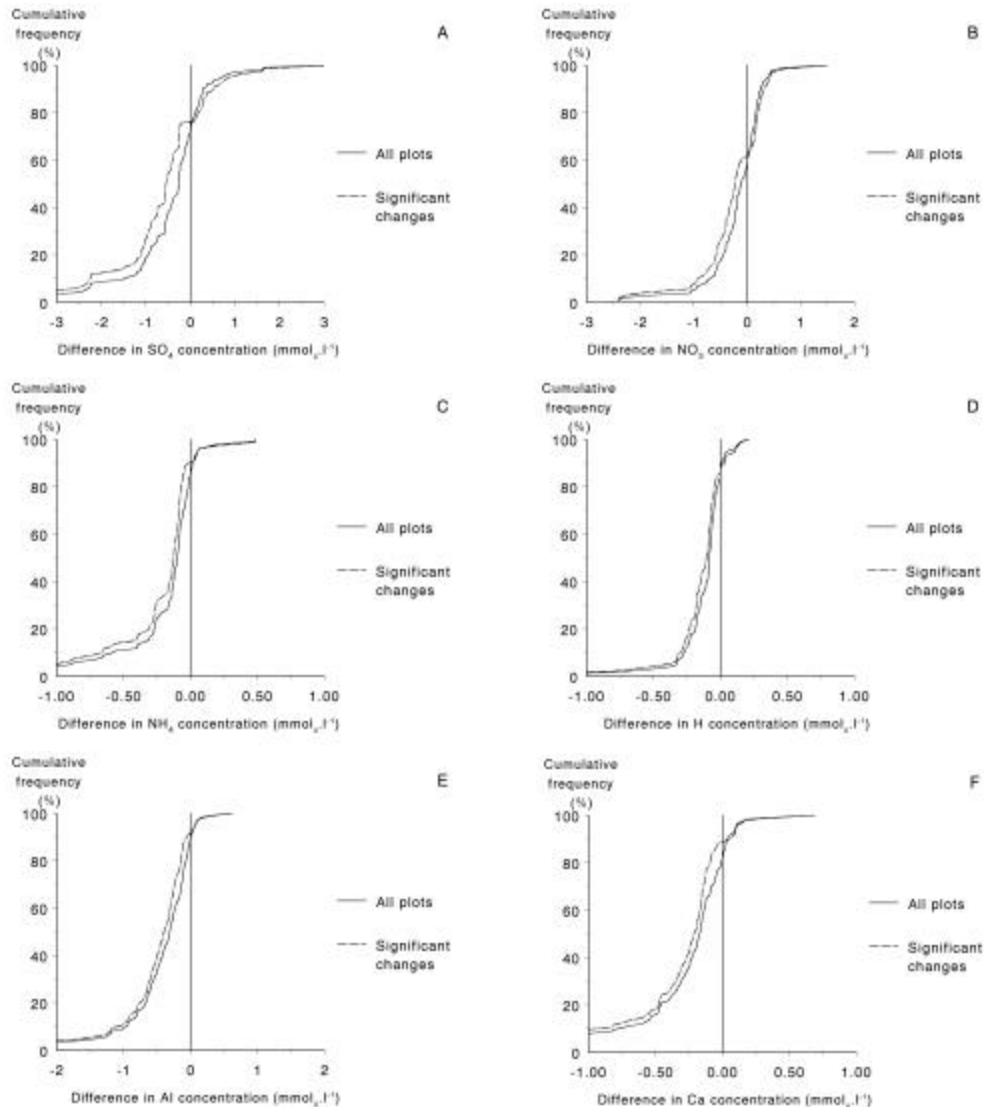


Figure 13 Cumulative frequency distributions of the measured differences in concentrations of SO₄ (A), NO₃ (B), NH₄ (C), H (D), Al (E) and Ca (F) in the mineral layer (0-30 cm) for all plots and for those plots where the differences were significant

7.5 Summary and conclusions

Here we summarise the difference in results in 1990 and 1995 for the humus layer (solid phase chemistry data) and the mineral layer (soil solution chemistry), focusing on key parameters that in principle do react on changes in the atmospheric

deposition of sulphur, nitrogen and heavy metals. We thus present the results for the year 1990 and 1995 and the differences for the 124 stands that were identical. Furthermore, the significance of the average changes is discussed. The results for the differences in the total C, N and P contents and pools in the mineral topsoil (0-30cm) are not discussed anymore, since the repetition does not give reliable results because of the large amount of soil in a layer of 30 cm. For example, an increase of 0.01% (0.1 g.kg⁻¹), being the case for N, leads to an increase of several hundreds of kilograms, being unreliable. These results indicate that monitoring a mineral layer of this thickness during a relatively short time period is not adequate.

The chemical composition of the humus layer

Average contents and pools of key parameters in the humus layer of 124 forest stands in 1990 and 1995 and their differences are presented in Table 69. Results are limited to key parameters that do give an indication of eutrophication (major nutrients N and P), acidification (total contents of Ca, Mg and K, pH, CEC exchangeable bases and protons) and heavy metal depositions (Pb, Cd, Cu, Zn, Ni and Cr). Results are not presented as a function of tree species as it was done in the previous sections, since it is highly questionable whether those results can be interpreted in terms of differences in tree species impacts. It is more likely that those differences are just due to spatial variability and uncertainties in the measurements of the key parameters. The reliability of average changes will increase with an increase in the number of stands involved and as such, the overall differences for all 124 stands are more likely than those for tree species, which are often based on approximately 10-15 stands.

Table 69 Average contents and pools of major nutrients, pH, exchangeable cations and heavy metals in the humus layer of 124 forest stands in 1990 and 1995 and their differences (1995-1990).

