

Impact of acid atmospheric deposition on the biogeochemistry of moorland pools
and surrounding terrestrial environment

CENTRALE LANDBOUWCATALOGUS



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Abstract

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A monitoring programme was carried out to quantify the fluxes of solutes in terrestrial and aquatic oligotrophic ecosystems in The Netherlands. The programme focussed on five sites, three dominated by podzolic soils and two dominated by driftsand soils. Of the podzolic sites one was a *Calluna vulgaris* heathland and the other two were *Pinus sylvestris* forests. Moorland pools were present at these three sites. The driftsand sites were a *Pinus sylvestris* forest and a site without vegetation, located close to each other. Also here a moorland pool was present. A number of other sites was studied less intensively.

The monitoring programme included measurement at regular time intervals of concentrations of all major solutes present in bulk precipitation, throughfall, stemflow, unsaturated soil solution, groundwater and poolwater. In addition, water fluxes were measured (bulk precipitation, throughfall and stemflow) or estimated (unsaturated water transport, groundwater transport, and in- and outflux of moorland pools). Besides the monitoring of hydrological and chemical parameters, hydrobiological parameters were also monitored in the pools. The programme was conducted between 1982 and 1987, but particularly for the hydrobiological monitoring larger datasets were available.

The chemical composition of bulk precipitation, throughfall and stemflow was dominated by NH_4 and SO_4 . In throughfall their fluxes were c. four times higher than in bulk deposition, however. Dry deposition of SO_4 , which is probably largely derived from atmospheric SO_2 , may have been enhanced by co-deposition with NH_3 . The deposition of $(\text{NH}_4)_2\text{SO}_4$ was 1.5 to 2 times higher in the forested plots than in their non-forested counterparts. In the soils all deposited NH_4 was transformed into organic nitrogen (assimilation) or NO_3 (nitrification). Nitrification occurred even in the most acidic soils, which resulted in high atmospheric acid loads ($4\text{--}4.5 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ in the forest plots and c. $2.5 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ in the heathland and bare sand). Neutralization of this acidity was primarily accomplished through dissolution of soil bound Al, particularly in the spodic horizon. This raises the question if depodzolization (i.e., dissolution of Al-organics in the spodic horizon) is currently in operation.

Na, Cl and Mg are probably largely sea-salt derived. Our data suggest that, particularly in the forest plots, base cation weathering rates are hardly large enough to provide the amount taken up by vegetation. It is probably not uncommon that forest ecosystems on these soils largely rely on atmospheric input as a source for base cations.

Estimates of the water budgets for the four moorland pools obtained from model calculations suggests that all pools were largely fed by precipitation water, even where the bottom of the pools was occasionally below the groundwater table. In retrospect, this means that our initial intent to study the coupling between chemical processes in the terrestrial and the aquatic environments was not possible at the selected sites.

Solute budgets for two of the pools where data over 5-6 consecutive hydrological years were present indicate that over 85% of deposited NO_3 was lost to the sediments (assimilation) or to the air (probably by denitrification). Also SO_4 was lost, probably due to reduction and subsequent immobilization in the sediment. The largest loss of SO_4 (54% of bulk deposition) was found in the pool with the highest average pH of sediment interstitial water (5.9). The output of K was 2-3 times as high as the input by bulk deposition. This depletion of K may be due to replacement on sorption sites by NH_4 which is deposited in very large amounts.

Diatom analysis of herbarium samples (1916-1973) and recent samples (1977-1984) demonstrates a long-term acidification of the moorland pools by c. 1-1.5 units. The largest decrease in pH (c. 2 units) has occurred in pools where over 50% of the bottom desiccates in extremely dry years; the smallest decrease (0.5 unit) in a pool where only 20% of the bottom desiccates in such years. We hypothesize that during desiccation oxidation of reduced sulphur compounds results in the formation of H_2SO_4 . The absence of acidification after the extreme drought of 1921 may be related to lower atmospheric inputs and a consequently lower reduced sulphur store in the sediment at that time. Serious acidification occurred after the drought periods of 1959 and 1976. Acidification reduced the diversity of diatom assemblages and aquatic macrophytes (dominance of *Juncus bulbosus* and *Sphagnum*).

Preface

This book summarizes the results of six years (1981-1987) of biogeochemical monitoring of oligotrophic ecosystems in The Netherlands. The project started in 1981 as two independent monitoring programmes carried out by the Research Institute for Nature Management (RIN-DLO) and the Department of Soil Science and Geology of the Agricultural University at Wageningen. The latter programme was a follow-up of an earlier monitoring project carried out at an oak-birch woodland site and published as Agricultural Research Report 930 (Van Breemen et al., 1988). In comparison, the present project extends to more localities (four instead of one) and a wider range of ecosystems (pine forest, heathland, open sand, moorland pools). Between 1982 and 1984 the project was partly financed by the EEC (Contract No. ENN-650-N(N)). During this period three institutions closely cooperated and were responsible for the following activities:

- Agricultural University, Department of Soil Science and Geology: monitoring of soil solution, groundwater and poolwater.
- Research Institute for Nature Management: monitoring of groundwater, poolwater and pool microbiology.
- National Institute for Public Health and Environmental Hygiene: monitoring of rainwater, throughfall and stemflow.

After 1984 the monitoring was continued at a number of sites, partly financed by the Netherlands Technology Foundation (STW).

Many persons have significantly contributed to this study. We are grateful to N. van Breemen for his stimulating interest and guidance throughout this study. H.F.R. Reijnders was responsible for the chemical analyses of rainwater, throughfall and stemflow, and E. Velthorst for the analyses of soil solution. J.J.M. van Grinsven assisted with the simulation of the hydrology in the unsaturated zone. C.N. Beljaars analysed the majority of the diatom slides. A.A.N. de Wit, P. Bremer, W. Oostveen, C.N. Beljaars and H. Booltink assisted with the field work. Old plankton samples were put at disposal by P.F.M. Coesel and H. Kooyman-van Blokland (University of Amsterdam) and B.Z. Salomé (Limnological Institute, Royal Netherlands Academy of Sciences). The figures were prepared by A. Griffioen (RIN-DLO). We are grateful to the State Forestry Service (SBB), the Society for the Preservation of Nature Reserves in The Netherlands and W.A.M. Rijken for permission to carry out the monitoring at their sites.

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1 Introduction

During the last decade atmospheric deposition and its ecological effects have received considerable attention. The current high input of atmospheric pollutants is largely due to the increased emission of SO_2 and NO_x from fossil fuels, and in The Netherlands to NH_3 from agricultural origin (Van Breemen et al. 1982; Buijsman et al. 1985). One of the major effects of these pollutants is a considerable acidification and eutrophication of terrestrial and aquatic environments. The current anthropogenic acid loads in The Netherlands are extreme compared to values reported for many other forested areas in Europe and North America (Van Breemen et al. 1984). In acidic soils the increased acidification may result in a decrease in pH and base saturation and in an increased solubility of Al and heavy metals. The increased solubility of Al in soil solution and drainage water is believed to one of the causes for the widespread forest dieback and also to have adverse effects on aquatic ecosystems (Driscoll & Schecher 1988).

In Dutch forests the dry deposited amounts of both NH_3 and SO_4 are c. two times the amounts deposited in bulk deposition (Van Breemen et al. 1982). This demonstrates the effectiveness of a forest canopy in scavenging atmospheric pollutants. The high acid input into the Dutch forest soils is primarily neutralized by Al dissolution, and the resulting high concentrations of dissolved Al are counterbalanced by NO_3 and SO_4 (Van Breemen & Jordens 1983). These observations for forested sites in The Netherlands made us hypothesize that (1) due to dry deposition the atmospheric acid load in forest soils is considerably higher than in non-forest soils, so that (2) also the mobilization of Al is higher in forest soils than in non-forest soils.

In the sandy areas of The Netherlands, which have a low acid neutralizing capacity, many poorly buffered small seepage pools exist with a surface area of a few ha or less. These moorland pools may be particularly sensitive to acidification, and acid loads probably depend on the vegetation in the catchment area, with forest being most effective in scavenging dry atmospheric acidity. We hypothesized that pools without a terrestrial catchment (i.e. fed by precipitation alone) or pools without forest in their catchment have less dry deposition and therefore lower anthropogenic acid inputs and lower acidification rates than pools with a forest in their catchment.

In an earlier study Van Dam et al. (1981) hypothesised that reduction of sulphate considerably reduces surface water acidity in moorland pools. Reduction processes, which result in transformation of sulphate into either insoluble sulphides or hydrogen sulphide which escapes as a gas, takes place primarily in the soft bottom sediment of the pools. In addition, Van Dam et al. (1981) suggested that during prolonged drought

periods, when the sediment is partly exposed to the atmosphere, re-oxidation of reduced compounds takes place. As re-oxidation causes high acid inputs into the pools, periods of drought and low water tables are expected to result in severe surface water acidification, which may have a strong impact on the diatom assemblages.

To test our hypotheses, a hydrochemical and hydrobiological monitoring programme was carried out at five sites in The Netherlands. The selected sites, all of which include a terrestrial study plot and a moorland pool, are representative for the most acid sensitive sandy areas in The Netherlands. Of the five moorland pools, two are rainwater-fed, (i.e. without lateral flow of groundwater from a terrestrial catchment), and three were believed to be fed by groundwater from the surrounding environment, at least part of the year. The catchments of all three groundwater fed pools have similar acidic soil types. In order to establish a difference in dry deposition in the catchments, two groundwater-fed pools were selected with a forested catchment, while the third one is surrounded by heathland.

The hydrochemical monitoring included the estimation of chemical fluxes in bulk deposition, throughfall, stemflow, litterfall, soil solution, groundwater and poolwater. To quantify the effect of vegetation cover (forest or heathland) on acid load, soil acidification and the composition of soil solution, drainage water, and poolwater, we studied hydrochemical processes in similar soils as well as the chemical composition of groundwater draining into the pools in the heathland and in one of the forested catchments. The effect of vegetation cover on anthropogenic soil acidification was also studied in two adjacent driftsand plots, one having a forest and one a bare surface with scattered algae and mosses.

The meteoric water monitoring data were also used to gain more insight into the regional and temporal variation of atmospheric deposition and their origin. Hydrobiological monitoring data, which were available over a long period of time, were used to estimate long-term fluctuations in poolwater chemical composition.

In this report materials and methods are described in detail, while the main results and conclusions are more of a general nature. A compilation of all collected data is given on microfiche. Publications, in which selected parts of this study are discussed in detail, are indicated in a separate reference list (Appendix 4) and are available upon request.

2 Description of study sites

The selected research sites are Hasselsven (HV), Goorven (GV), Tongbersven (TV), Gerritsfles (GF) and Kliplo (KL). The names used for the sites are the names of the pools present at each of the sites. Topographic positions of these sites, given in Figs 2.1 to 2.4, indicate that three are located in the south (Hasselsven, Goorven and Tongbersven), one in the centre (Gerritsfles) and one in the north of the Netherlands (Kliplo). The monitoring activities carried out at the various sites are summarized in Table 2.1. At the Tongbersven Scots pine stand throughfall and stemflow were monitored at two locations, one close to the soil solution monitoring plot (TVA), the other c. 1 km to the east (TVB). At Gerritsfles soil solution monitoring took place at two locations, one in a Scots pine forest (GFF) and the other in a bare driftsand c. 40 m

Table 2.1. Monitoring programme carried out at the various sites. In brackets: abbreviation of sites. At Tongbersven throughfall and stemflow monitoring took place at two locations TVA and TVB, and at Gerritsfles soil solution monitoring took place at two locations GFF and GFB. For Hasselsven precipitation quality data were taken from the meteorological station Eindhoven (c. 15 km North of HV), and precipitation quantity data were taken from the meteorological station Maarheze (c. 10 km Southeast of HV).

Monitoring activity	Hasselsven (HV)	Goorven (GV)	Tongbersven (TV)		Gerritsfles (GF)		Kliplo (KL)
			(TVA)	(TVB)	(GFF)	(GFB)	
precipitation quantity				*		*	*
precipitation chemistry				*		*	*
throughfall quantity	*		*	*	*		*
throughfall chemistry	*		*	*	*		*
stemflow quantity			*	*	*		*
stemflow chemistry			*	*	*		*
litterfall quantity				*		*	
litterfall chemistry				*		*	
soil solution quantity	*			*	*	*	
soil solution chemistry	*			*	*	*	
forest growth				*		*	
groundwater hydrology	*			*			
groundwater chemistry	*			*			
pool hydrology	*			*			*
pool chemistry	*	*		*	*		*
pool hydrobiology	*	*		*	*		*

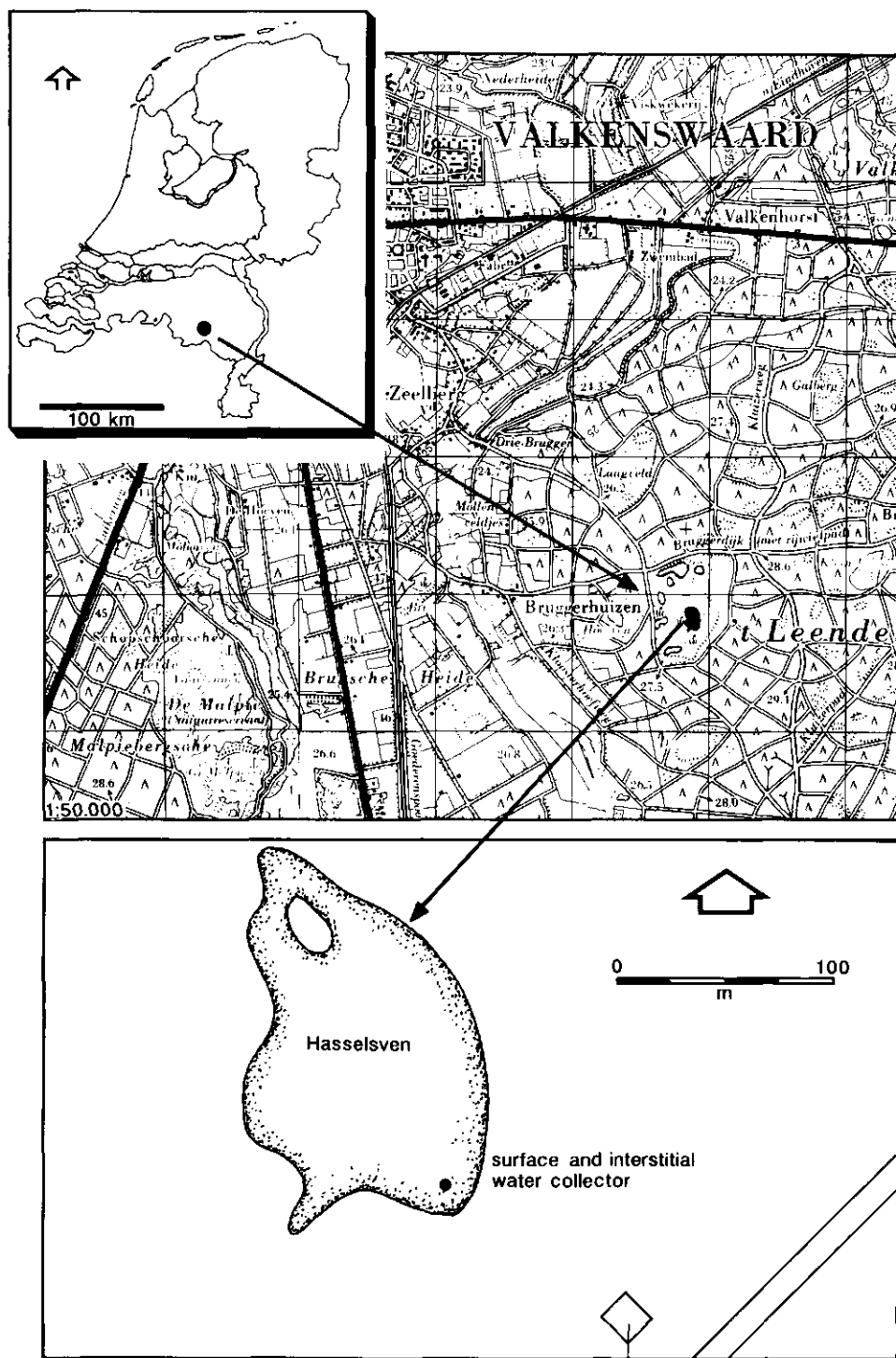


Figure 2.1. Topographic position of Hasselsven (HV).

see Fig.3.1.

to the south (GFB).

Gerritsfles and Kliplo are rainwater-fed pools, whereas at the outset of this study the other three pools were believed to be groundwater influenced at least during part of the year. Of these three, Goorven and Tongbersven have a forested catchment, and Hasselsven is surrounded by heathland. Details on the research sites are given below.

2.1 Description and short history of the monitoring sites

2.1.1 Hasselsven

Hasselsven (Fig. 2.1) is situated in the Leenderbos, 3 km SW of the village of Leende (51°20'N, 5°30'E), at 26.3 m above NAP (mean sea water level). The site includes the moorland pool 'Groot Hasselsven', which has a surface area of c. 1.3 ha. Hasselsven is owned by the State Forestry Service, and is closed to the public.

Until the 19th century the wide surroundings of the site consisted of heath and moorland. Beginning in the late 19th century the soils were partly reclaimed for agriculture. Some parcels of arable land, indicated on cadastral maps of the late 19th and early 20th century at the northeastern, southern and southwestern sides of the pool, were abandoned later. Between 1932 and 1941, the area surrounding the reserve was planted with trees, mainly Scots pine (Iven & Van Gerwen 1974). The reserve itself consists of c. 40 ha of wet and dry heathland, gently sloping towards the pool.

2.1.2 Goorven

Goorven (Fig. 2.2) is situated 2 km south of the village of Oisterwijk (51°34'N, 5°13'E), at 8.3 m above NAP. The site includes the pool 'Achterste Goorven', with a surface area of c. 2.4 ha, and is a part of the nature reserve 'De Oisterwijkse Bossen en Vennen'. This reserve contains numerous moorland pools, with a large variation in chemistry and biota (Van Dam & Kooyman-van Blokland 1978, Coesel et al. 1978, Van Dam 1983). It is owned by the 'Vereniging tot Behoud van Natuurmonumenten in Nederland'. Only the paths around the pool are open to the public. In winter the pool is often used as a skating-rink.

In the Middle Ages the originally forested area was transformed into a landscape of heath and moorland, and used for sheep grazing and peat excavation. Drifting sand dunes were formed as a result of overgrazing. The undulating terrain with only weak soil profile development and fragments of overblown podzolic profiles still bears witness of these changes (Geenen 1977). The site was planted with Scots pine in 1840, as can be concluded from topographical maps (see also Van Hees & Van den Wijngaard 1977). Presently, pine reaches up to the shores of the pool, and no heathland remains. More detail on the history of the pool are given by Van Dam (1987).

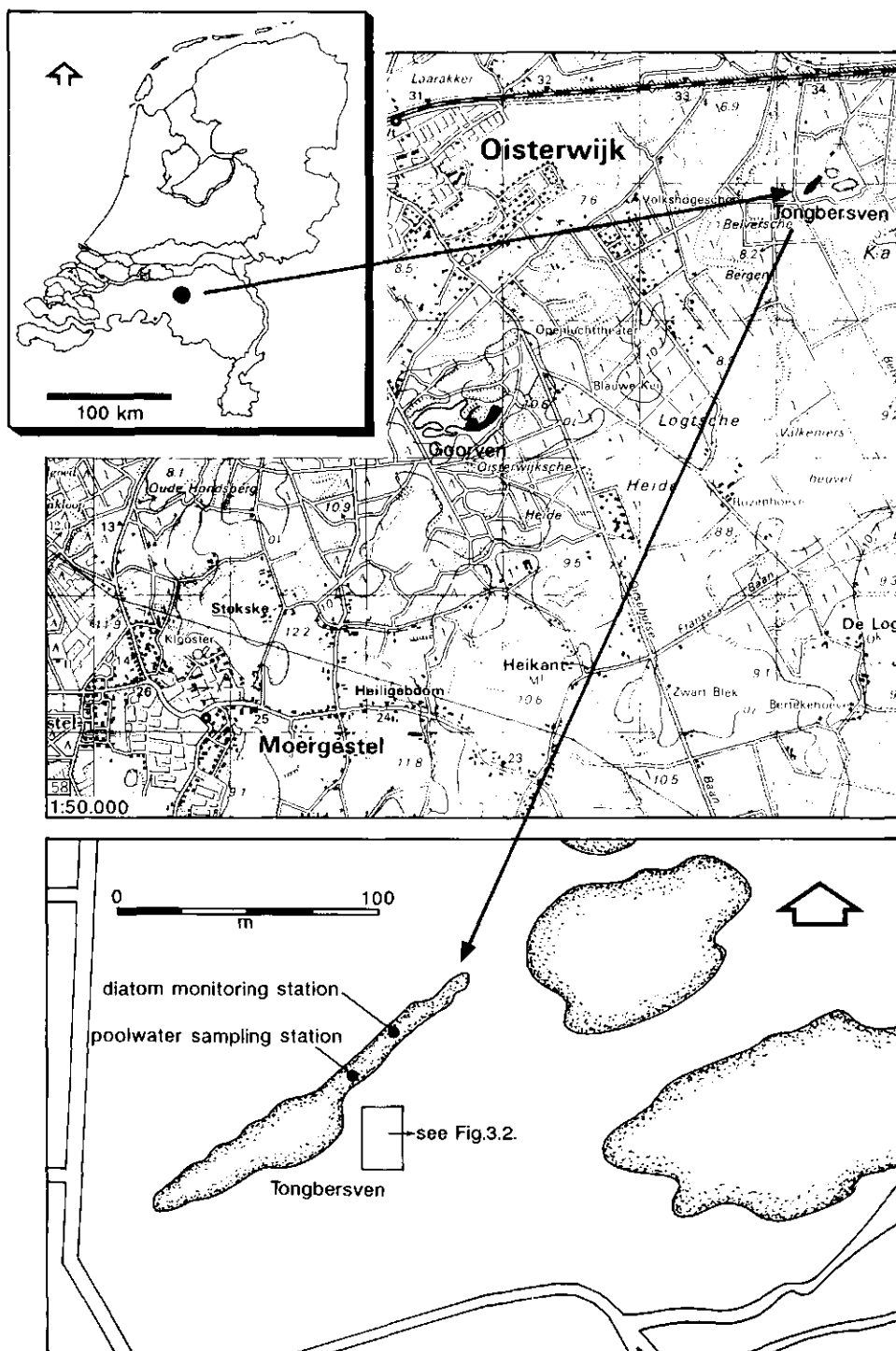


Figure 2.2. Topographic position of Goorven (GV) and Tongbersven (TV).

2.1.3 Tongbersven

Tongbersven (Fig. 2.2) is situated 4 km east of the village of Oisterwijk (51°34'N, 5°14'E), at 8.2 m above NAP. The site includes the pool 'Tongbersven-West', with a surface area of c. 0.46 ha. It is a part of the nature reserve 'Kampina' which is very rich in moorland pools. Hydrobiological aspects of a number of pools in this area were studied by Van Dam & Kooyman-van Blokland (1978), Coesel et al. (1978) and Van Dam (1983). Most of this area is owned by the 'Vereniging tot Behoud van Natuurmonumenten in Nederland'. In this part the paths are open to the public. A smaller part, in which the research site is located, is privately owned and closed to the public. A small cottage at the northern side of the pool is used as a weekend house. Some researchers have used other names for Tongbersven-West, including Palingven-West (Glas 1957), Palingvennen and Tongbersvennen (Verschoor 1977).

In the beginning of the 19th century, the Tongbersven site was transformed from heathland into a Scots pine forest (Van Hees & Van den Wijngaard 1977). On the 1:25 000 topographical map from 1930 the northern shore is indicated as a tree plantation, while spontaneous regrowth of trees occurred south of the pool. On the 1949 map part of the forest at the northern side of the pool was cut, while in 1961 and later the pool was totally surrounded by forest.

2.1.4 Gerritsfles

Gerritsfles (Fig. 2.3) is situated 4.5 km SE from the village of Kootwijk (52°10'N, 5°49'E), at 39.9 m above NAP. The site includes the moorland pool 'Gerritsfles', with a surface area of c. 6.8 ha. The pool and its surroundings are a nature reserve owned by the State Forestry Service, and closed to the public. Bathing occurred until 1965 (Bink and Schimmel 1975).

Until 1921 the Gerritsfles pool was situated in an entirely open landscape (topographic maps 1:25 000). This situation was recorded vividly by photographs in Tesch et al. (1926). On the maps of 1899 bare sand dunes occurred on the southwestern side, while the rest of surrounding area consisted of heathland. In 1928 a grassland parcel existed on the northwestern side of the pool, while spontaneous regrowth of trees occurred at the southwestern side. The size of this small forest lot increased in later years.

The moorland pool Gerritsfles is a classical site for hydrobiological research in the Netherlands. After preliminary studies by De Beaufort (1913) the pool was surveyed by a team under the guidance of Prof. M. Weber and Dr. J. Romijn in 1918. Since then the pool was regularly visited by hydrobiologists, particularly Redeke & De Vos (1932), Dresscher et al. (1952) and Van Dam et al. 1983 (see also Higler 1979). The scientists were attracted by the nearly undisturbed habitat, the presence of so-called glacial relict species, e.g. *Eurycercus glacialis* and *Dytiscus lapponicus*, and the characteristic hydrology of this rainwater-fed pool.

The finding that the pool is fed by rainwater only was published as early as 1952

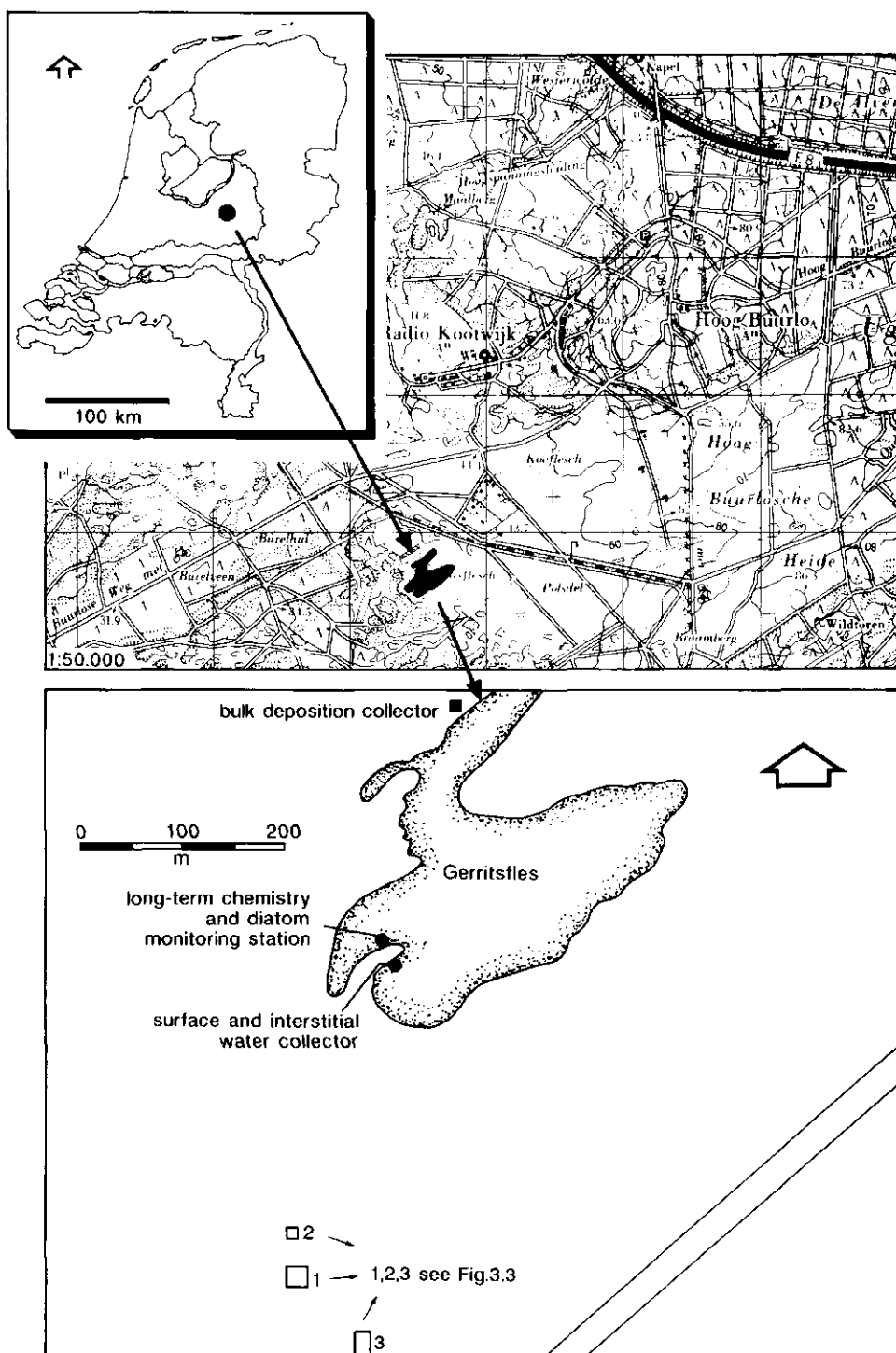


Figure 2.3. Topographic position of Gerritsfles (GF).

(Schimmel & Ter Hoeve). Seepage of water through the pool bottom is probably of limited importance, due to a practically impermeable ferruginous hard pan. However, excess water may leave the pool by periodic underground overflow over the ore-wall formed by the vertical extension of the iron pan. Fluctuations of the water-level in the pool are small. The groundwater table is c. 15 m beneath the bottom of the pool.

2.1.5 *Kliplo*

Kliplo (Fig. 2.4) is situated 4 km east of the village of Dwingeloo (52°50'N, 6°26'E), at c. 13.0 m above NAP. The site includes the pool 'Kliplo', also known as 'Kiplo' or 'Kipelo', which has a surface area of c. 0.6 ha. It is in a nature reserve owned by the State Forestry Service, and also includes a number of other pools, differing in chemistry and biota (Coesel & Smit 1977). The site is closed to the public now, but until 1971 the pool was used for bathing (Brouwer 1968, Londo 1973). In winter the pool is used as a skating-rink.

The heathland originally surrounding the pool was afforested, mainly with Scots pine, between 1910 and 1925. At the pool's northwestern side is a remnant of a small ditch, which may have been a pipe of a duck decoy. Probably the pool has been used for catching ducks in the 19th century, and therefore nutrients may have been introduced into the pool.

Kliplo was one of the pools which was intensively studied by Beijerinck (1926) in his classical thesis on the distribution and periodicity of fresh water algae in the province of Drenthe. Most of the pools in this region harbour only a small number of species of algae, except for a few pools, including Kliplo, which appeared to be mines of algae. These findings inspired the members of the Hydrobiological Club to make a more complete inventory of this relatively small pool (see e.g. Redeke & De Vos 1932). Later on, the site was regularly sampled by other investigators, which permits the construction of a time series of plankton samples.

Like the Gerritsfles pool, Kliplo is fed by rainwater only. This is also evident from the forest floor surface some tens of metres north of the pool, which is situated below the water surface of the pool.

2.2 Geology and physiography

2.2.1 *Hasselsven*

The Hasselsven site is part of the southern coversand landscape, which is weakly undulating and intersected by brook valleys. At greater depth below soil surface various deposits are present, e.g. Formation of Sterksel (mainly consisting of interglacial Rhine deposits), Formation of Eindhoven (local material deposited during the Saalien glaciation, consisting of stratified coarse and fine sand, including loamy material) and Formation of Asten (deposition of peaty and humous sandy or loamy material formed in the warmer climate of the Eemien). Near the surface thick layers (up to 30 m) of

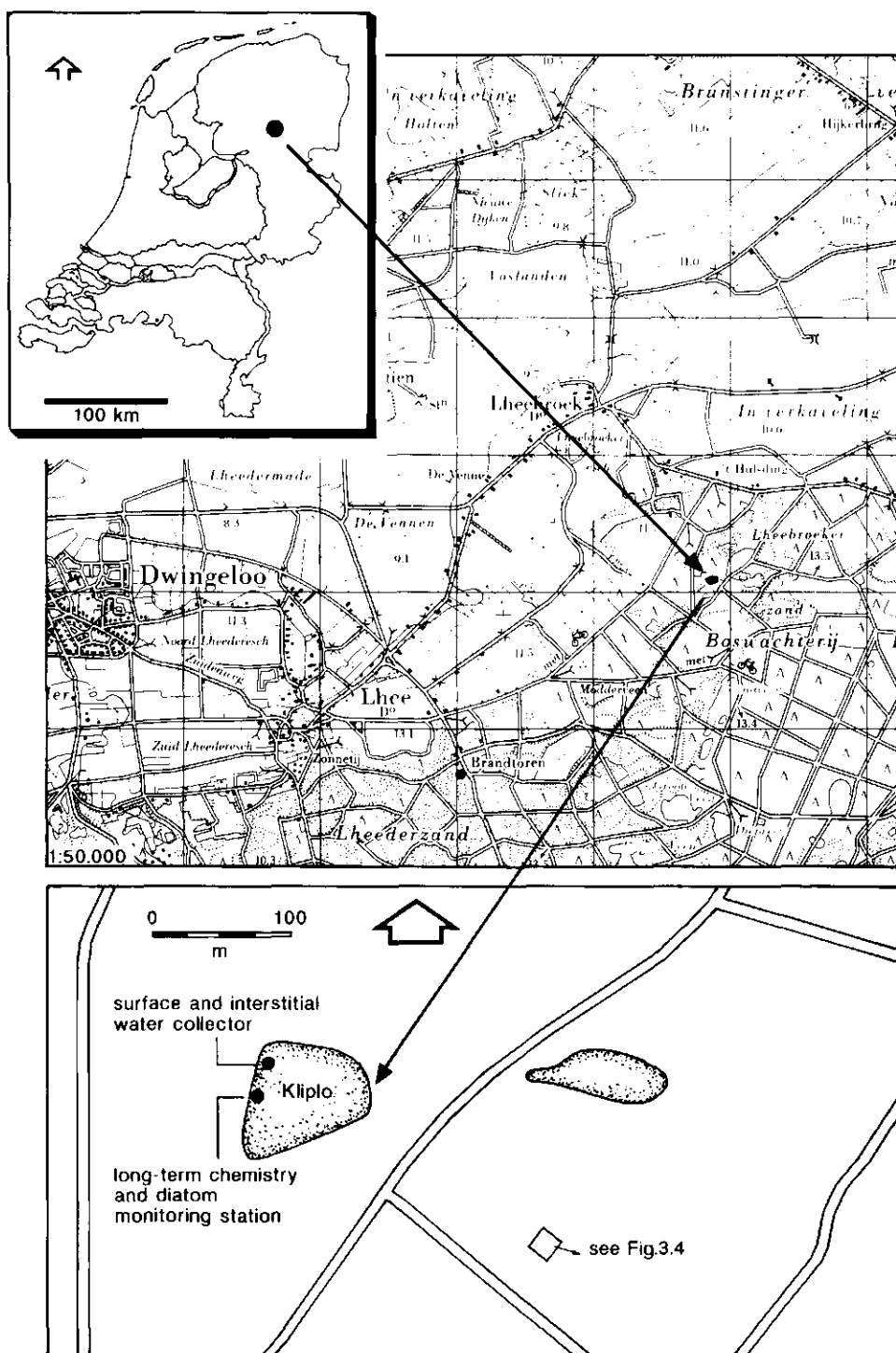


Figure 2.4. Topographic position of Kliplo (KL).

local material were deposited during the Weichselien glaciation (Formations of Eindhoven and Twente). The older part of the Twente formation is influenced by fluvio-periglacial processes and consists of fine sand, loamy fine sand and inclusions of sandy loam. The younger parts of the Eindhoven formation are of aeolian origin and vary in thickness (Older Coversand I and II, and Younger Coversand I and II, respectively). The Younger Coversand I is generally better sorted and therefore less stratified, but often shows a stronger relief than the Older Coversand. After the Allerød period the Younger Coversand II was deposited at only a few places during the last glaciation. Holocene deposits are found in the brook valleys or as local driftsands due to overcropping of forests and heathlands.

2.2.2 Tongbersven and Goorven

Both sites are situated in the western part of the so-called 'Central Rift Valley'. During the greater part of Tertiary and Quarternary this rift valley was filled with hundreds of meters of sediment. The upper 10 to 40 m are sediments originating from the last three glacial periods and belong to the so-called 'Nuenen group'. These sediments consist of loamy deposits, fluvio-periglacial sands and coversands. Like in the Hasselsven area aeolian coversand deposits were formed in the Pleistocene during the last glaciation. In the late Pleistocene and the early Holocene dunes and depressions were formed in the weakly undulating landscape under the influence of predominantly western winds. These sand dunes, which are poor in loamy material and more loosely packed than the underlying Pleistocene coversand, generally show less soil formation. Other early Holocene deposits consist of peat and (sometimes loamy) brook sediments. Later in the Holocene local driftsands were formed.

2.2.3 Gerritsfles

The deposits at greater depth originate from eastern rivers and consist of very pale sands (Formations of Harderwijk and Enschede). These sands were covered by Rhine deposits (Formation of Urk) which have a richer mineralogical composition. During the Saalien glaciation part of the ice cap, advancing to the south, pushed up ridges of the earlier deposits. The area of the Gerritsfles is situated at the foot of a south-west slope of such a ridge. During the last glaciation (Weichselien) aeolian sands were deposited, known as Old Coversand and Young Coversand I and II. In the Holocene Young Coversand II was locally blown and resedimentated (drift sands), giving the landscape a more pronounced relief. The terrestrial research site is situated in such a drift sands area, which is locally still active. The moorland pool is at the borderline of driftsand and coversand.

2.2.4 *Kliplo*

Like at Gerritsfles deposits of eastern rivers (Formations of Harderwijk and Enschede) overly Tertiary deposits. In the Elsterian glaciation these early pleistocene deposits were covered by fluvio-glacial and aeolian material (Formations of Peelo and Eindhoven, respectively). During the Saalien glaciation moraine material was deposited (boulder clay) in which during the warmer Eemien period weathering and soil formation took place. The last glaciation (Weichselien) in this area was mainly characterized by the deposition of aeolian sands. In the research area these coversands mainly consist of Young coversand I and II and to a lesser extent of Old coversands.

2.3 Soils

2.3.1 *Soil distribution at the research sites*

In the **Hasselsven** coversands 'dry' (moderately well drained) and 'wet' (poorly drained) podzolic soils have developed (soil map of the Netherlands 1:50 000, sheet 57 O, Stiboka 1972). A detailed soil survey of the area indicated that the gley features present from 40-95 cm below soil surface in the dry podzolic soils become less pronounced or even disappear in the wet ones (Hootsmans & Wallis de Vries 1985). In the dry podzols, the top of the C horizon is very shallow (c. 30 cm below the soil surface) while in wet podzols the C horizon may even start below 200 cm depth. A distinct textural change in the coversand deposits was observed at c. 65 cm depth, with a median between 150 and 210 μm above and between 105 and 150 μm below this depth. This textural change may be related to different coversand formations. The soil solution monitoring plot is located in the drier part of the area. The profile is classified as a 'Haarpodzol' soil according to the Dutch classification system (De Bakker & Schelling 1966). The groundwater table at the soil solution monitoring plot varies between 1.3 and 2.9 m below soil surface.

In both the **Goorven** and **Tongbersven** areas three soil types are distinguished (soil map of the Netherlands 1:50 000, sheet 51 W, Stiboka 1985): sand dunes with little soil development, dry podzol soils (both with a groundwater table at least several metres below soil surface) and wet podzol soils (with a groundwater table temporarily within one metre below soil surface). All soils have a texture of fine sand, poor in loamy material. A detailed soil survey (scale 1:2500) at the Tongbersven site revealed three other soil types: transitional podzol soils, having pronounced gley features; wet soils with little soil formation characteristics, and wet soils with an A1/Ap horizon of at least 15 cm (Schipper, 1984). The soil solution monitoring plot at the Tongbersven site is situated on a dry podzol soil ('Haarpodzol'), one of the major soil types surrounding the moorland pool. The groundwater table at the Tongbersven plot varies between 3.5 and 4.8 m below soil surface.