Element	Content (mass.kg ⁻¹)				Pool (mass.ha ⁻¹)			
	Unit	1990	1995	Difference	Unit	1990	1995	Difference
<i>Nutrients</i>								
OM	g.kg ⁻¹	651	634	-16.7	ton.ha ⁻¹	62.6	62.0	-0.65
N	g.kg ⁻¹	14.4	13.7	-0.677 s	kg.ha ⁻¹	1386	1332	-53
P	g.kg ⁻¹	0.562	0.530	-0.032 s	kg.ha ⁻¹	53.2	52.3	-0.92
Ca	g.kg ⁻¹	2.30	2.00	-0.299 s	kg.ha ⁻¹	202	177	-24.7 s
Mg	g.kg ⁻¹	0.448	0.448	-0.000	kg.ha ⁻¹	42.9	43.2	0.30
K	g.kg ⁻¹	0.788	0.625	-0.163 s	kg.ha ⁻¹	78.0	64.1	-13.9 s
<i>Acidity</i>								
pH-H ₂ O	-	3.87	3.97	0.10 s	-	-	-	-
pH-KCl	-	2.90	2.91	0.005	-	-	-	-
CEC	mmolc.kg ⁻¹	299	295	-4.3	kmolc.ha ⁻¹	29.6	29.4	-0.20
Bases	mmolc.kg ⁻¹	122	111	-11.0 s	kmolc.ha ⁻¹	11.6	10.4	-1.12 s
Protons	mmolc.kg ⁻¹	129	136	7.6 s	kmolc.ha ⁻¹	13.2	13.9	0.66
<i>Metals</i>								
Pb	mg.kg ⁻¹	116	95	-21.1 s	kg.ha ⁻¹	11.5	10.4	-1.15
Cd	mg.kg ⁻¹	0.80	0.67	-0.13 s	kg.ha ⁻¹	0.075	0.071	-0.004
Cu	mg.kg ⁻¹	19.9	18.4	-1.45 s	kg.ha ⁻¹	2.00	1.94	-0.053
Zn	mg.kg ⁻¹	89.2	80.9	-8.3 s	kg.ha ⁻¹	8.27	8.36	0.09
Ni	mg.kg ⁻¹	13.7	7.6	-6.1 s	kg.ha ⁻¹	1.19	0.82	-0.37 s
Cr	mg.kg ⁻¹	14.0	14.7	0.71 s	kg.ha ⁻¹	1.38	1.55	0.17

The results that are obtained when considering all plots together, as presented in Table 69, show (see also the conclusions that were drawn before in the various sections in Chapter 7):

- A rather constant pool of organic matter, while the organic matter content decreased with nearly 17 g.kg^{-1} . The latter result implies that the contamination with mineral soil was slightly higher in 1995 than in 1990, leading to a larger pool of total mass in the organic layer in 1995
- An average decrease in all nutrient contents and nutrient pools in the humus layer, except for Mg. Changes in nutrient contents were significant for all nutrients except Mg, whereas changes in nutrient pools were only significant for Ca and K.
- An average significant increase in pH-H₂O by 0.1 over the 5 year-period, whereas the pH-KCl did hardly change.
- A rather constant pool of exchangeable cations (total CEC), whereas the contents and pools of exchangeable bases decreased significantly while the contents and pools of exchangeable protons increased.
- A significant decrease in the average total contents of all heavy metals, except Cr, whereas a significant decrease in pools was only found for Ni.

In general, the results do indicate:

- A release in N from the humus layer in response to the decrease in N deposition in the period 1990-1995. The decrease in N content of approximately 0.68 g.kg^{-1} and in N pool of $11 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ ($53 \text{ kg N.ha}^{-1}.\text{yr}^{-1}$ in 5 year) seems likely, although the difference is not statistically significant with respect to pools.
- An ongoing acidification, considering the decrease in total pools of Ca and K and the decrease in base saturation, combined with increase in H saturation, despite the decrease in acid deposition between 1990 and 1995. The relatively constant pH-KCL and even the small increase in pH-H₂O is, however, not in line with these results. The decrease of approximately $5 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ for Ca seems possible but the decrease of nearly $3 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ for K is questionable, since K leaches very fast from the freshly fallen litter and the period in which the samples were taken might have influenced this result. The decrease in base cation pools and the increase in H pools of less than $1 \text{ kmol}_c.\text{ha}^{-1}$ in 5 years, being less than $200 \text{ mol}_c.\text{ha}^{-1}.\text{yr}^{-1}$, seems likely in view of the average acid input near $5 \text{ kmol}_c.\text{ha}^{-1}.\text{yr}^{-1}$ in this period.
- A release of heavy metals from the humus layer in response to the general decrease in metal deposition in the last decade, specifically with respect to Pb and Cd, although the results are not very convincing when pool changes are considered.

The above mentioned conclusions have to be considered with care. Spatial variability and uncertainties in the measurements of the key parameters influence the differences. The data for the humus layer are based on 10 samples per stand with an average reliability of the mean value of 80% (De Vries and Leeters, 2001), implying that changes between two samples can just be due to impacts of spatial variability on the mean value. Furthermore, soil sampling in 1990 was based on a systematic grid net while soil samples in 1995 were chosen near the trees of which the crown

condition was measured. The reliability of average changes do, however, increase with an increase in the number of stands involved and as such, significant differences for all 124 stands are a strong indication for average changes taking place in the forests. In general a 5-year period seems, however, too small for definite conclusions, specifically when distinctions are made in tree species or soil types.

The chemical composition of the soil solution in the mineral layer

Average values for pH and for concentrations and ratio's of major elements in the soil solution in the layer 0-30 cm for 124 stands in 1990 and 1995 and their differences are given in Table 70.

Table 70 Average values for pH, concentrations and ratio's in the soil solution in the layer 0-30 cm for 124 stands in 1990 and 1995 and their differences (1995-1990)

Parameter	Concentration/Ratio			
	Unit	1990	1995	Difference
pH	-	3.7	3.9	0.2
Al	mol _c .m ⁻³	0.88	0.36	-0.52
Ca	mol _c .m ⁻³	0.65	0.36	-0.29
Mg	mol _c .m ⁻³	0.32	0.16	-0.15
K	mol _c .m ⁻³	0.23	0.10	-0.13
Na	mol _c .m ⁻³	0.99	0.35	-0.64
NH ₄	mol _c .m ⁻³	0.33	0.15	-0.18
NO ₃	mol _c .m ⁻³	0.72	0.55	-0.17
SO ₄	mol _c .m ⁻³	1.35	0.81	-0.53
Cl	mol _c .m ⁻³	1.42	0.43	-0.99
KAT	mol _c .m ⁻³	3.73	1.68	-2.06
AN	mol _c .m ⁻³	3.77	1.87	-1.90
HCO ₃	mol _c .m ⁻³	-0.04	-0.19	-0.15
NH ₄ /K	mol.mol ⁻¹	1.83	1.43	-0.39
NH ₄ /Mg	mol.mol ⁻¹	2.27	2.19	-0.07
Al/Ca	mol.mol ⁻¹	1.26	1.01	-0.25
N/(N+S)	mol _c .mol _c ⁻¹	0.87	0.98	0.10

The most important conclusion that can be drawn from Table 70 is that there is a strong decrease in the concentration of all major cations and anions. On average, the decrease is larger in SO₄ than in NO₃, reflecting the larger decrease in S deposition than in N deposition. This has led to a decrease in the concentration of toxic Al and an increase in pH. This seems to indicate a positive response of the soil solution chemistry to the decreasing acid input.

This is, however, not an unambiguous proof, since the concentrations of Cl decreased even more strongly and thus the impact might be due to hydrological differences between the years. Scaling the concentrations of all ions to Cl even leads to the result that relative to Cl all major ions have increased. This is, however, due to the fact that Cl concentrations in 1990 were extremely high in the forest topsoil because of very high Cl inputs in early spring in that period. Neither the original nor the scaled concentrations thus give a good indication of a possible recovery (original concentrations) or worsening (scaled concentrations) of the soil solution chemistry.

The most important indication of a positive response of the soil solution chemistry to a decrease in S and N deposition in the period between 1990 and 1995 is the decrease in the ratio's of aluminium to calcium and of ammonium to potassium. This is a clear indication for an improvement of the environmental circumstances in the root zone. Furthermore, the larger decrease in the average SO_4 concentration ($0.53 \text{ mol}_c \cdot \text{m}^{-3}$) compared to the sum of the NH_4 and NO_3 concentration ($0.35 \text{ mol}_c \cdot \text{m}^{-3}$) is a clear indication of the positive response to the larger decrease in S deposition compared to the decrease in N deposition in this period.

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Appendix 1 Sampling method

Tracing the forest stand and marked trees

- The locations are pointed out on topographical maps. They are situated on intersections of co-ordinates, marked by a circle on the map.
- The place within the forest stand where the activities start, usually the South-West corner is indicated on the map by an arrow (sometimes outside the circle). From this point it is easy to find the marked trees.
- The trees are marked with yellow dots and metal number plates (mostly low at the surface) and divided in five groups of five. The first group (numbers 1-5) is situated in the South-West corner. These are border trees, they are not part of the sample area. The other groups (with tree numbers 6-10, 11-15, 16-20 and 21-25 respectively) can be found by walking diagonal through the forest stand. They are situated approximately 20 m apart. In most forest stands the groups are situated in a right line (0). In several cases the situations differs (0).
- At the first sampling of the soil, the middle of the groups 2 to 5 are marked with metal stakes buried in the ground (ca 20 cm below surface). The places of these stakes are registered on a situation drawing and can be located for future samplings by a metal detector.

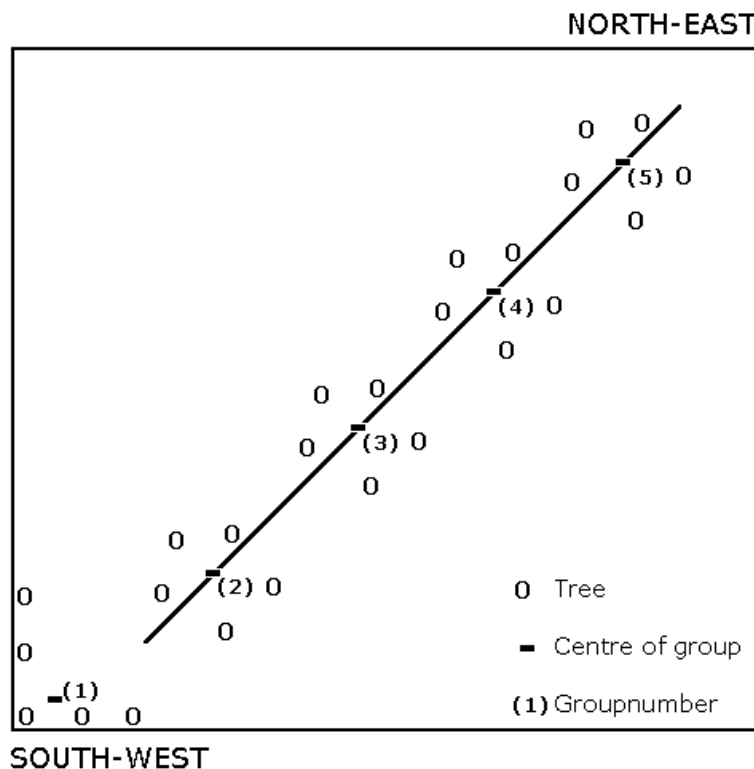


Fig A1.1 Standard structure of a sampling plot

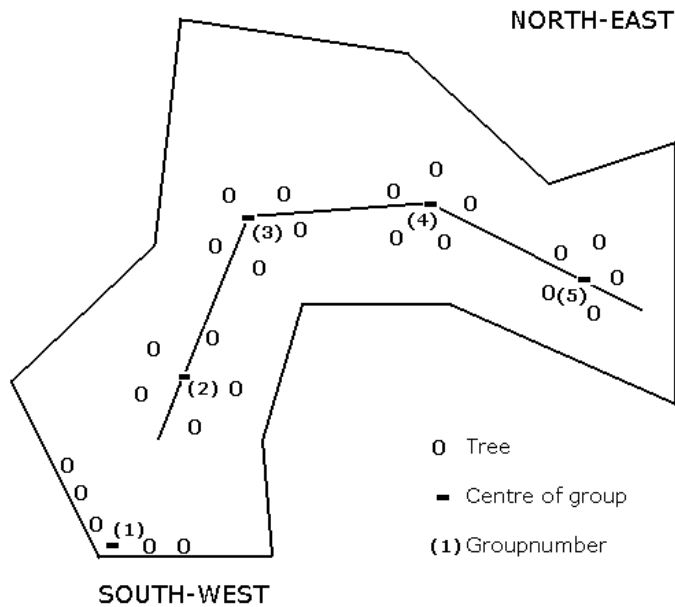


Fig A1.2 Possible exception of the standard structure of a sampling plot: connection line in a curve

Sampling the soil

When the groups are situated in a right line and on regular distances. This line will never be completely right, even when it has a curve (0) this method is valid.

- The middles of the groups 2 to 5 are connected and form so the baseline. This baseline has to be stretched out 10 m at both ends. The total of this the baseline becomes then ca. 80 m.
- Pickets are placed on the baseline every 8 m, starting at 4 m from the beginning at group 2. As a result pickets are placed at 4, 12, 20, 28, 36, 44, 52, 60, 68 and 76 m (0). When the baseline is not 80 m but longer or shorter the distances for the pickets have to be fitted. Fit the distances by dividing the total length of the baseline by 10 and start at half that outcome.