In the sandy area of the **Gerritsfles** different soil types exist depending on the nature of the parent material and the hydrological conditions. In the relatively poor, but well

drained sands from the early Pleistocene (formations of Harderwijk and Enschede) mainly dry podzolic soils ('Haarpodzol' soils) occur. In the richer materials from the river Rhine (formation of Urk) coarse sandy and gravelly brown soils ('Holtpodzol') are developed. In the Young Coversand II alternating dry and wet podzolic soils ('Haarpodzol' and 'Veldpodzol' soils) occur, depending on topography and related hydrological conditions. The moorland pool is surrounded by a zone of wet podzolic soils developed in fine sand. To the east mainly dry podzols occur, developed in fine and coarse sands, often with gravelly material at shallow depth. To the west mainly drift sands are present, in many cases with gravel in the subsoil ('Duinvaag' soils; 1:50 000 soil map of the Netherlands, sheet 33 W, Stiboka 1979). The two soil solution monitoring plots at the Gerritsfles (GFF and GFB) were established in the driftsand area with 'Duinvaag' soils. Groundwater depth at this site is c. 15 m below soil surface.

Kliplo is situated in an area with a complex of wet and dry soils without distinct soil formation (soil map of the Netherlands 1:50 000 sheet 17 W, Stiboka 1979). Parent material consists of non-loamy or weakly loamy fine sands. At greater distance from the pool other soil types occur: dry podzols, wet podzols (sometimes with a peaty topsoil) and soils with a plaggen epipedon. All these soil types may have a boulder clay layer between 40 and 120 cm below soil surface. Depending on the topographical position the groundwater table varies from about 20 to >100 cm below soil surface.

2.3.2 Soil classification, chemistry and mineralogy

Detailed soil descriptions were made for the four plots where soil solution monitoring took place: Hasselsven (heath vegetation) Tongbersven (forest vegetation), Gerritsfles (forest vegetation) and Gerritsfles (scattered algae and mosses).

2.3.2.1 Methods

All soils were described using the 'Guidelines for soil description' (FAO 1977) and classified according to De Bakker & Schelling (1966) and Soil Survey Staff (1975). Soil particle size analysis was done at the 'Laboratorium voor grond- en gewasanalyse Mariendaal' at Oosterbeek, by sieving and gravity sedimentation, after treatment with hydrogenperoxide to remove organic matter. Bulk density measurements were carried out at the Dept. of Tillage Research, Agric. University Wageningen.

The analytical methods used are as follows (for details of most of the methods see Begheijn 1980):

Air-dried soil was crushed and sieved (2 mm), so that all analyses refer to the fine earth (< 2 mm) fraction. Soil pH was determined in a 1:2.5 (mass to volume) extract in water and in 0.01 mol/l CaCl_2 . Total organic C was measured potentiometrically as CO_2 , after wet combustion in a phosphoric-chromic acid mixture. Nitrogen was transferred to ammonia with sulfuric acid and selenium, followed by steam distillation into boric acid and back titration of ammonium borate. 'Free' Al_2O_3 and Fe_2O_3 refer to dithionite-oxalate extractable fractions, assayed colorimetrically with ortho-

phenantroline (Fe) and pyrocatechol violet (Al). 'Amorphous' Fe_2O_3 was extracted by oxalic acid-ammonium oxalate and measured by Atomic Absorption Spectrometry (AAS). Various fractions of free Al were extracted sequentially with: 1) 1.0 mol/l KCl (exchangeable), 2) 0.1 mol/l $\text{Na}_4\text{P}_2\text{O}_7$ (organic), 3) 0.2 mol/l $(\text{NH}_4)_2\text{C}_2\text{O}_4$ adjusted to pH 2 (amorphous), and 4) dithionite-oxalate (crystalline, free) (USDA 1972, Driscoll et al. 1985). The $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and dithionite-oxalate extracts were oxidized with heat and aqua regia before analysis. Aluminium in the pyrophosphate extracts was determined by AAS with a nitrous oxide acetylene flame, while the other extracts were analyzed colorimetrically using pyrocatechol violet. Organic C dissolved in the pyrophosphate extracts was measured by combustion followed by infrared detection. The cation exchange capacity (CEC) and the exchangeable cations were measured using Bascomb's (1964) $\text{BaCl}_2\text{-MgSO}_4$ method. Soil elemental analysis, except for FeO, Fe_2O_3 , Na_2O and MgO, was done by X-ray fluorescence spectroscopy of a Li-tetraborate melt of the soil material. FeO, Fe_2O_3 , Na_2O and MgO were analysed colorimetrically with orthophenantroline before (Fe(II)) and after reduction (Fe(II) + Fe(III)) by hydroquinone, or by AAS (Na_2O , MgO) after a 10 second HF- H_2SO_4 destruction at 60 °C.

2.3.2.2 Results

The main features of the four sites will be discussed below, in the order driftsand without (GFB) and with forest (GFF) and coversand without (HV) and with forest (TV). Since the parent material and the profile development of GFF and GFB on the one hand and of TV and HV on the other are similar, the soil characteristics of GFF and GFB and of TV and HV will be discussed together. Soil profile descriptions are given in Appendix 1. Mass fractions given in Tables 2.2 tot 2.8 refer to oven dried (105 °C) soil.

Gerritsfles bare and Gerritsfles forest. The well-sorted parent material consists for 75% of very fine and fine sand and for 20% of medium sand, with a clear sedimentary layering resulting from slight differences in the organic matter content. The clay fraction is only 1% of the mineral soil (Table 2.2). The texture is uniform with depth in both profiles, with medians ranging from 158 to 172 μm (GFB) and 154 to 159 μm (GFF).

Both soils are young driftsands, show few signs of soil formation, and are classified as Typic Udipsamments (Soil Survey Staff 1975). The most striking visible differences between the two soils are (1) the seven to ten cm thick forest floor at GFF, consisting of little decomposed pine litter in which roots are abundant, (2) the slightly darker colour of the GFF soil, which is probably due to the presence of translocated organic C originating from the forest floor and (3) the presence of fine roots in the upper 60 cm of the mineral soil at GFF. The bulk density at GFF ranges from 1.37 $\text{kg}\cdot\text{dm}^{-3}$ in the surface soil to 1.49 $\text{kg}\cdot\text{dm}^{-3}$ at 100 cm soil depth, and is distinctly lower than that at GFB (1.6 $\text{kg}\cdot\text{dm}^{-3}$). At GFB the bulk density is constant over the whole soil

Table 2.2. Particle size distribution (μm) of the four soils studied.

Site	Depth	Horizon	% of mineral soil, size						Median
			0-2	2-50	50-105	105-210	210-420	420-2000	
GFF	0-0.5	C	1.1	2.7	9.2	71.0	14.3	1.7	154
	0.5-25	C	1.1	1.4	9.0	71.3	15.9	1.3	157
	25-75	C	0.8	1.1	8.5	66.7	21.0	2.0	159
	75-150	C	0.6	1.4	10.8	65.5	18.9	2.8	157
GFB	0-0.5	C	0.8	1.1	8.7	70.9	16.5	2.0	158
	0.5-25	C	0.9	1.2	6.6	62.7	23.3	5.3	172
	25-75	C	1.0	0.9	5.8	68.9	22.8	0.6	169
	75-150	C	1.1	0.6	4.6	72.4	20.5	0.8	167
TV	0-10	E	1.2	3.6	18.6	57.0	17.1	2.5	146
	10-20	E	0.4	3.9	15.9	59.6	18.9	1.4	147
	20-40	Bhs	1.8	3.0	17.0	58.0	18.7	1.7	150
	40-58	Bs	1.3	4.8	19.0	58.9	15.2	0.8	142
	58-90	BC1	0.1	2.1	14.5	58.7	22.7	1.7	158
	90-150	BC2	0.2	2.5	18.2	62.3	16.2	0.7	147
HV	0-9	E	1.3	6.9	16.2	50.3	18.5	6.9	146
	9-15	Bhs	1.2	7.5	14.3	51.0	19.2	6.1	147
	15-33	Bhs2	1.6	7.5	15.8	49.4	19.9	5.8	149
	33-73	Bs	2.1	4.4	18.3	53.2	14.8	7.4	141
	73-120	C	1.7	3.5	28.6	54.7	6.9	4.7	125

Table 2.3. Mean and standard deviation of the bulk densities of the four soils studied ($\text{kg}\cdot\text{dm}^{-3}$). sd = standard deviation. Depth in cm.

Site	Depth	Hor.	Mean	sd
GFF	0-25	C	1.37	0.01
	25-75	C	1.47	0.09
	75-150	C	1.49	0.05
GFB	0-25	C	1.62	0.04
	25-75	C	1.62	0.02
	75-150	C	1.60	0.02
TV	0-10	E	1.31	0.07
	25-40	Bhs	1.23	0.02
	40-58	Bs	1.32	0.02
	70-88	BC1	1.41	0.01
	90-150	BC2	1.56	0.03
HV	0-9	E	1.47	0.00
	9-15	Bhs1	1.33	0.01
	15-33	Bhs2	1.16	0.09
	33-73	Bs	1.45	0.02
	73-120	C	1.52	0.01

Table 2.4. pH and exchangeable cations ($\text{mmol}_c \cdot \text{kg}^{-1}$) of the four soils studied. Depth in cm.

Site	Depth	Hor.	pH(H ₂ O)	pH(CaCl ₂)	Ca	Mg	Na	K	Al	H	Sum
GFF	0-0.5	C	3.63	2.77	3	1	0	0	18	30	52
	0.5-25	C	4.05	3.52	0	0	0	0	6	5	11
	25-75	C	4.08	3.95	0	0	0	0	2	7	9
	75-150	C	4.16	4.00	0	0	0	0	2	2	4
GFB	0-0.5	C	5.87	4.54	0	0	0	0	0	4	4
	0.5-25	C	5.43	4.10	0	0	0	0	0	3	3
	25-75	C	4.40	4.38	0	0	0	0	0	2	2
	75-150	C	4.82	4.33	0	0	0	0	0	2	2
TV	0-10	E	3.77	2.95	1	0	0	0	11	15	27
	10-20	E	3.86	3.07	0	0	0	0	8	14	22
	20-40	Bhs	3.93	3.63	0	0	0	0	109	18	127
	40-58	Bs	4.20	4.21	0	0	0	0	11	3	14
	58-90	BC1	4.35	4.29	0	0	0	0	0	4	4
	90-150	BC2	4.38	4.25	0	0	0	0	0	5	5
HV	0-9	E	3.90	3.00	2	1	0	1	34	26	64
	9-15	Bhs1	4.17	3.49	2	1	0	0	49	25	77
	15-33	Bhs2	4.29	4.04	1	1	0	0	29	2	33
	33-73	Bs	4.56	4.34	1	1	0	0	7	0	9
	73-120	C	4.49	4.27	1	1	4	0	5	1	12

profile (Table 2.3).

Chemically, the most pronounced difference between GFF and GFB is the soil pH (Table 2.4). The unvegetated GFB soil is slightly less acidic, with a lowest pH(H₂O) of 4.4 between 25 and 75 cm depth, than the forested site (GFF), where pH ranges from 3.6 in the surface centimeters to 4.2 in the subsoil. The lower soil pH at GFF may be related to (1) soil acidification due to nutrient uptake, (2) production and leaching of organic acids in the forest soil and (3) higher acid loadings from atmospheric sources in the pine stand, due to increased dry deposition of (NH₄)₂SO₄ (Van Breemen et al. 1982).

Although a marked difference in organic C content of the GFF soil relative to that in GFB is suggested by the darker colour of the forest soil throughout the profile, Table 2.5 indicates only slightly higher carbon contents below 25 cm depth (0.24 and 0.33% at GFF vs. 0.22 and 0.08% at GFB). The clear difference in organic C content of the surface layers of the mineral soil (5.38 and 0.45% at GFF vs. 0.48 and 0.25% at GFB) is mainly due to the presence of discrete organic particles (e.g. from dead roots) at the forested site. The surface layer at GFB has a slightly raised organic C level relative to that in the subsoil due to the growth of algae and mosses on the soil surface. The N content is highest in the forest floor and shows elevated levels in the surface layer of the mineral soil at the forested site. Below 0.5 cm depth the N content does not exceed 0.03% (weight basis) in neither of the two soils. The C/N ratios in the GFF forest floor and in both mineral soils are low and are indicative for a luxurious N supply.

Table 2.5. Soil organic carbon and nitrogen contents (% of dry weight), as well as C/N ratio of the four soils studied. Depth in cm.

Site	Depth	Hor.	C	N	C/N
GFF	10-0	O1	49.60	2.00	24.8
	0-0.5	C	5.38	0.23	23.4
	0.5-25	C	0.45	0.03	15.0
	25-75	C	0.24	0.02	12.0
	75-150	C	0.33	0.01	33.0
GFB	0-0.5	C	0.48	<0.01	—
	0.5-25	C	0.24	0.02	12.0
	25-75	C	0.22	0.01	22.0
	75-150	C	0.08	<0.01	—
TV	5-0	O1	44.40	1.60	27.8
	0-10	E	2.13	0.05	42.6
	10-20	E	1.06	0.02	53.0
	20-40	Bhs	4.54	0.09	50.0
	40-58	Bs	0.62	0.01	62.0
	58-90	BC1	0.02	<0.01	—
	90-150	BC2	0.05	<0.01	—
HV	3-0	O1	41.80	1.60	26.1
	0-9	E	2.48	0.12	20.7
	9-15	Bhs1	2.27	0.17	13.4
	15-33	Bhs2	1.17	0.08	14.6
	33-73	Bs	0.00	0.14	—
	73-120	C	0.00	0.05	—

Associated with the low clay and organic matter contents, CEC's are also low in both soils, except in the surface layer of GFF ($52 \text{ mmol}_c \cdot \text{kg}^{-1}$). Exchangeable cations are primarily aluminium and hydrogen ions (Table 2.4).

In both soils the content of free Fe (III)-oxides is low (0.19 to 0.21% at GFB and 0.20 to 0.27% at GFF) and constant with depth. Only a minor portion of this free Fe_2O_3 is in an amorphous form (Table 2.6). Levels of dithionite-oxalate extractable, so-called 'free', Al in the two soils are low too (0.25 to 0.39% at GFB and 0.17 to 0.40% at GFF; Table 2.6). Sequential extraction of Al (Fig. 2.5) demonstrates two distinct differences between GFB and GFF: (1) in the upper 0.5 cm the free Al level is lower at GFF than at GFB, while at greater depth the two sites do not differ in this respect, and (2) free Al in the bare soil is primarily in an oxalate extractable (amorphous, non organically complexed) form, while the forested soil has higher pyrophosphate extractable (organically complexed) Al levels. Apparently the organic Al fraction in the forest soil has increased at the expense of oxalate extractable Al.

Although Al is the second most abundant element in the soil (on an oxide mass basis), total Al_2O_3 contents amount to only 2.0 to 2.3% (GFB) and 2.2 to 2.4% (GFF) of the soil solid phase. This indicates that roughly 10 to 20% of the total Al in these soils is in a free form (Al hydroxides and organic Al compounds), while the

rest is present in aluminium silicates (Table 2.7). The very high contents of SiO_2 (more than 95% of the mineral soil) and the extremely low contents of MgO , CaO , Na_2O and K_2O (roughly 0.05, 0.10, 0.45 and 0.90%, respectively; Microfiche) indicate that both the GFF and GFB soils are mineralogically very poor.

Table 2.6. Amorphous and free Fe_2O_3 , as well as free, total, and total minus free (Δ) Al_2O_3 as a percentage of fine earth in the four soils studied. Depth in cm.

Site	Depth (cm)	Hor.	Fe_2O_3		Al_2O_3		
			amorph.	free	free	total	Δ
GFF	0-0.5	C	0.10	0.27	0.17	2.38	2.21
	0.5-25	C	0.07	0.22	0.26	2.34	2.08
	25-75	C	0.10	0.21	0.40	2.22	1.82
	75-150	C	0.07	0.20	0.29	2.34	2.05
GFB	0-0.5	C	0.08	0.19	0.26	2.31	2.05
	0.5-25	C	0.06	0.19	0.25	2.02	1.77
	25-75	C	0.06	0.21	0.30	2.29	1.99
	75-150	C	0.07	0.19	0.39	2.33	1.94
TV	0-10	E	0.04	0.04	0.07	0.50	0.43
	10-20	E	0.02	0.04	0.05	0.55	0.50
	20-40	Bhs	0.41	0.44	1.17	2.32	1.15
	40-58	Bs	0.14	0.28	0.70	2.39	1.69
	58-90	BC1	0.06	0.16	0.31	1.61	1.30
	90-150	BC2	0.06	0.20	0.33	1.84	1.51
HV	0-9	E	0.09	0.21	0.12	1.15	1.03
	9-15	Bhs1	0.50	0.66	0.31	1.42	1.11
	15-33	Bhs2	0.30	0.44	0.54	1.77	1.23
	33-73	Bs	0.11	0.39	0.42	2.37	1.95
	73-120	C	0.09	0.33	0.44	2.51	2.07

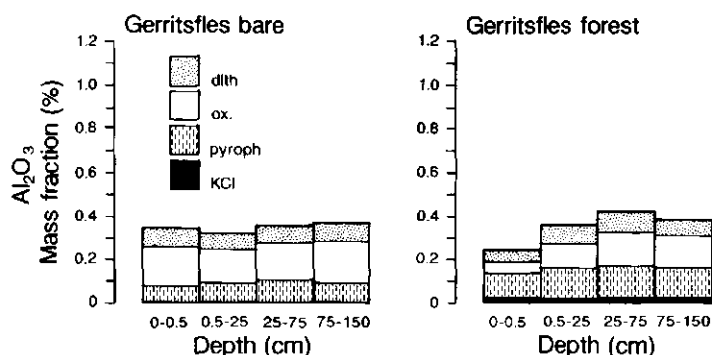


Figure 2.5. Gerritsfles bare and Gerritsfles forest, sequentially extracted Al_2O_3 in % of the mass fraction.

Table 2.7. Molar amounts of Si and base cations relative to the amount of ΔAl in Table 2.6. Depth in cm.

Site	Depth	Hor.	Si	Al	Mg	Ca	Na	K
GFF	0-0.5	C	33.17	1.00	0.04	0.06	0.34	0.44
	0.5-25	C	38.65	1.00	0.03	0.05	0.38	0.46
	25-75	C	45.26	1.00	0.04	0.06	0.41	0.52
	75-150	C	40.14	1.00	0.04	0.05	0.43	0.48
GFB	0-0.5	C	40.03	1.00	0.04	0.05	0.39	0.48
	0.5-25	C	46.34	1.00	0.02	0.05	0.41	0.51
	25-75	C	41.35	1.00	0.04	0.04	0.36	0.51
	75-150	C	42.60	1.00	0.02	0.05	0.36	0.52
TV	0-10	E	192.67	1.00	0.00	0.02	0.50	0.71
	10-20	E	167.72	1.00	0.00	0.02	0.33	0.74
	20-40	Bhs	64.44	1.00	0.00	0.04	0.30	0.54
	40-58	Bs	48.27	1.00	0.04	0.04	0.29	0.46
	58-90	BC1	64.16	1.00	0.03	0.04	0.34	0.52
	90-150	BC2	55.33	1.00	0.05	0.04	0.32	0.51
HV	0-9	E	77.68	1.00	0.06	0.04	0.29	0.46
	9-15	Bhs1	71.05	1.00	0.05	0.03	0.27	0.47
	15-33	Bhs2	65.44	1.00	0.04	0.04	0.27	0.44
	33-73	Bs	40.97	1.00	0.05	0.04	0.23	0.45
	73-120	C	39.08	1.00	0.04	0.04	0.29	0.47

Table 2.8. Mineralogical composition (%) of the 75-106 μm fraction of the Gerritsfles soils. Depth in cm.

Site	Depth	Heavy min.	Alkali feldsp.	plagioclase	quartz
GFF	0-10	0.38	7.4	0	92.2
	100-130	0.44	7.4	—	—
GFB	0-10	0.39	4.7	2.4	92.5
	100-130	0.52	5.7	0.8	93.0

Quartz is by far the most important mineral phase present in both soils. About 7% of the grains in all sand and silt fractions of both soils were identified as feldspars by SEM and staining techniques (Table 2.8). The relative elemental composition of the soil indicates that the feldspars present are primarily K and Na feldspars (Table 2.7). Contents of heavy minerals (primarily opaque, tourmaline, granate) are similar for both soils and range from about 5% (volume fraction) in the 2 to 75 μm fraction to 0.4% in the 106 to 212 μm fraction (Wopereis 1985).

X-ray diffraction analyses of the 0 to 2 μm mineral fractions of GFB and the subsoil of GFF indicate the presence of primarily amorphous material with small amounts of illite, kaolinite and soil chlorites. In addition, traces of kaolinite were found the upper 10 cm of GFF (Wopereis 1985).

Hasselsven and Tongbersven. The parent materials at Hasselsven and Tongbersven are well-sorted (TV) and fairly well-sorted (HV) coversands and consist for 75 to 81% (TV) and 65 to 83% (HV) of very fine and fine sand (50 to 210 μm). The mass fraction of clay (particles $< 2 \mu\text{m}$) ranges from 0.1 to 1.8% (TV) and 1.3 to 2.1% (HV) of the mineral soil and reaches its maximum in the Bhs horizons. In contrast to the GFB, GFF and TV soils, the HV soil contains considerable amounts (4.7 to 7.4%) of coarse and very coarse sand (420 to 2000 μm ; Table 2.2). The textures are fairly uniform with depth in both profiles and the medians are slightly lower than in the GFB and GFF soils (142 to 158 μm at TV and 125 to 149 μm at HV).

Soils at both plots are well drained Spodosols (Typic Haplorthods), although the Spodosol characteristics are more pronounced in the forest soil (TV) than in the heathland soil (HV). At both sites the bulk densities are lowest in the spodic horizons (1.2 to 1.3 $\text{kg}\cdot\text{dm}^{-3}$) and increase with depth to c. 1.5 $\text{kg}\cdot\text{dm}^{-3}$ in the BC2 (TV) and C (HV) horizon (Table 2.3).

The Tongbersven soil is slightly more acidic than the Hasselsven soil (Table 2.4). In both soils pH(H_2O) increases with depth: at TV from 3.77 (upper E) to 4.38 (BC2) and at HV from 3.90 (E) to 4.49 (C). Compared to the forested GFF site these Spodosols have a strongly acidic surface soil which extends to a much greater depth (0 to 40 cm at TV and 0 to 9 cm at HV).

The forest floor at TV is similar to the one at GFF, but less deep (Appendix 1). The organic surface layer of the heathland soil (HV) is only three cm thick and consists of *Calluna* litter in various stages of decomposition (Appendix 1). The organic C distribution in the TV mineral soil is characteristic for a Spodosol, with a maximum in the Bhs (4.54%) and a rapid decrease at greater depth (Table 2.5). In accordance with the faint Spodosol characteristics visible in the heathland soil, the organic C content in the HV E horizon (2.48%) is even slightly higher than the organic C content in the Bhs1 horizon (2.27%), and decreases rapidly with depth. Note that the organic C content in the GFF and GFB (driftsand) parent material is higher than in the Spodosol BC and C horizons, which may be due to intermixing of mineral soil with organic top-soil during the deposition of the driftsands.

The N content of the TV and HV surface layers (1.6%) is slightly lower than that in the GFF forest floor (2%). In contrast, the N content in the mineral horizons of both Spodosols is higher than in the two driftsands (Table 2.5). The relatively high N content of the mineral soil at the heathland site HV is somewhat unexpected. Although C/N ratios are similar in the organic surface layers at TV, HV and GFF (25 to 28), they differ considerably for the mineral soil horizons at the three sites, with highest values at TV (> 43) and lowest at HV and GFF (< 33) (Table 2.5).

Due to the low clay contents CEC values are primarily related to the organic matter content and are highest in the Tongbersven Bhs horizon (127 $\text{mmol}\cdot\text{kg}^{-1}$) and the Hasselsven E and Bhs1 horizons (64 and 77 $\text{mmol}\cdot\text{kg}^{-1}$, respectively). These values are substantially higher than those reported for the GFF and GFB soils. Subsoil (Bs, BC and C horizon) CEC values for the Spodosols are less than 10 $\text{mmol}\cdot\text{kg}^{-1}$ and similar to values found in the GFB and GFF soils. Like in both Gerritsfles soils the

exchangeable cations consist almost exclusively of Al and H (Table 2.4).

Contents of 'free' Fe_2O_3 are lowest in the E horizon (0.04% at TV and 0.21% at HV), increase to a maximum in the Bhs horizon (0.44% at TV and 0.66% at HV) and drops to 0.20% in the BC2 (TV) and 0.33% in the C (HV) (Table 2.6). Free iron in the Bhs horizons is largely in an amorphous (oxalate extractable) form. A comparison of all four profiles with respect to free Fe contents reveals that (1) in the sub-soils the levels are highest at HV and lower at the other three sites, (2) its distribution at TV and HV is typical for a Spodosol with high contents in the spodic horizons, and (3) amorphous Fe only contributes significantly in the Bhs horizons at TV and HV (Table 2.6).

Dithionite-oxalate extractable 'free' Al at TV and HV also exhibits a typical Spodosol distribution pattern with lowest values in the E (0.05% and 0.12%, respectively) and highest in the Bhs (1.17% and 0.54%, respectively; Table 2.6). In the sub-soils (BC2 and C, respectively) free Al levels decrease again to 0.33% (TV) and 0.44% (HV). As can also be seen from organic C and free Fe distribution patterns, Spodosol characteristics are most pronounced at TV. Sequential extraction of the free Al fraction (Fig. 2.6) clearly demonstrates the importance of pyrophosphate extractable (organically complexed) Al forms in the two Spodosols. Only in both subsoils (BC and C, respectively) oxalate and dithionite extractable Al become relatively important; at these depths both level and chemical form of free Al are similar for the Spodosols and the much younger driftsands at GF.

A total chemical analysis of both Spodosols indicates that Al, although present in small amounts, is the second most abundant element (on an oxide mass basis) in all soil horizons (Microfiche). Assuming that the difference between total and free Al is due to silicate-bound Al, a continuous increase of silicate bound Al with depth is found in both Spodosols. This increase ranges from 0.4% and 1.0% in the E horizons at TV and HV, respectively, to 1.5% and 2.1% in the BC2 (TV) and C (HV) (Table 2.6). Note that not only the E horizons, but also the Bhs horizons in both Spodosols have low contents of silicate bound Al relative to the amounts present in the BC2 (TV)

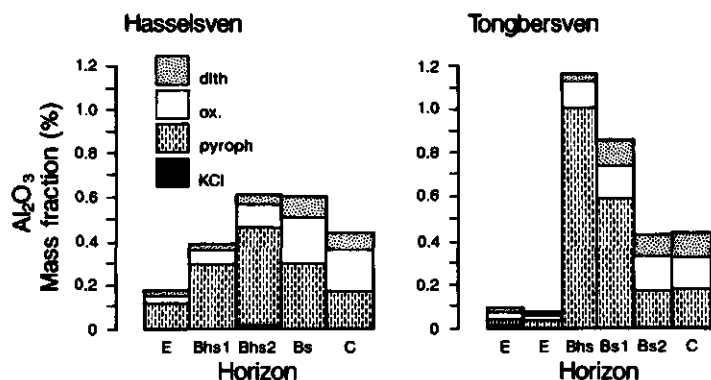


Figure 2.6. Hasselsven and Tongbersven, sequentially extracted Al_2O_3 in % of the mass fraction.

Table 2.9. Water content (volume fraction, in %) as a function of water potential (mbar) for the various soil layers. Values are means and standard deviations of three observations. Depth in cm.

Site	Depth	Porosity		Water potential									
				- 10		- 32		- 100		- 200		- 500	
		mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
HV	0-5	42.9	0.4	41.4	2.0	40.8	1.7	27.9	1.7	17.6	0.6	13.2	0.8
	9-14	48.8	0.4	47.1	0.6	45.0	0.9	28.9	1.4	20.4	0.6	15.8	0.5
	15-20	55.6	4.3	49.3	0.8	43.2	2.0	23.1	3.5	18.0	3.0	14.3	2.5
	43-48	45.4	0.9	37.2	0.9	33.4	1.2	10.9	0.3	6.4	0.2	4.3	0.2
	95-100	43.1	0.6	35.4	0.6	32.8	0.7	9.6	0.8	4.8	0.8	2.9	0.6
TV	2-7	49.2	3.3	43.8	3.7	41.8	3.3	25.3	4.7	16.7	3.2	13.6	2.8
	25-30	52.2	0.6	45.4	2.5	40.6	2.9	29.5	1.8	24.1	1.4	20.3	1.3
	33-38	49.8	0.8	45.7	1.2	40.1	1.3	17.4	1.9	13.6	2.0	11.3	1.9
	43-48	46.8	0.5	43.6	1.1	38.8	0.4	9.6	0.5	6.1	0.0	4.5	0.1
	90-95	41.1	1.4	36.3	1.3	33.6	2.4	7.1	0.1	4.1	0.6	2.5	0.1
GFF	0-5	47.9	0.6	25.5	10.1	19.7	8.4	7.0	0.7	5.6	0.6	4.7	0.5
	25-30	47.6	2.8	29.2	10.6	22.7	8.0	5.1	0.6	3.4	0.3	2.2	0.3
	50-55	41.5	0.8	36.6	0.6	28.7	0.6	5.3	0.2	4.1	0.7	2.9	0.1
	75-80	44.6	2.9	37.0	1.9	27.8	2.6	4.9	0.3	3.8	0.4	2.8	0.2
	100-105	42.6	0.7	37.3	0.4	29.8	0.3	4.8	0.1	3.7	0.3	2.5	0.2
GFB	0-5	38.8	2.1	36.2	0.7	32.6	1.6	5.9	0.3	4.8	0.7	3.1	0.7
	25-30	38.2	1.4	33.5	0.5	30.7	0.9	5.5	0.5	4.2	1.0	2.4	0.2
	50-55	38.8	1.6	33.8	0.8	30.5	1.3	4.5	0.4	3.2	0.1	2.0	0.0
	75-80	39.8	1.1	34.5	0.3	32.0	1.0	4.5	0.6	3.1	0.3	1.8	0.2
	100-105	39.4	0.3	34.9	1.1	32.7	1.1	4.7	0.6	3.4	0.4	2.0	0.3

and C (HV) horizon. The levels of silicate bound Al in the HV C horizon are similar to those found in the GFF and GFB soils (2.0 and 1.9%, respectively). However, in the TV sub-soil amounts are lower (1.5%), which may be due to (1) lower contents of silicate minerals of the parent material at TV, or (2) leaching of Al to deeper soil horizons at this site.

The soil material of the Spodosols is very rich in SiO_2 and extremely poor in K, Na, Ca and Mg (Microfiche). The relative composition of elements in silica bound form in the Spodosols indicates that basic cations are probably present as feldspars. Table 2.7 shows that the alumino-silicate composition is similar for Spodosols and drift-sands, all presumably having K-feldspar as the major Al-silicate. No mineralogical data are available for the TV and HV Spodosols.

2.3.3 Soil physical properties

Soil water characteristics were measured by equilibrating 5 cm long and 5 cm wide undisturbed soil cores at 10, 32, 100, 200, 500 mbar suction and small disturbed samples at 2500 and 16000 mbar suction (Van Breemen et al. 1988). In general tripli-

Table 2.10. Parameters for the closed-form equation for the soil water characteristic ($h(\theta)$; Van Genuchten 1980). WCS = saturated water content, WCR = residual water content (both vol %), a = reciprocal of the air entry value (mbar^{-1}), N = Van Genuchten parameter, exp-K10 = measured conductivity at 10 mbar suction, opt-K10 = optimized conductivity at 10 mbar suction (both $\text{cm} \cdot \text{d}^{-1}$). Depth in cm.

Horizon	Depth	WCS	WCR	a	N	exp-K10	opt-K10
HV							
E	0-10	42.2	1.9	0.2038	1.451	7	7
Bhs1	10-15	47.9	8.5	0.1907	1.794	41	41
Bhs2	15-30	52.4	4.4	0.1945	1.682	120	120
Bs	30-80	45.4	0.9	0.1870	1.552	163	163
C	80-300	43.1	1.1	0.0320	2.154	202	202
TV							
E	0-20	46.7	2.5	0.0875	1.712	46	46
Bhs	20-40	40.8	2.5	0.0485	1.431	36	50
Bs	40-60	47.8	1.6	0.5958	1.323	169	169
BC1	60-90	45.2	0.5	0.4255	1.523	202	202
C2	90-130	38.7	0.6	0.6531	1.502	162	20
GFF							
01	10-0	61.0	0.0	0.0296	1.291	—	500
C	0-30	34.2	0.0	0.3331	1.524	97	50
C	30-120	39.9	1.0	0.0451	2.345	350	70
C	120-130	39.9	1.3	0.0451	2.345	350	20
GFB							
C	0-20	40.0	0.21	0.0306	2.615	255	285
C	20-130	40.0	0.21	0.0306	2.615	255	200

cate samples were analysed at 25 cm depth intervals (GF) or in every soil genetic horizon (TV and HV). Results are shown in Table 2.9.

Hydraulic conductivity was measured by the two plate steady state method (Klute 1972) at 10 mbar suction for two 5 cm long and 5 cm wide cores at the same depth intervals as for the soil water characteristic (Table 2.10).

Soil water potential (h) as a function of water content (θ) was parameterized according to the closed-form equation suggested by Van Genuchten (1980). Hydraulic conductivity (K) as a function of θ was calculated according to Mualem (see Van Breemen et al. 1988) (Table 2.10).

2.4 Pool morphometry

2.4.1 Methods

Enlargements of aerial photographs from the Topographical Service (scale approx. 1 : 18 000) were made to a scale of c. 1 : 1000 to serve as a base for field maps of bathy-

metry and sediment thickness of the moorland pools. Distortion of the photographs was corrected by field measurements.

Water depth was measured by lowering a stick with a white disc (diameter 20 cm) from a dinghy to the depth where the disc touched the sediment surface. Thickness of the soft bottom sediment was estimated from the maximum depth to which a stick (2 cm² cross-section) could be pushed manually into the sediment. Thickness of quacking bog carpets was measured by pushing through the moss carpet a calibrated rod equipped with two 'flapping-down' side-sticks at the rod's lower end, and pulling up the rod until the side-sticks touched the bottom of the quacking bog. Maps were constructed from water depth and sediment thickness measurements that were carried out in a regular pattern (grid distance 10 or 20 m).

2.4.2 *Hasselsven*

No bathymetric map of this pool was made. However, incident field observations indicate that the bottom of the pool is very flat. During the summers of 1982 and 1983 the depth of the water in the largest part of the pool was estimated to be only 0.2-0.4 m. In winter the depth is c. 0.5-0.6 m. Data on the surface area are available from topographic maps (see 2.1.1).

2.4.3 *Goorven*

The results of the survey of bathymetry and sediment thickness on 11, 12 and 13 September 1984 are presented in Figs 2.7-2.9 and Microfiche. The water level on these days was 6 cm below the average water level recorded during the period 1979-1985 (8.34 m + NAP). Data on surface area, volume and other parameters are presented on Microfiche. Depth-area (hypso-graphic) and depth-volume curves are presented in Figs 2.10-2.13.

Goorven has a complex morphology. It consists of a series of smaller and larger basins interconnected by natural channels and man-made ditches. Especially in basin III (Fig. 2.8) a number of small (natural?) islands occur. Consequently, the shore line development (defined as the circumference of the pool divided by the circumference of a circle of the same area) is high (3.98; Microfiche).

The area and volume at mean water level were calculated by extrapolation from Figs. 2.10 and 2.11, respectively. The mean volume is $14.5 \cdot 10^3$ m³ and the mean surface area $23.5 \cdot 10^3$ m², giving a mean depth at mean water level of 0.62 m (Microfiche). The mean depth of basin III, where sampling station E is situated, is only 0.54 m.

Depth to the mineral soil (Fig. 2.7) and waterdepth (Fig. 2.8) have a rather similar distribution. The deepest parts are in basin II, where the maximum water depth is 1.85 m. To the east the depth is generally decreasing (Microfiche; Figs. 2.7 and 2.8). The thickness of the soft bottom sediment layer (Fig. 2.9) is very uneven. The thinnest parts are only 0.1 cm thick, the thickest parts (in wind-sheltered places) more than 1 m.

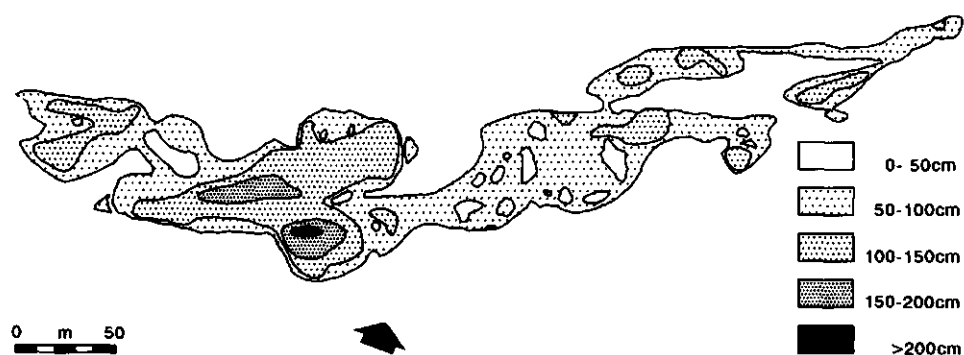


Figure 2.7. Goorven, generalized depth of mineral soil relative to water level on September 11-13, 1984 (water level 8.28 m above NAP).

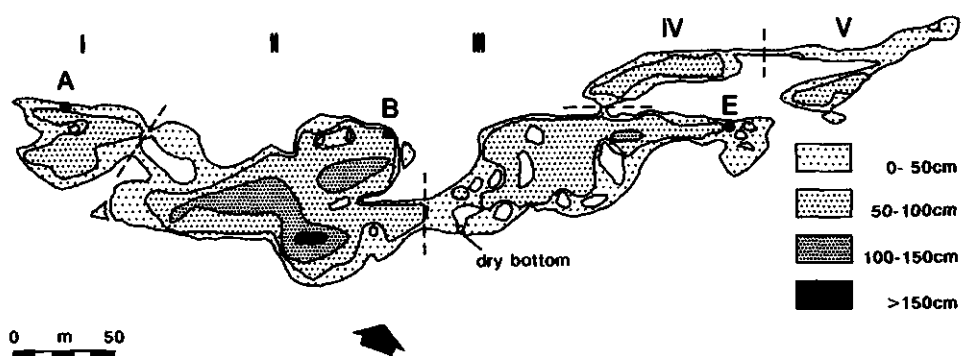


Figure 2.8. Goorven, generalized bathymetric map on September 11-13, 1984 (water level 8.28 m above NAP). I - V = basin numbers, A, B and E = sampling stations.

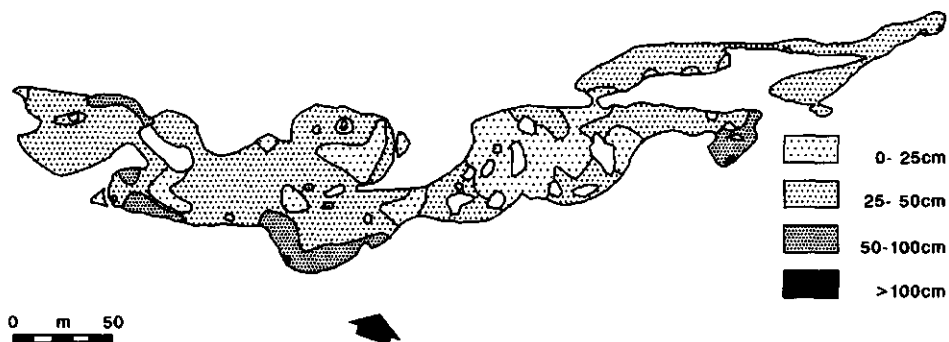


Figure 2.9. Goorven, Generalized thickness of mud layer on September 11-13, 1984.