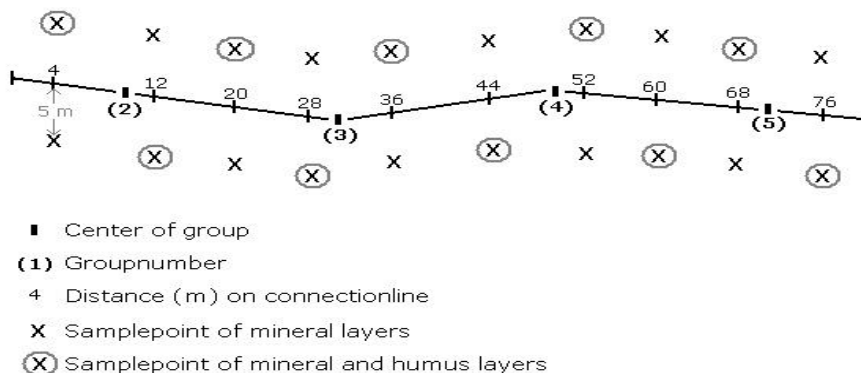


Fig A1.3 Location of sample points in a standard plot

- Subsamples of the soil (20) are taken at a distance of 5 m sheer and on both sides of the baseline on the by pickets marked points. Subsamples of the humus layer (10) are taken alternately on different sides of the baseline (0).

When the groups are not situated on a right line, but also next to each other (0).

- Again connect the middles of the groups 2 to 5. This time the result is not one right line, but two line that touch each other. Stretch the baseline out at every ending group.
- Pickets are placed on the longest line on regular distances the same way as described above. For the second line idem, starting at the loose end.
- Sub samples of soil and humus layer are taken as described above. Attention has to be paid to the area where the two line meet. Don't take sub samples on more or less the same place. These points of attention are indicated in 0 with an '*'.

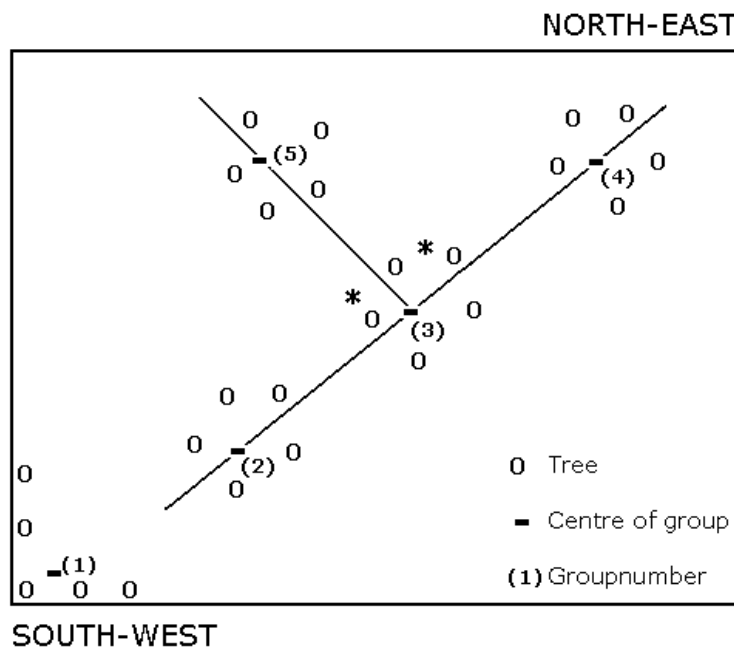


Fig A1.4 Possible exception of the standard structure of a sampling plot: connection line in an angle

Appendix 2 List of locations with their main characteristics

number	map	coordinate		sample date	tree species		soil type	groundwater level		
		x	y					class	mhl	mll
22	11D	199	551	21-mrt-95	EI	1972	cHn21	VIIId	120	201
24	11F	215	568	7-mrt-95	EI	1960	aVz	IIC	45	65
26	11H	212	558	7-mrt-95	DG	1940	Hn21F	VIIo	135	170
31	12C	223	559	6-mrt-95	JL	1942	Hn21F	VIIo	85	170
37	12G	246	551	20-mrt-95	JL	1950	Hn21F	Vao	20	150
39	12G	246	555	3-apr-95	DG	1948	cHd23	VIIIId	170	270
40	12G	246	556	18-apr-95	FS	1935	Hn23xF	VIIIId	200	350
42	12G	247	553	20-mrt-95	JL	1943	Hn21xF	VIIId	130	200
43	12G	248	553	18-apr-95	JL	1943	Zd21	VIIIId	180	300
45	13B	274	565	18-apr-95	EI	1950	zWz	VIo	75	140
48	16C	182	533	10-apr-95	CD	1958	Hn21F	IVu	60	115
49	16C	183	533	10-apr-95	JL	1953	kZn21F	VIo	70	130
52	16E	206	547	25-apr-95	EI	1971	Hn23x	sVad	20	201
55	16F	217	545	27-mrt-95	CD	1960	Zn21	Vbo	30	140
57	16F	218	548	27-mrt-95	GD	1965	Zn21	VIIIId	201	201
58	16F	219	544	3-apr-95	GD	1949	Zn21	Vad/VId	30	201
61	16F	220	544	3-apr-95	GD	1945	Zn21	Vad/VId	30	201
62	16F	220	545	24-apr-95	FS	1973	Hn23xF	Vad	15	121
66	17A	227	538	11-apr-95	FS	1970	Hn21	VId	70	201
71	17C	221	526	8-mrt-95	FS	1960	Hn21F	VIo	75	175
72	17C	221	527	8-mrt-95	FS	1960	Hn21F	VIIId	120	300
75	17B	240	548	21-mrt-95	FS	1937	Hn21F	Vbo	30	150
76	17B	240	549	21-mrt-95	EI	1935	Hn21xF	Vao	25	150
79	17E	243	544	11-apr-95	JL	1932	Hn30F	Va	15	121
82	17E	245	547	3-apr-95	DG	1973	Hn21gF	VIo	45	140
93	17G	242	537	11-apr-95	JL	1938	Hn21F	VIIId	100	201
106	22D	234	507	5-apr-95	DG	1920	Zn21	VId	60	180
112	28C	225	487	8-mei-95	GD	1913	Y23	VIIIId	200	300
116	32A	144	469	23-mrt-95	GD	1961	Hn21	VIIIId	181	181
118	32A	145	470	6-apr-95	BU	1875	zEZ21	Vo	70	160
120	32A	146	468	23-mrt-95	GD	1892	Zd21F	VIIIId	201	201
121	32A	147	468	23-mrt-95	DG	1946	gY30F	VIIIId	251	251
125	32F	175	469	6-apr-95	GD	1908	zY21	VIIIId	250	500
127	32F	178	467	6-apr-95	GD	1979	Hn21	VIIIId	175	300
129	33A	180	466	5-apr-95	DG	1950	Y21	VIIIId	182	182
130	34C	226	455	6-mrt-95	FS	1955	pZn23F	Vao	15	130
134	41A	222	442	6-mrt-95	BU	1961	KX	VIo	60	165
135	41E	247	439	8-mei-95	EI	1885	KX	Vbd	26	200
140	45D	154	401	3-mei-95	EI	1945	pZg23xF	IIIb	30	115
144	46A	183	423	3-mei-95	GD	1918	Zn30	VIIo	100	160
150	50B	111	395	28-mrt-95	DG	1951	cHd21	VIIId	110	220
156	50E	122	392	29-mrt-95	GD	1916	Hn23	VIIIId	200	300
157	50E	123	389	8-mrt-95	CD	1962	Zd21	VIIIId	200	300
158	50E	123	390	8-mrt-95	GD	1925	Hn21	VIIId	120	250
159	50G	124	386	29-mrt-95	EI	1924	Hd23	VIIIId	170	250
160	51D	154	377	22-mrt-95	DG	1956	Y21F	VIIIId	185	400
166	52G	206	380	6-apr-95	GD	1927	Zb23	VIIIId	300	400
169	57A	146	365	22-mrt-95	CD	1958	Zd21F	VIIIId	145	250
170	57A	146	371	22-mrt-95	JL	1933	Hn23F	Vbo	25	120
171	57A	148	371	22-mrt-95	FS	1966	Zn30F	IIIb	25	115
173	57E	163	372	2-mei-95	CD	1934	Hn23F	VId	70	181
174	57E	164	370	4-apr-95	GD	1939	Hn21F	VIIIId	175	250
175	57E	164	371	4-apr-95	GD	1935	Zd21F	VIIIId	250	350