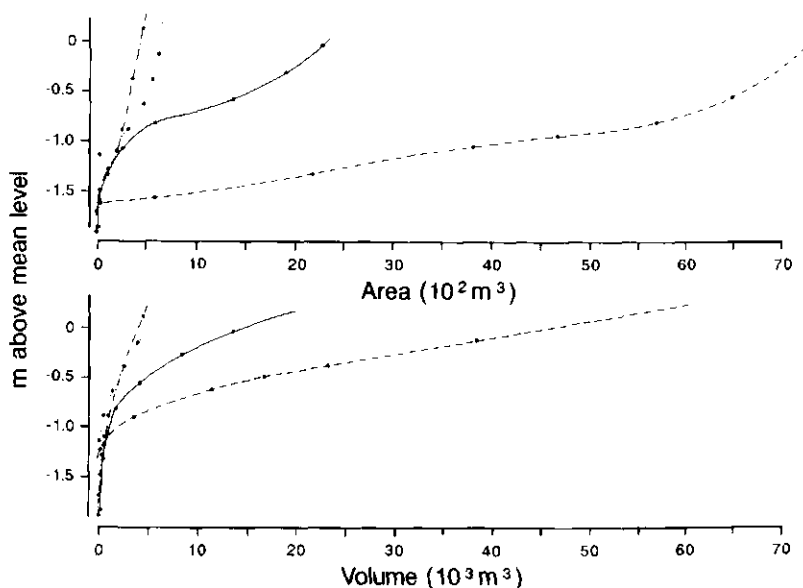


Figure 2.10 (top). Tongbersven (dashed-dotted line), Goorven (solid line), Gerritsfles (broken line), and Kliplo (dotted line): water depth vs. area.

Figure 2.11 (bottom). Tongbersven (dashed-dotted line), Goorven (solid line), Gerritsfles (broken line), and Kliplo (dotted line): water depth vs. volume.

2.4.4 Tongbersven

The results of the survey on 8 January 1985 are presented in Fig. 2.14. The water level on this day was 9 cm above the mean level recorded over the period 1983-1984. Data on volume, area and other parameters are presented on Microfiche. Depth-area and depth-volume curves are presented in Figs 2.10-2.13.

The morphometric parameters of Tongbersven cannot be compared directly to those of the other pools. Below the quacking bog (which covers a large part of the pool) the thickness of the soft bottom sediment could not be measured with the method used. Therefore all morphometric parameters include the soft bottom sediment layer, which can be considerable (maximum measured thickness 85 cm, minimum 7 cm). The quacking bog has a mean thickness of 54 cm. This value should be regarded with caution, however, as the boundary between the bog and the underlying water is difficult to assess.

The area and volume at mean water level, calculated by interpolation are 4380 m^2

Figure 2.14. Tongbersven, January 8, 1985. A. Depth of mineral soil in cm below water level. B. Bathymetric map (depth in cm). C. Thickness of the quacking bog layer in cm (*italics*), thickness of the mud layer (normal). Shortly dashed line: borderline between open water and quacking bog. Long-dashed line: borderline between inundated lagg zone and quacking bog. Water level 8.28 m above NAP.

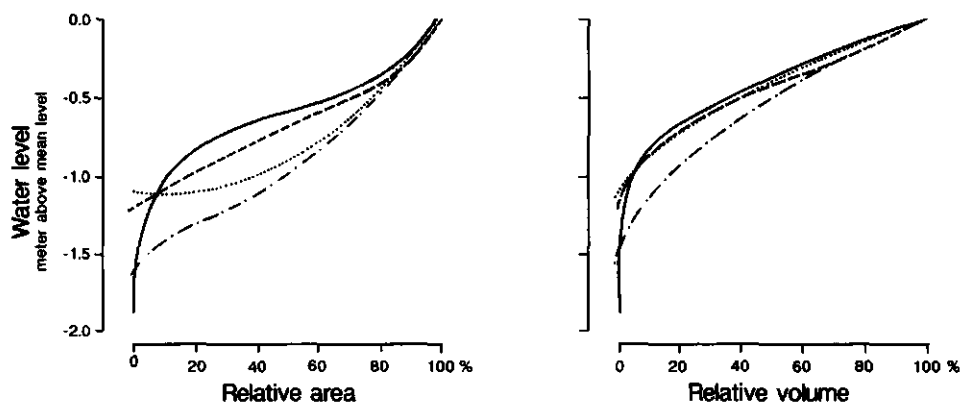
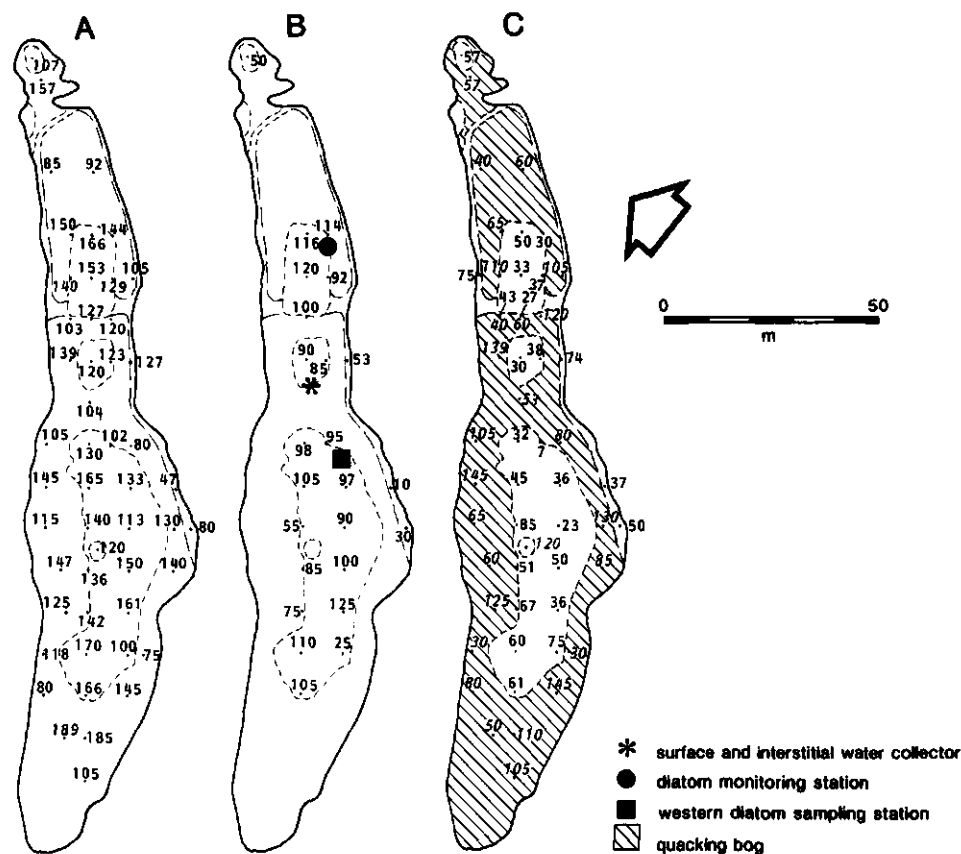


Figure 2.12 (left). Tongbersven (dashed-dotted line), Goorven (solid line), Gerritsfles (broken line), and Kliplo (dotted line): water depth vs. area relative to area at mean water level.

Figure 2.13 (right). Tongbersven (dashed-dotted line), Goorven (solid line), Gerritsfles (broken line), and Kliplo (dotted line): water depth vs. volume relative to volume at mean water level.



and 4000 m³ respectively. The area of the quacking bog (including the relatively narrow lagg zone) is c. 3100 m². The depth of water to the firm bottom at mean water level is 0.94 m (Microfiche). Oostveen (1985) estimated the mean thickness of the soft bottom sediment to be 40 cm, which would give a mean water depth of 54 cm. The maximum depth of the open water (measured to the top of the soft bottom sediment at mean water level) is 1.16 m and is found in the largest open water area.

2.4.5 Gerritsfles

The results of the survey on 18 and 19 September 1984 are presented on Microfiche and in Figs. 2.15-2.17. The water level at these dates was 14 cm below the average level recorded during the period 1979-1985 (39.91 m + NAP). Depth-area and depth-volume curves are presented in Figs 2.10-2.13.

The morphology of Gerritsfles is relatively simple. One large and three small islands are present. The shore line development is c. 2.0. The area and volume at mean water level, calculated by extrapolation from Figs. 2.10 and 2.11, are $67.8 \cdot 10^3$ m² and $45.8 \cdot 10^3$ m³, respectively. The mean depth at mean water level is 0.68 m (Microfiche). Depth of mineral soil and waterdepth (Figs 2.15-2.17) have a rather similar distribu-

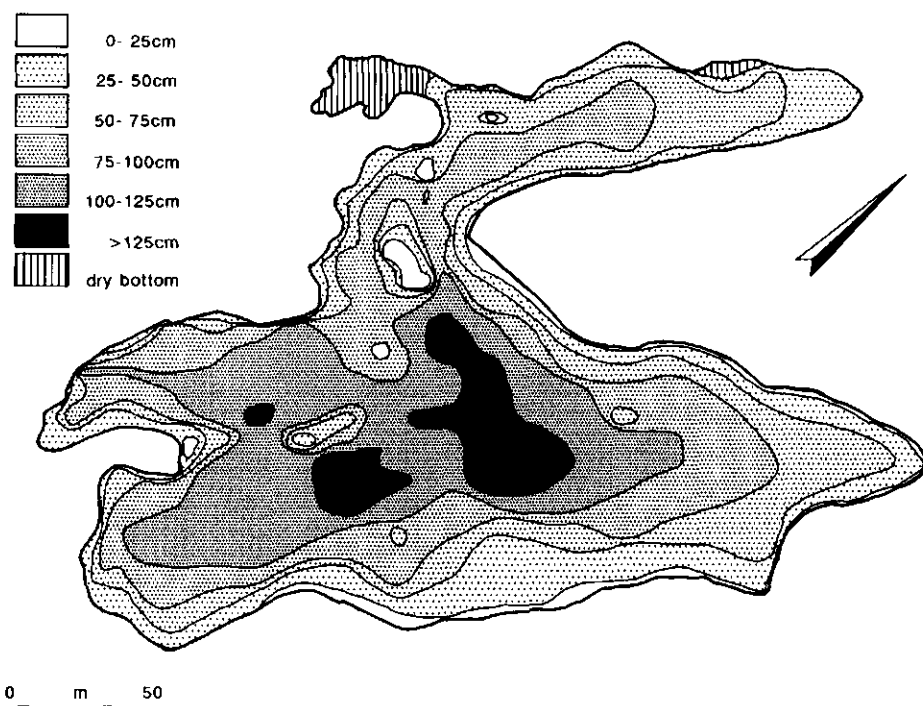


Figure 2.15. Gerritsfles, generalized depth of mineral soil relative to water level on September 18-19, 1984 (water level 39.77 m above NAP).

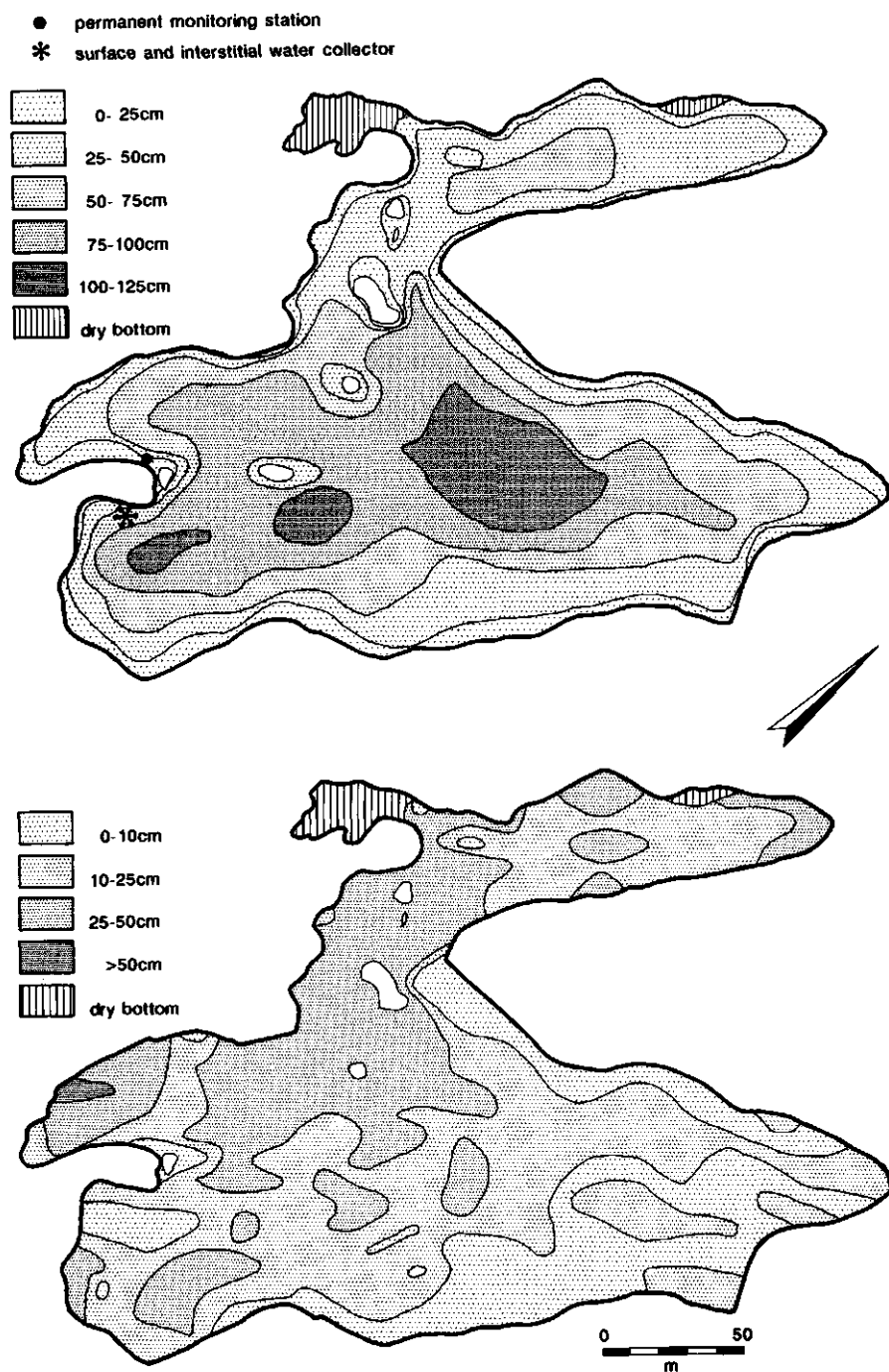


Figure 2.16 (top). Gerritsfles, generalized bathymetric map on September 18-19, 1984 (water level 39.77 m above NAP).

Figure 2.17 (bottom). Gerritsfles, generalized thickness of mud layer on September 18-19, 1984.

0.82 m. Consequently Kliplo has the largest mean depth of the investigated pools. Depth to the mineral bottom and waterdepth (Fig. 2.18) have a different pattern. The surface of the sediment layer is shaped like a soup-plate. The surface of the mineral bottom has a deep depression (maximum 1.96 m below mean water level) near the quacking bog at the western side. Presumably this depression extends under the quacking bog. Here the sediment soft bottom is up to 1.24 m thick. At the southeastern sandy shore the sediment soft bottom is absent.

2.5 Terrestrial and aquatic vegetation

The most prominent aquatic species were recorded during the bathymetric mapping of Goorven, Gerritsfles and Kliplo; the nearshore species of these pools were recorded in September 1984. Both aquatic and nearshore plants of Tongbersven and Groot Hasselsven were recorded during short visits in September 1984. The most important species found during these surveys and in historic records are given in Table 2.11, classified according to the autecological information tabulated by Iversen (1929), Zólyomi (1967), Pietsch (1976, 1982), Landolt (1977) and Ellenberg (1979). More details are given by Van Dam (1987).

Nomenclature of vascular plants and mosses follows Van der Meijden et al. (1983) and Margadant & During (1982), respectively. Details on the vegetation and its history are given by Van Dam (1987).

2.5.1 Hasselsven

On a sketch-map of the vegetation from 1955 (see Van Dam 1987) there is no separate sign for sociations of *Molinia caerulea*, which is currently very common in the moorland surrounding the pool. The former **Ericetum** at the western and northern side of the pool is now a sward of *Molinia caerulea*. The former **Callunetum** east of the pool is currently a stand of *Erica tetralix*, *Calluna vulgaris* and *Molinia caerulea*. Only in a small area south of the pool, near the soil solution monitoring plot the **Ericetum** is still free of *Molinia*.

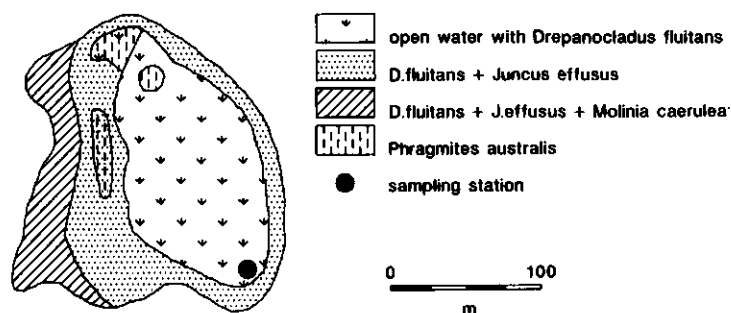


Figure 2.19. Hasselsven, sketch-map of vegetation.

Table 2.11. Macrophytes of open water and nearshore areas. R is indicator value for pH (1 = acidobiontic, 2 = acidophilous, 3 = circumneutral, 4 = alkaliphilous, - = indifferent). Symbols indicate estimated abundance (· = rare, o = frequent, O = common, * = dominant). See Fig. 2.8 for locations of sampling stations in Goorven. Data from Van Dam (1987).

POOL Station		HV		GV						TV		GF		KL	
				A	B	E	ABE	ABE							
From 19..		57	82	12	12	12	75	84		17	76	26	73	54	65
To 19..		57	84	59	59	59	76	84		57	84	58	84	58	84
R	Species														
1	<i>Drepanocladus fluitans</i>		*
1	<i>Drosera intermedia</i>				o	o	.	.	.	o	o			.	.
1	<i>Drosera rotundifolia</i>				o	o	.	.	.	o	o
1	<i>Eleocharis multicaulis</i>			o	.	o	.	.	.	o	o
1	<i>Juncus bulbosus</i>	o	o	.	.	.	o	O	.	o	.	.	o	.	.
1	<i>Rhynchospora alba</i>				o	o	.	.	.	o	o			.	.
1	<i>Sphagnum spec.</i>	o	o	o	o	O	o	o	.	O	O	O	*	o	o
2	<i>Agrostis canina</i>				o	o	o	.
2	<i>Carex rostrata</i>	.		o	o	o	o	o	.	o	o	o	o	o	o
2	<i>Deschampsia setacea</i>								.			.			
2	<i>Eriophorum angustifolium</i>		.	o	o	o	o	o	.	o	o	o	o	o	o
2	<i>Hydrocotyle vulgaris</i>			.	.	.	o	o	.	o
2	<i>Hypericum elodes</i>			O	o	.	o	.	.						
2	<i>Juncus acutiflorus</i>								
2	<i>Juncus effusus</i>	*	*	O	.	.
2	<i>Lobelia dortmanna</i>							
2	<i>Luronium natans</i>							
2	<i>Molinia caerulea</i>	o	O	o	o	O	O	O	.	O	O	o	o	o	o
2	<i>Myrica gale</i>				O	O	O	O	.	o	o				
2	<i>Potamogeton polygonifolius</i>			O						
2	<i>Potentilla palustris</i>			o		o	.	o	o
2	<i>Sparganium angustifolium</i>								.			o	.	O	.
2	<i>Utricularia minor</i>				o	o	.	.	o	.
2	<i>Viola palustris</i>			

The belt of marshy vegetation is inundated and united with the pool at high water levels in winter and spring. The most conspicuous plant species of the marshy zone is *Juncus effusus*, which is present all around the pool. On the outer side it is mixed with *Molinia caerulea*. *Juncus effusus* is generally accompanied by the moss *Drepanocladus fluitans*. *Juncus bulbosus* is also common near the open water. Clumps of *Phragmites australis* are present in the NW area of this zone. Scattered stems of this species are present in the rush belt at the western side of the pool.

The flat and shallow sandy bottom of the pool is covered with a dense mat of the moss *Drepanocladus fluitans* with some *Juncus effusus* (Fig. 2.19). The vegetation of the open water gradually changes into the belt of marshy vegetation.

Table 2.11. Continued.

POOL Station	HV		GV					TV		GF		KL	
			A	B	E	ABE	ABE						
From 19..	57	82	12	12	12	75	84	17	76	26	73	54	65
To 19..	57	84	59	59	59	76	84	57	84	58	84	58	84
R Species													
3 Carex lasiocarpa			o		.			.					
3 Menyanthes trifoliata			
3 Myriophyllum alterniflorum			o										
3 Potamogeton natans				o	O
3 Scirpus fluitans				o	O					.			
3 Utricularia intermedia			o	.									
4 Alisma plantago-aquatica			.										
4 Eupatorium cannabinum			.										
4 Lycopodium europaeus			.										.
4 Lysimachia vulgaris			.	.									
4 Mentha aquatica			.										.
4 Scirpus lacustris			.										
4 Typha angustifolia			.										
- Eleocharis palustris		o			.					.	o	o	.
- Glyceria fluitans										o	.		
- Juncus articulatus												.	.
- Lemna minor													
- Nuphar lutea													
- Nymphaea alba			O	O	O	o	o	o	.				
- Phragmites australis		O o	o			.	.					o	o
Number of species	7	7	26	28	18	20	15	29	18	22	16	10	24
Average R	1.6	1.5	2.5	2.0	1.8	1.6	1.6	1.7	1.5	1.9	1.6	1.8	2.0

Van Donselaar (1957) recorded essentially the same zonation in the marsh at the western side (Table 2.11), although *Phragmites* appeared to be more common at that time. He recorded prolific growth of *Juncus bulbosus* and *Sphagnum cuspidatum* between the reed. *Drepanocladus fluitans* was not recorded in 1957.

Juncus effusus, *Phragmites australis* and *Drepanocladus fluitans* indicate eutrophication. According to Iven & Van Gerwen (1974) the pool has been eutrophied by a colony of black headed gulls (*Larus ridibundus*). In the 1940s numerous gulls were present, in the 1960s only some tens of pairs were breeding in the marsh. The last birds were dislodged in 1970 (Iven & Van Gerwen 1974).

2.5.2 Goorven

Pinus sylvestris is the main tree species surrounding the pool, but it is often mixed with *Quercus robur* and *Q. rubra*. *Picea* sp. and *Castanea sativa* occur sporadically. Near the pool, where the water table is close to the soil surface, *Betula pubescens*, and to a lesser extent *Frangula alnus* grow spontaneously. *Betula* also occurs on some of the islands, where *Myrica gale* and *Molinia caerulea* are particularly abundant. The understorey of the dry soils is dominated by *Vaccinium myrtillus* and *Deschampsia flexuosa*, especially on the tops of the sand dunes. *Molinia caerulea* is dominating on wet soils nearshore, but intrudes also into the vegetation of dry soils. The present state of the surrounding forest and its vegetation does not differ from the earlier one, as described by Thijssse (1912) and Koster (1942).

The majority of the pines on the irregularly formed peninsula northeast of station E was logged in 1950 (Westhoff & Van Dijk 1950). The vegetation of this peninsula is dominated by *Molinia caerulea*, *Calluna vulgaris* and *Erica tetralix*. In addition, a lot of *Pinus* and *Betula* saplings are present. The present macrophytic vegetation of the interconnected basins is quite uniform (Fig. 2.20). A belt of *Myrica gale* and *Molinia caerulea*, with a minimum width of about one metre and extending to several tens of metres in marshy places, separates the pool with its boggy margins from the surrounding forest. The belt is inundated during periods of high water. *Salix (aurita/cinerea group)* is often mixed with *Myrica gale*.

Nymphaea alba is the most conspicuous water plant although its total coverage is less than one percent of the pool's surface area. Next important is *Juncus bulbosus*, which occurs in loose patches throughout the pool, particularly near the shores and in the shallower eastern basins. *Sphagnum* and *Molinia caerulea* often occur nearshore, the former species never forming floating mats. *Eriophorum angustifolium* and *Carex rostrata* locally form patches. *Juncus effusus* also occurs locally. *Rhynchospora alba* and *Batrachospermum* are rare, while *Drosera intermedia* occurs at one locality in the eastern basin. The westernmost basin differs from the others by the presence of *Phragmites australis*.

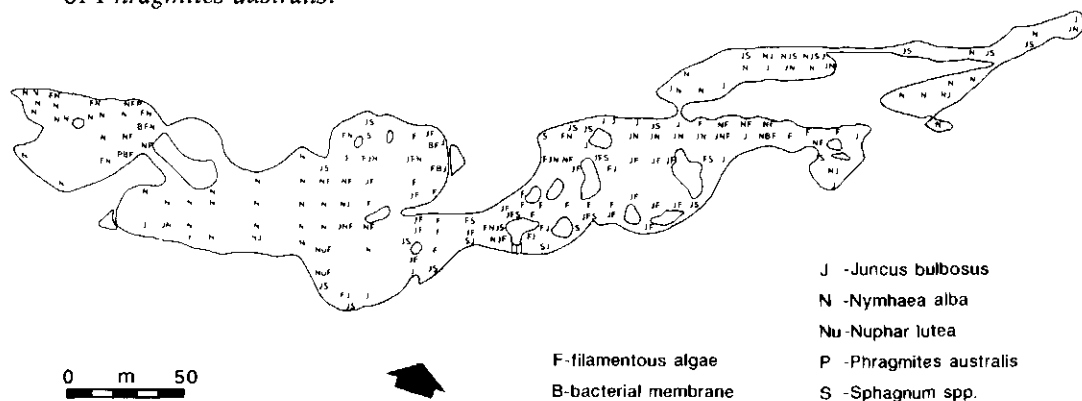


Figure 2.20. Goorven, plant species at gauging stations.

The present, very simple zonation is an impoverished stage of the former vegetation pattern (Van Dam 1987, Table 2.11). The species number decreased from 37 before 1960 to 20 after 1970. The average R (pH indication value, see Section 4.2.6) varied from 2.5 near station A to 1.8 near station E before 1960. In the period 1976-1984 the average R was 1.6 throughout the pool. The vanished species are characteristic for meso-eutrophic, not extremely acid waters (e.g. *Myriophyllum alterniflorum*, *Scirpus fluitans*, *Carex lasiocarpa*, *Mentha aquatica*). During the last decade five species disappeared (*Drosera rotundifolia*, *Eleocharis multicaulis*, *Hypericum elodes*, *Potamogeton natans*, *Utricularia minor*). The latter three cannot thrive well in acidified waters.

2.5.3 Tongbersven

This pool is completely surrounded by forest, with *Pinus sylvestris* as the dominant species. Locally *Prunus serotina* and *Quercus robur* occur. *Picea abies*, *Castanea sativa* and *Rhododendron* sp. are present sporadically. *Molinia caerulea* and *Deschampsia flexuosa* dominate the understorey (Table 2.11; see also Hofman & Janssen 1986).

A sketch of the aquatic vegetation of the pool is given in Fig. 2.21. This pool is rather different from the other investigated pools because it is largely filled with quacking bog. The open water of the westernmost (largest) basin is partly colonized by *Utricularia minor* (Hofman & Janssen 1986). One of the first pioneers of the terrestrial phase is *Eleocharis multicaulis*. In the quacking bog around and between the three patches of open water *Molinia caerulea*, *Sphagnum* spp., *Rhynchospora alba*, *Drosera rotundifolia*, *Oxycoccus palustris*, *Eriophorum angustifolium*, *Erica tetralix*, *Polytrichum* spp. and *Drosera intermedia* occur, the latter in small quantities (Table 2.11; Hofman & Janssen 1986).

At the transition between the floating bog and mineral soil is a lagg zone with bare mud, *Sphagnum* species and *Molinia caerulea* and, more rarely, *Utricularia minor*. Especially in the western part *Juncus effusus* occurs. *Betula pubescens* grows very close to the mineral soils.

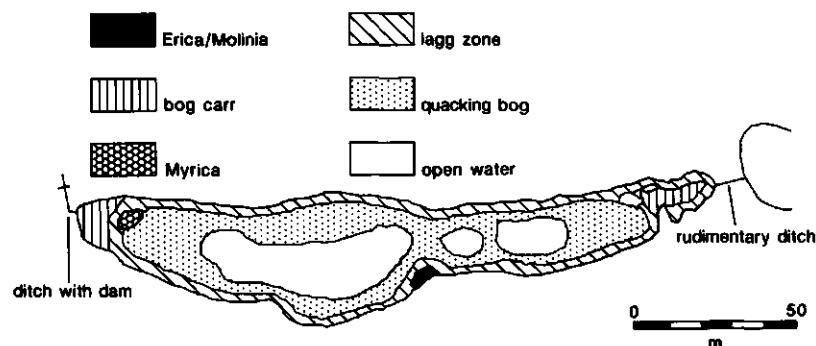


Figure 2.21. Tongbersven, sketch-map of vegetation.

The flora and vegetation were studied before by Glas (1957), Beijer (1976) and Verschoor (1977). Changes over the last decades are of minor importance.

2.5.4 Gerritsfles

This pool is directly surrounded by heathland, presently with *Molinia caerulea* as the dominant species. Only at the southwestern side of the pool *Calluna vulgaris* is still dominant. At the northwestern side a grassland lot has its border about ten metres from the shoreline. The poolwater is not affected by the grassland's drainage water, because this meadow falls outside the iron pan. According to H.J.W. Schimmel (pers. comm.), however, fertilizer formerly applied to the grassland and scattered by wind

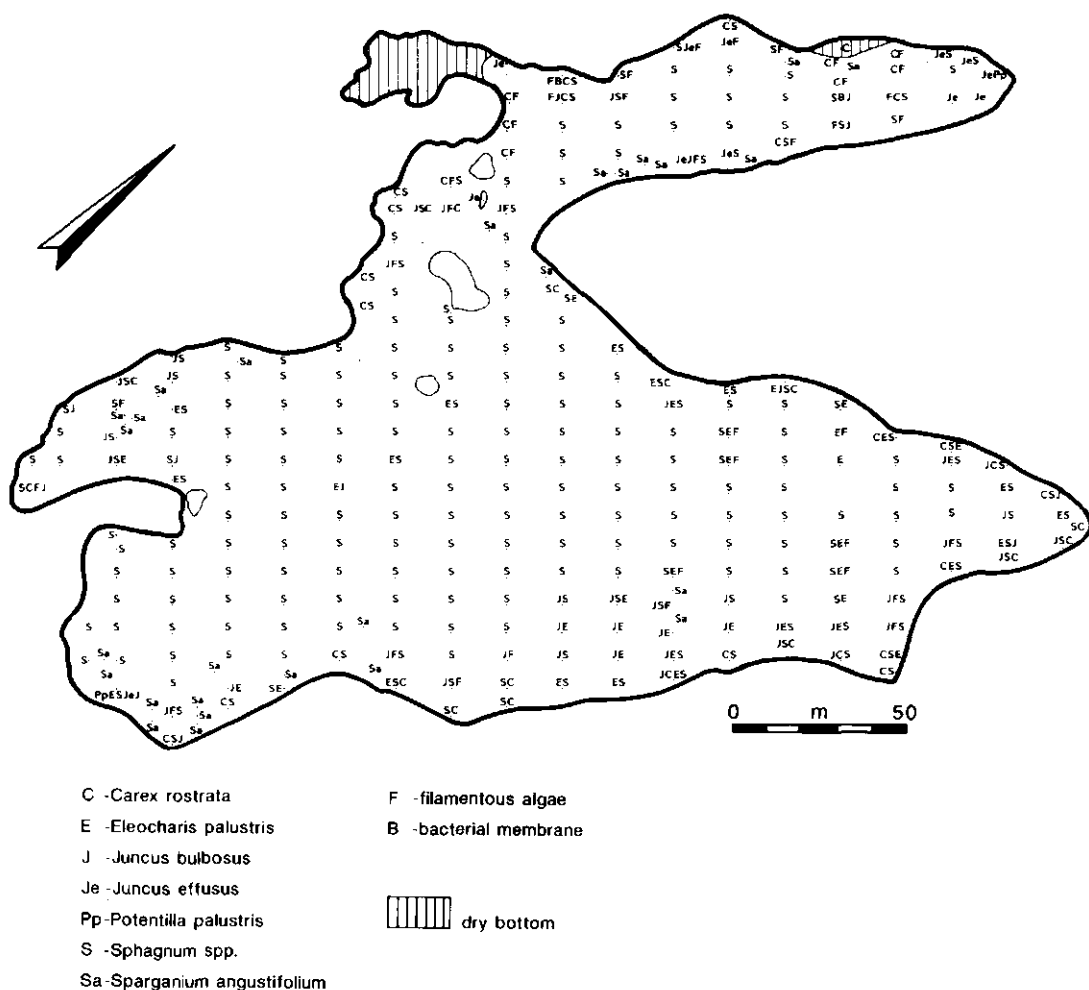


Figure 2.22. Gerritsfles, plant species at gauging stations.

could have reached the pool. No fertilizer has been applied since about 1965.

At the northwestern shore of the pool a marshy vegetation is found with *Molinia caerulea* and *Eriophorum angustifolium* as the dominant species (Schimmel & Ter Hoeve 1952, Van de Beld 1978).

The vegetation of the nearby forest belongs to the **Frangulo-Salicetum auritae** with mainly *Betula pubescens* and *Salix aurita* and also *Prunus serotina*. *Polytrichum commune* and *Molinia caerulea* are dominant in the herb layer (Van de Beld 1978). The meteoric and soil solution monitoring stations are located in a forest lot some hundreds of metres southwest of the pool (Fig. 2.3). This forest, which was partly planted in 1924 and partly originates from spontaneous regrowth, has *Pinus sylvestris* as the dominant tree species, while the understorey consists of a dense mat of *Deschampsia flexuosa*. The forest is fairly open and exhibits a rather poor vitality.

The most prominent aquatic species in the Gerritsfles pool are mapped in Fig. 2.22. The bottom of the open water is almost completely covered with a dense layer of *Sphagnum* spp. The vegetation zonation shows the following general pattern (from open water to shore): (1) Submerged mosses, mainly *Sphagnum* spp.; (2) Submerged mosses and *Juncus bulbosus*; (3) *Eleocharis palustris* or *Carex rostrata* and *J. bulbosus*; (4) Optimal development of *J. bulbosus*; (5) *J. effusus*; (6) *Eriophorum angustifolium*. After the extreme drought of 1976 *Juncus bulbosus* encroached the pool from the shores during several years, but receded again from c. 1978 onward.

All present-day species were already present before, probably with the exception of *Juncus effusus*. This species was present in very small quantities in 1950 and much more frequent in 1958 (Table 2.11). The abundance of submerged *Sphagnum* probably increased over the years, as open sandy places, which are hardly present now, did occur formerly. *Lobelia dortmanna*, a **Litorellion** species which grows exclusively on bare sandy bottoms, occurred until c. 1927 and not in later years. The decline of species which are characteristic for low alkalinity waters is typical for acidifying moorland pools (Van Dam & Kooyman-van Blokland 1978, Roelofs 1983). The average R (pH indication value) decreased from 1.9 in the period 1916-58 to 1.6 in the period 1973-84; Table 2.11).

2.5.5 Kliplo

The pool Kliplo is surrounded by fairly open *Pinus sylvestris* forest at all sides except the western, where a strip of quacking bog, c. 5-10 m wide and c. 50 m long, borders the shore. The vegetation of this bog includes, apart from *Sphagnum* spp., *Polytrichum* and other mosses, *Andromeda polifolia*, *Oxycoccus palustris*, *Carex rostrata* and *Eriophorum angustifolium* (Wartena 1954, Glas 1958). To the West of the bog strip is an open heathland with *Empetrum nigrum*, *Calluna vulgaris*, *Erica tetralix* and *Juniperus communis* as important species. Spontaneous regrowth of *Pinus sylvestris*, which occurred since 1925, was removed in 1965.

In the southwestern and northeastern corners of the pool small patches of carr occur, with birch, peat-mosses and *Molinia*. At the northern side a belt, several metres

wide, of birch separates the pool from the dry pine forest. At the southern side the pool borders to a dry complex of *Juniperus*-heathland and bare sand dunes, with birches overhanging the pool. The meteoric water sampling station is located in a forest c. 200 m East of the pool. In this forest *Pinus sylvestris* is the dominant tree species. In the understory *Empetrum nigrum* and *Deschampsia flexuosa* occur.

The present submerged vegetation is dominated by *Potamogeton natans*. The floating leaves cover only one or a few percents of the surface area, but the submerged stems with small leaves form a dense underwater network. Only in the northeastern and southeastern corner the species is locally absent (Fig. 2.18). *Sphagnum* spp. are present at some nearshore localities. The very rare *Sparganium angustifolium* is present with a few individuals near the northeastern shore.

On the sandy beach in the southeastern corner *Juncus bulbosus*, *Hydrocotyle vulgaris* and *Eriophorum angustifolium* are present. The latter species forms a small stand in the southwestern corner of the pool. The northern shore has a belt of *Phragmites australis*, which also locally occurs on the southern shore. *Potentilla palustris* is found everywhere along the western and northern shore and *Carex rostrata* is also common along the shores. Furthermore, *Menyanthes trifoliata* is present near the small island. These species were also recorded during earlier investigations.

3 Field and laboratory methods

The locations of the monitoring equipment used at the various research sites are indicated in Figs 3.1 to 3.4. The locations of the sampling stations in Goorven are shown in Fig. 2.9. Table 3.1 shows the numbers and types of collectors that were used. In this section the applied methods will be discussed.

3.1 Solution sampling techniques

3.1.1 Meteoric water

Rainwater and forest canopy throughfall were collected by means of simple open collectors. Funnels with an opening of 390 cm² were used, connected to a polythene bottle kept in the dark. In 1981 an older model was used with a collection bottle wrapped in aluminium foil instead of a dark chamber. Both models are described in detail by KNMI/RIVM (1982). As no measures were taken to prevent dry deposition from reaching the collectors, the rainwater samples also contained a fraction of dry deposition, probably less than 15% of the wet deposition (Slanina & Asman 1980). Deposition measured in this way is denoted as bulk deposition.

Table 3.1. Numbers and types of collectors used at the various sites. 'Soil solution collector' indicates a set of collectors at various depths within one profile (see Table 3.2); manual surface water collection gives the number of sampling stations. Not all samplers were used simultaneously; see section 3.2 for details on sampling periods.

Site sampler	HV	GV	TV		GF		KL
			TVA	TVB	GFF	GFB	
bulk prec. funnel	—	—		1		1	1
throughfall funnel	—	—	—	2	2		4
throughfall gutter	—	—	2	—	2		—
throughfall box	4	—	—	—	—		—
stemflow collar	—	—	1	2	1		2
soil solution collector	2	—	2		2	2	—
piezometer	12	—	17			—	—
surface water collector	1	—		1		1	1
interstitial water coll.	2	—		2		2	2
manual surf. water coll.	1	3		1		1	1

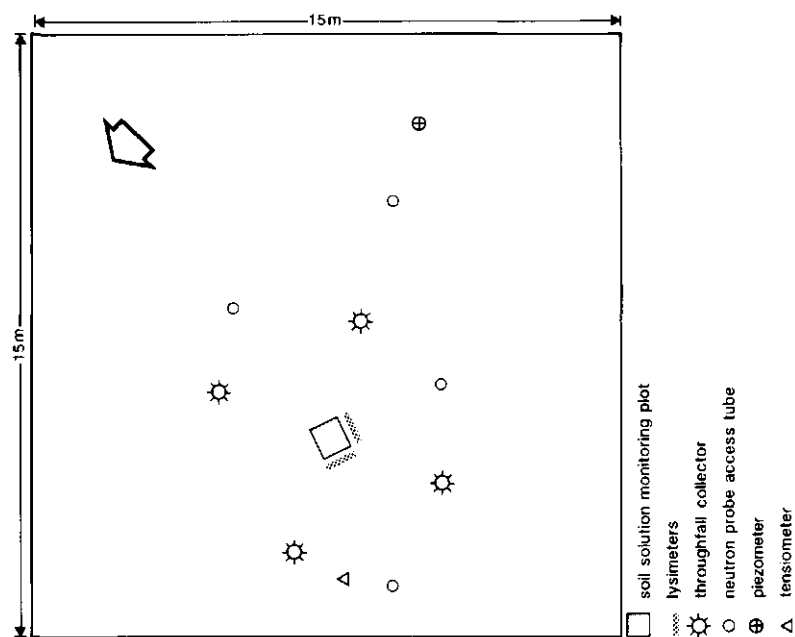


Figure 3.1. Location of the equipment used at Hasselstven.