number	map	coordinate		sample date	tree species		soil type	groundwater level		
		x	y					class	mhl	mll
178	57F	174	372	2-mei-95	CD	1948	Hd21	VIIId	130	220
201	11F	213	563	7-mrt-95	JL	1955	Hn21F	VIIIId	160	250
202	11H	217	555	21-mrt-95	EI	1975	zEZ21	Vlo	75	135
203	11H	218	551	24-apr-95	GD	1918	Zn21	VIIIId	175	300
205	12G	246	553	20-mrt-95	JL	1936	Hn23F	VIIId	130	220
207	16C	182	535	10-apr-95	EI	1948	Zn10AF	Vlo	70	150
209	16F	217	548	27-mrt-95	FS	1932	Hn21F	VIIIId	180	300
213	17C	222	527	8-mrt-95	DG	1949	Hn23xF	VId	75	201
214	17E	243	549	21-mrt-95	EI	1940	Hn21xF	VIIId	100	190
215	17F	253	546	20-mrt-95	GD	1976	mY23xF	sVId	70	201
216	22D	234	510	26-apr-95	CD	1961	Hn21F	VIIIId	150	300
217	27A	185	488	6-apr-95	CD	1935	gZd30F	VIIIId	401	501
218	28A	228	492	26-apr-95	EI	1976	zEZ21	VIIIId	250	251
219	28E	248	491	12-apr-95	GD	1897	Hn21	Vao	15	140
220	28F	257	489	12-apr-95	EI	1870	KX	Vao	0	160
222	44D	118	402	28-mrt-95	CD	1977	Zd21	VIIIId	200	250
224	46B	191	422	3-mei-95	GD	1974	gY30F	VIIIId	400	500
226	50B	112	396	5-apr-95	EI	1947	Hn23	Vb	35	140
227	50E	121	390	8-mrt-95	GD	1947	Hn23xF	VIIId	90	201
228	51D	152	377	22-mrt-95	GD	1954	Y23	VIIIId	165	250
230	52B	198	400	20-apr-95	EI	1955	Zn23F	Vlo	60	160
231	52C	186	377	6-apr-95	EI	1972	cHn21v	Vlo	55	150
232	52C	187	376	6-apr-95	EI	1972	Hn21F	Vlo	50	130
233	57A	145	371	3-mei-95	FS	1936	Hn21F	Vlo	50	150
515	11H	216	551	24-apr-95	CD	1959	Zn21	VIIId	120	250
519	11G	209	552	25-apr-95	BU	1900	vWpxF	sVad	20	190
533	11D	198	551	21-mrt-95	FS	1958	Hn21F	Vlo	75	175
536	12G	243	551	25-apr-95	FS	1949	Hn23F	Vlo	60	125
559	12C	222	561	6-mrt-95	BU	1915	zVpF	VIIId	115	200
571	12A	225	571	6-mrt-95	GD	1935	Hn23	Va	20	125
592	15E	167	544	25-apr-95	EI	1940	KXH	Vbo	35	130
640	17F	255	539	20-mrt-95	BU	1929	Hd23F	VIIIId	141	201
644	17F	252	542	20-mrt-95	BU	1930	Hd21F	VIIIId	141	201
740	22B	235	523	25-apr-95	EI	1960	zWp	sVId	60	201
794	27H	216	477	19-apr-95	FS	1965	Hn21F	Vlo	70	170
806	27H	217	486	19-apr-95	DG	1951	Hn21F	Vlo	65	170
815	27F	212	496	25-apr-95	JL	1936	zEZ21	VIIIId	201	201
881	27B	197	491	26-apr-95	CD	1970	gHd30F	VIIIId	300	400
906	28G	243	484	7-mrt-95	JL	1946	Hn21F	Vlo	65	160
912	28F	257	495	12-apr-95	GD	1905	Zd21	VIIIId	201	301
928	28C	222	483	19-apr-95	GD	1886	gHn21F	Vb	40	182
934	28D	234	484	26-apr-95	GD	1940	Hn21	Vb	35	140
941	28C	227	487	8-mei-95	GD	1945	Hd21g	VIIIId	182	182
969	32H	176	451	23-mrt-95	BU	1975	gHd30	VIIIId	501	801
979	32G	163	456	30-mrt-95	JL	1930	Hd23F	VIIo	85	170
1010	32F	173	471	7-mei-95	BU	1925	Y30F	VIIIId	250	500
1012	32F	172	472	5-apr-95	EI	1928	gY30gF	VIIIId	141	201
1034	32D	153	456	30-mrt-95	BU	1876	gY30F	VIIIId	182	182
1036	32C	148	457	30-mrt-95	BU	1970	gHd30	VIIIId	500	750
1040	32C	144	458	6-apr-95	EI	1928	zEZ21g	VIIIId	181	181
1078	33H	219	457	6-mrt-95	BU	1891	pZn21H	IVu	50	115
1096	33C	182	451	23-mrt-95	GD	1930	Y23	VIIIId	301	501
1115	33C	183	455	23-mrt-95	GD	1946	Zd21F	VIIIId	301	501
1134	33C	181	459	16-mei-95	GD	1940	Hn21	Vlo	50	140
1135	33C	182	459	16-mei-95	GD	1919	Zn21	Vlo	55	140

number	map	coordinate		sample date	tree species		soil type	groundwater level		
		x	y					class	mhl	mll
1136	33C	185	459	11-mei-95	GD	1910	Zd21/Zn21	Vbo	30	130
1210	34E	247	473	7-mrt-95	GD	1945	Zn23	IIIa	5	85
1212	34E	247	474	7-mrt-95	BU	1898	EZg23	IIIa	15	115
1251	39E	161	448	8-mei-95	GD	1907	gY21	VIIIId	182	182
1257	39B	159	446	8-mei-95	BU	1780	gbEZ30	VIIId	130	182
1273	40H	212	435	3-mei-95	GD	1918	Zb23x	VIIIId	501	601
1358	45H	171	404	3-mei-95	CD	1939	Hn21F	VIIo	85	170
1424	50H	139	383	1-mei-95	DG	1902	zEZ21	VId	45	182
1428	50H	139	384	1-mei-95	BU	1910	Hn21	VId	65	182
1438	50F	133	388	1-mei-95	DG	1933	zEZ21	VIIIId	150	280
1463	50B	114	392	29-mrt-95	GD	1943	Hn21	VId	75	185
1470	50B	115	396	28-mrt-95	EI	1882	pZn23	VIo	55	145
1476	51G	166	379	22-mrt-95	DG	1957	zEZ23	VIIIId	180	300
1562	52E	205	400	20-apr-95	CD	1960	Hn21	sVa	25	182
1593	52B	199	397	20-apr-95	EI	1890	Ln5	Va	10	150
1602	57H	172	362	2-mei-95	GD	1930	Zd21	VIIIId	182	182
2001	13A	261	572	25-apr-95	EI	1969	zWp	VIIo	95	180
2002	14C	107	534	21-mrt-95	CD	1960	Zd21	VIIIId	181	181
2003	14F	130	546	20-mrt-95	EI	1947	Zn21	VIo	55	130
2004	14F	131	547	20-mrt-95	CD	1948	Hn21	VIIo	95	150
2005	14F	134	544	21-mrt-95	BU	1946	Zn21	IVu	45	115
2006	16C	181	534	26-apr-95	EI	1952	vWp	IIIa	5	100
2007	16F	219	549	27-mrt-95	DG	1972	Hn21	VIIIId	160	260
2008	17A	220	547	15-mei-95	DG	1974	Hn21	VIIId	95	200
2009	17E	244	545	24-apr-95	GD	1952	Hn21	VId	60	180
2010	17F	251	541	24-apr-95	GD	1973	Hn21F	Vbo	35	150
2011	19A	107	523	4-apr-95	CD	1924	Zd30	VIIIId	181	181
2012	19C	104	507	4-apr-95	EI	1950	Zn50A	VIIo	85	160
2013	21C	184	508	7-mrt-95	EI	1957	kZn30A	VIIo	85	170
2014	21C	186	506	7-mrt-95	BU	1959	Mn15A	Vbo	30	140
2015	21F	217	515	23-mrt-95	DG	1937	Hn21	VIo	70	170
2016	22C	224	503	23-mrt-95	EI	1908	Zn21	VIIo	100	170
2017	22D	235	509	22-mrt-95	EI	1926	Hn21	Vbo	26	150
2018	22E	232	509	22-mrt-95	FS	1960	Hn21	VIo	60	170
2019	24H	96	479	18-apr-95	EI	1950	Zd21	VIIIId	201	301
2020	24H	99	486	18-apr-95	CD	1935	Zd20A	VIIIId	201	301
2022	26H	173	477	3-apr-95	DG	1934	Y30	VIIIId	181	181
2023	27B	195	488	19-apr-95	DG	1932	Hd30	VIIIId	201	301
2024	27B	198	493	3-apr-95	DG	1973	Hd30	VIIIId	181	181
2025	27C	183	486	10-apr-95	DG	1940	gY30	VIIIId	181	181
2026	27C	185	477	28-mrt-95	EI	1950	gY30	VIIIId	181	181
2027	27C	187	477	28-mrt-95	FS	1905	Zd21	VIIIId	181	181
2028	27C	187	485	10-apr-95	EI	1910	Zd30	VIIIId	181	181
2029	27C	188	480	25-apr-95	BU	1780	Y21	VIIIId	201	301
2030	27E	201	496	19-apr-95	EI	1905	zHd21	VIIIId	201	301
2031	27G	206	478	29-mrt-95	EI	1900	Zn23	Vbo	35	140
2032	27G	206	482	29-mrt-95	EI	1907	pZn23	VId	60	185
2035	28C	228	482	26-apr-95	DG	1936	Hn21	VIIIId	160	230
2036	28G	245	477	26-apr-95	EI	1828	bEZ23	Vbd	35	201
2037	29A	264	488	5-apr-95	EI	1937	kZn23	Iib	35	75
2039	32D	153	455	19-apr-95	DG	1893	Hd21F	VIIIId	181	181
2040	32D	159	452	19-apr-95	EI	1917	Zn21	VIo	50	140
2041	32F	172	474	2-mei-95	DG	1939	Y23	VIIIId	181	181
2042	32F	173	472	8-mei-95	BU	1950	cY23	VIIIId	201	201
2043	32F	174	469	10-apr-95	FS	1955	Hd21	VIIIId	251	351