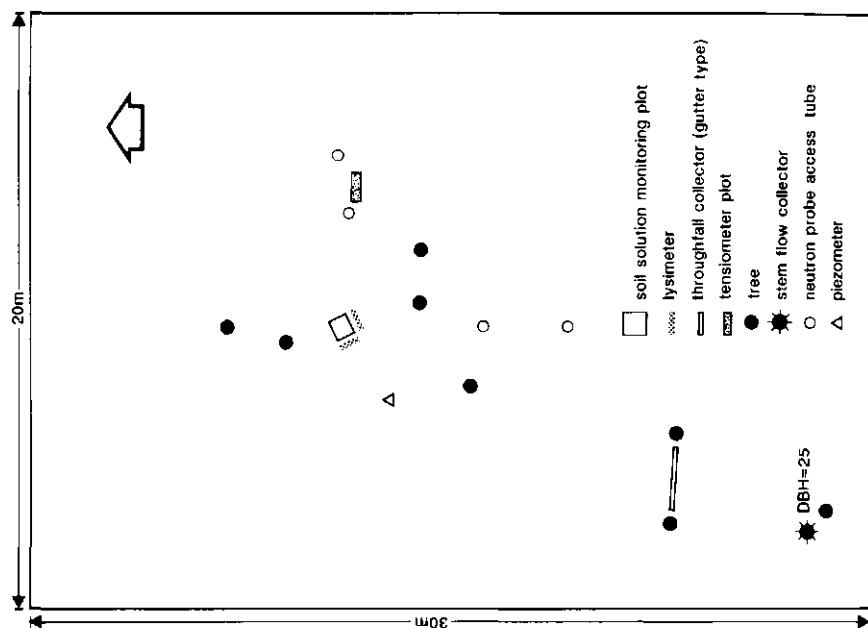


Figure 3.2. Location of the equipment used at Tongbersven.

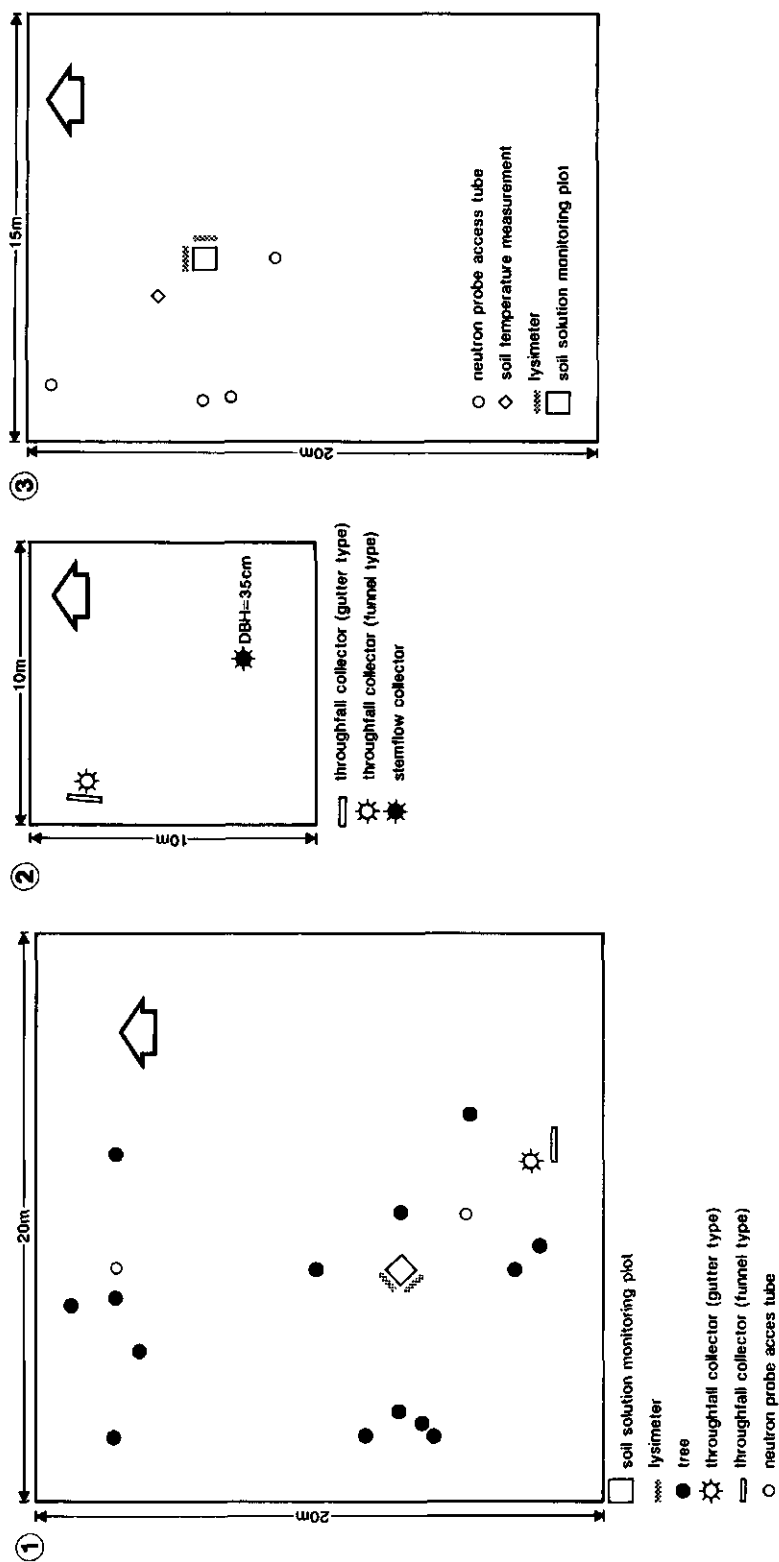


Figure 3.3. Location of the equipment used at Gerritsfles (1, 2 = Gerritsfles-forest, 3 = Gerritsfles-bare).

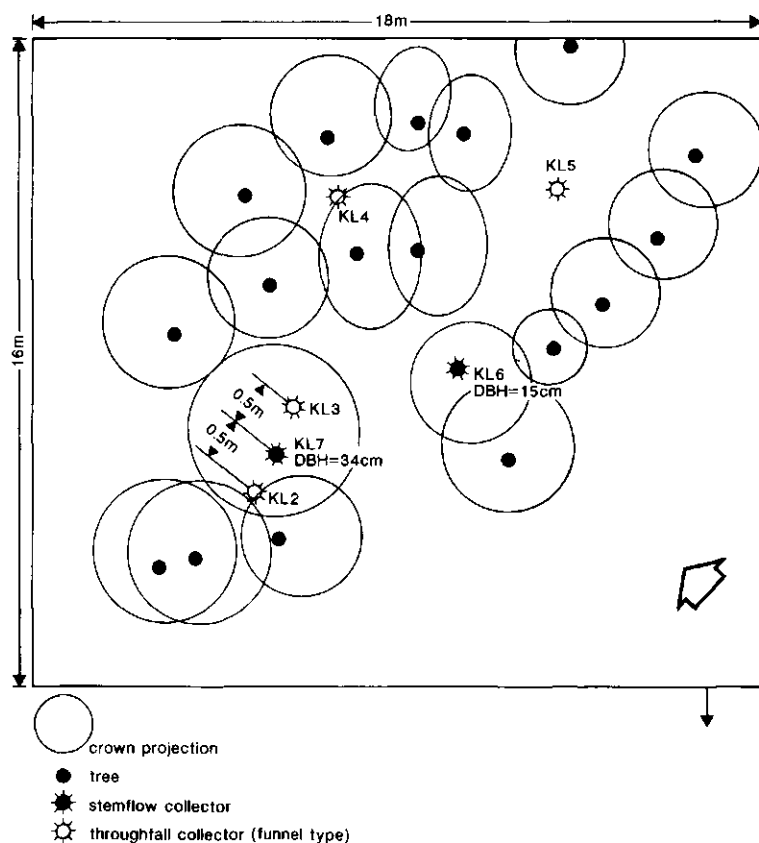


Figure 3.4. location of the equipment used at Kliplo.

For throughfall also a second type of collector was developed to minimise spatial variation in throughfall quantity and composition. This type consisted of a gutter which was made by lengthwise cutting away a section of a PVC pipe (length 2 m, diameter 125 mm). In this way an opening was formed with a surface area of c. 1800 cm². The pipe was closed at both ends, and placed at c. 1 m above ground level at an inclination of c. 30°. The lower end of the gutter was equipped with a connection tube and a nylon filter (as described by KNMI/RIVM 1982). Nylon wires were used to prevent bird from perching on the gutters' edges. Each throughfall sampler consisted of two such gutters, one being placed with its drainage tube near a tree trunk and extending radially from the tree, and the other one in the opposite direction. Both were connected to the same 50 l polythene collection vessel which was placed below soil surface in a covered pit.

Stemflow was trapped by 5 cm wide polythene collars fixed around tree trunks, using silicone sealant. The collars spiralled down at an angle of c. 30°. At the lower end the collars had a connection tube with a nylon filter. Stemflow was collected in

50 l polythene collection vessels which were wrapped in aluminium foil except samplers B7 and B8 (Microfiche) which were placed below soil surface and covered with a lid.

Throughfall under *Calluna* was collected in four rectangular open-top PVC boxes (6 cm high, $5 \cdot 20 \text{ cm}^2$ surface area) with a $5 \cdot 20 \text{ cm}^2$ trough as a lid. The troughs were perforated with five 0.5 cm diameter holes.

From all types of meteoric water subsamples for chemical analysis were taken in polythene containers which were rinsed with distilled water and sample before filling.

3.1.2 Soil solution

Soil solution was sampled by means of newly designed suction lysimeters (Fig. 3.5). Conventional ceramic cups or plates may leach Al under acidic conditions or sorb Al from solutions of more neutral pH. A circular filter ($0.2 \mu\text{m}$ acrylic copolymer, Versapor 200; Fig. 3.5b) with internal nylon support was used to hold the applied suction and filter particulates. This membrane was supported by a circular, porous ($40 \mu\text{m}$) polyethylene material (Supralen RCH 1000; Fig. 3.5d). The filter and porous polyethylene support were placed in a machined circular PVC frame (Fig. 3.5a, c) and on a circular PVC plate (Fig. 3.5e). A hole was drilled into the lysimeter (Fig. 3.5d) to accomodate a nylon tube (Fig. 3.5f) and flexible (tygon) tubing (Fig. 3.5g) to transport solution to a polypropylene collection vessel (500 ml).

When soil solutions (pH 4.4; $\text{EC } 31 \mu\text{S} \cdot \text{cm}^{-1}$; 0.07 m mol/l Al) were passed through the lysimeters no significant change in pH and Al concentrations in the leachates could be detected. Driscoll et al. (1985) observed no Al leaching from similar lysimeters upon passing 0.1 mol/l HNO_3 , nor did they find Al retention in the lysimeters when passing synthetic and natural solutions, which were undersaturated with

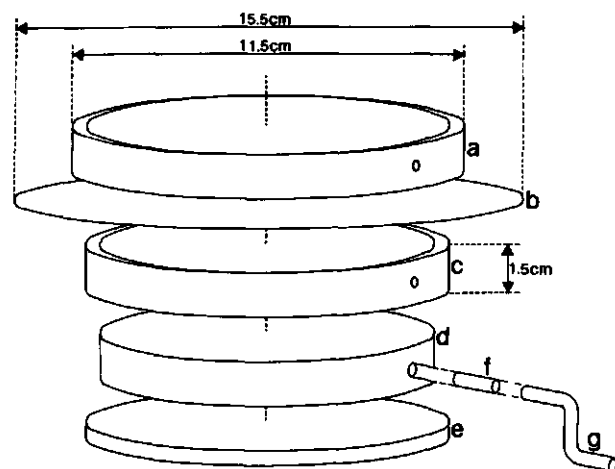


Figure 3.5. Diagram of the suction lysimeter used to collect soil solutions.

respect to gibbsite. However, solutions that were highly oversaturated with gibbsite were reported to show Al retention.

At all sites one soil pit was dug in which two series of lysimeters were installed (roughly 2 m apart) in adjacent walls. Lysimeter installation was carried out by digging a small cavity (20 to 30 cm long) sideways in the wall of a soil profile, inserting the lysimeter and pressing it upward to ensure good contact between filtercloth and undisturbed soil. The remainder of the cavity was backfilled (as tightly as possible) with the original soil material. When all lysimeters were installed the pit walls were covered with plastic sheets and the pits were backfilled. The lysimeters were connected through tygon tubing with 500 ml polypropylene collection vessels, which were placed in an insulated wooden box (75·75·50 cm) underground, a few meters from the lysimeters.

Soil solutions were sampled using a permanent vacuum of 150 mbar, maintained by means of a hanging drop (Fig. 3.6). The hanging drop was created by a waterfilled 5 liter bottle in the wooden box as the upper syphon reservoir and a container situated approximately 150 cm lower as the lower reservoir. By keeping both soil solution, collection system, and hanging drop below the soil surface, freezing was prevented, so that even in periods with temperatures well below 0 °C sampling could continue.

Lysimeters were installed in twofold at various depths (Table 3.2). The lysimeters placed at 0 cm depth had an extended circular PVC frame (Fig. 3.5a), which is 1 to 2 cm higher than the thickness of the forest floor. This rim served to (1) allow for the

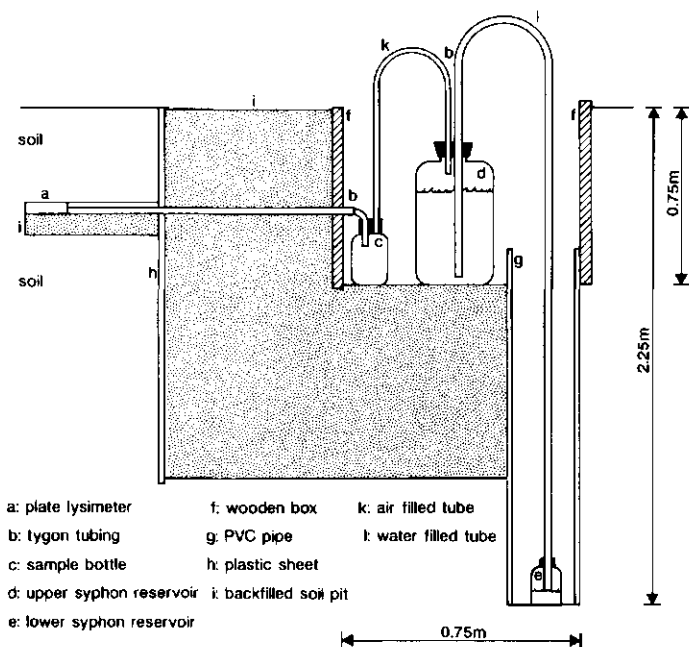


Figure 3.6. Diagram of hanging drop lysimeter set-up.

Table 3.2. Depths of duplicate lysimeters at the four sites. The depth is in cm relative to the surface of the mineral soil (e.g. 0 cm is below the forest floor)

Site	Placed below horizon	Depth
HV	O1	0
	E	7
	Bhs2	22
	Bs	70
	C*	110
TV	O1	0
	E	12
	Bhs	35
	Bs	57
	BC2*	100
GFF	O1	0
	C*	10
	C*	40
	C*	100
GFB	C*	2
	C*	40
	C*	100

* Lysimeter was not placed below, but within this horizon (see also Appendix 1 for soil profile descriptions).

measurement of mineralization, since root penetration in these lysimeters (and hence nutrient uptake by plants) was prevented and (2) prevent inflow of water from the mineral soil.

In this set-up soil solutions were collected continuously, in contrast to the commonly employed procedure with other tension lysimeters (ceramic cups or plates), where point samples are assumed to be representative for a certain period of time (week, month). However, it should be stressed that although an integrated soil solution sample over time is collected, this sample is by no means a flux-weighted mean of the passing soil solution: with constant suction waterfluxes tend to be overestimated in wet periods and underestimated in dry periods.

The soil solution sampling method is sensitive to air entry (which occurs upon drying or mechanical/chemical damage the filter cloth). Air entry causes vacuum loss and subsequently syphoning of all water from the upper hanging drop reservoir, so that sampling stops. However, during the monitoring period no vacuum loss was observed due to drought or frost except in the '0 cm' lysimeters and on a few occasions in the Hasselsven E and Bhs1 lysimeters. Damage of the filter cloth, due to mechanical and/or chemical action has only been observed at the HV E lysimeters. Every year in May and June numerous air leaks developed, which appeared to be 1 to 5 mm wide

brown, fluffy stains, probably as a result of chewing by soil fauna. Mending was easy by using a small amount of PVC glue.

Because the '0 cm' lysimeters had a rim which separated the forest floor or thin soil layer above the filter plate from the surrounding soil, vacuum loss would not only prevent the collection of sample, but also cause water saturation of the organic top soil in the lysimeters if drought or frost was followed by precipitation or snowmelt. To avoid this problem the hanging drop of the '0 cm' lysimeters was replaced by a specially designed pump. This pump evacuated the '0 cm' lysimeters and the attached collection vessels to a pre-set vacuum of 100 to 150 mbar. Every three minutes the vacuum was measured by means of a built-in transducer and if necessary increased to the pre-set value. If air entered the filter the vacuum was lost and the pump was not able to evacuate the system to the pre-set value within 16 sec (the pump's maximum run time). In that case the pump's pumping/checking interval was changed to one hour. This one hour interval changed back to a three minute interval as soon as the pre-set value between 100 and 150 mbar could be created within 16 sec (this was the case when the filter cloth had been remoistened). The pump was driven by a six Volt battery, which was recharged every fortnight.

3.1.3 *Groundwater*

Groundwater was sampled only at Tongbersven and Hasselsven because at these sites interaction between groundwater and poolwater was expected at the outset of the monitoring. Figs 3.1 and 3.2 show the location of the piezometers that were used for groundwater sampling. Groundwater in piezometers TV4 (Tongbersven) and HV12 (Hasselsven) was monitored for all major solutes. The monitoring programme focused on these two piezometers because they were located near the soil solution monitoring plots. Groundwater from the other piezometers was monitored only for pH, EC and Cl, and on two occasions for all major solutes. Piezometers TV4 and HV12 were PVC tubes with an inner diameter of 36 mm and a 350 mm long filter, covered with a nylon cloth to prevent silting up. They were sampled by means of a PVC pipe with a stainless steel valve at the bottom. The other piezometers were PVC tubes with an inner diameter of 20 mm and a 0.5 m long filter consisting of c. 100 slits, each 25 mm long and 0.1 mm wide and a wooden stopper at the bottom. These piezometers were sampled by means of a vacuum pump.

The length of the piezometers varied from 200 to 521 cm depending on the lowest groundwater table (Table 3.3). Where a layer with high hydraulic resistance was met during installation an additional shallower piezometer with the filter just above this layer was placed. In this case indices (.1 and .2) for piezometer pairs are used (Table 3.3), with the .1 piezometer being the shallower of the two. The piezometers were placed in a hole made with a motor driven drill with an outer diameter of 93 mm. After placing the piezometer the hole was backfilled with the original material. At the level of layers with high hydraulic resistance, bentonite clay was inserted to restore the resistance. Most piezometers reached up to about 50 mm below soil surface, were

Table 3.3. Piezometers (HV and TV) and poolwater level gauges (P). The reference level corresponds to the top of the piezometer or the zero of the gauge. Length in cm, levels in cm above NAP.

HV			TV		
code	length	ref. level	code	length	ref. level
1	300	2810	1	300	904
2.1	190	2734	2	300	924
2.2	380	2733	3.1	240	968
3.1	120	2718	3.2	425	973
3.2	300	2717	4	521	1191
4	200	2650	5.1	240	973
5	300	2754	5.2	350	971
6	300	2708	6.1	200	959
7	300	2704	6.2	300	956
8	300	2700	7	300	934
9	300	2781	8	300	904
10	300	2770	9	300	872
11	300	2725	10	280	879
12	322	2808	11	300	925
			12	300	921
			13	250	856
			14	250	890
			15	300	977
			16.1	100	848
			16.2	250	901
			17	250	865
P					
P1	—	2670	P1	—	868
P2	—	2668	P2	—	872
P3	—	2650	P3	—	904
			P4	—	856

closed with a PVC cap and covered with a tile. Only TV4 and HV12 reached 100 mm above soil surface. The PVC caps had a 2 mm diameter hole to allow for air transport.

Groundwater samples were collected in 100 ml polythene containers. Before sampling c. three times the volume of water in the piezometers was pumped out to renew the water. This water was used to rinse the sample container.

3.1.4 Surface and interstitial water from moorland pools: intensive monitoring

Monthly surface and interstitial water samples from the moorland pools were taken by means of newly designed solution collectors (Fig. 3.7), using a 500 mbar vacuum. A circular nylon screen (Fig. 3.7d) with a filter on both sides (0.2 μ m acrylic co-

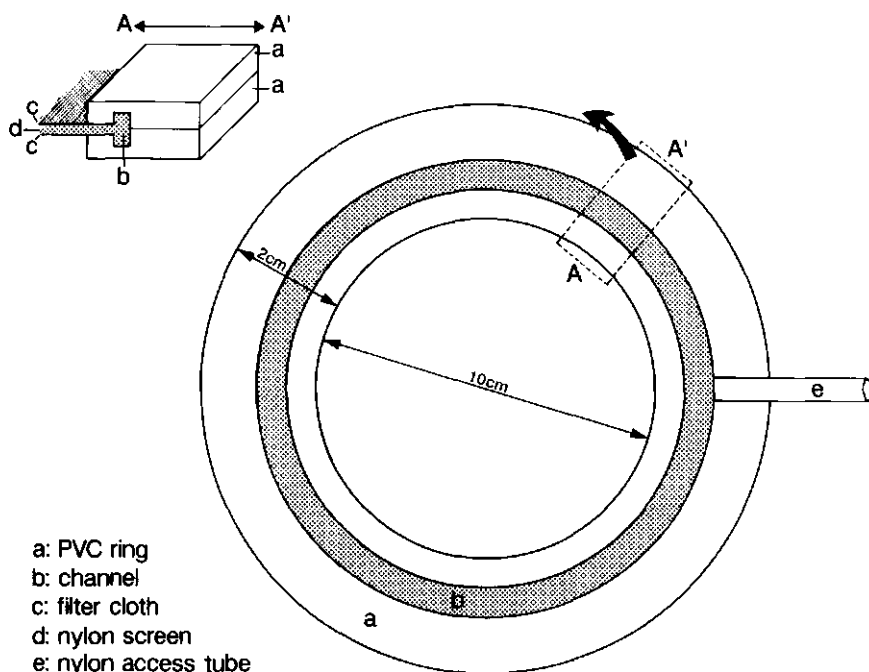


Figure 3.7. Diagram of interstitial and poolwater collector.

polymer, Versapor 200; Fig. 3.7c) was fitted between two symmetrical PVC rings (5 mm high, inner diameter 10 cm and outer diameter 14 cm; Fig. 3.7a). On the sides of the PVC rings a 1 mm deep and 3 mm wide circular channel was machined (Fig. 3.7b), and the rings were glued together. In this way a vacuum applied to the channel is distributed evenly over the whole filter.

Samples were collected in 500 ml polypropylene bottles through tygon tubes with a length of 5 to 10 meter and an internal diameter of 1 mm, after discarding the first 20 ml of sample. In all four moorland pools one collector was installed in the surface water about 20 cm above the soft sediment bottom, two were installed c. 5 cm below the surface of the soft sediment bottom and another two in the lower part of the sediment, c. 5 cm above the mineral pool bottom. Thickness of the soft sediment varied from pool to pool (section 2.4). Sampling points in the pools are indicated in Figs 3.1 to 3.4. Collected samples were about 100 ml, indicating that a water layer less than 1 cm both below and above the collector was sampled. However, the collected volume is likely to be spherical rather than a layer so that the depth resolution is presumably in the order of a few cm. Therefore this technique is probably less suitable for sampling reduced compounds, that show steep concentration gradients with depth.

3.1.5 Surface water from moorland pools: monitoring of longterm composition

Surface water samples for monitoring of longterm chemical composition and microflora were taken quarterly from the shore with a bucket. In this way the surface 10-20 cm water layer of the pool could be sampled. Surface water was collected filling a 2 l and a 0.5 l polythene container from the bucket after rinsing with surface water.

3.2 Sampling periods

The period in which the various monitoring activities took place are indicated in Table 3.4.

Precipitation, throughfall and stemflow sampling started in 1981 at the Tongbersven B site and in 1982 at the Gerritsfles and Kliplo sites. At Kliplo, four throughfall funnels

Table 3.4. Summary of monitoring periods. Prec = precipitation, Thr = throughfall and stemflow, SS = soil solution, Grw = groundwater, Poolw = poolwater, Longt = longterm poolwater monitoring. The longterm monitoring of Goorven and Gerritsfles started in 1979.

	+ ----1981---- + ----1982---- + ----1983---- + ----1984---- + ----1985---- + ----1986---- + ----1987---- +
Prec TV	-----
Prec GF	-----
Prec KL	-----
Thr HV	-----
Thr TVA	-----
Thr TVB	-----
Thr GF	-----
Thr KL	-----
SS HV	-----
SS TV	-----
SS GF	-----
Grw HV	-----
Grw TV	-----
Poolw HV	-----
Poolw TV	-----
Poolw GF	-----
Poolw KL	-----
Longt GV	<-----
Longt GF	<-----
Longt KL	----->
	+ ----1981---- + ----1982---- + ----1983---- + ----1984---- + ----1985---- + ----1986---- + ----1987---- +

and two stemflow samplers were installed close to each other to get more insight in the variation in precipitation quantity and chemical composition within a forest stand. A throughfall gutter was installed at Tongbersven A, together with a stemflow collector in March 1983. At the same time a throughfall gutter was installed at Gerritsfles close to one of the throughfall funnels. In 1984 one additional throughfall gutter was installed at both Tongbersven A and Gerritsfles. Throughfall under *Calluna* at Hasselsven was sampled from April 1984 onwards.

Monitoring of soil solution composition at Hasselsven, Tongbersven and Gerritsfles (both forested and unvegetated) and monitoring of groundwater level and composition at Hasselsven and Tongbersven (piezometers TV4 and HV12) was conducted from November 1982 to May 1987. Groundwater from the other piezometers at Hasselsven and Tongbersven was sampled from 20 May 1983 to 6 July 1984. At two occasions (20 November 1983 and 28 March 1984) groundwater from all piezometers was analysed for the major solutes. Throughfall and stemflow sampling was stopped in February 1985 except at Tongbersven A and Gerritsfles, where sampling continued until May 1987.

Surface and interstitial water from the moorland pools were sampled from March 1983 to February 1985, but for the detection of long-term variation longer series were used: for Goorven from July 1979 to February 1985, for Gerritsfles from July 1979 to February 1987, and for Kliplo from May 1981 to February 1985. Historic records were also used.

3.3 Sampling intervals and handling of samples

Meteoric water was collected on a monthly basis, using the same dates as the KNMI/RIVM network (see KNMI/RIVM 1981-1987). In 1981 the samples were left in the field for a full month. The samplers were inspected and cleaned weekly; filters were changed monthly or more often when contamination (e.g. with bird droppings) was suspected. From 1982 onward samples were collected weekly and stored in the dark at 4 °C. At the end of each sampling period the weekly samples were pooled to one monthly sample. Amounts of stemflow and throughfall collected with the gutters were sometimes so large that subsamples of 10 or 20% of the total sample had to be taken in the field. In that case, subsamples of the same relative size were taken from the other weekly samples in the same month and pooled later to obtain a volume-averaged sample. Throughfall under *Calluna* was collected fortnightly from the four samplers and was pooled in the field. The fortnightly samples were pooled to one monthly sample before analysis.

Soil solutions were collected every fortnight and stored at 4 °C in the dark. Solutions were pooled to monthly samples before analysis. Groundwater and poolwater were collected monthly and stored at 4 °C in the dark until analysis. Poolwater samples for the detection of long-term variation were taken monthly in Gerritsfles and Goorven before June 1980, and quarterly in Kliplo and in Gerritsfles and Goorven after June 1980.

In general, all containers were cleaned by rinsing with distilled water; the same container was always used for a sample from a specific collector. Meteoric water was filtered through a 250 μm polyethene filter, except throughfall solutions from the heathland which were filtered through a paper filter (Schleicher and Schull no. 604).

Groundwater samples for intensive monitoring were filtered through a 0.2 μm membrane filter (Schleicher and Schull BA83). The first 50 ml of the percolate was discarded. Groundwater samples which were analysed for Cl only were not filtered. Soil solutions and monthly moorland pool water samples were not filtered again after sampling because the collection involved filtering (see 3.1.2, 3.1.4). Quarterly moorland poolwater samples were not filtered except the subsamples used for the determination of sulphate which were filtered through ordinary filter paper, and those for the determination of permanganate consumption which were filtered through asbestos.

In the sampling procedure for interstitial water in moorland pools no precautions were taken against oxidation (see also Section 6.4.1, Sulphate). To minimize changes in chemical composition, pool water samples were analysed as soon as possible after collection. However, dissolved reduced compounds may have become oxidized before analysis.

3.4 Sample analysis

Chemical analyses carried out in the various solution samples are summarized in Table 3.5. Analyses were carried out by the following laboratories:

- Meteoric water except throughfall *Calluna*: National Institute of Public Health and Environmental Hygiene, Bilthoven (RIVM)
- Throughfall *Calluna*, soil solutions, groundwater, monthly pool water samples: Dept. of Soil Science and Geology, Agricultural University, Wageningen (LUW)
- Longterm pool water: Waterleidingbedrijf Midden-Nederland, Utrecht (WMN).

In addition some field measurements were carried out. In monthly poolwater samples field pH was measured with a Metrohm Herisau E 588 field pH meter with a combination electrode (EA 152). In groundwater samples except those from TV4 and HV12 field pH was measured with a WTW-pH90 pH meter with a combination electrode E50, and conductivity was measured with a WTW-LF91 conductivity meter with a standard measuring cell KLE 1/T. In quarterly poolwater samples field pH was measured with a Metrohm E488 pH-meter, a WTW 91 pH-meter or a Gallenkamp pH-stick, and conductivity was measured with a Yellow Springs Instrument 33 conductivity meter or a WTW-LF91 conductivity meter. When air temperature was below 10 °C 'field' values for pH and conductivity were often measured in the laboratory within a few hours after sampling. In quarterly poolwater samples oxygen content was also measured in the field, using a Yellow Springs Instrument 54 oxygen meter.

Table 3.5. Components analysed in various water samples:

- (1) meteoric water
 (2) soil solution, groundwater at soil solution monitoring plots
 (3) other groundwater
 (4) poolwater, monthly monitoring
 (5) poolwater, longterm monitoring
 1 mmol_c = 1 mmol / absolute value of ionic charge

Component	(1)	(2)	(3)	(4)	(5)
water quantity (g)	*				
pH (lab)	*	*	*	*	*
pH (field)			*	*	*
EC (lab) ($\mu\text{S}\cdot\text{cm}^{-1}$)	*	*	*	*	*
EC (field) ($\mu\text{S}\cdot\text{cm}^{-1}$)	*				
free acid ($\text{mmol}\cdot\text{m}^{-3}$)	*				
silica ($\text{mmol}\cdot\text{m}^{-3}$)		*		*	*
potassium ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	*
sodium ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	*
calcium ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	*
magnesium ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	*
aluminium ($\text{mmol}_c\cdot\text{m}^{-3}$)		*		*	*
iron ($\text{mmol}_c\cdot\text{m}^{-3}$)		*		*	*
manganese ($\text{mmol}_c\cdot\text{m}^{-3}$)		*		*	*
zinc ($\text{mmol}_c\cdot\text{m}^{-3}$)	*				
ammonium ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	*
chloride ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*	*	*	*
nitrate ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	*
sulphate ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	*
phosphate ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	* ^a
fluoride ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	
bicarbonate ($\text{mmol}_c\cdot\text{m}^{-3}$)	*	*		*	
alkalinity ($\text{mmol}_c\cdot\text{m}^{-3}$)					*
Kjeldahl nitrogen ($\text{mmol}_c\cdot\text{m}^{-3}$)	* ^b				
organic ammonium ($\text{mmol}_c\cdot\text{m}^{-3}$)					*
organic carbon ($\text{mmol}_c\cdot\text{m}^{-3}$)		*		*	
inorganic carbon ($\text{mmol}_c\cdot\text{m}^{-3}$)		*		*	* ^c
temperature (°C)					*
KMnO ₄ -consumption ($\text{mg}\cdot\text{l}^{-1}$)					*
COD ($\text{mg O}_2\cdot\text{l}^{-1}$) ^d					*
Colour ($\text{mg Pt}\cdot\text{l}^{-1}$)					*
oxygen ($\text{mol}_c\cdot\text{m}^{-3}$)					*
total hardness ($\text{mmol}_c\cdot\text{m}^{-3}$)					*

^a as total phosphate and H₂PO₄^b from August 1982 onward^c as CO₂ and CO₃^d chemical oxygen demand

3.4.1 Analytical methods: RIVM

The analyses for pH, NH_4 and NO_3 were carried out within a week after pooling. Analyses for the other solutes were also carried out within a week or, if this was not possible, subsamples were taken, stored at 4 °C in the dark and analysed within a month.

Precipitation amount: with a balance the amount was determined from the difference in weight of the collection bottle with and without the sample.

pH: a pH-meter with a combination electrode were used after addition of a small volume of saturated sodium chloride solution (NEN 6411, 1981).

Total acidity: bicarbonate was removed by adding a known amount of sulfuric acid to a pH < 4 and passing air through the sample. The sample was then titrated to pH 5.6 with hydroxyl ions which were generated coulometrically (WMO 1978). The endpoint of the titration was detected with a combination electrode. The difference between the amounts of hydroxyl ions and sulphuric acid added was marked as total acidity if positive and as bicarbonate if negative.

Ammonium: after reaction with sodium salicylate and sodium hypochlorite at 35 °C for 5 min in the presence of sodium nitroprusside as a catalyst, the absorption at 660 nm was determined with a photometer (ontwerp NEN 6643).

Sulphate: after passing through a cation exchanger the sample was mixed with a barium perchlorate solution. Barium sulphate was formed and the excess of barium was coloured with thorin. The absorption at 660 nm was determined in a flow-through cuvet with a photometer (EMEP 1977).

Chloride: the sample was titrated with a silver nitrate solution. The endpoint of the titration was determined potentiometrically with a silver/silver chloride indicator electrode and a silver/silver chloride reference electrode which was connected with the sample solution through a potassium nitrate bridge (set-point titration; NEN 6476, 1981).

Nitrate: the sample was pumped through a filter with activated carbon to remove interfering organic substances. The absorption was determined at 206 nm with an UV-photometer (Slanina et al. 1976).

Sodium and potassium: after addition of a cesium chloride solution as an ionic buffer the concentration was determined by atomic absorption spectrometry (flame method; ontwerp NEN 6423, ontwerp NEN 6424)

Calcium and magnesium: after addition of a lanthanum chloride solution to suppress possible interferences, concentration was determined with atomic absorption spectrometry (flame method; NEN 6446, 1980, NEN 6455, 1981).

Fluoride: after addition of an acetate buffer solution containing the de-complexing reagent HEDTA the concentration was determined potentiometrically in a flow-through system with an ion-selective electrode (Cowell 1977).

Conductivity: the sample was pumped through a thermostated (20 °C) flow-through conductivity measurement cell. Values at 25 °C were obtained by multiplying measured conductivity with a factor 1.11034 (NEN 6412, 1981).

Phosphate: after reaction with ammonium molybdate in a strong sulphuric acid solution in the presence of potassium antimonyltartrate as a catalyst, a compound was formed which was transformed to a coloured substance by reaction with ascorbic acid. The absorption was measured at 880 nm with a photometer in a flow-through cuvet (NEN 6663, 1981).

Total nitrogen: after addition of sulphuric acid the sample was evaporated and destructed at high temperature with potassium peroxydisulphate. The volume of the residue was brought back to the original volume with distilled water. In the obtained solution ammonium was measured in a flow-through system as described under ammonium.

Bicarbonate: see total acidity.

3.4.2 Analytical methods: LUW

During analysis samples were kept at lab temperature, but as much as possible in the dark. Analysis of pH and conductivity was generally done within one day after sampling or pooling. Next the samples were divided into two parts. One part was used for the analysis of organic and inorganic carbon (by infra-red analysis of CO_2 evolution from the sample using a Beckman carbon analyser), fluoride, chloride, nitrate and sulphate (all by ion chromatography, Dionex), ammonium and phosphate (colorimetrically as described in 3.4.1). The other part was acidified to pH 2 or 3 with hydrochloric acid and used to determine potassium and sodium (by atomic emission spectroscopy), calcium, magnesium, iron and manganese (by atomic absorption spectroscopy), and aluminium and silica (colorimetrically with pyrocatechol violet and molybdene blue, respectively). Short descriptions of the analytical methods are given by Van Breemen et al. (1988). For details reference is made to Begheijn (1980).

To check the analyses, six artificially made samples of known composition, similar to the natural samples were prepared according to Begheijn (1981). Two of such standard samples were analysed during every analytical run, and a statistical analysis of the results is given by Van Breemen et al. (1988). This showed a reasonable to good recovery (95 to 105%) of solutes present in relatively high concentrations ($> 50 \text{ mmol} \cdot \text{m}^{-3}$), except for chloride in the artificial soil solution (recovery 110%). At lower concentrations some elements were underestimated, particularly potassium (80 to 90%), ammonium (80%) and, most seriously, fluoride (40 to 80%) and phosphate (30 to 120%). The coefficients of variation were reasonable ($< 10\%$) for most dominant solutes, except chloride (8 to 20%), but much poorer when concentrations were below 50 to 100 $\text{mmol} \cdot \text{m}^{-3}$ (particularly so for fluoride (30 to 200%) and phosphate (42 to 200%)). However, analysis for the trace elements F and P was never optimized. The poor results for potassium mentioned by Van Breemen et al. (1988) were mainly due to analytical problems in 1981; by the time the present monitoring programme started (November 1982) the analytical performance had increased considerably.

3.4.3 Analytical methods: WMN

Samples which were analysed for all major solutes were processed the day after sampling, while those analyzed for Cl were stored at 4 °C for a maximum of 60 days. Iron, Ca and Mg were determined by atomic absorption spectrometry using a Perkin Elmer model 703. Aluminium was determined by flameless atomic absorption spectrometry using a Perkin Elmer model 306. Nitrate was measured by colorimetric determination of nitro-salicylic acid, formed by reduction of sodium salicylate by nitrate in an acid environment (Müller & Widemann 1955). All other determinations were carried out according to NEN standards as described in 3.4.1. The concentration of organic acid was estimated according to Oliver et al. (1983) from DOC, assuming a weak acidity contribution of organic carbon of $5.5 \text{ mmol}_c \cdot \text{g}^{-1} \text{ C}$ (Henriksen & Seip (1980).

3.4.4 Analytical methods: RIN

For the monthly or fortnightly determination of chloride in piezometers and pool water at Tongbersven and Hasselsven the sample was titrated with a mercury(II) nitrate solution. The endpoint was indicated by a violet coloured complex of the surplus of mercury(II) with difenylcarbazon in an acid environment (Golterman et al. 1978). The accuracy of the determination was $15 \text{ mmol} \cdot \text{m}^{-3}$.

3.5 Soil physical monitoring

Soil water content in the field at the four soil solution monitoring plots (Figs 3.1 to 3.3) was measured by the neutron scattering method (Graecen 1981) with a CPN corp. 503 DR Hydroprobe Moisture Depth Gauge. The probe was calibrated gravimetrically. Monitoring started in March 1983 at monthly intervals in at least two tubes at every site. Measurements were taken at 25 cm depth intervals. Readings refer to a spherical volume rather than to a specific soil layer (Van Vuuren 1984). The volume of the sphere increases with decreasing water content. Therefore the neutron method is not very well suited to measure the water content in thin, distinct soil horizons (e.g. the spodic horizon).

Preliminary measurements of soil water potential were started at the four sites at the same time and with the same monitoring intensity using Soil Moisture Corp. Jet Fill Tensiometers. Measurements were made in duplicate at 50 and 90 cm depth. At Gerrietsfles measurements were stopped soon after it became clear that in most cases hydraulic contact between cup and the coarse sand was insufficient to establish hydraulic equilibrium with the soil.