number	map	coordinate		sample date	tree species	soil type	groundwater level		
		x	y				class	mhl	mll
2044	32F	176	475	2-mei-95	BU 1871	Y30	VIIIId	181	181
2045	32F	177	467	10-apr-95	EI 1937	Zn21	IIa	0	75
2046	32H	176	456	20-apr-95	EI 1910	gY30	VIIIId	181	181
2047	33B	191	473	25-apr-95	DG 1885	Hd30	VIIIId	201	301
2048	34A	221	463	30-mrt-95	DG 1970	Zn23	VIo	75	170
2049	34A	224	470	30-mrt-95	EI 1950	Hn23	IIIa	20	110
2050	34C	220	455	8-mrt-95	BU 1974	Hn23	IIIb	30	115
2051	39B	156	448	6-mrt-95	EI 1910	Y21	VIIIId	181	181
2052	39B	156	449	6-mrt-95	DG 1939	Y21	VIIIId	181	181
2053	39E	161	446	20-apr-95	BU 1957	gY30	VIIIId	181	181
2054	40E	202	449	12-apr-95	BU 1931	Ld5	VIIIId	181	181
2055	40E	205	445	12-apr-95	BU 1911	Rd10C	VIIId	130	181
2056	41A	220	440	8-mrt-95	GD 1953	zEZ30	VIo	70	150
2057	42E	38	412	20-apr-95	CD 1933	Zd20A	VIIIId	201	301
2059	46C	183	408	27-apr-95	EI 1980	Zn21	VIo	45	160
2060	50F	135	388	5-apr-95	FS 1968	Hd21	VIIId	130	181
2062	50H	135	377	27-apr-95	GD 1964	Hn23	VIo	75	160
2064	50H	138	383	27-apr-95	EI 1915	Hn21	Vbo	35	170
2065	51B	151	396	20-apr-95	FS 1955	Zn21	IIIa	25	110
2067	57A	141	371	1-mei-95	FS 1975	Hn21F	Vbo	35	150
2068	57A	146	372	1-mei-95	GD 1960	Hn21	VIIId	130	230
2069	57E	162	371	12-apr-95	FS 1939	Hn23	VIo	50	140
2070	57E	163	369	12-apr-95	CD 1952	Hn21	VIIId	110	210
2072	58G	209	352	11-apr-95	BU 1940	Y23	VIIIId	181	181
2073	60C	187	327	2-mei-95	BU 1891	BLb6	VIIIId	201	301
2074	60D	198	330	2-mei-95	EI 1940	Zn23	Vad	10	200
2075	60E	203	348	11-mei-95	EI 1937	Zb23	VIIIId	181	181
2076	62A	188	319	11-apr-95	EI 1890	KK	VIIIId	251	351
2077	62A	188	321	11-apr-95	BU 1926	Ld6g	VIIIId	201	301
2078	62E	202	319	1-mei-95	EI 1905	Zn23t	VIIIId	201	301
2079	45F	172	414	27-apr-95	CD 1950	Hd21	VIIId	130	181
2080	33C	189	462	3-mei-95	EI 1917	gcY30	VIIIId	201	301
2081	33D	195	454	11-mei-95	GD *	Hd30	VIIIId	201	201
2082	33H	215	459	3-mei-95	EI 1917	pZg23	VIo	65	130
2083	46B	191	418	11-mei-95	BU 1915	BLd6	VIIIId	201	201
2084	32F	175	473	15-mei-95	DG 1962	gY30F	VIIIId	181	181
2085	17A	226	539	15-mei-95	GD 1925	Zd21	VIIId	130	251

Location numbers < 2000 indicate that these locations are also measured in 1990 (De Vries and Leeters, 2001). Grey backgrounds indicate an observation of the characteristic that differs from the observation in 1990.

Appendix 3 Calculation of the required changes in element concentrations and element pools to derive significant trends

Element concentrations

Repeated measurements of the concentration of an element X at times t1 and t2 gives information on the change in that concentration according to:

$$\Delta \hat{X} = \hat{X}_2 - \hat{X}_1 \quad (\text{A1.1})$$

with \hat{X} being equal to the estimated average concentration of element X based on a number of samples (or a number of sub samples in a pooled sample). Whether the calculated differences, based on repeated measurements are significant, depends on (i) the spatial variability (in terms of the standard deviation, s) of the concentration of the considered element and (ii) the number of samples (n) that were taken at each survey to assess an estimated average element concentration (\hat{X}). Statistically spoken, repeated measurements are two random samples from one population with characteristics n1 and n2, \hat{X}_1 and \hat{X}_2 and s1 and s2. The standard deviations (sd) of the two estimated means are equal to:

$$\text{sd}(\hat{X}_1) = s_1 / \sqrt{n_1} \quad (\text{A1.2a})$$

$$\text{sd}(\hat{X}_2) = s_2 / \sqrt{n_2} \quad (\text{A1.2b})$$

The standard deviation of the difference in the two estimated means equals:

$$\text{sd}(\Delta \hat{X}) = \text{sd}(\hat{X}_2 - \hat{X}_1) = s_X \sqrt{1/n_1 + 1/n_2} \quad (\text{A1.3a})$$

with s_X being equal to:

$$s_X = \sqrt{\frac{(n_1 - 1) \cdot s_{X_1}^2 + (n_2 - 1) \cdot s_{X_2}^2}{(n_1 - 1) + (n_2 - 1)}} \quad (\text{A1.3b})$$

Assuming that the same number of soil samples are taken at two repeated measurements ($n_1 = n_2$) leads to the following simplification:

$$\text{sd}(\Delta \hat{X}) = \text{sd}(\hat{X}_2 - \hat{X}_1) = \sqrt{(s_{X_1}^2 + s_{X_2}^2) / n} \quad (\text{A1.4})$$

Assuming that there is no change in standard deviation ($s_{X_1} = s_{X_2}$), further simplifies Eq. (A1.4) to:

$$\text{sd}(\hat{X}_2 - \hat{X}_1) = s_{x_1} \cdot \sqrt{2/n} \quad (\text{A1.5})$$

Assuming that the standard deviation is similar in both cases (which is to be expected in the same population when n is large) implies that one only needs a value of s during one sampling period. In statistical terms, the difference between \hat{X}_1 and \hat{X}_2 is only significant when:

$$|\hat{X}_2 - \hat{X}_1| \geq t_a \cdot s_{x_1} \cdot \sqrt{2/n} \quad (\text{A1.6})$$

where:

t_a = tabled student t factor for a given uncertainty; for $a = 0.05$, $t_a \sim 2$

The term $t_a \cdot s_{x_1} \cdot \sqrt{2/n}$ equals the 95% probability interval for the difference between the two means \hat{X}_1 and \hat{X}_2 ($\Delta\hat{X}$).

Element pools

The variation in element pools is the variation of the product of the amount of solid material and the element concentration in the organic layer or of the bulk density, thickness and element concentration in the mineral layer. In order to reduce the costs of analyses use is made of pooled samples in which both the amount of solid material and the element concentration is determined separately. Assuming that the element concentrations are spatially independent of the amount of solid material or bulk density and thickness, one can say that the expectation of the product equals the product of the expectations (Eq. A1.7a).

$$E[\hat{X}\hat{Y}] = E[\hat{X}] \cdot E[\hat{Y}] \quad (\text{A1.7a})$$

We also assume that the values for the element concentration and the amount of solid material or bulk density and thickness are the average values of a simple random sample. Therefore, the average of the sample is an unbiased estimator and equals the expectation of the average (Eq. A1.7b).

$$E[\hat{X}] \cdot E[\hat{Y}] = XY \quad (\text{A1.7b})$$

with:

X = the actual average element concentration

Y = the actual average pool of solid material in the humus layer or the bulk density times thickness in the mineral layer

\hat{X} = the estimated average element concentration

\hat{Y} = the estimated average pool of solid material in the humus layer or the bulk density times thickness in the mineral layer

Because \hat{X} and \hat{Y} are unbiased estimators, the variance error of the estimated element pool equals the expectation of the square of the difference of the estimated average with the actual average (which is unknown) and can be given as:

$$\text{var}[\hat{X}\hat{Y} - XY] = E[(\hat{X}\hat{Y} - XY)^2] \quad (\text{A1.7c})$$

Substitution of $\hat{X} = X + X'$ and $\hat{Y} = Y + Y'$ with $E[X'] = E[Y'] = 0$ and using the fact that \hat{X} and \hat{Y} are independent, Eq. (A1.7c) can also be written as:

$$\text{var}[\hat{X}\hat{Y} - XY] = Y^2 E[X'^2] + X^2 E[Y'^2] + E[X'^2] \cdot E[Y'^2] \quad (\text{A1.7d})$$

or

$$s_{\hat{X}\hat{Y}}^2 = Y^2 s_X^2 + X^2 s_Y^2 + s_X^2 \cdot s_Y^2 \quad (\text{A1.7e})$$

Repeated sampling of element pools in both humus and mineral layer at two different times gives information on the change in element pools. If both samples are taken independently, the variance of this difference can be given as:

$$\text{var}[\hat{Z}_2 - \hat{Z}_1] = \hat{Y}_1 s_{\hat{X}_1}^2 + \hat{X}_1 s_{\hat{Y}_1}^2 + s_{\hat{X}_1}^2 \cdot s_{\hat{Y}_1}^2 + \hat{Y}_2 s_{\hat{X}_2}^2 + \hat{X}_2 s_{\hat{Y}_2}^2 + s_{\hat{X}_2}^2 \cdot s_{\hat{Y}_2}^2 \quad (\text{A1.8})$$

with:

$$\hat{Z} = \hat{X}\hat{Y}$$

$$\hat{Z}_1 = \text{estimated Z at time t=1}$$

$$\hat{Z}_2 = \text{estimated Z at time t=2}$$

The variance of the average values for X and Y at time t1 and t2 can be estimated by the variance in those values divided by the number of samples as illustrated for X1 :

$$\sigma_{\hat{X}_1}^2 = \frac{S_{X_1}^2}{n} \quad (\text{A1.9})$$

Assuming that the variance remains constant ($S_{X_1}^2 = S_{X_2}^2 = S_X^2$) and combining Eq. (A1.8) and Eq. (A1.9) gives the following estimation for the variance (Eq. A1.10a) or standard deviation (Eq. A1.10b) for the differences in the element pools:

$$\text{var}[\hat{Z}_2 - \hat{Z}_1] = \frac{2}{n^2} \cdot S_X^2 \cdot S_Y^2 + \left(\frac{\hat{Y}_1^2 + \hat{Y}_2^2}{n} \right) \cdot S_X^2 + \left(\frac{\hat{X}_1^2 + \hat{X}_2^2}{n} \right) \cdot S_Y^2 \quad (\text{A1.10a})$$

or

$$\text{sd}(\hat{Z}) = \sqrt{\frac{2}{n^2} \cdot S_X^2 \cdot S_Y^2 + \left(\frac{\hat{Y}_1^2 + \hat{Y}_2^2}{n}\right) \cdot S_X^2 + \left(\frac{\hat{X}_1^2 + \hat{X}_2^2}{n}\right) \cdot S_Y^2} \quad (\text{A1.10b})$$

Information on the standard deviation in the element concentration (X) and the solid phase pool (Y) in the first assessment can be used for a first indicator of the required change by assuming that $\hat{X}_1 = \hat{X}_2$ and $\hat{Y}_1 = \hat{Y}_2$. Eq. (A1.10b) then simplifies to:

$$\text{sd}(\hat{Z}) = \sqrt{\frac{2}{n^2} \cdot S_X^2 \cdot S_Y^2 + \left(\frac{2\hat{Y}^2}{n}\right) \cdot S_X^2 + \left(\frac{2\hat{X}^2}{n}\right) \cdot S_Y^2} \quad (\text{A1.11})$$

The measured difference in element pools between two time periods is only statistically significant when:

$$|\hat{Z}| \geq t_a \cdot \text{sd}(\hat{Z}) \quad (\text{A1.12})$$

Appendix 4 Calculation of critical heavy metal content levels

The contents of heavy metals have been analysed in the humus and are given in Section 4.3. In order to classify the observed contents into pollution classes, the regular Dutch evaluation system has been applied.

In the Netherlands a system of critical levels is used for the evaluation of the contents of pollutants in soil and groundwater. For the heavy metal contents of the soil these levels depend on the clay (Dutch: *lutum*, L) and humus (organic matter, H) content of the soil. This relation is based on the assumed background values of the polluting substances in relation with the mineral characteristics of the soil material and the origin and history of the soils.

The Dutch system recognises three critical levels for each pollutant:

- the Target Value (Dutch: *Streefwaarde*, S), i.e. the assumed maximum for the range of background values as measured in the top (10 cm) of agricultural and forest soils (Edelman, 1983; Edelman and De Bruin, 1986),
- the Intervention Value (Dutch: *Interventiewaarde*, I), i.e. the minimum value for serious pollution, indicating that any action to clean, remove or isolate the polluted part of the soil is necessary,
- the Examination Value (Dutch: *Toetsingswaarde*, T), i.e. the value above which more research to the extent and the source of the pollution is necessary, calculated as the mean value of the Target and Intervention Value.

For each pollutant the same formula can be used for the calculation of the Target and Intervention Value. This formula consists of the value for the separate pollutants in a standard or reference soil (L=25%, H=10%) and a formula to correct for non-standard soils. If the organic matter content is lower than 2%, the calculation is done with an organic matter content of 2%. In case of the humus layer, the calculation is done with a clay content of 0%. The formulas for the Target (S) and the Intervention (I) Values follow here:

$$S = S_{st} \cdot \frac{A + B \cdot L + C \cdot H}{A + B \cdot 25 + C \cdot 10}$$

$$I = I_{st} \cdot \frac{A + B \cdot L + C \cdot H}{A + B \cdot 25 + C \cdot 10}$$

These formulas apply for all considered heavy metals. The height of the critical values for the reference soil and the coefficients in the formulas, however, are different for the various heavy metals (0).

Table A4.1 Critical heavy metal contents for the reference soil (L=25%, H=10%) and adjustment coefficients for non-standard soils.

Element	Reference soil		Coefficients		
	S_{st} (ppm)	I_{st} (ppm)	A	B	C
Lead (Pb)	85	530	50	1	1
Cadmium (Cd)	0.8	12	0.4	0.007	0.021
Copper (Cu)	36	190	15	0.6	0.6
Zinc (Zn)	140	720	50	3	1.5
Nickel (Ni)	35	210	10	1	0
Chromium (Cr)	100	380	50	2	0