In August 1984 homemade tensiometers (for details, see Van Breemen et al. 1988) were installed at Tongbersven and Hasselsven. Tensiometer cups were installed horizontally in two profiles at 10 cm intervals, to a depth of 100 cm. Tensiometers were read monthly using a pressure transducer (National Semiconductor type 1604 GB).

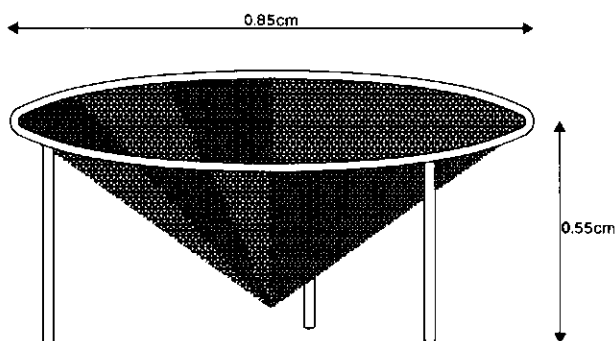


Figure 3.8. Diagram of litterfall collector.

3.6 Litterfall; sampling and analysis

From May 1984 to May 1985 tree litter was sampled at the forested monitoring plots (GFF and TV) from 5 randomly placed funnel-shaped, sheet plastic collectors. The collecting surface was 0.5 m^2 with the top about 50 cm above the soil surface (Fig. 3.8).

Litter was sampled fortnightly, oven-dried at 70°C within one day of collection, weighed and stored for analysis. Samples contained not only needles, but also twigs and cones. Chemical analysis was carried out at the Department of Soil Science and Plant Nutrition of the Agricultural University, Wageningen, according to Houba et al. (1985).

3.7 Hydrological monitoring of ground- and poolwater

Groundwater levels at Hasselsven and Tongbersven were recorded fortnightly starting in December 1982 in piezometers HV12 and TV4 (located at the soil solution monitoring plots), using a plummet with a light signal. In the other piezometers at Hasselsven the groundwater depth was measured fortnightly from July 1983 to July 1984 and monthly until March 1985. At Tongbersven the piezometers except TV4 were read fortnightly from June 1983 to June 1984 and monthly until July 1985. In these piezometers groundwater depth were recorded using an acoustic sounding device.

Poolwater levels of Tongbersven were measured fortnightly from July 1983 to July 1984, and monthly from this date to March 1985. At Hasselsven poolwater levels were measured fortnightly from June 1983 to June 1984 and monthly from this date to July 1985. Measurements of poolwater levels at Goorven, Gerritsfles and Kliplo were made every three months, starting in November 1979 in Goorven and Gerritsfles and in february 1982 in Kliplo, until May 1987. These measurements had an accuracy of 0.005 m.

3.8 Sampling and analysis of diatoms

Old diatom samples were obtained from the collections of the Hugo de Vries-laboratory (University of Amsterdam), the Research Institute for Nature Management (Ministry of Agriculture), the Limnological Institute (Royal Netherlands Academy of Sciences) and the Zoological Laboratory (University of Ghent). Recent samples were taken in Goorven and Kliplo at irregular intervals between 1977 and 1979 and twice a year between 1980 and 1984, and in Tongbersven and Hasselsven twice a year in 1983 and 1984.

Sampling, slide preparation, identification and counting are described in detail by Van Dam & Kooyman-van Blokland (1978) and Van Dam et al. (1981). The old plankton samples were taken with a net with a mesh width of 60 μm (A. van der Werff, pers. comm.) and the recent ones with a net with a mesh width of 40 μm . Replica slides were deposited in the collection of the Hugo de Vries-laboratory. The references for identification are listed by Van Dam (1984). Nomenclatorial and taxonomical changes, suggested by Krammer & Lange-Bertalot (1985) and Ross in Hartley (1986) were followed.

In each diatom slide 400 valves were identified and counted. Additionally the slide was searched for the most prominent species outside the count. The relative abundance is reported here as the number of valves of each taxon recorded in the count.

4 Data handling and computational procedures

4.1 Data handling

4.1.1 *Zero, missing and below detection limit values*

The volume of a number of samples was too small to permit estimation of all parameters listed in Table 3.5. Some samples were lost by disturbance or contamination. Missing values are indicated on Microfiche as -1. Concentrations below detection limit are indicated as < (detection limit). In further computations values below detection limit were replaced by an arbitrary value of (detection limit) · 0.5. Zero values have been assigned only to concentrations of free acidity and bicarbonate.

4.1.2 *Detection of outliers*

4.1.2.1 Meteoric water

Outliers were simply removed by hand; no statistical tests were used. Histograms were drawn for deposition (volume · concentration) of all components and all samplers, and values > 2 · (next highest value) were treated as outliers. Outliers in phosphate and pH > 8 were considered as indications of contamination; data for such samples were discarded. For most other solutes, only the outliers themselves were removed (i.e., replaced by missing values), except when they occurred for a number of components in one sample; such samples were also completely removed.

Ionic activity coefficients were calculated for each sample using the Güntelberg equation (Stumm & Morgan 1970). The ionic activities were multiplied with ionic conductivity values (Vogel 1961, see Golterman et al. 1978 for Al^{3+}) and added to give a calculated electrical conductivity for each sample. In most cases the calculated EC proved to be c. 10% higher than the measured EC. A number of samples had very aberrant values and these were excluded. Sum and difference in charge equivalent concentration of cations and anions were also calculated for each sample. Samples for which the difference was more than 15% of the sum were excluded.

As a result of these computations, 20 out of a total of 619 samples were considered unreliable and removed.

4.1.2.2 Soil solution, groundwater and poolwater

Raw chemical data were checked by means of ionic balances. For this purpose Mn, Fe and Al were supposed to be present as Mn^{2+} , Fe^{3+} and Al^{3+} respectively, although the charge of these ions is highly dependent on pH and – in the case of Mn and Fe – redox conditions (Stumm & Morgan 1970). Nevertheless, sums of anions and cations generally did not differ by more than 5%. Only when large concentrations of Fe ($> 100 \text{ mmol}_c \cdot \text{m}^{-3}$) or dissolved organic C (more than c. $1500 \text{ mmol} \cdot \text{m}^{-3}$) were present the cation sum exceeded the anion sum by more than 10%. To account for organic anion concentrations, estimates were made using the procedure outlined by Oliver et al. (1983). If the sum of anions (including organic anions) and the sum of cations differed more than 10%, concentrations of the major solutes were compared to the values from the months before and after, and apparently erroneous values were eliminated from the data set.

4.1.3 Comparison of poolwater analyses

Poolwater samples were analyzed by two laboratories: samples for quarterly monitoring of Goorven, Gerritsfles and Kliplo by WMN and samples for monthly monitoring of Hasselsven, Tongbersven, Gerritsfles and Kliplo by LUW. Thus for Gerritsfles and Kliplo parallel series were available for comparison. Sampling stations were close together (Figs 3.3 and 3.4) but sampling techniques were different (see 3.1.4 and 3.1.5). Samples of both series were usually taken one or a few days apart. In addition, eight parallel samples from other pools are available for comparison. These samples were taken at the same locations and dates, using the same sampling techniques (see 3.1.5). In Table 4.1 the average values for the three groups (Gerritsfles, Kliplo and other pools) of samples for both laboratories and the grand mean of all samples for each parameter are given. Results of regression analyses are given in Table 4.2.

No appreciable differences were found in mean values over all pools for lab pH, lab electrical conductivity, Na, K, Ca, Mg, Al, Mn and Cl, although considerable differences between individual samples can occur, especially for Al. For Fe the mean values correspond well, but in Gerritsfles and Kliplo the LUW-values are considerably lower than the WMN-values, while the reverse is true for the other pools. In the LUW-sample from Goorven E very high values were found for some parameters while other samples showed more normal values for these parameters, e.g. lab pH, Ca and Mg. Presumably this sample has been stored too long before analysis. The LUW-values for ammonium and phosphate are nearly always higher than the corresponding WMN-values. The grand mean of ammonium in the LUW-samples is 26% higher than the mean of WMN. The relative difference varies between 10 and 69% for each of the three groups (Gerritsfles, Kliplo and other pools). Phosphate in the LUW samples is 2-4 times higher than in the WMN-samples. However, phosphate analysis was not optimised in the LUW laboratory.

Hydrogen bicarbonate is often higher in the WMN-samples than in the LUW-

Table 4.1. Comparison of chemical data from WMN and LUW. ? : probably erroneous data, excluded from calculation of mean values and regression analysis, ! : outlier, excluded from regression analysis. Names of pools: GF = Gerritsfles, KL = Kliplo, D = Diepveen, P = Poort 2, Z = Echterzand, H = Groot Huisven, M = Midden Wolffspuilen, S = Schaapsven, W = Deelse Was, E = Goorven station E. EC in $\mu\text{S}\cdot\text{cm}^{-1}$, SiO_2 in $\text{mmol}\cdot\text{m}^{-3}$, ions in $\text{mmol}\cdot\text{m}^{-3}$.

Pool	date	pH field		pH lab		EC lab		SiO ₂		K		Na		Ca		Mg		Al		Fe		Mn		
		WMN	LUW	WMN	LUW	WMN	LUW	WMN	LUW	WMN	LUW	WMN	LUW	WMN	LUW	WMN	LUW	WMN	LUW	WMN	LUW	WMN	LUW	
GF	830517	830527	4.1	4.50	4.8	4.3	80	79	8	0	23	20	174	176	50	95	49	37	11	15	20	23	2	3
GF	830817	830819	4.0	4.55	4.5	4.7	97	90	22	6	33	33	239	213	50	80	58	61	20	35	26	29	2	3
GF	831116	831118	4.9	5.35	5.2	5.3	96	84	5	1	38	31	261	211	50	33	58	45	14	13	16	66	2	3
GF	840216	840217	5.1	4.85	5.6	5.0	59	63	3	1	28	27	174	183	50	13	41	41	10	2	12	21	1	2
GF	840518	840517	5.5	5.55	4.6	5.4	73	55	13	1	26	27	174	170	25	50	41	33	10	16	9	90	1	1
GF	840814	840817	3.9	5.15	4.5	4.5	76	81	13	6	26	29	196	187	15	48	49	49	16	16	20	41	2	2
GF	841113	841114	4.4	4.40	4.4	4.6	69	61	5	1	18	8	174	161	100	30	41	49	26	12	3	24	1	2
KL	830517	830527	5.3	-	5.4	4.7	63	55	1	0	26	22	239	241	50	23	58	57	12	22	46	48	-	4
KL	830817	830818	4.4	-	5.2	5.2	66	71	13	7	26	2	261	243	100	70	74	66	12	0	91	54	4	4
KL	831115	831125	5.5	-	5.7	5.7	64	68	3	1	36	31	261	317	50	-	74	74	20	24	64	69	4	2
KL	840216	840217	4.6	-	5.3	5.8	65	64	2	1	33	41	261	257	50	48	74	70	11	5	19	84	3	4
KL	840518	840517	5.2	-	4.8	5.8	64	63	30	1	36	41	261	267	50	88	66	70	7	7	35	89	2	3
KL	840814	840817	4.8	-	5.2	5.3	57	59	25	5	23	23	261	250	50	75	66	70	9	4	32	39	4	4
KL	841113	841114	5.2	-	5.3	5.6	54	59	13	1	28	28	261	243	100	70	58	66	13	33	18	42	3	6
D	820929	820929	4.5	-	4.4	4.8	86	83	17	15	64	65	304	303	75	65	99	92	26	11	54	38	1	4
P	820929	820929	4.5	-	4.5	4.7	64	64	1	6	56	54	283	302	50	32	74	66	10	16	51	44	1	4
Z	820929	820929	5.4	-	5.5	5.4	80	80	50	46	61	67	326	324	50	39	58	49	19	7	419!	221!	1	4
H	821001	821001	3.9	-	4.1	3.8	1126	130	1	9	36	41	304	293	200	142	156	152	43	29	8	6	4	4
M	821001	821001	4.4	-	4.7	4.9	52	53	83	66	36	42	174	217	125	95	58	51	23	11	91	53	3	4
S	821001	821001	4.3	-	4.5	4.1	53	52	17	19	10	14	130	156	100	104	49	55	10	4	35	6	3	4
W	830126	830126	4.2	-	4.4	4.0	1126	125	1	16	23	20	217	200	299	297	90	93	211!	303!	3	2	8	6
E	830818	830818	3.9	-	4.4	6.8	1110	127?	47	90	38	43	326	359	100	340?	901	172?	39	25	150	62	2	1
Mean Gerritsfles			4.6	4.91	4.8	4.8	79	73	10	2	27	25	199	186	48	50	48	45	15	16	15	42	2	2
Mean Kliplo			5.0	-	5.3	5.4	62	63	12	2	30	30	258	260	64	62	67	68	12	14	44	61	3	4
Mean other pools			4.4	-	4.6	4.5	87	89	27	33	41	43	258	269	125	111	84	80	48	51	101	54	3	4
Grand mean			4.6	4.91	4.9	4.9	76	76	17	13	33	33	239	240	81	75	67	64	26	28	56	52	3	3

(contd. next page)

Table 4.1. Continued.

Pool	date	NH ₄		Cl		NO ₃		SO ₄		H ₂ PO ₄		CO ₂		alk HCO ₃	
		WMN	LWU	WMN	LWU	WMN	LWU	WMN	LWU	WMN	LWU	WMN	LWU	WMN	LWU
GF	830517	830527	133	143	240	304	304	16	0	250	267	0.05	0.0	91	75
GF	830817	830819	155	172	296	320	320	5	0	291	317	0.42	0.5	136	0
GF	831116	831118	261	278	310	321	321	5	1	291	294	0.05	0.4	114	222
GF	840216	840217	161	192	226	254	254	8	15	167	213	0.11	0.0	136	44
GF	840518	840517	155	195	240	256	256	8	1	312	81?	0.05	0.5	114	461?
GF	840814	840817	144	146	254	239	239	5	1	208	263	0.05	0.4	114	82
GF	841113	841114	94	142	212	202	202	10	1	208	229	0.21	0.5	114	66
KL	830517	830527	47	76	310	299	299	11	0	167	133	0.11	0.0	136	295
KL	830817	830818	19	6	324	307	307	1	0	146	96	0.11	0.0	204	196
KL	831115	831125	94	38	339	400	400	5	1	83	115	0.21	0.5	159	212
KL	840216	840217	72	90	339	344	344	6	1	146	97	0.11	0.0	182	229
KL	840518	840517	36	74	353	324	324	3	2	-	87	0.05	0.3	136	165
KL	840814	840817	6	4	339	309	309	3	1	42	76	0.05	0.4	227	140
KL	841113	841114	17	33	296	371	371	3	6	104	57	0.11	0.5	136	86
D	820929	820929	67	111	367	372	372	3	5	271	227	0.32	1.3	409	107!
P	820929	820929	4	39	324	313	313	5	5	187	107	0.21	2.3	295	177!
Z	820929	820929	155	150	381	394	394	5	5	229	171	1.37	1.5	114	100!
H	821001	821001	6	79	353	349	349	2	5	521	475	0.05	0.8	159	59!
M	821001	821001	14	107	240	254	254	8	5	208	100	0.05	1.5	227	78!
S	821001	821001	3	41	169	186	186	2	5	187	147	0.05	0.5	227	138!
W	830126	830126	25	43	254	264	264	29	45	708	732	0.05	0.5	295	138
E	830818	830818	111	80	494	523	523	3	59?	437	282	0.21	0.6	204	38!
Mean Gerritflies			158	181	254	271	271	8	2	247	264	0.14	0.3	117	82
Mean Klippo			42	46	328	336	336	5	1	115	95	0.11	0.2	169	189
Mean other pools			48	81	323	332	332	7	11	346	280	0.29	1.1	241	104
Grand mean			81	102	303	314	314	7	5	246	214	0.18	0.6	179	120

Table 4.2. Regression analysis of chemical data of WMN and LUW, taken from Table 4.1.

Fitted equations:

LUW = $a_1 + b_1 \cdot \text{WMN}$; v_1 = percentage variance accounted forLUW = $b_2 \cdot \text{WMN}$; v_2 = percentage variance accounted for

	pH/l	EC/l	K	Na	Ca	Mg	Al	Fe	Mn	NH ₄	Cl	NO ₃	SO ₄	H ₂ PO ₄
a_1	0.76	-2.04	-2.05	10.2	8.2	0.07	-9.67	28.6	2.22	30.9	22.2	-3.07	-12.3	0.43
b_1	0.853	1.019	1.075	0.959	0.815	0.967	1.437	0.423	0.433	0.877	0.964	1.163	0.957	0.902
v_1	44	91	91	83	75	94	96	66	25	79	85	52	87	15
b_2	1.008	0.994	1.021	1.000	0.877	0.968	1.332	0.573	1.047	1.098	1.034	0.912	0.921	1.618
v_2	45	91	91	83	76	94	94	39	19	71	85	52	88	-

Table 4.3. Comparison of mean charge balances of WMN and LUW analyses given in Table 4.1. HCO_3^- = alkalinity determined by WMN or HCO_3^- determined by LUW, ORG = organic anions, $\text{diff/sum} = 100 \cdot (\Sigma \text{CATIONS} - \Sigma \text{ANIONS}) / (\Sigma \text{CATIONS} + \Sigma \text{ANIONS})$, GF = Gerritsfles, KL = Kliplo, OT = other pools, AL = all pools. Ions in $\text{mmol} \cdot \text{m}^{-3}$.

	Cations										Anions					
	H	K	Na	Ca	Mg	Al	Fe	Mn	NH ₄	SUM	HCO ₃	Cl	NO ₃	SO ₄	H ₂ PO ₄	diff/sum
GF WMN	19	27	199	48	48	15	15	2	158	531	20	254	8	247	0	-3
LUW	21	25	186	50	45	16	42	2	181	568	11	271	2	264	0	-2
KL WMN	7	30	258	64	67	12	44	3	42	527	52	328	5	115	0	-2
LUW	6	30	260	62	68	14	61	4	46	551	26	336	1	95	0	4
OT WMN	36	41	258	125	84	48	101	3	48	744	14	323	7	346	0	0
LUW	56	43	269	111	80	51	54	4	81	749	18	332	11	280	1	4
AL WMN	17	33	239	81	67	26	56	3	81	603	28	303	7	246	0	-2
LUW	27	33	240	75	40	28	52	3	102	600	18	314	5	214	1	0

samples. This is caused by a difference in methods. The WMN uses an alkalinity titration and supposes all the alkalinity to be present as hydrogen bicarbonate. Part of the weakly acid organic anions are also titrated by this method. However, this is not always the case as the highly stained samples from the pools D and P (Table 4.1) have negligible alkalinity. In the LUW-samples bicarbonate was calculated from total inorganic carbon and pH. For bicarbonate and alkalinity large differences are found between individual samples. The average values for Kliplo and Gerritsfles correspond reasonably well but in the other pools the average bicarbonate value by LUW is only 43% of the average alkalinity value by WMN.

In Table 4.3 ionic balances from samples of both laboratories are compared. In the analyses of both laboratories the sum of anions (including organic anions estimated according to Oliver et al. (1983)) and cations, generally deviates less than a few percents which indicates that the analyses are of good quality.

4.2 Flux calculations

One of the main research objectives was to study the impact of atmospheric deposition on the solution composition as water moves through the system. To get more insight in the processes involved chemical budgets for various soil-vegetation and moorland pool systems were estimated. Chemical budgets summarize the net fluxes for chemical compounds for specified time and depth intervals. The fluxes estimated in the present study refer to water and dissolved compounds in rain, throughfall, stemflow, soil solution, groundwater and moorland poolwater.

Solute fluxes in rain, throughfall and stemflow were obtained directly from measured water fluxes and concentrations. Because open collectors (bulk samplers) were used solute fluxes may have been overestimated as a result of contamination. Procedures used to minimise errors in meteoric fluxes are described in 4.1.2.1 and 4.2.1. Fluxes obtained from the bulk samplers collectors were checked against data from nearby official weather stations (Table 6.3).

Monthly chemical fluxes of soil solution, groundwater flow to and seepage from moorland pools were calculated by multiplying a simulated waterflux and a measured solute concentration. The continuous collection of soil solution over a one-month period is assumed to give a sample representative for the soil solution composition of that month. Unsaturated soil water fluxes were calculated with a deterministic model for soil water flow (SWATRE), based on the Darcy flow equation (Feddes et al. 1978; Belmans et al. 1983). Primary input data are precipitation and evapotranspiration. The same model was used for other budget studies in The Netherlands and is extensively discussed by Van Breemen et al. (1988). In 4.2.2 a brief description of this model is given and the procedures to obtain the input data and the calibration of the unknown model parameters is discussed.

Hydrological models for the moorland pools are presented in 4.2.3 and 4.2.4, and the modelling of chemical budgets for the pools is discussed in 4.2.5.

4.2.1 *Calculation of chemical fluxes in meteoric water*

For each sampler chemical fluxes were obtained by multiplying concentrations and water fluxes. Water fluxes per unit area were calculated from the water amount and the surface area of the funnels (c. 390 cm²) and gutters (c. 4000 cm²). No corrections for wind error were made. Stemflow per unit area was estimated using a standard number of 600 trees·ha⁻¹. This is a rough estimate, but, because the quantity of stemflow is very low compared to throughfall, the effect on total flux is small.

Fluxes for the forest stands were calculated as the mean of the fluxes found in the throughfall samplers plus the mean of the stemflow collectors. At Tongbersven the TVA samplers B6, B7 and B8 (Microfiche), which were located close to the moorland pool, were used for the calculation of chemical budgets of the soil-moorland pool system, and the TVB samplers B2, B3, B4 and B5 (Microfiche), which had longer time series, were used for comparison with the other meteoric water samplers and the estimation of dry deposition. At Gerritsfles the gutters (which were used for a much shorter time than the funnels) were not used in the calculation of mean fluxes. Because of the large variation between the individual collectors (see Section 7.2.1) missing values could not be simply omitted, and they were estimated by means of regression of fluxes found in each sampler on the values of all other samplers at the same site. A fixed intercept of zero was used. For stemflow, missing values were estimated from the other stemflow collectors, if present, and otherwise from throughfall. In the open field single collectors were used and missing values were replaced by values from the nearest meteorological station (KNMI/RIVM 1981-1985). This was done only three times (Gerritsfles May and June '82, replaced by data from Deelen, and Tongbersven June '83, replaced by data from Eindhoven).

4.2.2 *The flow model SWATRE for the unsaturated soil zone*

The model SWATRE, used for the unsaturated soil water flux calculations, is one-dimensional, so that lateral water and energy transport as well as spatial variability of infiltration and soil properties were not considered. The boundary conditions and system parameters used are reviewed in Table 4.4.

4.2.2.1 *Evapotranspiration*

Procedures to calculate potential transpiration, soil evaporation and interception are described elsewhere (Van Breemen et al. 1988). The amount of meteoric water intercepted by the canopy was estimated from the difference between bulk precipitation and throughfall. The evapotranspiration parameters used to calculate potential transpiration and soil evaporation are given in Table 4.5. Parameter f_3 (transpiration/evaporation of intercepted water) has no meaning for GFB. The values of f_3 for GFF and TV are based on Singh and Szeicz (1979). The trees are assumed to be inactive from December 1 to May 1.

Table 4.4. Boundary conditions and input parameters for the SWATRE model.

Input data	Source
Top of soil system	
Precipitation	Only used as input for the bare Gerritsfles site (daily precipitation taken from KNMI station Harskamp).
Throughfall	Daily throughfall was calculated from monthly throughfall, distributed per day according to the distribution of precipitation (taken from daily precipitation recorded at the nearest KNMI meteorological station ^a).
Potential evapotranspiration	Calculated with empirical formulations from Penman open water evaporation, using synoptic data from the nearest weather station ^b , and field data of monthly cumulative throughfall.
Bottom of soil system	
Groundwater level	Linear interpolation of fortnightly field measurements at Tongbersven and Hasselsven. At both Gerritsfles sites free drainage was assumed.
Soil Hydrology	
Water retentivity function	Optimization of closed form equation, using experimental data from undisturbed soil columns. One time correction of average field hysteresis state at Tongbersven and Hasselsven (with the exception of both spodic horizons).
Conductivity function	First estimate from water retentivity function by Mualem, calibrated with experimental value at -10 mbar pressure head. Fine tuning with SWATRE.
Root wateruptake distribution	First estimate from root distribution (soil description); fine tuning with SWATRE. Hyperbolic reduction of transpiration with pressure head below reduction point.
Initial condition	Equilibrium with phreatic level at start of growing season.

^a The nearest meteorological stations are: Harskamp (Gerritsfles), Tilburg (Tongbersven) and Maarheze (Hasselsven).

^b The nearest weather stations are: de Bilt (Gerritsfles) and Eindhoven (Tongbersven and Hasselsven).

4.2.2.2 Soil hydraulic properties

Model calculations were done first with the fitted water retention and hydraulic conductivity functions. Hydraulic properties for the model compartments were grouped according to the genetic soil horizons.

For Tongbersven and Hasselsven simultaneous field measurements of soil water content and soil water potential were used to adjust the water retention characteristic based on lab data. However, neutron data were not accurate enough to determine a

Table 4.5. Evapotranspiration parameters used for the SWATRE simulations. IC = Interception capacity (mm), TF = fraction of throughfall not intercepted in groundvegetation, f_1 = crop factor, f_2 = fraction of potential soil evaporation, f_3 = ratio of the actual rates of transpiration and evaporation of intercepted water.

Parameter	Day	Site			
		HV	TV	GFF	GFB
IC		0.50	2.00	2.00	0.00
TF		0.82	1.00	0.90	1.00
f_1	000-090	0.50	0.50	0.50	1.00
	090-120	0.50	0.50	0.90	1.00
	120-300	0.80	0.80	0.90	1.00
	300-335	0.50	0.60	0.70	1.00
	335-365	0.50	0.50	0.50	1.00
f_2	000-120	1.00	1.00	1.00	1.00
	120-300	0.30	0.10	0.20	1.00
	300-335	1.00	1.00	0.90	1.00
	335-365	1.00	1.00	1.00	1.00
f_3		0.66	0.33	0.33	0.00

field water characteristic for the Bhs horizon at Tongbersven and Hasselsven. For the parameterization of the water retention data, the mean of θ ($h = -10$ mbar suction) and the saturated water content was used instead of the saturated water content (cf. Van Breemen et al. 1988). For the initial model calculations the potential root water uptake was assumed to be distributed according to the root mass distribution for GFF. For TV and HV root water uptake was assumed to be distributed evenly to depths of 60 cm (TV) or 20 cm (HV). The sink term variables are identical to those described for the 'Oude Maat' soils (Van Breemen et al. 1988).

4.2.2.3 Model calibration

The SWATRE model was calibrated by minimizing the sum of squared differences between measured and simulated soil water contents. Calculations were carried out for the hydrological years from April 1, 1983 to April 2, 1987. For Gerritsfles and Tongbersven a free drainage and for Hasselsven a potential boundary condition was imposed at the bottom of the soil system. Simulations were carried out for 10 cm thick soil compartments. In general model calibration started by adjusting the hydraulic conductivity (cf. Van Breemen et al. 1988). For Hasselsven and Tongbersven, where field soil water retention characteristics were available, these adjustments were generally small (Table 2.10). Fine tuning of the calibration was carried out by adjusting the

root water uptake patterns. A major problem in the calibration procedure was the high spatial variability of soil water contents (Figs 4.1 to 4.4 and Appendix 2).

Hasselsven. Simulation of the unsaturated hydrology in the Hasselsven soils is difficult due to the presence of an open vegetation (heath). Field measurements of rainfall and interception were not available for the simulated hydrological year 1983-1984. Based on an estimate of soil cover and field observations of throughfall, interception was calculated per unit surface area. Simulated and measured water storage for 1983 and 1984 (Fig. 4.1) agree reasonably well for the complete soil profile. This also holds true for the water contents at various soil depths (Appendix 2). The water content in the HV soil has a pronounced seasonal variation with lows (8 to 10 cm water per 130 cm profile) around October and highs (16 to 26 cm water) around April. The exceptionally high water contents in the spring of 1983 and 1985 are due to upwelling of groundwater (Appendix 2).

Tongbersven. Initial simulations gave values for transpiration which were low compared to literature values (Galoux 1981). The simulated transpiration was increased by reducing the water retention of the Bhs and Bs horizons by 8% (from -500 to 0 mbar). Decreased water contents will reduce conductivity of the Bhs and will increase the water storage in the soil overlying the Bhs.

Simulated and measured water storage in the soil profile are shown in Fig. 4.2. At the end of the first growing season (from September 1983, i.e. day 240 onwards) measured water storage is significantly lower than simulated values, which may be due to measurement errors. During the same period similar low values for water contents were observed in the individual soil layers. The discrepancy between measured and simulated values may also be due to the assumption that only vertical flow takes place, while percolating water may be drained laterally over the compact Bhs horizon. However, no evidence was found for temporary saturation above and interflow over the Bhs horizon (see 5.3.1). Possibly surface runoff occurs occasionally when the forest floor has become hydrophobic near the end of the summer.

Water contents in the TV soil also exhibits a seasonal trend: lowest water content (9 to 11 cm water per 130 cm soil profile) in the autumn and highest values (15 to 17 cm water) in the spring (Fig. 4.2).

Gerritsfles Forest. Distribution of water uptake by roots was estimated to be 50% in the litter layer, 22% from 0-10 cm depth and 38% evenly distributed between 10 and 60 cm depth. Initial SWATRE simulations gave unrealistically low transpiration values, as indicated by too high simulated Cl fluxes from the soil system. To increase transpiration, and thus improve the calibration, the forest floor, with estimated hydraulic properties, was introduced as a separate compartment in the model. This increased the water retention capacity of the soil profile, but still did not give the expected result, illustrating the complex interplay between water retention, hydraulic conductivity and transpiration. However, the calibration could be improved by a

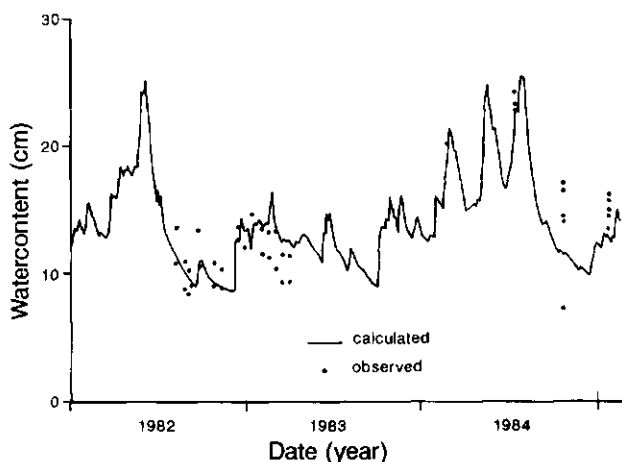


Figure 4.1. Hasselsven, simulated and measured water storage in the profile.

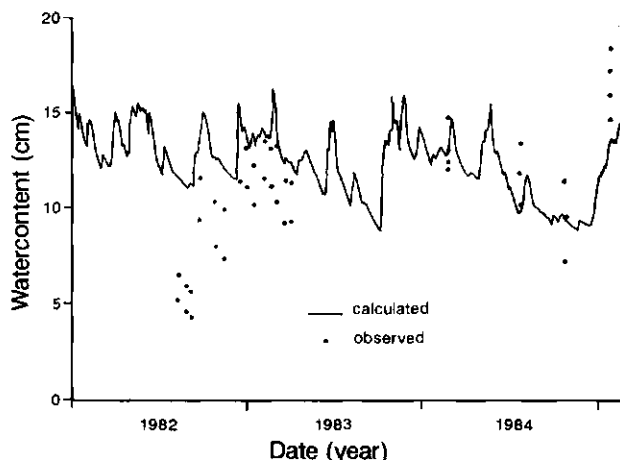


Figure 4.2. Tongbersven, simulated and measured water storage in the profile.

Reduction of conductivity (Table 2.10). Simulated and measured water storage in the soil profile is shown in Fig. 4.3.

Simulated water storage at GFF shows the most pronounced seasonal variation of all research sites, with lows (c. 4 cm water per 130 cm profile) at the end of the summer and early autumn, and highs (12 to 18 cm water) in winter and spring. The strong seasonality is probably caused by: (1) the high evaporative demand in summer and (2) a relatively low holding capacity in all soil layers. Simulations were not fully satisfactory (Fig. 4.3), particularly not in the summer of 1985, where measured values were significantly higher than simulated ones. This discrepancy originates primarily in the surface horizon (Appendix 2).

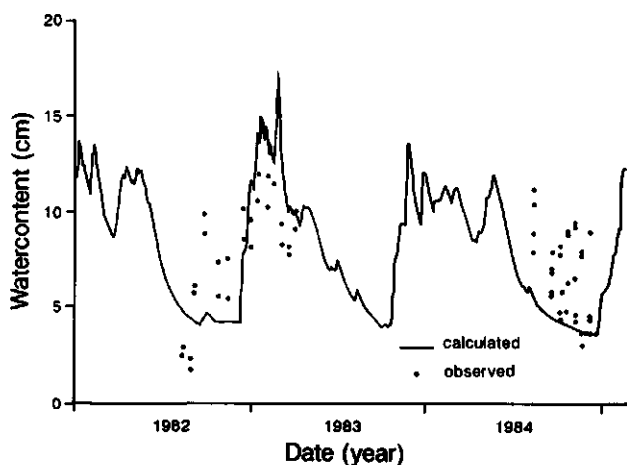


Figure 4.3. Gerritsfles forest, simulated and measured water storage in the profile.

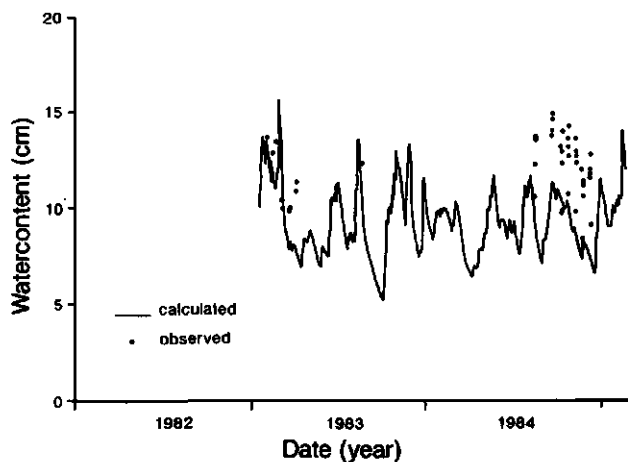


Figure 4.4. Gerritsfles bare, simulated and measured water storage in the profile.

Gerritsfles Bare. The soil profile of GFB was divided into two layers: 0-20 cm and 20-130 cm. Rooting depth and root water uptake distribution are not relevant as there is no vegetation. The most critical parameter in the simulation for this site is the 'crop factor'. In SWATRE evaporation from bare soil is described according to the method of Black et al. (1969). This method calculates evaporation from a bare soil from the diffusivity relationship:

$$E = 2(\theta_i - \theta_o) \sqrt{Dt/\pi} \quad (4.1)$$

with:

E evaporation in cm

θ_i initial volumetric water content in $\text{cm}^3 \cdot \text{cm}^{-3}$

θ_o residual water content

D hydraulic diffusivity ($\text{cm}^2 \cdot \text{d}^{-1}$)

t time after start of evaporation from θ_i in day

In general θ_i is equal to field capacity, which is attained approximately two days after saturation of the soil profile. This relation can be simplified to:

$$E = C \sqrt{t} \quad (4.2)$$

The value of C strongly depends on the definition of field capacity. Field capacity is an operational parameter; in practice saturation seldomly appears in the field and the number of days to reach field capacity will depend on soil type and the degree of saturation which is actually attained after a rain event. The value of C can also be interpreted as the maximum evaporation from a soil at field capacity. In SWATRE a value of $0.35 \text{ cm} \cdot \text{d}^{-1}$ is taken for C. The calculated evaporation was verified in two ways:

- (1) by comparison of simulated and measured water contents;
- (2) by comparison of simulated annual evaporation with data from the lysimeter at Castricum filled with bare dune sand.

The conductivity of the topsoil (0-20 cm) was slightly increased, the values for the subsoil (20-130 cm) were lowered somewhat (Table 2.10) to match simulated and measured water content and water storage (Fig. 4.4).

Evapotranspiration from the large ($25 \cdot 25 \cdot 2 \text{ m}^3$) sandbox lysimeters at Castricum was analysed by Ter Hoeve (1978). Based on precipitation and drainage output data over 35 years, an empirical relationship was derived between actual evapotranspiration (ET_{act}) and the precipitation excess (P_e):

$$P_e = N - ET_{\text{act}} = N - f_1 \cdot E_o \quad (4.3)$$

with:

P_e precipitation excess in cm

N precipitation in cm

ET_{act} actual evapotranspiration in cm

E_o open water evaporation according to Penman, in cm

f_1 crop factor

For the lysimeter with bare dune sand a value of 0.3 was found for f_1 . Applying this value to GFB gives 200 mm actual evapotranspiration for the hydrological year 1983/'84. The simulated evapotranspiration is 202 mm. The bare driftsand at GFB is

the only soil without a pronounced seasonal variation in water content, which must be due to the absence of transpiration from this soil.

4.2.3 The model VENSIM for pool water hydrology

The model VENSIM (Houweling 1991) was used to simulate the water volume and Cl concentrations of the pool water of Tongbersven, Hasselsven, Kliplo, and Gerritsfles, in order to calculate water budgets. For any watershed the equilibrium between water influx, efflux and storage can be described by the budget equation

$$dV_v/dt + \Sigma Q_i = 0 \quad (4.4)$$

with:

V_v stored water volume

ΣQ_i sum of inflow and outflow fluxes (inflow and storage decrease positive, outflow and storage increase negative).

When Cl is conservative and the pool is well mixed, a simple mass budget for the Cl ions can be written as:

$$d(V_v \cdot C_v)/dt + \Sigma(Q_i \cdot C_i) = 0 \quad (4.5)$$

with:

C_v concentration of Cl in the pool,

C_i concentration of Cl in Q_i .

Fig. 4.5 is a schematic representation of a pool system. The surface area of the pool depends on the water level and the hydraulic resistance of the pool bottom decreases near the border. The variables and parameters of the model are listed in Table 4.6. The budget equations (4.4) and (4.5) can be rewritten as:

$$Q_p + Q_e + Q_l + Q_r + dV_v/dt = 0 \quad (4.6)$$

$$Q_p \cdot C_p + Q_l \cdot C_l + Q_r \cdot C_r + d(V_v \cdot C_v)dt = 0 \quad (4.7)$$

with:

Q_p precipitation water influx

Q_e evaporation water loss

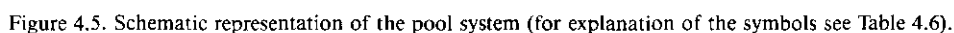
Q_l seepage water loss

Q_r surface water inflow from adjacent pool (if any)

C_p Cl concentration in Q_p

C_l Cl concentration in Q_l

C_r Cl concentration in Q_r .



	Symbol	Unit
Input variables		
Precipitation per 10 days	P	(mm)
Evaporation per 10 days	E _o	(mm)
Cl concentration in precipitation	C _p	(mmol · m ⁻³)
Groundwater level	H _g	(m + NAP)
Cl concentration in groundwater	C _g	(mmol · m ⁻³)
Water level in adjacent pool	H _s	(m + NAP)
State variables		
Water level	H _v	(m + NAP)
Cl concentration in poolwater	C _v	(mmol · m ⁻³)
Poolwater area	A _v	(m ²)
Poolwater volume	V _v	(m ³)
Mean simulated poolwater level	H _v *	(m)
Mean simulated Cl concentration in poolwater	C _v *	(mmol · m ⁻³)
Parameters		
Catchment area	A _s	(m ²)
Empirical evaporation coefficient in resp. around pool	f ₁ , f ₂	(-)
Hydraulic resistance of pool bottom	c _b	(day)
Highest level where hydraulic bottom resistance is c _b	H _p	(m + NAP)
Hydraulic resistance of pool bottom above H _p + dH	c _p	(day)
Range over which c _b reduces to c _p	dH	(m)
Surface area of the border strip with hydraulic bottom resistance c _p	A _p	(m ²)
Surface area of the central part of the pool with hydraulic bottom resistance c _b	A _b	(m ²)
Level of the pool bottom	H _m	(m + NAP)
Hydraulic resistance of the the connection with the adjacent pool	K _s	(m ² · d ⁻¹)

The components of equations (4.6) and (4.7) are calculated from:

$$\begin{aligned} Q_p &= P \cdot A_s \\ Q_e &= f_1 \cdot E_o \cdot A_v + F_2 \cdot (A_s - A_v) \\ Q_l &= (H_v - H_r) \cdot A_b / c_b + (H_v - H_r) \cdot A_p / c_p \\ Q_r &= (H_v - H_s) \cdot K_s \end{aligned}$$

with:

$$\begin{aligned} H_r &= H_g & \text{if } H_g > H_m \\ H_r &= H_m & \text{if } H_g \leq H_m \\ F_2 &= f_2 \cdot E_o & \text{if } P > f_2 \cdot E_o \\ F_2 &= P & \text{if } P \leq f_2 \cdot E_o \\ C_l &= C_v & \text{if } H_v \geq H_g \\ C_l &= G_g & \text{if } H_v < H_g \\ C_r &= C_v & \text{if } H_v \geq H_s \\ C_r &= C_s & \text{if } H_v < H_s \end{aligned}$$

Further explanation of the symbols is given in Table 4.6.

VENSIM integrates the equations (4.4) and (4.5). The initial values of the state variables H_v and C_v are taken from observations (if available) or estimated during calibration. A_v and V_v are related to H_v by the pool morphometric data.

The VENSIM model was calibrated by minimizing J , the weighted root mean square difference between observed and calculated poolwater levels and between observed and calculated Cl concentrations using the equation

$$J = \sqrt{(\Sigma(H_j - H'_j)^2/n)} + K\sqrt{(\Sigma(C_j - C'_j)^2/m)} \quad (4.8)$$

with:

- H_j, H'_j calculated and observed water level respectively (m) ($j = 1, \dots, n$)
- C_j, C'_j calculated and observed Cl concentration respectively ($\text{mmol} \cdot \text{m}^{-3}$) ($j = 1, \dots, m$)
- n number of water level observations
- m number of Cl concentration observations
- K weighing factor ($1/2000$), the ratio of the measuring accuracy of water level (0.005 m) and Cl concentration ($10 \text{ mmol} \cdot \text{m}^{-3}$).

The sources of input variables are given in Table 4.7. Poolwater levels at the end of ten day periods were estimated from fortnightly, monthly or three-monthly measurements using linear interpolation. The evaporation coefficient of the land-part of the catchment was fixed on 0.7 and the distance dH over which C_b reduces to C_p was fixed on 0.1 m. The estimated parameter values are shown in Table 4.8. Because monitoring of the groundwater level near Tongbersven started in May 1983, H_g values

Table 4.7. Sources of information on precipitation, evaporation and groundwater level used for the calibration of VENSIM. Precipitation (P) data for Leende from KNMI (1980-1987), evaporation data (E_o) for Eindhoven, Andel and Eelde from KNMI (1982-1988), evaporation data for Deelen from KNMI (pers. comm.) and Cl in precipitation (C_p) at Eindhoven from KNMI/RIVM (1978-1986). L = local bulk sampler at the site (Microfiche). TV32, TV4, HV22 and HV4 are local piezometers (Oostveen 1985).

Variable	HV	TV	GF	KL
P	Leende	L	L	L
E_o	Eindhoven	Eindhoven/Andel ^a	Deelen	Eelde
C_p	Eindhoven	L	L	L
H_g	HV22, HV4	TV32, TV4	—	—

^a mean value

Table 4.8. Synopsis of calibration results of VENSIM. In the HV* a dry Cl deposition of $0.780 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ is assumed in the terrestrial part of the catchment.

Parameter or variable	HV	HV*	TV	GF	KL
Catchment area (m^2)	21177	21650	4650	68812	7887
Evaporation coefficient of poolwater	0.79	0.78	0.79	0.79	1.00
Hydr. resist. of pool bottom below H_p (day)	265	253	1290	1025	1312
Level above which C_b reduces to C_p ($\text{m} + \text{NAP}$)	26.20	26.20	7.89	39.47	12.61
Hydr. resist. of pool bottom above H_p (day)	827	807	38	59	66
Retention time of poolwater (year)	0.62	0.38	0.40	0.86	1.14
Ratio A_v/A_s	0.87	0.85	0.97	0.85	0.88
Root mean square error of level (m)	0.024	0.023	0.015	0.026	0.026
Root mean square error of Cl conc. ($\text{mmol} \cdot \text{m}^{-3}$)	39.44	22.59	30.58	11.94	13.61

for the period January 1, 1983 to May 1, 1983 at this site had to be estimated by regression, using the observed water levels in piezometer TV7. Simulated and observed pool-water levels for the four pools are given in Figs 4.6 to 4.9.

Poolwater level and concentration data were screened for outliers. When after the initial calibration the difference between a calculated value and the corresponding measured value exceeded 2.5 times the root mean square error, the measurement was excluded from the final calibration. These observations are marked with \circ in Figs 4.6 to 4.9. The root mean squared differences of levels and concentrations are given in Table 4.8. For Hasselven the root mean squared difference between observed and calculated concentration of Cl is $39 \text{ mmol} \cdot \text{m}^{-3}$. This value decreases to $23 \text{ mmol} \cdot \text{m}^{-3}$ if dry deposition of Cl ($0.730 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$) is included in the model.

The estimated evaporation coefficient for the open water of Tongbersven, Hasselven and Gerritsfles is slightly smaller than 0.8. At Kliplo, however, the coefficient is 1.0. This high value for Kliplo is probably caused by water withdrawal by the

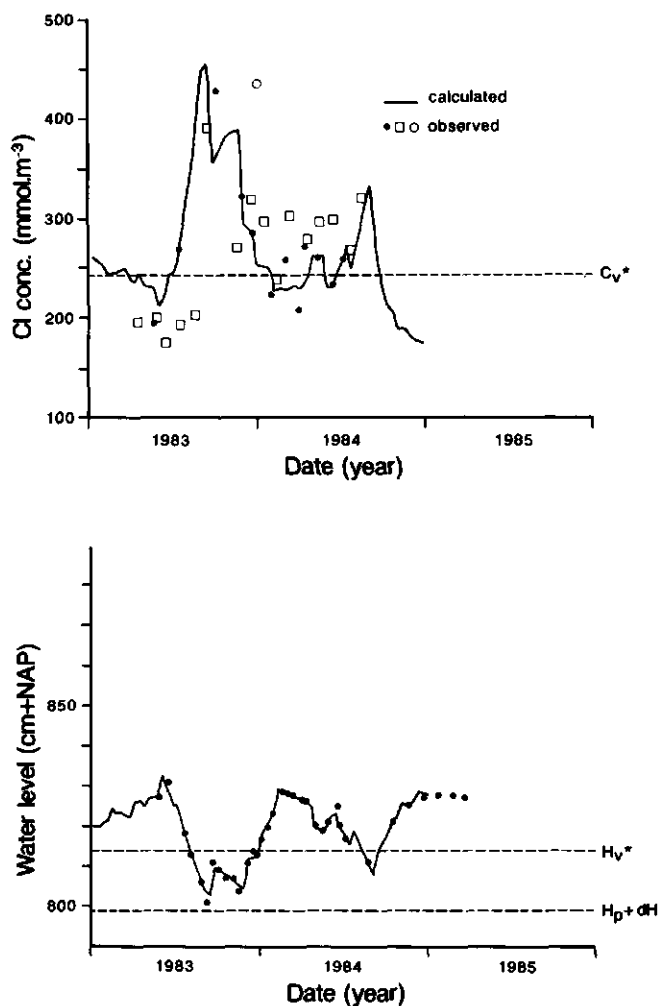


Figure 4.6. Tongbersven, simulated and observed poolwater levels and Cl concentrations. ● = observed by RIN, ○ = observed by RIN (not used for calibration), □ = observed by LUW (not used for calibration), C_v^* = simulated mean Cl concentration, H_v^* = simulated mean poolwater level, $H_p + dH$ = lowest level where hydraulic resistance of bottom is c_p .

birch carr at the northern side of the pool. The hydraulic resistance of the pool bottom is about 1300 day at Tongbersven and Kliplo and 1000 day at Gerritsfles. Above minimum poolwater level this resistance is lower than 100 day. At Gerritsfles and Kliplo the waterpressure below the poolbottom is assumed to be zero. If the pressure head is negative (Bannink et al. 1989) the hydraulic resistance of the poolbottom will be higher, but the seepage hardly changes. At Hasselsven the resistance of the sandy pool bottom is only about 250 day. Near the border the hydraulic resistance of the pool bottom increases to about 800 day. The mean open water surface covers about 85%

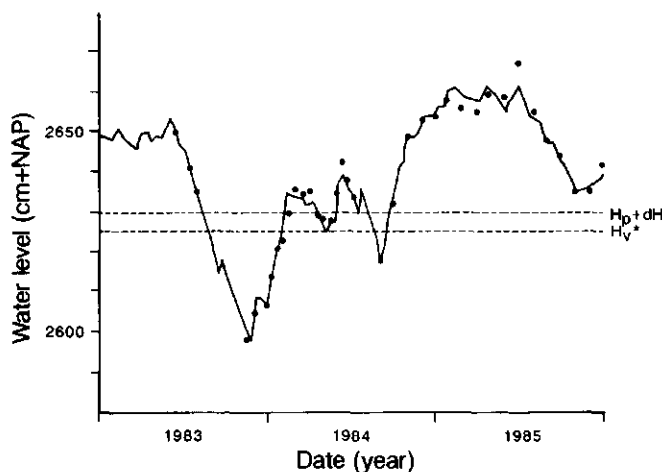
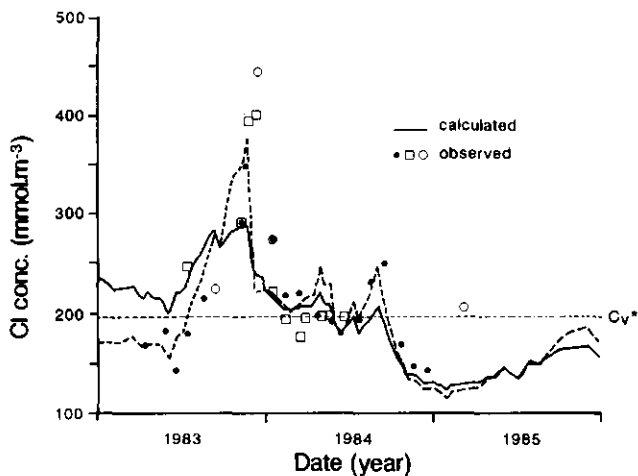


Figure 4.7. Hasselsven, simulated and observed poolwater levels and Cl concentrations. Solid line = model without dry deposition of Cl, broken line = model with dry deposition of $0.73 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1} \text{ Cl}$, \bullet = observed by RIN, \circ = observed by RIN (not used for calibration), \square = observed by LUW (not used for calibration), C_v^* = simulated mean Cl concentration, H_v^* = simulated mean pool water level, $H_p + dH$ = lowest level where hydraulic resistance of bottom is c_p .

Figure 4.8. Gerritsfles, simulated and observed poolwater levels and Cl concentrations. \bullet = observed by RIN, \circ = observed by RIN (not used for calibration), \square = observed by LUW (not used for calibration), C_v^* = simulated mean Cl concentration, H_v^* = simulated mean poolwater level, $H_p + dH$ = lowest level where hydraulic resistance of bottom is c_p .

Figure 4.9. Kliplo, simulated and observed poolwater levels and Cl concentrations. \bullet = observed by RIN, \circ = observed by RIN (not used for calibration), \square = observed by LUW (not used for calibration), C_v^* = simulated mean Cl concentration, H_v^* = simulated mean poolwater level, $H_p + dH$ = lowest level where hydraulic resistance of bottom is c_p .

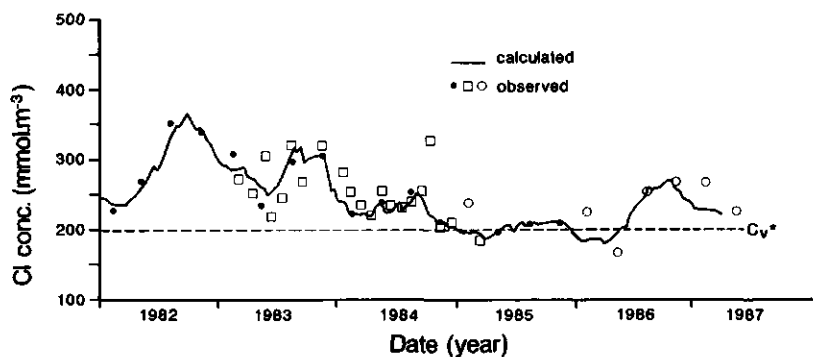


Fig. 4.8

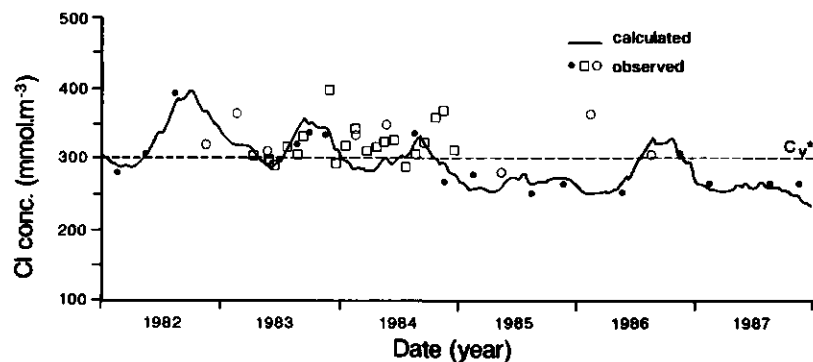
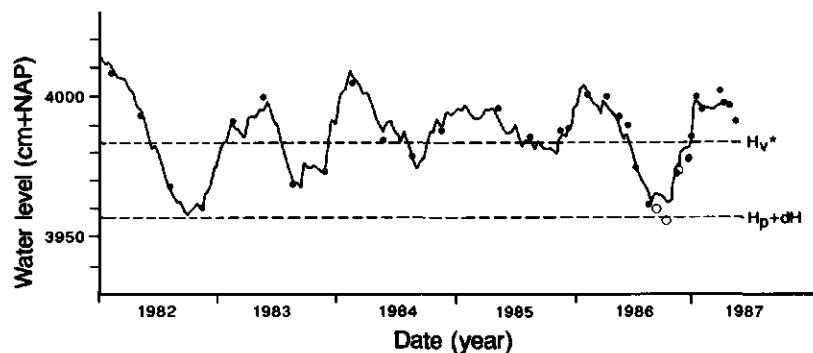
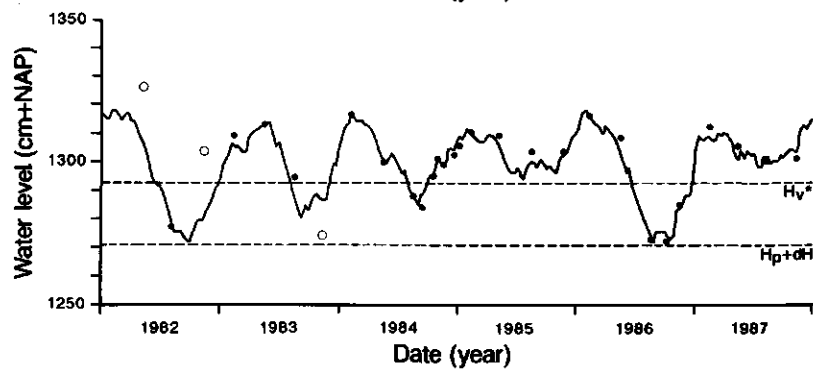


Fig. 4.9



of the catchment area at Hasselsven, Gerritsfles and Kliplo. At Tongbersven the open water area is nearly equal to the catchment area. According to the calibration results storage of water in the bank of the pools is unimportant. The calibration results do not indicate any important exchange of ground or surface water in the observation period between Tongbersven and Palingven, which are separated by a strip of land of c. 25 m wide.

Poolwater levels and Cl concentrations were calculated with mean (1950-1980) values for precipitation and evaporation (KNMI 1982) and mean values for the concentration of Cl in precipitation (1978-1985) at the KNMI/RIVM stations in Table 4.9. The calculated mean water level (H_v^*) and Cl concentration (C_v^*) were compared to the mean observed levels and concentrations in Table 4.10. The mean observed water level is 0.03 to 0.14 m above the mean simulated level (H_v^*). These

Table 4.9. Sources of information on precipitation, evaporation and groundwater level used to calculate mean values of state variables in VENSIM. Precipitation (P) and evaporation (E_o) are means for 1951-1980 (KNMI 1982). Chloride in precipitation (C_p) is mean for 1978-1985 (KNMI/RIVM 1978-1987). Values for H_g are mean values for local piezometers in 1983-1984 (Oostveen 1985).

Variable	HV	TV	GF	KL
P	Eindhoven	Boxtel	Kootwijk	Dwingeloo
E_o	Eindhoven	Eindhoven/Andel ^a	Deelen	Eelde
C_p	Eindhoven	Eindhoven	Deelen	Witteveen
H_g	HV22, HV4	TV32, TV4	—	—

^a mean value

Table 4.10. Mean observed and simulated values of water levels (m above NAP) and Cl concentrations ($\text{mmol} \cdot \text{m}^{-3}$). H_v^* and C_v^* values are based on mean values of precipitation and evaporation in 1951-1980 and mean concentration of Cl in precipitation in 1978-1985. Observed values are means over the periods January 1, 1983 to January 1, 1986 (HV and HV^*), January 1, 1982 to January 1, 1984 (TV), January 1, 1982 to April 1, 1987 (GF), and January 1, 1982 to April 1, 1988 (KL). In HV^* a dry Cl deposition of $0.730 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ is assumed in the terrestrial part of the catchment.

Variable	HV	HV^*	TV	GF	KL
Cl concentration					
observed	191	191	266	250	294
simulated (C_v^*)	195	303	239	198	303
water level					
observed	26.39	26.39	8.20	39.87	13.01
simulated (H_v^*)	26.25	26.25	8.14	39.84	12.93

Table 4.11. Deviation (S) of the annual precipitation excess ($P - 0.8 \cdot E_o$) from the mean values over 1951-1980 (KNMI 1982).

	Eindhoven			Elde		
	P	E_o	S	P	E_o	S
Mean	735	690		780	632	
1981	846	681	118	792	586	49
1982	724	738	-49	649	658	-152
1983	783	745	4	801	646	10
1984	891	647	190	770	551	55
1985	785	643	88	793	590	47
1986	846	698	105	779	632	-1
1987	940	636	248	800	602	44

differences seem reasonable. The high value at Hasselsven is caused by a positive deviation of the precipitation excess in 1984 and 1985 from the mean annual precipitation excess at the station Eindhoven (Table 4.11).

At Kliplo the mean observed Cl concentration in the period 1982-1987 corresponds well with the mean simulated concentration (C_v^*). In 1982 and 1983 the observed concentration is above C_v^* , in 1985 and 1987 it is below C_v^* . The Cl concentration at Tongbersven is 27 $\text{mmol} \cdot \text{m}^{-3}$ above C_v^* in the period 1983-1984. Particularly the high concentration of Cl, due to the high evaporation in the summer of 1983, causes the departure from C_v^* . The Cl concentration at Gerritsfles over the period 1982-1986 is 52 $\text{mmol} \cdot \text{m}^{-3}$ above C_v^* . This might indicate an underestimation of the evaporation coefficient f_1 .

The mean Cl concentration at Hasselsven agrees well with the observed concentration when dry deposition is assumed to be zero. The extremely high value for C_v^* when a dry deposition of $0.73 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ is assumed rules out the possibility of dry deposition of Cl. The observed differences can probably be attributed to the small precipitation excess in 1982 and also in 1985 and 1986. Probably the assumption of a perfectly mixed pool does not hold. The simultaneous rise of the concentration of Cl and the water level in December 1983 (Fig. 4.7) indicates a delayed inflow of Cl from the surrounding zone of the pool. Therefore the dry deposition term was set to zero in further computations.

4.2.4 The analytical model ANSIM for poolwater hydrology

Because no groundwater depths were recorded near the Goorven pool the importance of regional ground water inflow into the pool was estimated using the pool's Cl budget. As in the VENSIM model, Cl is considered to be geochemically and biologically conservative.

Let A_{\max} , A_{mean} and A_{\min} be the area and V_{\max} , V_{mean} and V_{\min} the volume of the pool at maximum, mean, and minimum water levels respectively. A_{\max} is used as an approximation for the surface area of the catchment basin.

The annual input of Cl (F_i) can be approximated by

$$F_i = P \cdot A_{\max} \cdot C_p \quad (4.9)$$

with:

P precipitation amount in mm

C_p Cl concentration in $\text{mmol} \cdot \text{kg}^{-1}$

If evaporation is assumed to be only important during summer (at minimum water level) and no net change in water storage takes place, the annual output of Cl (F_o) can be approximated by

$$F_o = (P \cdot A_{\max} - f_1 \cdot E_o \cdot A_{\min}) \cdot C_o \quad (4.10)$$

with:

E_o evaporation of an open water surface (Penman-evaporation)

f_1 empirical evaporation coefficient

C_o concentration of Cl in the overflowing water

If all Cl output is assumed to take place during the overflow (at maximum water level), C_o can be approximated by

$$C_o = C_e \cdot V_{\text{mean}} / V_{\max} \quad (4.11)$$

with:

C_e mean Cl concentration of the surface water.

In a steady state $F_i = F_o$ and combination of the expressions (4.9), (4.10) and (4.11) gives:

$$C_e = \frac{P \cdot A_{\max}}{P \cdot A_{\max} - f_1 \cdot E_o \cdot A_{\min}} \cdot \frac{V_{\max}}{V_{\text{mean}}} \cdot C_p \quad (4.12)$$

To test the model it was also applied to the other pools (Hasselsven, Tongbersven, Gerritsfles and Kliplo). The in- and output parameters, the water renewal time and the observed Cl concentrations (C_m) are presented in Table 4.12. For Tongbersven a modification is necessary, because of the uncertainty in the thickness of the sediment and the presence of a quacking bog. Oostveen (1985) estimated the volumes of the sediment and the quacking bog to be 1680 and 1779 m^3 , respectively. According to Vegt (1978) the water storage capacity of a peatmoss dominated quacking bog is c. 0.4. Thus

Table 4.12. Parameters of the ANSIM hydrological model. A_{\max} , A_{\min} = maximum and minimum pool surface area (m^2), V_{\max} , V_{mean} = maximum and mean pool volume (m^3), P = precipitation ($\text{mm} \cdot \text{y}^{-1}$), E_o = evaporation ($\text{mm} \cdot \text{y}^{-1}$), f_1 = evaporation coefficient, C_p = Cl concentration in precipitation ($\text{mmol} \cdot \text{m}^{-3}$), C_e = estimated mean Cl concentration in poolwater ($\text{mmol} \cdot \text{m}^{-3}$), C_m = observed mean Cl concentration in poolwater ($\text{mmol} \cdot \text{m}^{-3}$), τ = retention time (year).

Parameter	GV	TV	GF	KL
A_{\max}^a	25000	4599	69900	6300
A_{\min}^a	22200	4070	63800	5800
V_{\max}^a	17170	1816	52300	5900
V_{mean}^a	14500	1365	45800	5100
p^b	739	743	853	821
E_o	676	676	662	632
f_1^c	1.00	0.79	0.79	1.00
C_p^d	69	69	84	90
C_e	435	252	218	357
C_m^e	455	246	254	324
τ	0.78	0.40	0.77	0.98

^a V_{mean} from Microfiche. A_{\min} , A_{\max} and V_{\max} calculated from Figs 2.10 and 2.11, using mean lowest and mean highest water levels in the periods 1979-1985 (Goorven, Gerritsfles) and 1982-1985 (Kliplo). For Tongbersven the lowest and highest water levels over the period 1983-1984 were taken from Oostveen (1985).

^b Sources for P and E_o in TV, GF and KL as in Table 4.9. For GV P and E_o values at the stations Boxtel/Tilburg and Eindhoven/Andel respectively in 1951-1980 were used (KNMI 1982).

^c Values for f_1 in TV, GF and KL taken from Table 4.8.

^d mean over 1982-1984 in bulk precipitation

^e measured Cl concentration 1983-1985 (Table 6.12)

the volume of Tongbersven (Microfiche) has to be reduced by $(1680 + (1 - 0.4) \cdot 1779) \text{ m}^3$ before the model can be applied.

For the empirical evaporation coefficient of Goorven a value of 1.0, similar to that of Kliplo, was arbitrarily chosen, as small patches of birches and other trees were present in the catchment basin of both pools. The amount of overflowing water can be calculated as

$$P \cdot A_{\max} - f_1 \cdot E_o \cdot A_{\min} / A_{\max}$$

For Tongbersven, Gerritsfles and Kliplo the calculated amounts are 270, 411 and 239 $\text{mm} \cdot \text{y}^{-1}$, respectively. This is in the same order of magnitude as the mean leakage over the period 1951-1980 from Tables 5.7 to 5.9, where values of 199, 385 and 238 $\text{mm} \cdot \text{y}^{-1}$ are given.

The sensitivity of the model to changes of f_1 is shown in Table 4.13. It appears that

Table 4.13. Sensitivity analysis of estimated Cl concentration (C_e) in $\text{mmol} \cdot \text{m}^{-3}$ in the ANSIM hydrological model against empirical evaporation coefficient (f_1).

f_1	GV	TV	GF	KL
0.7	189	210	190	207
0.8	233	258	221	240
0.9	304	333	265	287
1.0	435	471	329	357
1.1	767	803	434	472

relatively small changes in the evaporation coefficient can have considerable effects on the calculated concentration of Cl.

There is reasonable correspondence between the calculated and observed Cl concentrations (Table 4.12). Thus Goorven is not necessarily groundwater fed, contrary to view held by Ter Hoeve (1949).

4.2.5 The model BUDGET for ion mass budgets of moorland pools

In an isolated, well-mixed pool with a perched water table, a simple mass budget for solutes (Houweling & Van Dam 1991) can be written as

$$Q_p \cdot C_p + Q_l \cdot C_l + Q_s \cdot C_s + M_r = 0 \quad (4.13)$$

with:

- Q_p water influx by precipitation in $\text{m}^3 \cdot \text{y}^{-1}$
- Q_l water efflux by seepage and overflow in $\text{m}^3 \cdot \text{y}^{-1}$
- Q_s water storage change in $\text{m}^3 \cdot \text{y}^{-1}$
- C_p solute concentration in precipitation in $\text{mol}_c \cdot \text{m}^{-3}$
- C_l solute concentration in seepage and overflow in $\text{mol}_c \cdot \text{m}^{-3}$
- C_s solute concentration in stored water in $\text{mol}_c \cdot \text{m}^{-3}$
- M_r amount of solutes lost to air or sediment in $\text{mol}_c \cdot \text{y}^{-1}$

Inflow and storage decrease are counted positive, outflow and storage increase negative. Solute concentrations in evaporation water are assumed to be zero.

Q_l and Q_s were simulated by VENSIM, Q_p and C_p were measured, while C_l and C_s were calculated from the measured solute concentrations (C_v) in surface water. Subsequently M_r was calculated from (4.13).

The water volume V_v at the start and the end of each calendar month and Q_p , Q_l and Q_s for each month were obtained from the VENSIM model. Also the mean modelled Cl concentration Cl^* for each month was obtained from VENSIM. The

concentration C_i at the 15th of each month was calculated by linear interpolation from C_v at the nearest dates before and after this date and assumed to be the mean concentration over the whole month. The concentration C_s at the last day of each month was calculated similarly from C_v .

All components of the budget were calculated for the whole pool and converted to $\text{kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ (solutes) or $\text{mm} \cdot \text{y}^{-1}$ (water), using the area of the watershed as the surface area. The relative loss R is defined as the amount of solutes lost to air and sediment as a fraction of the input:

$$R = \frac{M_r}{Q_p \cdot C_p} \quad (4.14)$$

For water R is equal to the evaporation as a fraction of the precipitation and can be calculated by VENSIM. The residence time or retention time τ for water and solutes is defined as the mass in the pool divided by the supply and can be calculated as

$$\tau = \frac{C_s \cdot V_{\text{mean}}}{C_p \cdot Q_p} \quad (4.15)$$

To obtain the water retention time C_s and C_p should be fixed at 1 in equation (4.15).

4.2.6 Calculation of diatom-inferred pH of moorland pools

For the pH-classification of the diatom taxa the system of Hustedt (1939) was followed:

R	abbreviation	group	pH-range
1	acb	acidobiontic	only in acid waters, generally below pH 5.5
2	acph	acidophilic	generally only in acid waters
3	cir	circumneutral	at pH c. 7
4	alph	alkaliphilous	generally only in alkaline waters
5	alb	alkalibiontic	only in alkaline waters
0	noph	unclassified	unknown

pH-Spectra were calculated from data listed by Renberg (1976) and Van Dam et al. (1981). Diatom-inferred pH values (pH-RENBE) were calculated with the formulas of Renberg & Hellberg (1982):

$$\text{pH-RENBE} = 6.40 - 0.85(^{10}\log B) \quad (4.16)$$

with:

$$B = (\text{cir} + 5\text{alph} + 40\text{acb})/(\text{cir} + 3.5\text{alph} + 108\text{alb}) \quad (4.17)$$

cir, alph, acb and alb: relative abundance of each pH-group in the count.

A second method to estimate the pH from the diatom assemblage composition is weighted averaging. Ter Braak & Van Dam (1989) investigated the diatom assemblages in 97 pristine soft-water lakes and pools in Western Europe, with pH values between 3.3 and 7.3. For the most abundant diatom taxa the pH optimum was calculated as the weighted average of the pH values of the water bodies in which the taxon was present as

$$\hat{u}_k = \frac{\sum_{i=1, n} y_{ik} \cdot x_i}{\sum_{i=1, n} y_{ik}} \quad (4.18)$$

with:

\hat{u}_k estimated pH optimum of taxon k
 y_{ik} relative abundance of taxon k in sample i
 x_i observed pH in sample i.

Conversely, the pH can be inferred from the diatom taxa according to

$$\hat{x} = \frac{\sum_{k=1, m} \hat{u}_k}{\sum_{k=1, m} y_{ik}} \quad (4.18)$$

with:

\hat{x} diatom-inferred pH of sample i.

5 Hydrology

5.1 Above ground hydrology

5.1.1 Precipitation amount

The annual amounts of precipitation at Tongbersven, Gerritsfles and Kliplo, and their coefficients of variation (CV = standard error as a percentage of mean) are given in Table 5.1. Table 5.2 gives these values relative to observations from the nearest meteorological stations, together with values found in 'chemical' samplers (funnel-type samplers used for monitoring chemical composition) at the same stations (KNMI/RIVM 1981, 1982, 1983, 1984).

Table 5.1. Annual bulk precipitation: mean (mm) and coefficients of variation (percentage of grand mean) of monthly values at the three research sites. — = no data.

Site	1981		1982		1983		1984	
	prec	CV	prec	CV	prec	CV	prec	CV
TV	826	44	687	61	777	58	843	60
GF	—	—	557	46	986	43	878	53
KL	—	—	659	45	945	44	854	57

Table 5.2. Annual bulk precipitation in 'chemical' samplers at meteorological stations (KNMI) and at the monitoring sites (RIN) as a percentage of the 'official' annual precipitation. Meteorological stations: for TV Eindhoven (at c. 16 km), for GF Deelen (at c. 12 km), for KL Witteveen (at c. 15 km). — = no data.

Site	1981		1982		1983		1984	
	KNMI	RIN	KNMI	RIN	KNMI	RIN	KNMI	RIN
TV	88	98	85	95	88	102	90	95
GF	—	—	87	91	91	119	89	95
KL	—	—	90	110	93	116	94	103

Table 5.3. Mean annual throughfall and stemflow amount (mm) for the five research sites and their coefficients of variation (%). HV represents throughfall under *Calluna* measured from April 1984 to April 1985, other data refer to *Pinus* and calendar years. — = no data.

Site	1981		1982		1983		1984	
	mean	CV	mean	CV	mean	CV	mean	CV
TVA thr	—	—	—	—	445	76	544	67
TVA stem	—	—	—	—	12	102	16	91
TVB thr	799	46	668	65	763	63	879	0
TVB stem	6	68	6	94	10	86	16	0
GF thr	—	—	435	77	699	44	641	60
GF stem	—	—	5	130	20	91	18	121
KL thr	—	—	455	48	748	44	704	59
KL stem	—	—	3	141	11	73	11	98
HV thr	—	—	—	—	—	—	446	—

Chemical rainfall samplers usually yield lower water volumes than official precipitation gauges, because of their larger wind error (Dekker 1979, KNMI/RIVM 1982). In the present study there was generally a good correspondence between the chemical samplers and the official gauges. Discrepancies may arise from differences in wind exposure, and from real differences due to spatial variation in precipitation (the study sites were 12 to 16 km from meteorological stations, see Table 5.2). Chemical samplers used in this study always yielded higher volumes than the chemical samplers at meteorological stations although they were constructed similarly. This may be due to a more sheltered position of our samplers.

5.1.2 Throughfall and stemflow amount

The annual amounts of throughfall and their CV's are given in Table 5.3. Throughfall under heath at Hasselsven was 58% of the precipitation, indicating that the relative canopy interception in the heathland plot (42%) was similar to that found under pine at Tongbersven, and much higher than values found in the Gerritsfles and Kliplo pine stands (25 and 21%, respectively). However, interception at Hasselsven has been overestimated because the heathplants only cover about 50% of the soil surface. Furthermore, a part of the precipitation may have reached the soil as stemflow which was not measured.

5.2 Soil water fluxes in the unsaturated zone

The fluxes of soil water in the unsaturated zone were estimated using model calculations (see 4.2.2). The main terms of the water balances of the four systems are shown in Table 5.4. The precipitation (infiltration + interception) varied from 735 mm·y⁻¹

Table 5.4. The simulated components of the water balance ($\text{mm} \cdot \text{y}^{-1}$) for the hydrological years: 1983 (I), 1984 (II), 1985 (III) and 1986 (IV). Hydrological years run from April 1 tot March 31 in the next year.

Term	HV				TV				GFF				GFB			
	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
precipitation	785	807	771	777	775	735	849	840	976	748	864	770	976	748	864	770
infiltration	614	649	659	611	473	507	490	504	701	521	528	434	976	748	864	770
interception	171	158	112	166	302	228	359	336	275	227	336	301	0	0	0	0
transpiration																
potential	—	219	227	234	—	299	295	373	—	286	298	341	0	0	0	0
actual	172	136	180	163	187	171	197	168	185	195	230	159	0	0	0	0
soil evaporation																
potential	—	153	163	154	—	77	87	83	—	152	158	157	—	531	569	610
actual	113	92	99	105	80	64	77	79	89	98	86	67	208	171	189	160
evapotranspiration																
actual	456	386	391	434	569	463	633	583	549	520	652	527	208	171	189	160
drainage	365	371	354	284	230	260	202	267	438	223	213	243	882	552	642	639
storage change	-35	50	26	60	-24	13	15	-10	-11	5	0	1	-14	16	9	-15

(Tongbersven) to $976 \text{ mm} \cdot \text{y}^{-1}$ (Gerritsfles), so that calculated drainage fluxes cannot be compared directly. The estimated drainage fluxes at the unvegetated site at Gerritsfles are by far the largest due to the absence of transpiration. Surprisingly, the actual transpiration for both pine stands was only slightly higher than for the open heath cover, while potential transpiration was nearly 50% higher for the pine forests. This suggests that both pine stands suffer from water stress in the growing season.

The accuracy of the simulated soil water fluxes is determined largely by the uncertainty in the potential evapotranspiration. The error in the soil water fluxes calculated by SWATRE for oak-birch sites at Hackfort (The Netherlands) was estimated at only $14 \text{ mm} \cdot \text{y}^{-1}$ (Van Grinsven et al. 1987). Relative errors increased from 3% at 10 cm to 8% at 90 cm depth. However, relative errors for the pine sites (Gerritsfles and Tongbersven) can be larger because interception for coniferous forest is generally higher than for deciduous forest and the corresponding soil water fluxes are smaller. For Hasselsven and for the unvegetated Gerritsfles site relative errors are probably lower than for the forested sites, because at these sites evapotranspiration is lowest.

5.3 Groundwater and moorland pool hydrology

5.3.1 Interflow at Tongbersven and Hasselsven

The moorland pools at Hasselsven and Tongbersven are surrounded by Spodosols, sloping towards the pools. Therefore, any water stagnating on the spodic horizon may result in interflow into the pools. Interflow may occur when infiltration rates are high, e.g. during rainstorms or snowmelt. However, such events are rare and may not affect

the annual water balance of the pools. Nevertheless, its chemical impact may be significant because of the large differences in chemical composition of the solution from the surface soil layers, compared to precipitation and groundwater (see 6.2 and 6.3).

The hydraulic conductivities of the Bhs horizon, measured by the two plate steady state method at 10 mbar suction, are 51 and 36 $\text{cm} \cdot \text{d}^{-1}$ for Hasselsven and Tongbersven, respectively. These conductivities are far too high to permit interflow at

Table 5.5. Interflow measurement: pressure heads (cm water layer) on October 19 and November 7, 1984 and January 23, 1985 at Tongbersven and Hasselsven. For location of the plots, see text and Figs 3.1 and 3.2. x = above, y = in and z = below the Bhs horizon.

Hasselsven					
Date	Depth	Interflow plots			
		a	b	c	d
841019	x	-70	-30	-21	-16
	y	-34	-54	-19	-18
	z	-53	-52	-17	-15
841107	x	-63	-57	-19	-13
	y	-58	-34	-14	-12
	z	-59	-54	-9	-7
850123	x	-68	-51	-6	-6
	y	-58	-38	+7 ^c	+5 ^c
	z	-39	-3 ^d	-	+13 ^c

Date	Depth (cm)	Permanent plots			
		a	b	c	d
841019	10	-116	-119	-113	-100
	20	+2 ^d	-118	-13 ^a	-112
	30	-50	-120	-114	-58
	50	-106	-110	-107	-57
	100	+31 ^a	-106	-8 ^a	-55
841107	10	-103	-123	-101	-98
	20	-17 ^d	-115	-14 ^d	-101
	30	-60	-108	-103	-58
	50	-95	-95	-87	-86
	100	-51	-45	-40	-25
850123	10	-64	-43	-58	-57
	20	-9 ^d	-63	-17 ^d	-65
	30	-34	-74	-81	-38
	50	-84	-100	-104	-100
	100	-72	-52	-66	-72

ambient Dutch rainfall intensities (Dekker et al. 1984). However, the development of water repellency of the Bhs horizon after drying in late summer and early fall or the presence of frozen conditions right after the start of snowmelt could significantly decrease the permeability, and thus promote lateral water transport.

At Tongbersven subsurface runoff seems most likely because the slopes are short and steep (c. 40%) and the hard, compact B horizon continues close to the border of

Table 5.5. Continued.

Tongbersven					
Date	Depth	Interflow plots			
		a	b	c	d
841019	x	-58	-93	-56	-
	y	-101	-94	+6 ^a	-
	z	-85	-30	-	-
841107	x	-14	-60	-26	-57
	y	-	-67	-31	-53
	z	-53	-	-	-58
850123	x	-5	-48	-78	-56
	y	-49	-37	-58	-32 ^d
	z	-18 ^d	+8 ^b	-8 ^d	-76
Date	Depth (cm)	Permanent plots			
		1	2	3	4
841019	10	-91	-87	-65	-83
	20	-89	-101	-78	-92
	30	-81	-96	-81	-21 ^a
	50	-72	-79	-87	-77
	100	-60	-81	-71	-58
841107	10	-95	-98	-93	-104
	20	-84	-104	-94	-104
	30	-88	-98	-90	-113
	50	-80	-84	-90	-84
	100	-83	-86	-90	-67
850123	10	-38	-102	-39	-50
	20	-84	-44 ^d	-45 ^d	-43 ^d
	30	-95	-104	-69 ^d	-16 ^d
	50	-97	-74	-93	-75
	100	-87	-55	-62	-26

Remarks: ^a = air in tubing

^b = leak in tubing

^c = cups below groundwater level

^d = probable water stagnation

the pool. At Hasselsven the situation is opposite as the slopes are gentle (c. 2%) and the B horizon is less compact, especially near the pool.

A short term field study was designed to investigate the occurrence of water saturation above or in the Bhs horizon during periods of high water input. At both Hasselsven and Tongbersven sets of three ceramic tensiometer cups (Soil Moisture Equipment Corporation type 655X1-B1M3) were installed at four points along a transect on the slope towards the pools. Two points were located at some distance from the pools (a and b), and two near the shore (c and d; Figs 3.1 and 3.2). Of every set of three tensiometers one was installed in, one just above and one just below the Bhs horizon. Tensiometer cups were installed horizontally from a small soil pit in such a way that all tubing was at the same level as the cup. In this way the presence of air inside the cup or tubing would not affect the pressure head measurements. Due to the hardness of the Bhs horizon at Tongbersven installation of the tensiometer cups was difficult, which for some cups resulted in poor contact with the soil.

Pressure head measurements were carried out on November, 19 and November, 11 in 1984 and at January, 23 in 1985. Results are presented in Table 5.5. In addition to the pressure heads at a, b, c and d, the tensiometers at 10, 20, 30, 50 and 100 cm depth at the permanent soil solution monitoring plots (at the upper side of the slope) were also monitored.

The conditions for water saturation above the Bhs horizon were most favourable on January 23, 1985, because of snowmelt on the previous day. However, there was no evidence for saturation, although the topsoils at both sites were clearly wetter than at the other measuring dates. At Tongbersven less negative pressure heads in and below the Bhs horizon (20-39 cm depth) than in the adjoining soil layers indicate some water stagnation.

At Hasselsven there was even less evidence for water stagnation. On January 23, 1985 tensiometer cups in permanent plots 1 and 3 (see Fig. 3.1) at 20 cm depth also gave less negative pressure heads than the cups in the adjoining soil layers, but this was also the case on the other measuring dates. Consistently less negative pressure head readings at all three measuring dates could indicate either leakage of the tensiometer system or bad contact between cup and soil. Nevertheless our data do not present strong evidence for water stagnation in the surface soil near the Hasselsven pool.

In conclusion, field measurements suggest some water stagnation, especially at Tongbersven, but no waterlogging. Saturation near the B horizon may be short-lived, and therefore hard to detect by separate pressure head measurements. Continuous monitoring of pressure head is probably more appropriate. At Hasselsven the Bhs horizon near the pool is too permeable to allow interflow of perched water.

5.3.2 Water and chloride budgets of moorland pools, using VENSIM

Pool and groundwater levels of Tongbersven are plotted in Fig. 5.1. In autumn the water level in the Tongbersven pool is more than 1 m above the groundwater level near the pool. However, in winter and spring the difference between groundwater level and

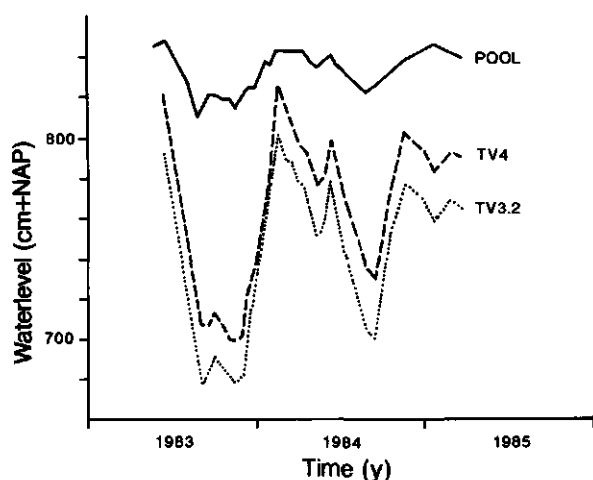


Figure 5.1 Tongbersven, observed water levels in pool and piezometers TV3.2 and TV4 (location see Fig. 3.2).

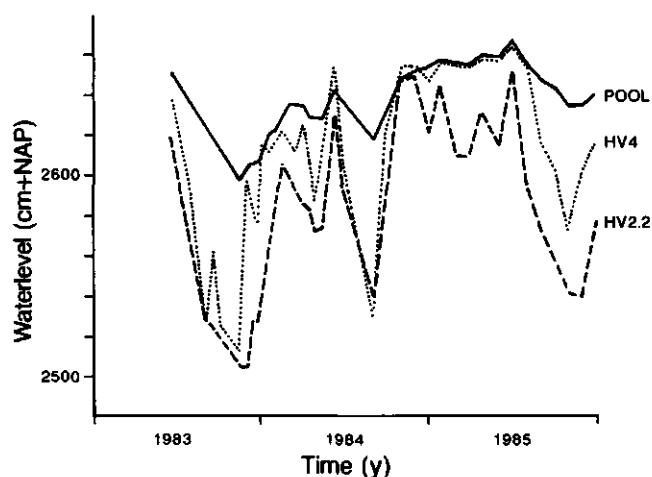


Figure 5.2 Hasselsven, observed water levels in pool and piezometers HV2.2 and HV4 (location see Fig. 3.1).

poolwater level decreases to values close to zero. Some inflow of groundwater into the pool may occur in this period, but this is probably only a minor contribution to the pool's water budget.

The poolwater and groundwater levels at Hasselsven are plotted in Fig. 5.2. As a consequence of the smaller storage coefficient of the soil, the groundwater level close to the pool (piezometer HV4) can rise above the poolwater level for a short period if precipitation intensity is high. In that case groundwater may enter the pool. At some distance of the pool (piezometer HV2.2) however, the groundwater level is always

below poolwater level. Therefore, groundwater inflow is probably not an important component in the water budget of the pool.

The calculated mean water levels and Cl concentrations for the observation periods (Table 4.11), as well as the mean fluxes of water over the period 1951-1980 and Cl over the period 1978-1985 for the pools Hasselsven, Tongbersven, Gerritsfles, and Kliplo are presented in the Tables 5.6-5.9. As was already known at the start of the investigations the groundwater levels at Gerritsfles and Kliplo are far below the pool bottoms and do not influence the pool water systems. The initial assumption that the pools at Tongbersven and Hasselsven were fed by groundwater from the surroundings, at least during a part of the year was invalidated by the observed groundwater levels.

The retention time of the poolwater (equation 4.15) was lowest for Tongbersven and highest for Kliplo (Table 4.8). The mean annual water budgets for the four pools can be compared for the period 1983-1984 (Table 5.10). For this comparison the evaporation, total leakage (the sum of seepage and overflow), and storage are expressed as

Table 5.6. Water and Cl budget of the Hasselsven pool (inflow and storage decrease are positive). Prec. = measured precipitation (from 1983 to 1986 at the monitoring sites, from 1951 to 1980 at the nearest meteorological stations, see Table 4.7), evap. = simulated evaporation, overfl. = simulated overflow at pool border, seep. = simulated seepage through pool bottom, dS = simulated storage change. Water in $\text{mm} \cdot \text{y}^{-1}$, Cl in $\text{kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$.

Water					
Period	prec.	evap.	overfl.	seep.	dS
830101-840101	774	-535	-12	-482	256
840101-850101	982	-424	-5	-228	-326
850101-860101	761	-507	-24	-357	126
mean	839	-489	-14	-356	19
mean as a fraction of prec.	1.00	-0.58	-0.02	-0.42	0.02
mean (1951-1980)	754	-503	-2	-249	0
mean (1951-1980) as a fraction on prec.	1.00	-0.67	0.00	-0.33	0.00
Chloride					
Period	prec.		overfl.	seep.	dS
830101-840101	0.56		-0.03	-1.19	0.66
840101-850101	0.58		-0.01	-0.44	-0.13
850101-860101	0.51		-0.03	-0.55	0.07
mean	0.55		-0.02	-0.73	0.20
mean (fraction of prec.)	1.00		-0.04	-1.32	0.36
mean (1978-1985)	0.50		0.00	-0.50	0
mean (1978-1985) as a fraction of prec.	1.00		-0.01	-0.99	0.00

Table 5.7. Water and Cl budget of the Tongbersven pool. For explanation see Table 5.6.

Water					
Period	prec.	evap.	overfl.	seep.	dS
830101-840101	777	-545	-89	-154	10
840101-850101	843	-485	-119	-122	-117
mean	810	-515	-104	-138	-53
mean (fraction of prec.)	1.00	-0.64	-0.13	-0.17	-0.07
mean (1951-1980)	738	-539	-58	-141	0
mean (1951-1980) as a fraction of prec.	1.00	-0.73	-0.08	-0.19	0.00
Chloride					
Period	prec.		overfl.	seep.	dS
830101-840101	0.64		-0.22	-0.50	0.08
840101-850101	0.54		-0.27	-0.30	0.03
mean	0.59		-0.25	-0.39	0.06
mean (fraction of prec.)	1.00		-0.42	-0.68	0.10
mean (1978-1985)	0.48		-0.13	-0.35	0
mean (1978-1985) as a fraction of prec.	1.00		-0.27	-0.72	0.00

fractions of the precipitation. Furthermore, the overflow is expressed as a fraction of the total leakage. The differences in the water budgets are mainly due to differences in the precipitation and evaporation. A high A_v/A_s ratio (Table 4.8) coincides with a high evaporation/precipitation ratio, because the evaporation from the terrestrial part of the catchment never exceeds precipitation. The mean evaporation/precipitation ratio in the pools with a high groundwater table (Hasselsven, Tongbersven) is similar to that in the pools with a deep groundwater table (Gerritsfles, Kliplo). The magnitude of the overflow as a fraction of the total leakage is 0.35-0.5. For HV the overflow is negligible.

Due to a higher precipitation amount and Cl concentration in precipitation, the pools Gerritsfles and Kliplo have a higher Cl input than the other two pools. In the long run Cl input by precipitation equals the Cl outflow by leakage. A high evaporation/precipitation ratio is associated with a low leakage/precipitation ratio and results in a high Cl concentration in the poolwater. Chloride leaks from Tongbersven in water with a high concentration, whereas Gerritsfles has a higher leakage with a lower concentration of Cl.

The fluctuations in the components of the water and Cl balances are due to fluctuations in precipitation amount and evaporation, and in the Cl concentration in precipitation. At Kliplo, Gerritsfles and Tongbersven precipitation excess exceeds leakage,

Table 5.8: Water and Cl budget of the Gerritsfles pool. For explanation see Table 5.6.

Water					
Period	prec.	evap.	overfl.	seep.	dS
820101-830101	564	-505	-196	-165	302
830101-840101	985	-536	-135	-167	-147
840101-850101	868	-457	-234	-182	5
850101-860101	811	-458	-169	-176	-7
860101-870101	778	-461	-155	-164	2
mean	801	-483	-178	-171	31
mean (fraction of prec.)	1.00	-0.60	-0.22	-0.21	0.04
mean (1951-1980)	888	-503	-155	-230	0
mean (1951-1980) as a fraction of prec.	1.00	-0.57	-0.17	-0.26	0.00
Chloride					
Period	prec.		overfl.	seep.	dS
820101-830101	0.55		-0.49	-0.47	0.41
830101-840101	0.86		-0.37	-0.47	-0.01
840101-850101	0.61		-0.53	-0.42	0.34
850101-860101	0.73		-0.34	-0.36	-0.03
860101-870101	0.90		-0.34	-0.39	-0.17
mean	0.73		-0.42	-0.42	0.11
mean (fraction of prec.)	1.00		-0.57	-0.58	0.15
mean (1978-1985)	0.75		-0.30	-0.45	0
mean (1978-1985) as a fraction of prec.	1.00		-0.40	-0.60	0.00

resulting in storage increase, at precipitation amounts above 375, 325 and 240 $\text{mm} \cdot \text{y}^{-1}$ respectively. On the average, precipitation excess and leakage more or less balance each other except in 1987 (without considering Hasselsven). In 1984 the Cl output by leakage exceeds the input by precipitation, due to the low concentration of Cl in precipitation. In 1983 the output of Cl exceeds the input at Gerritsfles because overflow is high due to a high precipitation excess. In 1986 the input of Cl exceeds the output at Gerritsfles due to the rather high concentration of Cl in precipitation ($130 \text{ mmol} \cdot \text{m}^{-3}$).

In 1983, 1985, 1986, and 1987 (with the exception of Gerritsfles in 1983 and 1986) the input of Cl by precipitation is balanced by the output by leakage. At Hasselsven there are larger discrepancies that cannot be accounted for (see 4.2.3.1.).

Table 5.9. Water and Cl budget of the Kliplo pool. For explanation see Table 5.6.

Water					
Period	prec.	evap.	overfl.	seep.	dS
820101-830101	685	-577	-98	-178	168
830101-840101	948	-581	-101	-186	-81
840101-850101	855	-497	-121	-192	-44
850101-860101	888	-551	-121	-194	-22
860101-870101	762	-549	-92	-178	56
870101-880101	893	-458	-135	-198	-102
mean	839	-535	-111	-188	-4
mean (fraction of prec.)	1.00	-0.64	-0.13	-0.22	-0.01
mean (1951-1980)	822	-583	-64	-174	0
mean (1951-1980) as a fraction of prec.	1.00	-0.71	-0.08	-0.21	0.00
Chloride					
Period	prec.		overfl.	seep.	dS
820101-830101	0.64		-0.29	-0.59	0.25
830101-840101	0.86		-0.31	-0.60	0.05
840101-850101	0.72		-0.36	-0.57	0.21
850101-860101	0.78		-0.32	-0.52	0.06
860101-870101	0.70		-0.24	-0.50	0.04
870101-880101	0.65		-0.35	-0.51	0.20
mean	0.72		-0.31	-0.55	0.14
mean (fraction of prec.)	1.00		-0.43	-0.76	0.19
mean (1978-1985)	0.70		-0.18	-0.52	0
mean (1978-1985) as a fraction of prec.	1.00		-0.26	-0.74	0.00

Table 5.10. Comparison of mean annual water budgets (1983-1984) of four pools. Total leakage is the sum of overflow and seepage. All units are in $\text{mm} \cdot \text{y}^{-1}$.

Pool	HV	TV	GF	KL
Precipitation	878	810	926	901
Penman evaporation	695	662	704	599
evaporation from system	480	515	496	539
evaporation/precipitation	0.55	0.64	0.54	0.60
total leakage/precipitation	0.41	0.30	0.39	0.33
storage change/precipitation	0.04	0.07	0.08	0.07
overflow/total leakage	-	0.50	0.50	0.36

5.4 Long-term fluctuation of poolwater level

Long-term fluctuations in pool water level will be evaluated in this section; levels measured during the current monitoring are presented on Microfiche.

5.4.1 *Hasselsven*

The mean water level of the Hasselsven pool during the monitoring period was 26.27 m above NAP, the minimum level 25.98 m above NAP (November 11, 1983), and the maximum level 26.50 m above NAP (June 15, 1983). On the manuscript chromotopographical map scale 1:25 000 of 1835 (Topographical Survey, Emmen) the surface area of the pool is considerably larger than in recent years. On the topographical maps 1:25 000 of 1898 and 1927 the area of the pool is about three times larger than presently. Apparently water tables were higher in the past. On the maps of 1950 and 1961 the surface area of the pool is about one fourth of the surface area on the map of 1970. The pool dried up in the summers of 1973 and 1976.

5.4.2 *Goorven*

Observed pool water levels are presented in Fig. 5.3. The quarterly mean level over the period November 1979 - February 1985 was 8.34 m above NAP. The annual amplitude (only 4 observations each year) is usually less than 0.3 m. Large fluctuations, especially during periods with a high net precipitation, are diminished by the presence of an outlet to another pool, which is effective at water levels above 8.44 m above NAP (= 0.1 m above mean water level).

No exact records exist about water levels in the past. However, during the dry summers of 1911 and 1921 large parts of the pools near Oisterwijk dried up (De Bruin 1979, Schuiling & Thijse 1928). Desiccated pool bottoms were exposed to wind and partly blew away. In the summer of 1922 the water level was not yet back to normal. On a photo of the Goorven pool in Zoetmulder (1922), which was probably taken in the summer of 1921, the water level is c. 0.5 m lower than the present mean water level.

From the hypsographic curve (Fig. 2.12) it appears that in extremely dry years such as 1921, 1959 and 1976, when the water level can drop about 0.7 m below the mean water level, the surface area of the pool can be reduced to about 25% of its area at mean water level. In the eastern, shallowest basins, this proportion will be even lower. The volume will then be reduced to only c. 10% of the normal volume (Fig. 2.13).

5.4.3 *Tongbersven*

The mean level was 8.17 m above NAP, the minimum level 8.01 m above NAP (September 2, 1983), the maximum level 8.31 above NAP (June 14, 1983). No historic water level data are available for this pool.

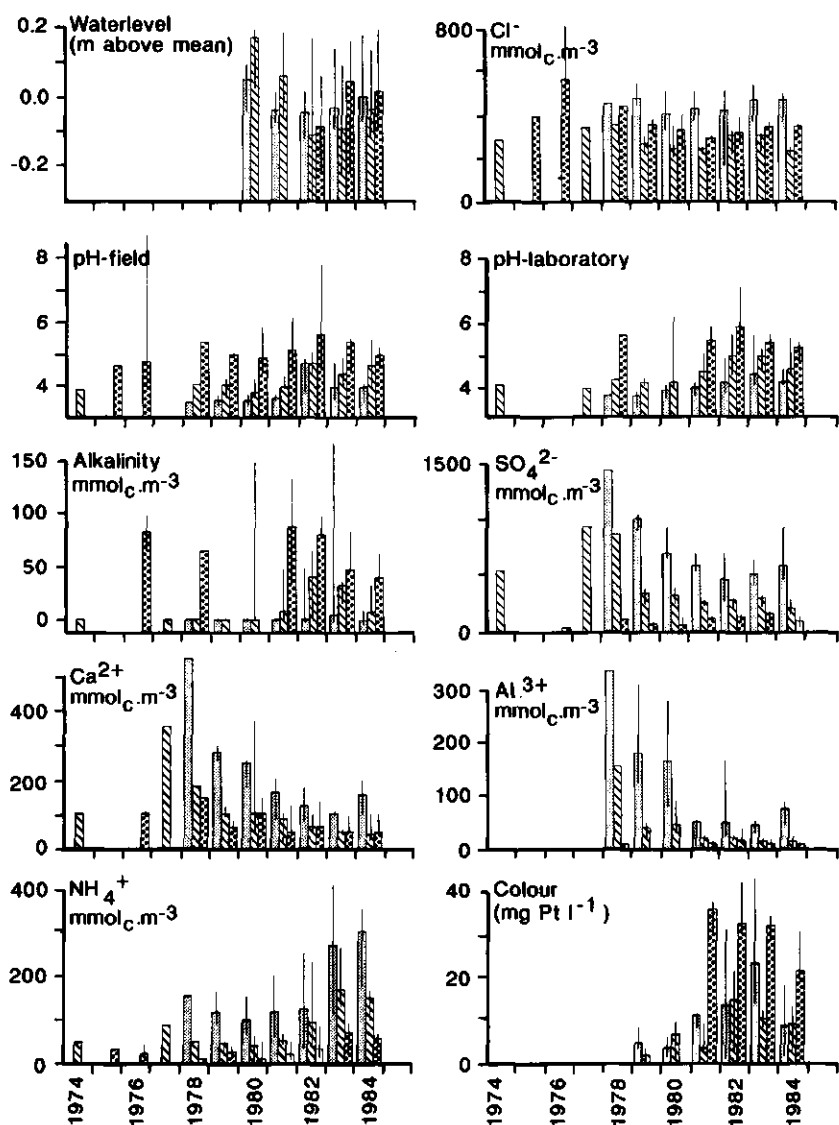


Figure 5.3. Annual mean values (bars) and amplitude (lines) of selected physical and chemical parameters in Goorven (finely dotted), Gerritsfles (hatched) and Kliplo (coarsely dotted) from 1974 to 1984.

5.4.4 Gerritsfles

Observed poolwater levels are presented in Fig. 5.3. The quarterly mean level over the period November 1979 - February 1985 was 39.91 m above NAP. The annual amplitude in 1980 and 1981 was c. 0.15 m. In the dryer years 1982 and 1983 the amplitude was larger (nearly 0.50 m).

Schimmel & Ter Hoeve (1952), who give a thorough description of the hydrology of the pool, recorded the water level at four occasions between August 1947 and February 1951. In August 1947, during a rather dry summer (De Bruin 1979, Schuurmans 1977) the water level was 39.50 m above NAP. This is 0.30 m lower than the mean August level from 1980 to 1984 and 0.11 m lower than the lowest level which was recorded during our observation period (November 1982). According to Fig. 2.12 c. 20% of the pool bottom area was exposed to the atmosphere at that moment, while the pool had only 45% of its mean volume (Fig. 2.13). On February 7, 1951 Schimmel & Ter Hoeve recorded 40.35 m above NAP, which is 0.33 m higher than the average February level in our observation period and 0.25 m higher than the maximum level we recorded (February 1980). The mean of the two extreme values from Schimmel & Ter Hoeve is 39.93 m above NAP and close to the mean level of 39.91 m above NAP over the period November 1979 - February 1985. On September 1, 1949 the level was 39.71 above NAP which is not far from the mean August level between 1979 and 1984. Thus since the late 1940's no large changes in the water level of the Gerritsfles pool have been recorded.

5.4.5 *Kliplo*

Observed poolwater levels are presented in Fig. 5.3. The mean level over the observation period was 12.98 m above NAP. The mean annual amplitude was 0.34 m.

In the northwestern corner of the pool, 10 m northeast of the small island, the pool has a protuberance, which is the remnant of an old ditch. The threshold of this ditch is at ca. 13.33 m above NAP, which is 0.19 m higher than the maximum level that was recorded. It cannot be excluded that this ditch occasionally acts as an overflow.

According to Beijerinck (1926) *Kliplo* always contains water. Also in recent dry years a large part of the bottom was still covered with water. In the extremely dry year 1959, when the water attained its lowest level, the pool was still used for bathing (P. Kerssies, pers. comm.). On August 10, 1976, H. van der Putten observed that the pool was still deeper than 0.5 m (B. Hoentjer, pers. comm., see also Van Gijsen & Claassen 1978). As the maximum depth at mean water level is 1.14 m (Microfiche) the water level during these episodes was ca. 0.5 m below the mean water level. According to Fig. 2.12 the surface area at that water level is still 80% while the volume is only 40% of the volume at mean water level (Fig. 2.13). As the mean Cl concentration is $324 \text{ mmol} \cdot \text{m}^{-3}$ the expected concentration at this volume is $810 \text{ mmol} \cdot \text{m}^{-3}$. The concentrations on 23 August 1976 and 6 October 1976 were 621 and 818 $\text{mmol} \cdot \text{m}^{-3}$ respectively (Microfiche). This corroborates the observation of the water level in August 1976.

6 Solute concentrations

6.1 Meteoric water

In Table 6.1 the volume-weighted mean concentrations in bulk deposition, throughfall and stemflow over the complete measuring periods indicated in Table 3.4 are given. The coefficients of variation can be found in Table 6.2. At Tongbersven the concentration of H in throughfall is lower than the concentration in bulk deposition. For the other ions and also for H at all other sites, concentrations in both throughfall and stemflow are higher than in bulk deposition. Mean H concentration ratios in throughfall relative to bulk deposition are 0.15 at Tongbersven and 1.25 at the other sites. Concentration ratios are c. 10-20 for K and c. 2-4 for the other ions at all sites. For stemflow concentration ratios are c. 20-40 for K and c. 10-20 for the other ions including H. A further discussion of these differences and the resulting differences in flux is given in 7.1. The coefficients of variation reflect temporal variability, and are generally low (< 100) for bulk deposition, moderate (c. 100) for throughfall and high (> 100) for stemflow.

Volume and concentrations of bulk deposition were checked against data from meteorological stations (KNMI/RIVM 1981-1985) (Table 6.3, see also Table 5.2). Our

Table 6.1. pH and volume-weighted mean ionic equivalent concentrations in bulk deposition, throughfall and stemflow ($\text{mmol}_e \cdot \text{m}^{-3}$), over the measuring periods indicated in Table 3.4. pH values are arithmetic means. n = number of observations.

		pH	H	K	Na	Ca	Mg	Zn	NH ₄	Cl	NO ₃	SO ₄	F	n
TV	bulk	4.7	40.2	6.6	62	32	16	1.0	136	75	56	147	3.1	50
TVA	thr	4.8	5.9	156.1	174	85	57	3.1	831	251	110	743	10.9	33
TVA	stem	3.7	485.7	319.1	674	339	218	5.4	2760	891	356	3090	33.7	24
TVB	thr	4.7	31.0	49.7	167	63	45	2.7	480	209	117	472	9.8	53
TVB	stem	3.5	483.7	120.1	549	186	123	4.1	2923	816	415	2921	26.4	34
GF	bulk	4.6	36.4	4.9	73	32	18	0.8	126	88	64	133	2.0	36
GF	thr	4.6	45.7	81.7	284	86	78	1.6	658	370	179	615	12.0	63
GF	stem	3.4	650.4	146.4	708	179	150	3.2	2101	968	497	2230	21.1	35
KL	bulk	4.6	35.5	4.4	74	25	17	0.6	112	89	59	118	1.4	36
KL	thr	4.6	43.3	66.9	297	66	76	1.0	583	366	151	545	6.7	144
KL	stem	3.8	310.4	137.9	721	123	119	1.5	1834	900	339	1763	15.7	67

Table 6.2. Coefficients of variation (percentage of grand mean) of concentrations in bulk deposition, throughfall and stemflow. For numbers of observations, see Table 6.1.

		pH	H	K	Na	Ca	Mg	Zn	NH ₄	Cl	NO ₃	SO ₄	F
TV	bulk	35	62	109	79	89	65	58	69	78	52	48	86
TVA	thr	12	185	74	114	113	97	99	87	111	112	108	83
TVB	stem	13	61	463	379	421	406	314	434	393	467	404	423
TVB	thr	10	88	78	57	71	55	67	43	54	83	44	47
TVB	stem	10	52	440	368	461	416	379	34	329	432	373	335
GF	bulk	22	56	62	91	111	69	61	67	87	53	58	62
GF	thr	13	79	71	61	64	48	57	47	61	89	47	49
GF	stem	18	66	284	235	385	350	329	55	266	411	63	345
KL	bulk	16	53	56	70	83	64	56	67	70	54	53	82
KL	thr	8	69	57	93	111	88	50	62	64	73	71	48
KL	stem	13	127	307	280	281	273	303	324	262	282	286	295

Table 6.3. Precipitation flux ($\text{mm} \cdot \text{y}^{-1}$) and volume-weighted mean ionic equivalent deposition ($\text{kmol}_e \cdot \text{ha}^{-1}$) over 1982 and 1983 for the bulk samplers. Data are absolute values and percentages of the values from the nearest meteorological stations (see Table 5.2).

	Site	Water	H	K	Na	Ca	Mg	Zn	NH ₄	Cl	NO ₃	SO ₄	F
1982	TV	686.6	0.46	0.052	0.45	0.294	0.116	0.010	1.24	0.59	0.53	1.36	0.024
	TV%	111	121	141	101	113	96	61	109	105	109	103	91
	GF	557.0	0.42	0.047	0.77	0.302	0.198	0.010	1.21	0.98	0.61	1.34	0.020
	GF%	95	99	103	102	116	109	79	92	103	101	94	66
	KL	659.2	0.47	0.038	0.73	0.238	0.162	0.006	1.07	0.93	0.61	1.16	0.011
	KL%	108	142	71	97	99	102	75	90	99	101	94	73
1983	TV	777.5	0.29	0.049	0.68	0.278	0.158	0.008	1.01	0.82	0.43	1.20	0.020
	TV%	110	161	153	129	116	131	71	113	139	111	117	92
	GF	985.8	0.30	0.036	0.73	0.182	0.172	0.004	0.89	0.87	0.46	0.98	0.014
	GF%	117	151	105	106	76	107	77	88	105	112	96	62
	KL	945.0	0.28	0.036	0.76	0.172	0.172	0.004	0.79	0.91	0.44	0.88	0.011
	KL%	114	133	97	113	96	111	94	114	106	101	89	92

values generally correspond well with those reported by KNMI/RIVM. Only for some solutes systematic differences occur, e.g. for Zn our values are c. 30% lower than those reported by KNMI/RIVM, while our H concentrations are c. 40% higher. At TVB values for K are c. 50% higher than the KNMI/RIVM values. The observed differences are difficult to explain. This is particularly the case after 1981, when our sampling methods and those used by the KNMI/RIVM network were almost identical, the only difference being that our samples were pooled weekly, whereas the KNMI/RIVM network used monthly or (after 1982) fortnightly samples. However, in light-protected

samplers (as we used) Ridder et al. (1984) did not find significant chemical differences between pooled weekly samples and monthly samples that were left in the field for the complete period.

6.2 Soil solutions

Arithmetic mean composition of the soil solutions at all four research sites from November 1982 up to May 1987 are given in Table 6.4. The variation in solute concentrations with time and depth is also illustrated by 3-D plots in Appendix 3. The variability in concentration during the monitoring period is given in Table 6.5. The difference between solute concentrations in the replicate lysimeters is small (cf. Mulder 1988), indicating that spatial variation in soil solution composition over a distance of c. 1 m is small (Microfiche). Therefore the coefficients of variation given in Table 6.5 primarily reflect temporal variation. The data on soil solution composition and its variation with time and depth will be discussed below for each of the solutes. The processes that determine the soil solution composition will be dealt with in chapter 8.

On a molar basis dissolved C, of which 90 to 95% is in organic form (Microfiche),

Table 6.4. pH, EC ($\mu\text{S}\cdot\text{cm}^{-1}$), DOC and SiO_2 ($\text{mmol}\cdot\text{m}^{-3}$) and ionic equivalent concentrations ($\text{mmol}_c\cdot\text{m}^{-3}$) in soil solutions from various depths at the four soil solution monitoring plots. Values are arithmetic means of data collected with two lysimeters at each depth from November 1982 up to 1987. Organic anion concentrations (A^-) are estimated from charge balance discrepancies. Numbers of samples are 80 to 100, except for HV 7, HV 22, TV 12, TV 57, GFF 100, GFB 40 and GFB 100 (60 to 80 samples), HV 70 (50 samples), and HV 110, TV 100 and GFF 10 (10 to 30 samples).

Site	Depth	pH	EC	DOC	SiO_2	K	Na	Ca	Mg	Al	Fe	Mn	NH_4	Cl	NO_3	SO_4	H_2PO_4	A^-
HV	0	3.93	174	3924	97	112	85	90	63	43	10	3	512	145	244	499	13.2	134
	7	3.59	249	2752	116	102	219	230	117	372	11	3	141	283	54	1124	1.4	-10
	22	4.22	118	814	69	64	153	73	63	551	2	1	64	188	80	724	0.3	39
	70	4.28	101	1285	75	25	149	93	72	488	2	1	10	149	103	583	0.3	57
	110	4.24	112	1916	97	21	124	96	52	364	3	2	3	148	40	660	1.1	-127
TV	0	4.10	312	5056	36	253	225	219	93	33	6	10	1423	341	607	1178	24.2	191
	12	3.41	351	6780	111	128	189	127	72	107	15	3	916	328	442	1044	8.9	123
	35	4.04	279	1772	176	67	267	61	104	1515	2	1	539	380	712	1446	0.8	108
	57	4.05	291	1859	187	57	325	69	112	2065	3	1	264	469	698	1757	0.5	61
	100	4.08	293	2835	157	59	323	173	163	1821	4	2	82	521	454	1497	0.3	238
GFF	0	4.17	266	6506	45	176	382	102	100	43	11	6	1193	515	607	718	20.4	220
	10	3.98	318	7845	166	92	503	120	143	839	32	2	948	644	1013	892	2.0	233
	40	4.00	339	2549	244	56	636	145	202	2073	4	7	50	907	1119	1142	0.4	105
	100	4.17	277	1104	171	48	576	113	168	1751	3	6	14	771	799	1173	0.2	3
GFB	0	4.46	70	697	37	10	98	49	35	178	2	1	81	145	111	256	0.2	-24
	40	4.43	62	873	56	11	87	46	28	239	3	1	13	116	110	223	0.6	16
	100	4.53	72	1085	79	9	224	40	28	188	3	2	10	114	128	298	0.3	-7

Table 6.5. Coefficients of variation (percentage of grand mean) of pH, EC and solute concentrations in soil solution. Data were collected with two lysimeters at each depth from November 1982 through May 1987. For number of samples see Table 6.4.

Site	Depth	pH	EC	DOC	SiO ₂	K	Na	Ca	Mg	Al	Fe	Mn	NH ₄	Cl	NO ₃	SO ₄	H ₂ PO ₄
HV	0	8	64	47	98	85	65	110	87	114	73	124	91	75	146	76	153
	7	7	34	68	46	109	59	67	55	68	45	92	215	59	224	47	298
	22	3	37	50	47	142	48	70	60	46	111	119	233	65	261	36	243
	70	4	30	74	23	62	39	57	50	65	111	110	336	40	246	24	166
	110	6	26	99	27	38	41	44	45	36	136	138	201	57	220	19	268
TV	0	11	38	59	110	49	47	96	90	102	81	116	47	50	86	47	115
	12	5	29	29	69	45	39	59	63	63	67	76	53	49	77	43	106
	35	3	17	38	39	49	29	50	57	31	92	110	51	41	58	21	240
	57	4	17	42	21	48	29	54	60	22	223	117	83	31	65	17	209
	100	5	30	50	25	48	19	106	70	23	81	55	172	20	68	19	155
GFF	0	7	56	73	83	72	44	97	104	128	94	134	87	61	166	42	184
	10	7	49	76	69	103	39	71	89	114	139	127	89	45	124	33	155
	40	4	49	54	43	86	53	80	63	66	75	126	162	62	92	40	176
	100	3	38	60	39	52	56	53	48	51	96	66	218	61	68	41	245
GFB	0	6	44	246	110	98	58	82	69	63	119	174	141	65	103	50	291
	40	4	28	167	49	84	64	142	62	33	144	115	440	70	87	32	403
	100	3	25	112	60	48	57	110	48	42	123	215	366	45	67	29	216

is the dominant solute in all soil solutions. The dominant anion is SO₄. This is in marked contrast to other soils in The Netherlands (e.g. the 'Oude Maat' soils with an oak-birch vegetation; Van Breemen et al. 1988), where NO₃ plays a more prominent role. Of the cations, NH₄ is dominant in all 0 horizons and in the upper 10 to 20 cm of the mineral soil under pine. In all other mineral soil horizons Al is the most important cation. The dominance of NH₄ in the 0 horizon and of Al at greater depth is a general phenomenon in sandy soils in The Netherlands (e.g. Van Breemen et al. 1988).

Total solute concentrations as indicated by the specific conductivity (EC) are significantly higher in the two forest soils (TV and GFF) than in the bare soil (GFB) and the heathland soil (HV). The difference can be attributed to (1) more dry deposition, (2) increased nutrient cycling, (3) more dissolved organic acids, and (4) increased evaporative concentration, in the forest plots. Also the concentrations of the individual solutes are higher in the pine soils than in those without vegetation or under heather, this being particularly so for Na, Al, NH₄, Cl, NO₃ and SO₄. The concentrations for the Hasselsven E horizon are generally high relative to the concentrations found above and below this horizon. This will be further discussed in 8.3.

The variability in solute concentrations, as indicated by CV, is small for pH (CV generally less than 8%), generally moderate (10 to 100%) for solutes occurring in concentrations above 100 mmol_c·m⁻³ and high (CV > 100%) for solutes occurring

in low concentrations ($< 100 \text{ mmol}_e \cdot \text{m}^{-3}$). The moderate CV values for solutes that form the bulk of the dissolved matter are primarily due to temporal variation in concentration, while the high CV values for solutes present in smaller amounts (H_2PO_4 , Fe, Mn) are also influenced by analytical errors.

Specific conductivity. The total ionic charge in solution, as indicated by the mean specific conductivity (EC), is highest in both forest soils (266 to $351 \mu\text{S} \cdot \text{cm}^{-1}$), intermediate in the heathland Spodosol (101 to $249 \mu\text{S} \cdot \text{cm}^{-1}$) and lowest in the bare drift-sand (62 to $72 \mu\text{S} \cdot \text{cm}^{-1}$). In both driftsand soils there is no clear trend in EC with depth. In the two Spodosols however, the EC is elevated in the 0 and E horizon and lower, but essentially constant in the Bhs horizon and below. The variation in EC is highest in the forest floor and upper mineral soil and relatively low at greater depth. The high CV at 100 cm depth in the Tongbersven soil is partly due to the small number of samples that were collected at this depth.

The specific conductivity has a strong seasonal variation in all soils, particularly in the surface layers (Appendix 3). Highest values are generally observed towards the end of the growing season (September, October), probably due to evaporative concentration of the soil solution. The EC values are lowest in late winter and spring, when soils are recharged with water (Figs. 4.1 to 4.4).

pH. The mean pH values of the soil solutions are lower in the forest soils than in their non-forested counterparts. The driftsand forest soil solutions at Gerritsfles have mean pH values from 3.98 to 4.17, which is 0.3 to 0.4 units lower than solutions from the bare plot. Mean pH values of the Spodosol solutions at the forested Tongbersven site range from 3.41 to 4.10, which is 0.1 to 0.2 pH units lower than in the heathland Spodosol at Hasselsven. In both driftsands, the soil solution pH is intermediate at the soil surface (forest floor (0 horizon) and top 2 cm of the mineral soil, respectively), decreases up to 40 cm depth and increases again below. In both Spodosols sharp changes occur in soil solution pH from the 0 horizon to the E horizon (-0.7 and -0.3 units at Tongbersven and Hasselsven, respectively), and from the E to the Bhs horizon ($+0.6$ units at both Tongbersven and Hasselsven). In the deeper soil horizons of the two Spodosols minor changes occur with depth. The variation in pH is largest in the 0 horizons and decreases with depth. The soil solutions are most acidic in the autumn and least acidic in the spring.

Dissolved carbon. Total dissolved organic carbon (DOC) concentrations are highest in the forest floor leachates and in the surface layers of the mineral forest soil (means of 5000 to 6500 $\text{mmol} \cdot \text{m}^{-3}$). 0 horizon leachates from the heathland Spodosol are considerably lower in total C than those from their forested counterpart. Because the bare driftsand has no 0 horizon, and only small amounts of organic C are present in the soil profile, the total mean dissolved C levels are lowest in this soil and even increase slightly with depth. In the forested driftsand mean total dissolved C concentrations gradually decrease with depth, whereas in both Spodosols the relatively high C

concentrations in the O and E horizons decrease sharply in the Bh horizon, but increase at greater depth. Variation in total dissolved C concentration is highest in the bare driftsand at all depths (CV = 112 to 246%) and lowest in the E and Bh horizons of both Spodosols (CV = 29 to 68%). Dissolved C exhibits a distinct seasonal pattern with highs in the late summer and autumn and lows in the spring.

Silica. Dissolved Si concentrations are highest in the mineral soil of the forested sites (111 to 244 $\text{mmol} \cdot \text{m}^{-3}$) and lowest in the bare driftsand and the heathland (37 to 116 $\text{mmol} \cdot \text{m}^{-3}$). In the heathland O horizon leachates Si levels are high compared to the forest floors leachates, which may be partly due to small inclusions of mineral soil in the shallow heathland O horizon during the installation of the lysimeters. In the bare driftsand dissolved Si gradually increases with depth. At the other sites Si reaches highest concentrations at 40 cm depth (GFF), in the BC horizon (TV) and in the E horizon (HV), respectively. The variation in Si concentration is relatively high in the surface soil (O horizons) and rapidly decreases with depth. Si concentrations are highest in the autumn and lowest in the spring. In general Si concentrations in the GFF and the TV forest soils are about $\frac{1}{3}$ of the values reported for acidic soils under oak developed in alluvial deposits in The Netherlands (Van Breemen et al. 1988). This difference may be partly due to a higher rate of mineral weathering in the loamy sands as well as a more pronounced biocycling of Si in deciduous forests (Bartoli 1983).

Potassium. Dissolved K concentrations are highest in the forest soils (48 to 253 $\text{mmol}_c \cdot \text{m}^{-3}$) and lowest in the bare driftsand (9 to 11 $\text{mmol}_c \cdot \text{m}^{-3}$). Concentrations peak in the O horizon leachates and rapidly decrease to concentrations of 20 to 60 $\text{mmol}_c \cdot \text{m}^{-3}$ at greater depths in the mineral soils, which indicates the importance of biocycling of this element (Appendix 3). Variation in K concentration is lowest in the TV soil, and higher in the other soils, particularly in the surface horizons. The variation in dissolved K is strongly seasonal with highs in the late summer and autumn.

Sodium. Dissolved Na concentrations reach highest values in the forest soils: 382 to 636 and 189 to 325 $\text{mmol}_c \cdot \text{m}^{-3}$ at GFF and TV, respectively. Mean concentrations are lowest in the bare driftsand (GFB, 87 to 224 $\text{mmol}_c \cdot \text{m}^{-3}$) and in the heathland soil (HV, 73 to 230 $\text{mmol}_c \cdot \text{m}^{-3}$). The higher Na concentrations in the GFF forest soil relative to the TV forest soil are probably related to the difference in Na concentration in throughfall (Table 6.1). The low Na concentrations in the bare and the heathland soils are due to a lower Na deposition at non-forested sites, and to a lower evaporative concentration of soil solutions. In the GFB soil Na concentrations increase strongly between 40 and 100 cm depth. Because transpiration is absent in this soil, this increase must be due to a Na release from the soil solid phase (i.e., chemical weathering of Na containing feldspars; see also chapter 8). At all sites the mean Na concentrations tend to increase with depth, with the exception of the Hasselsven E horizon leachate. In general, Na concentrations vary little with time. Dissolved Na concentrations in the mineral horizons of all four soils are correlated significantly at the 99% confidence

level with Cl concentrations; correlation coefficients are 0.87 (GFF, $n = 185$), 0.37 (GFB, $n = 212$), 0.66 (TV, $n = 203$), and 0.81 (HV, $n = 152$).

Calcium. Dissolved Ca concentrations are higher in the forest soils (61 to 219 $\text{mmol}_c \cdot \text{m}^{-3}$) than in their non-forested counterparts (40 to 96 $\text{mmol}_c \cdot \text{m}^{-3}$), with the exception of the extremely high concentration in the Hasselsven E horizon leachate (230 $\text{mmol}_c \cdot \text{m}^{-3}$). In the upper parts of the soils the variation in Ca concentration is generally highest, with increased concentrations in summer and autumn. The heathland Spodosol E horizon leachates, with their extremely high mean Ca concentrations, exhibit distinct concentration peaks in the summer and autumn (Fig. 6.1). These peaks coincide with elevated EC values and Mg, Cl and SO_4 concentrations, suggesting that increased mineralization of organic matter in the E horizon and evaporative concentration may cause the observed phenomena.

Magnesium. Magnesium and Ca concentrations and their temporal variation are similar. Mean dissolved Mg concentrations are highest in the GFF forest soil (100 to 202 $\text{mmol}_c \cdot \text{m}^{-3}$), slightly lower in the TV forest soil (72 to 163 $\text{mmol}_c \cdot \text{m}^{-3}$) and the heathland (HV) Spodosol (52 to 117 $\text{mmol}_c \cdot \text{m}^{-3}$) and lowest in the bare driftsand (GFB, 28 to 35 $\text{mmol}_c \cdot \text{m}^{-3}$). In the mineral horizons of all soils Mg concentrations are significantly correlated with Ca at the 99% confidence level; correlation coefficients are 0.88 (GFF, $n = 191$), 0.58 (GFB, $n = 218$), 0.36 (TV, $n = 208$) and 0.80 (HV, $n = 186$).

Aluminium. Dissolved Al is the dominant cation on a charge basis in all mineral soils and strongly increases in concentration with depth in the surface horizons. Organic monomeric Al concentrations were estimated using a regression model approach

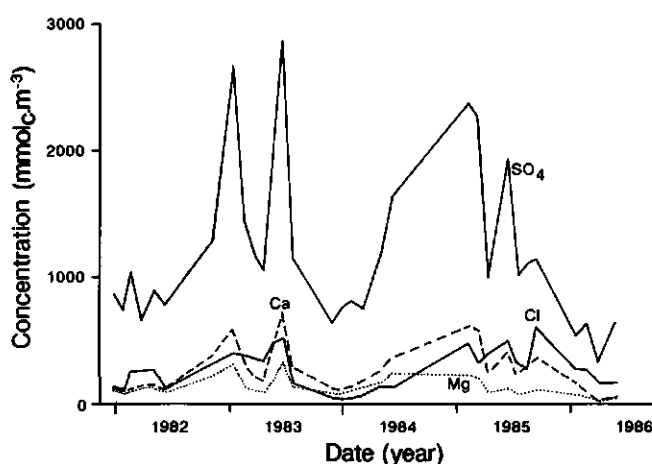


Figure 6.1. Concentration of Ca, Mg, Cl and SO_4 in the Hasselsven E horizon as a function of time.

(Mulder et al. 1989b). Only in the 0 horizon leachates Al is predominantly in an organically complexed form. In the E horizon of both Spodosols about 25% of the total dissolved Al is in an organic mononuclear form, while at greater depth as well as in both driftsands Al is for 90 to 100% in an inorganic mononuclear form. Mean concentrations are highest in the subsoils of the forested sites (maximum about $2000 \text{ mmol}_c \cdot \text{m}^{-3}$), lowest in the subsoil of the bare driftsand (GFB, about $200 \text{ mmol}_c \cdot \text{m}^{-3}$) and intermediate in the subsoil of the heathland Spodosol (HV, about $400 \text{ mmol}_c \cdot \text{m}^{-3}$). Coefficients of variation are generally low, except for the 0 horizons.

A clear seasonal trend in Al concentration could be observed in most of the soils (Figs. 6.2 and 6.3). This is similar to the findings for other acidic soils in The Netherlands (e.g. 'Oude Maat'; Van Breemen et al. 1988). The seasonality of the Al concen-

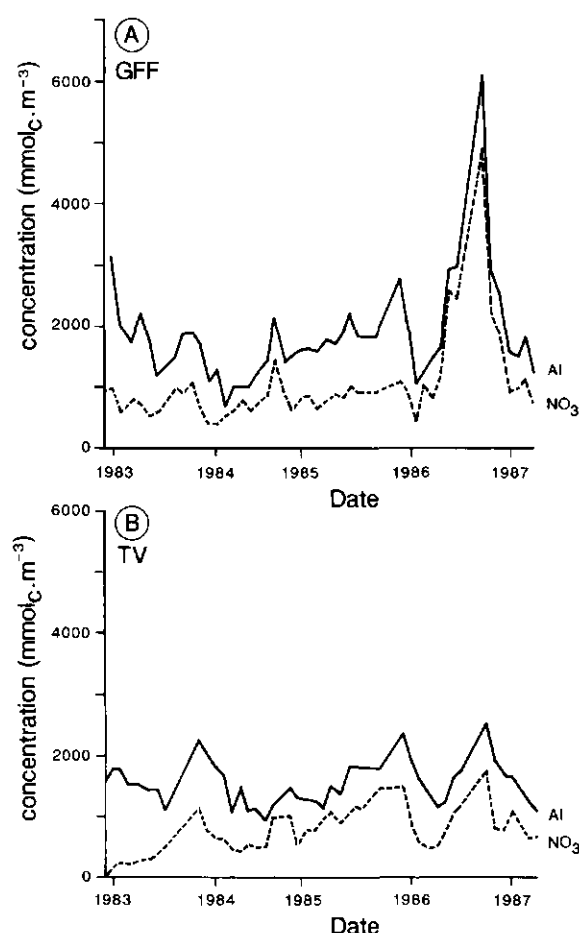


Figure 6.2. Concentration of dissolved Al and NO_3 in the Gerritsfles (A) and Tongbersven (B) forest soils as a function of time. Soil solutions were from 40 cm depth (GFF) and 35 cm depth (TV), respectively.

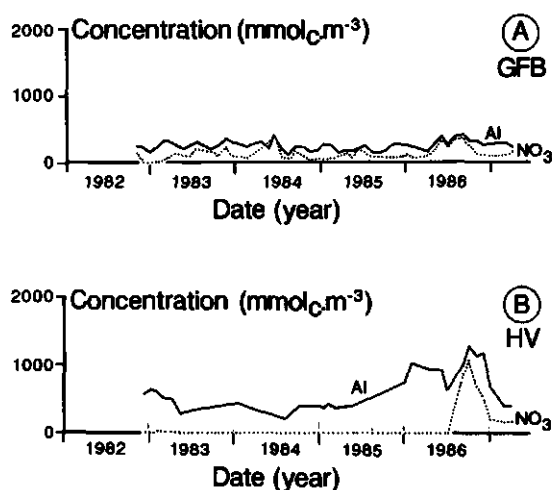


Figure 6.3. Concentration of dissolved Al and NO₃ in the Gerritsfles bare soil (A) and the Hasselsven heathland soil (B) as a function of time. Soil solutions were from 40 cm depth (GFB) and 22 cm depth (HV), respectively.

tration is largely due to the strong impact of nitrogen transformations on the Al chemistry in these soils, as can be seen from the NO₃ concentrations, which increase through summer. Van Breemen and Jordens (1983) reported a high correlation between dissolved Al and NO₃ in the 'Oude Maat' soils in The Netherlands. Also in our soils Al correlates better with dissolved NO₃ than with SO₄ (Table 6.6). However, this may be due to the less pronounced seasonal variation of SO₄ compared to NO₃ and may be unrelated to a different Al mobilizing potential for these two anions.

Aluminium toxicity is considered to be a predisposing factor in forest decline, reducing root growth and inhibiting nutrient uptake. Godbold et al. (1988) demonstrated an inhibiting effect of Al on root growth at 2400 mmol_c.m⁻³ (Al/Ca ratio 6.3). Also data from field studies suggest that Al/Ca ratios over 5 may cause damage to the fine

Table 6.6. Correlation coefficients of dissolved Al with Cl, NO₃, SO₄ and pH in the mineral horizons of the four research sites. Numbers of observations are 198 for HV, 206 for TV, 190 for GFF and 215 for GFB. Confidence levels are 99.9% (***) and 95% (*).

Site	Cl	NO ₃	SO ₄	pH
HV	0.21***	0.40***	0.38***	n.s.
TV	0.50***	0.43***	0.65***	0.73***
GFF	0.63***	0.89***	0.69***	-0.36***
GFB	0.12*	0.58***	0.13*	-0.50***

Table 6.7. Solute ratios (mol/mol) in soil solutions of Tongbersven and Gerritsfles (GFF). Values are arithmetic monthly means between November 1982 and May 1987. Depth in cm.

Site	Depth	Al/Ca	NH ₄ /K	NH ₄ /Mg
TV	0	0.1	5.6	30.6
	12	0.6	7.2	25.4
	35	16.6	8.0	10.4
	57	20.1	4.6	4.7
	100	7.1	1.4	1.0
GFF	0	0.3	6.8	23.9
	10	4.7	10.3	13.3
	40	9.6	0.9	0.5
	100	10.4	0.3	0.2

root system, resulting in forest decline (Ulrich 1989). In Table 6.7 Al/Ca ratios for the GFF and TV forest soils indicate that the critical ratio of 5 is reached at about 20 cm depth in the mineral soil.

Iron. Dissolved Fe concentrations are highest in the surface layers of the vegetated soils, and range from 6 to 32 mmol_c·m⁻³. Concentrations are lower in the the subsoils and in the bare driftsand (2 to 4 mmol_c·m⁻³). Complexation of dissolved Fe by organics in our soil solutions is indicated by the strong correlation between dissolved Fe and dissolved organic C in both 0 horizon leachates; correlation coefficients: 0.70 (GFF, n = 55), 0.78 (TV, n = 54) and 0.73 (HV, n = 48), and mineral soil solutions; correlation coefficients: 0.84 (GFF, n = 185), 0.25 (GFB, n = 210), 0.75 (TV, n = 197) and 0.50 (HV, n = 184), which are all significant at the 99% confidence level.

Manganese. In general dissolved Mn concentrations are low in all soils, with slightly elevated levels in the forest soils (maximum 10 mmol_c·m⁻³).

Mean dissolved Mn concentrations in our soil solutions are about 5 to 10 times lower than those reported for other acidic soils developed in alluvial deposits in The Netherlands (Van Breemen et al. 1988). Dissolved Mn concentrations in most of the soil horizons show significant positive correlations (95% confidence level) with Ca and Mg.

Ammonium. Dissolved NH₄ concentrations are highest in the forest floor leachate at Tongbersven (1423 mmol_c·m⁻³) and at Gerritsfles (1193 mmol_c·m⁻³). The ammonium concentrations are distinctly lower in the heathland 0 horizon (512 mmol_c·m⁻³) and in the top few cm of the bare Gerritsfles soil (81 mmol_c·m⁻³). In all soils except Tongbersven the NH₄ concentrations decrease sharply with depth to values less than

60 $\text{mmol}_c \cdot \text{m}^{-3}$ at 40 cm (see also Appendix 3). In the Tongbersven soil the decrease in concentration is more gradual, but also at this site the drainage water at 100 cm depth contains less than 100 $\text{mmol}_c \cdot \text{m}^{-3}$ NH_4 .

The variation in concentration is lowest for the 0 horizon leachates and increases with depth. In general NH_4 concentrations are highest in the summer and autumn and decrease during winter. Notwithstanding the continuous high input of atmospheric NH_4 , an increase in soil solution NH_4 concentration in the course of time was not found at the forested sites (cf. Fig. 6.4 and Appendix 3), except during the last monitoring year at HV (Fig. 6.5), when a significant increase in soil solution NH_4

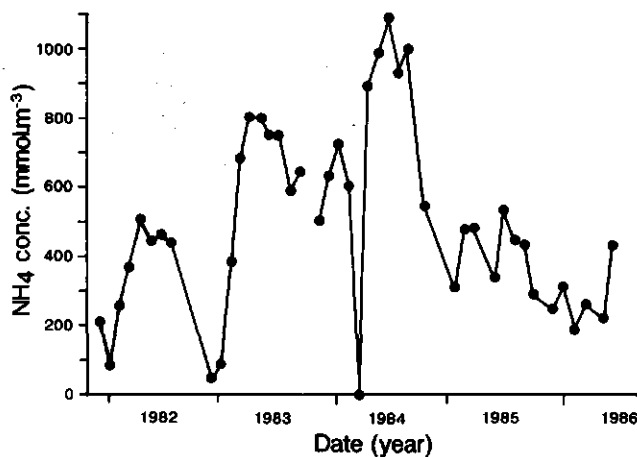
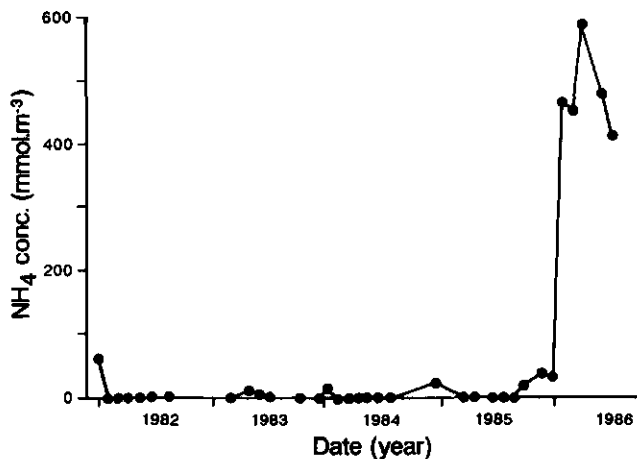


Figure 6.4. Concentrations of dissolved NH_4 in the Tongbersven soil solution at 35 cm depth, as a function of time.



concentration coincided with an increase in soil solution NO_3 concentration (see 6.2.15).

Like in throughfall, NH_4 concentrations in all 0 horizon leachates are strongly correlated with SO_4 ; correlation coefficients: 0.55 (GFF, $n = 105$), 0.79 (TV, $n = 99$) and 0.85 (HV, $n = 94$), all significant at the 95% confidence level.

In recent studies, Roelofs et al. (1985) attributed severe damage observed in pine and Douglas fir stands to increased NH_4/K and NH_4/Mg ratios, and concomitant inhibition of K and Mg uptake. In our forest soils, NH_4/K and particularly NH_4/Mg ratios are in the range where significant damage may be expected (Table 6.7). Negative effects due to elevated NH_4 concentrations are most likely to occur in the forest floor and the surface layer of the mineral soil, whereas negative effects of Al are more likely to occur below 20 cm depth.

Fluoride. Fluoride analysis by ion chromatography was not optimized, and the analytical data on this element (Microfiche) should be viewed with caution (see also Van Breemen et al. 1988). Dissolved F concentrations are generally below $30 \text{ mmol} \cdot \text{m}^{-3}$. Only in the GFF soil solutions, from both forest floor and mineral soil, the concentrations of F are somewhat higher but usually below $50 \text{ mmol} \cdot \text{m}^{-3}$.

Chloride. Dissolved Cl concentrations in the mineral soils are highest in the forest soils at Gerritsfles (600 to $900 \text{ mmol} \cdot \text{m}^{-3}$) and Tongbersven (300 to $500 \text{ mmol} \cdot \text{m}^{-3}$) and generally lower in the bare and heathland soil (100 to $200 \text{ mmol} \cdot \text{m}^{-3}$). As was discussed earlier Cl concentrations are strongly correlated with Na in all soil solutions. Chloride concentrations vary seasonally, particularly in the forest soils, with highs in the late summer and autumn, and lows in the late winter and spring.

Nitrate. Dissolved NO_3 concentrations are highest in the GFF soil (600 to $1100 \text{ mmol} \cdot \text{m}^{-3}$), considerably lower in the TV forest soil (400 to $700 \text{ mmol} \cdot \text{m}^{-3}$), and lowest in the non-forested soils (40 to $240 \text{ mmol} \cdot \text{m}^{-3}$). In the forest soils as well as in the bare driftsand NO_3 concentrations do not show a clear trend with depth. In the heathland soil, on the other hand, mean NO_3 concentrations sharply decrease from $244 \text{ mmol} \cdot \text{m}^{-3}$ in the 0 horizon to $40 \text{ mmol} \cdot \text{m}^{-3}$ in the mineral soil. The role of NO_3 in all our soil solutions is less prominent than in forest soil solutions reported by Van Breemen et al. (1988), where mean NO_3 concentrations were between 800 and $2300 \text{ mmol} \cdot \text{m}^{-3}$.

The variation in NO_3 concentration is highest in the surface soils layers (with the exception of the Hasselsven site, where the variation is high throughout the profile). The concentration of NO_3 shows a seasonal variation in the GFF and the TV forest soils, as well as in the bare driftsand (GFB) (Fig. 6.2 and 6.3, Appendix 3), with highs in autumn and winter. Nitrate not only shows a seasonal variation, but also increases steadily with time at all sites and at all depths (Appendix 3). The increase of NO_3 with time, which may be related to nitrogen saturation (Malanchuk & Nilsson 1989) was also observed in the groundwater at Tongbersven (see 6.3).

With respect to NO_3 the Hasselsven case is particularly interesting as NO_3 increased considerably during the last hydrological year at all depth (Appendix 3). At the start of the monitoring period the NO_3 concentrations were only elevated in the Hasselsven 0 horizons, and decreased to values below detection limit in the mineral soil. The nitrogen dynamics at this site illustrate that during favourable weather conditions, when ammonification and subsequent nitrification of organic N are high, a significant increase in NO_3 concentrations may occur. The associated acidification largely results in an increased dissolution of Al.

Sulphate. Dissolved SO_4 is the dominant anion in all soil solutions, with highest mean concentrations in the TV (1000 to 1800 $\text{mmol}_c \cdot \text{m}^{-3}$) and GFF forest soils (700 to 1200 $\text{mmol}_c \cdot \text{m}^{-3}$), lowest levels in the bare driftsand (GFB, about 250 $\text{mmol}_c \cdot \text{m}^{-3}$) and intermediate levels in the heathland soil (HV, 500 to 1100 $\text{mmol}_c \cdot \text{m}^{-3}$). As noted before, mean SO_4 concentrations in the Hasselsven E horizon (1124 $\text{mmol}_c \cdot \text{m}^{-3}$) are 2 to 3 times higher than those in the horizons above and below, which is possibly related to mineralization of organic sulphur in the E horizon.

The variation in SO_4 concentration is highest in the surface soil and generally decreases with depth. A distinct seasonality in SO_4 concentration with highs in the summer is present only in the GFB surface soil.

Phosphate. Like for F, the analysis for P was not optimized and therefore reported data should be viewed with caution. The data indicate that dissolved P, presumably present as H_2PO_4^- , reaches relatively high concentrations in the 0 horizon leachates (mean values 10 to 30 $\text{mmol}_c \cdot \text{m}^{-3}$), and decreases sharply with depth. In the mineral soils P concentrations are generally below 1 $\text{mmol}_c \cdot \text{m}^{-3}$.

Organic anions. Organic anion concentrations, as estimated from charge balance discrepancies, are only present in considerable amounts in the 0 horizon leachates (mean concentrations 134 to 220 $\text{mmol}_c \cdot \text{m}^{-3}$), where they make up 11% (GFF), 8% (TV) and 13% (HV) of the total anionic charge in solution. Below the forest floor only

Table 6.8. Correlation between concentrations of organic anions and total carbon in the O horizons and mineral soil of the research sites. Values are correlation coefficients significant at the 95% confidence level and numbers of observations (in brackets).

	O-horizon	Mineral soil
HV	0.74 (43)	0.67 (135)
TV	0.40 (49)	0.24 (97)
GFF	0.83 (54)	0.27 (98)
GFB	n.s.	0.51 (104)

the soil solutions from Tongbersven are somewhat elevated in organic anion concentrations (maximum $238 \text{ mmol}_c \cdot \text{m}^{-3}$), making up less than 10% of the total anionic charge. In both O horizons and mineral soils, organic anion concentrations are correlated at the 95% confidence level with total C concentrations (Table 6.8).

6.3 Groundwater

In Table 6.9 solute concentrations and their coefficients of variation are given for the Tongbersven and Hasselsven groundwater at the soil solution monitoring plots. The mean specific conductivity (EC) is almost five times higher in the groundwater of the forest soil (TV), than in the groundwater under heath (HV). The temporal variation in EC in both groundwaters is small, the groundwaters are acidic with elevated concentrations of Al, SO_4 and NO_3 at both sites.

At both sites the pH of the groundwater is slightly lower than soil solution pH at 100 cm. The total load of charged dissolved components in groundwater is higher than in soil solutions of the subsoils (groundwater EC values are 2.0 and 1.1 times the EC values of soil solutions below 100 cm depth of TV and HV, respectively). The solute concentration ratios between groundwater and soil solutions at 100 cm depth are given in Table 6.10. At Tongbersven all solutes except total C and NH_4 are more concentrated in the groundwater than in soil solutions at 100 cm depth. Most concentration ratios vary between 1.5 and 4 and are even higher for Mn (25) and Ca (5.6).

Table 6.11 gives mean solute concentrations and their coefficients of variation in samples collected at two occasions in the other piezometers at HV and TV. These

Table 6.9. Groundwater composition at the Hasselsven and Tongbersven soil solution monitoring plots between November 1982 and May 1987. Values are means (upper row) in $\mu\text{S} \cdot \text{cm}^{-1}$ (EC), $\text{mmol} \cdot \text{m}^{-3}$ (DOC and SiO_2) or $\text{mmol}_c \cdot \text{m}^{-3}$ (ions), and coefficients of variation (lower row). Numbers of observations are 45 to 50; CV values reflect temporal variation.

Site	pH	EC	DOC	SiO_2	K	Na	Ca	Mg	Al	Fe	Mn	NH_4	Cl	NO_3	SO_4	H_2PO_4
HV	4.22	119	333	129	36	164	107	52	526	8	2	7	149	187	647	0.7
	4	18	83	9	25	53	48	40	20	225	100	100	56	55	6	529
TV	4.02	576	965	239	106	1059	966	631	4031	11	50	10	1309	645	4698	0.3
	4	9	33	19	35	22	50	42	32	191	46	180	27	42	12	267

Table 6.10. Ratios of solute concentrations in groundwater relative to those in soil solution sampled at 100 cm depth at the Hasselsven and Tongbersven monitoring plots.

Site	EC	DOC	SiO_2	K	Na	Ca	Mg	Al	Fe	Mn	NH_4	Cl	NO_3	SO_4
HV	1.1	0.2	1.3	1.7	1.3	1.1	1.0	1.4	2.7	1.0	2.3	1.0	4.7	1.0
TV	2.0	0.3	1.5	1.8	3.3	5.6	3.9	2.2	2.8	25.0	0.1	2.5	2.1	3.1

Table 6.11. Groundwater composition at Tongbersven and Hasselsven. Values are means (upper row) and coefficients of variation (lower row) of all piezometers at two dates, in $\mu\text{S}\cdot\text{cm}^{-1}$ (EC), $\text{mmol}\cdot\text{m}^{-3}$ (DOC and SiO_2) and $\text{mmol}_c\cdot\text{m}^{-3}$ (ions). Numbers of observations are 22 (HV) and 30 (TV); CV values reflect spatial variation.

Date	Site	pH	EC	DOC	SiO_2	K	Na	Ca	Mg	Al	Fe	Mn	NH_4	Cl	NO_3	SO_4	H_2PO_4
831123	HV	4.3	122	585	143	30.9	140	240	83	449	16.7	4.6	6.2	173	117	756	0.3
		3	26	80	16	53	26	71	51	72	185	57	127	46	94	33	66
840328	HV	4.3	115	579	108	31.5	248	282	97	298	4.1	4.1	3.2	227	147	669	0.1
		4	29	56	16	65	18	49	36	79	34	48	170	36	130	21	104
831123	TV	4.2	312	929	172	27.1	515	308	197	2387	6.1	4.2	0.5	707	563	2485	0.3
		5	66	44	19	42	66	57	74	114	49	54	0	64	105	103	135
840328	TV	4.3	289	1047	95	30.5	634	305	203	2250	7.7	8.6	4.0	736	607	2154	0.2
		9	68	53	26	47	55	54	64	123	157	69	171	51	117	103	131

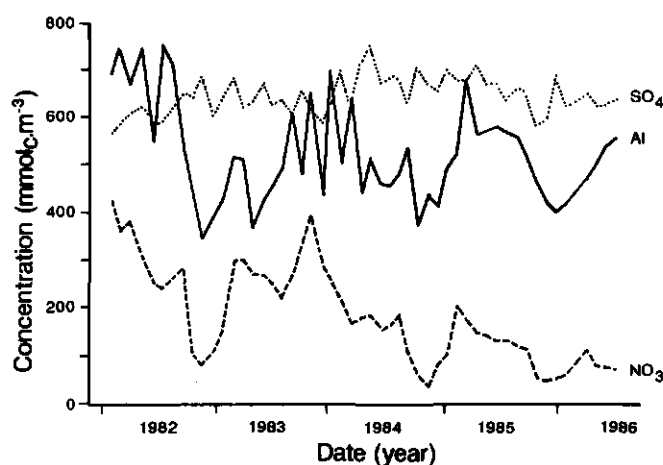


Figure 6.6. Concentrations of Al, NO_3 and SO_4 in groundwater at Hasselsven as a function of time.

concentrations are significantly lower (TV) and similar (HV) to the temporal means at the soil solution monitoring plots. This indicates that the groundwater samples collected at the TV monitoring plot are not representative for the TV site as a whole. The data in Table 6.11 also suggest that at both sites the spatial variation in most solute concentrations is significantly higher than the temporal variation at the monitoring plots (Table 6.9). Only for Na and Cl at the HV site the spatial variation is smaller than the temporal variation at the monitoring plot. Groundwater samples from inside or from the edge of the coniferous forest at HV do not differ considerably from those in the heathland area.

In the groundwater at Hasselsven no clear seasonal trends of element concentrations were observed (Fig. 6.6). In contrast to the groundwater at Tongbersven dissolved Al was negatively correlated with SO_4 ($r = -0.37$, $n = 69$) and positively correlated

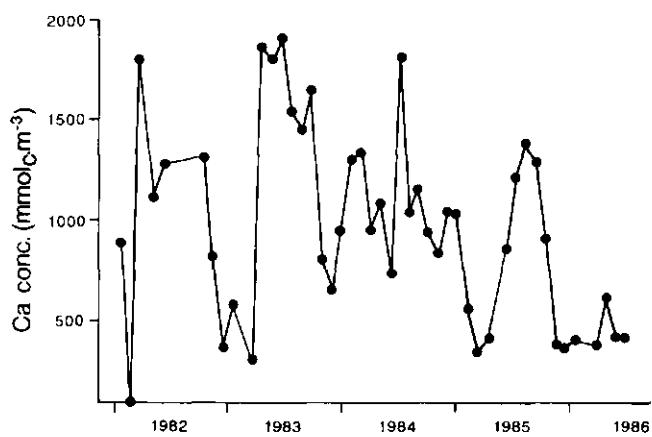


Figure 6.7. Concentration of Ca in groundwater at Hasselsven as a function of time.

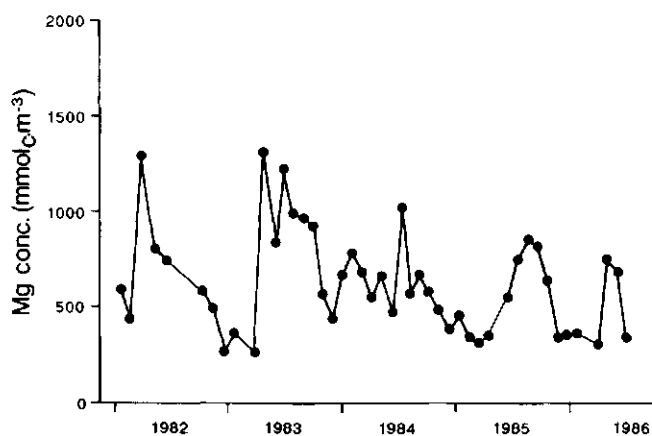


Figure 6.8. Concentration of Mg in groundwater at Hasselsven as a function of time.

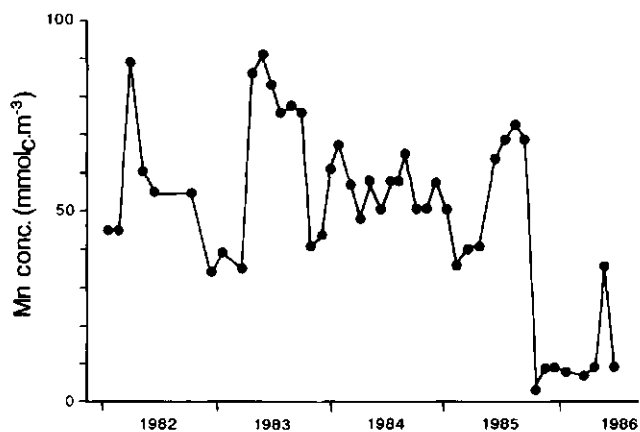


Figure 6.9. Concentration of Mn in groundwater at Hasselsven as a function of time.

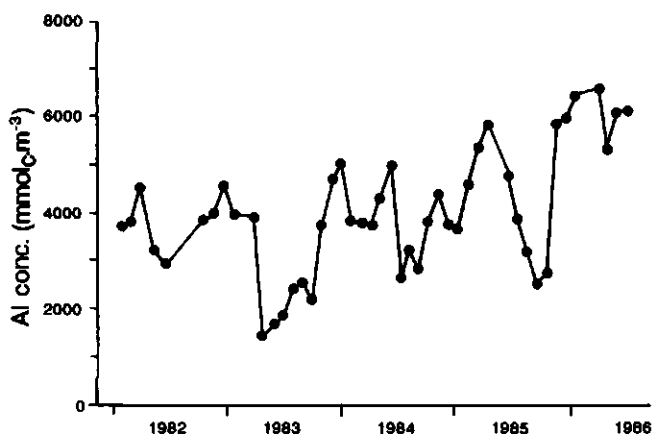


Figure 6.10. Concentration of Al in groundwater at Hasselsven as a function of time.

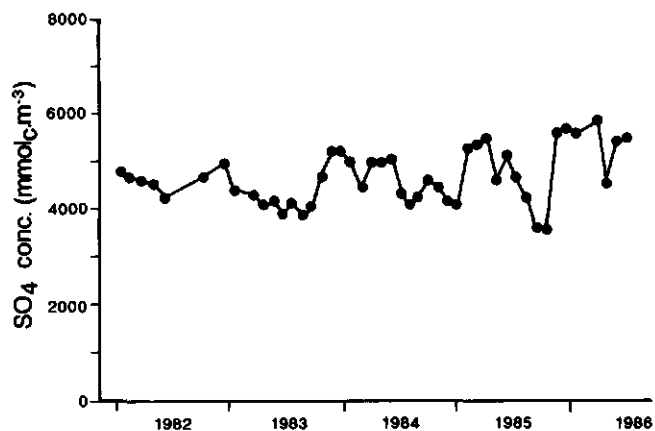


Figure 6.11. Concentration of SO₄ in groundwater at Hasselsven as a function of time.

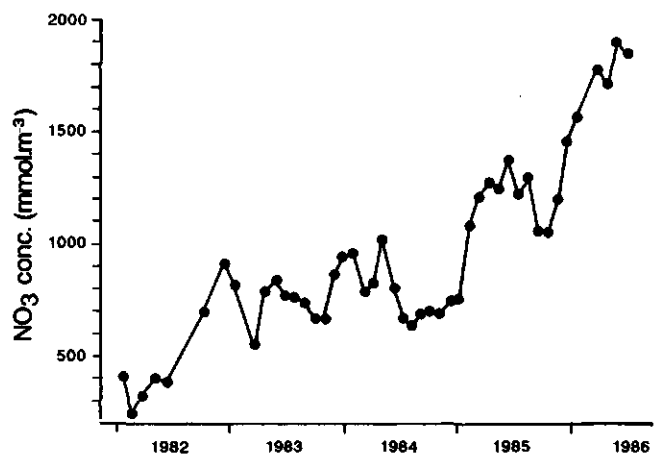


Figure 6.12. Concentration of NO₃ in groundwater at Hasselsven as a function of time.

Table 6.12. Chemical composition of the moorland pools. Values are pH measured in the lab (pH/l), pH measured in the field (pH/f), dissolved organic carbon (DOC), dissolved SiO_2 ($\text{mmol} \cdot \text{m}^{-3}$) and ionic equivalent concentrations ($\text{mmol}_e \cdot \text{m}^{-3}$) from the surface (S) and upper (I1) and lower (I2) part of the interstitial bottom water. Organic anion concentrations (A^-) were estimated from charge balance discrepancies. Values are means from March 1983 to March 1985. Numbers of samples are about 20 for the surface water and 35 for both interstitial waters, except for Tongbersven I1 (30) and Tongbersven I2 (18), and Goorven (8).

Site	Depth	pH/l	pH/f	DOC	SiO_2	K	Na	Ca	Mg	Al	Fe	Mn	NH_4	Cl	NO_3	SO_4	H_2PO_4	A^-	HCO_3
HV	S	3.94	3.84	466	6	62	173	108	64	26	12	5	46	217	6	398	0.11	-20	0
	I1	3.99	4.28	1854	33	54	133	77	49	32	153	4	61	245	3	321	3.23	88	2
	I2	3.99	4.09	3259	100	56	136	91	48	76	136	4	74	249	3	353	2.04	125	1
TV	S	5.07	4.85	1971	27	52	211	67	44	20	27	1	124	246	2	183	0.33	106	26
	I1	5.47	5.51	1824	118	65	171	54	43	13	33	1	188	214	4	157	0.78	90	109
	I2	5.45	5.56	2124	144	101	212	57	46	10	39	2	192	224	0	167	1.55	114	160
GV	S	4.44	3.89	1038	46	38	310	131	120	61	52	2	267	455	5	552	0.23	-2	15
GF	S	4.78	4.88	812	5	27	188	41	44	14	33	2	185	254	2	231	0.29	47	18
	I1	4.96	5.10	975	8	29	184	37	43	15	65	1	190	258	2	211	0.39	53	52
	I2	4.97	5.15	1168	9	28	186	43	46	16	84	1	193	256	0	214	0.33	86	59
KL	S	5.28	-	1043	2	27	253	63	66	12	37	4	45	324	1	96	0.24	62	27
	I1	5.91	-	1075	48	43	264	70	80	9	88	5	173	320	0	26	0.43	156	232
	I2	5.89	-	1276	112	67	280	81	97	10	184	6	260	320	0	20	0.55	241	399

with NO_3 ($r = 0.53$, $n = 69$), both significant at the 95% confidence level. Fig. 6.7 to 6.12, which show the seasonal variation in Ca, Mg, Mn, Al, SO_4 and NO_3 concentrations at the TV monitoring station, indicate that Al and SO_4 concentrations gradually increase through summer and rapidly drop in winter, while the reverse is true for Ca, Mg and Mn. Statistical analysis indicates a negative correlation at the 95% confidence level of Ca, Mg and Mn with Al ($r = -0.78$, $r = -0.67$ and $r = -0.73$, respectively; $n = 45$) and a positive correlation of Al with SO_4 ($r = 0.89$, $n = 45$). Both the seasonal variation of Al and SO_4 and the high correlation of Al with SO_4 were also observed in the TV soil solution. The sharp increase in Ca, Mg and Mn concentration in TV groundwater in winter (when the groundwater table rises) is in contrast to the seasonal variation of these solutes observed in soil solutions and may be due to mixing with groundwater of a higher pH, richer in base cations, possibly originating from outside the forest. The spatial variation in groundwater composition at TV indicates that pH and Ca levels 'upstream' of the monitoring plot are elevated in spring. However, the source of these high Ca concentrations in groundwater is unknown.

Nitrate in groundwater has a seasonal variation similar to that of Al and SO_4 . However, at Tongbersven this variation is superimposed on a continuous increase in concentration through the years, which runs parallel to the increase in NO_3 concentration in soil solutions at this site observed during the monitoring period (Fig. 6.12). This supports the hypothesis that the forest ecosystem at Tongbersven is increasingly unable to immobilize incoming N.

In contrast to the observations at the Tongbersven site, the NO_3 concentration in the groundwater at Hasselsven appears to decrease somewhat over the monitoring period. This suggests that the NO_3 pulse in the drainage water at this plot (Fig. 6.3) observed during the last hydrological year has not yet reached the groundwater.

6.4 Moorland poolwater

6.4.1 Short-term variation in poolwater composition

In Table 6.12 the mean chemical composition of surface and interstitial bottom water of the five moorland pools is given. Individual data are given on Microfiche. The variability in solute concentrations is given in Table 6.13. Data in Tables 6.12 and 6.13 are based on one (surface water) and 2 (both interstitial waters) collected samples per sampling period (month). No information is available on the spatial variation of solute concentrations, but this is probably rather small, so that CV values mainly reflect temporal variation. The data will be discussed below for each of the solutes.

Of all pools, Hasselsven and Goorven are the most acidic (pH c. 4.0), whereas Kliplo is the least acidic (pH c. 5.5). In both surface and interstitial water of all pools dissolved organic C is the dominant solute (on a molar basis). The dominant cation in all surface waters as well as interstitial waters is Na. In interstitial waters of Tongbersven, Gerritsfles and Kliplo dissolved NH_4 is also prominent. Chloride is the

Table 6.13. Coefficients of variation of the solutes given in Table 6.10.

Site	dpth	pH/l	pH/f	DOC	SiO ₂	K	Na	Ca	Mg	Al	Fe	Mn	NH ₄	Cl	NO ₃	SO ₄	H ₂ PO ₄	A ⁻	HCO ₃
HV	S	4	3	55	123	39	40	44	40	51	57	41	137	32	146	34	172	220	286
	I1	3	6	75	72	27	24	53	43	59	61	52	66	21	241	42	122	133	367
	I2	4	7	69	54	38	26	68	64	46	47	67	66	23	203	54	117	125	202
TV	S	1	5	19	67	30	29	40	20	63	35	68	54	21	191	26	110	43	207
	I1	4	3	22	49	17	13	29	18	75	25	44	33	12	407	29	137	79	75
	I2	4	3	24	78	59	35	25	15	73	19	55	60	18	-	23	278	88	105
GV	S	12	14	55	54	21	15	28	24	33	110	22	37	15	66	28	78	3288	51
	S	8	6	62	166	25	17	52	22	68	80	55	32	16	190	24	115	157	210
GF	I1	9	8	33	126	37	12	34	21	94	100	58	30	18	312	29	121	105	173
	I2	8	7	53	115	43	12	40	19	104	74	62	30	15	372	34	136	92	162
KL	S	6	-	22	95	28	8	39	6	78	38	33	74	9	189	27	145	75	78
	I1	4	-	36	58	32	5	27	15	69	21	22	35	11	608	87	231	79	60
	I2	4	-	44	20	20	5	23	7	78	20	15	22	9	600	101	174	80	49

dominant anion in all Tongbersven, Gerritsfles and Kliplo solutions, while the anions in both surface and interstitial water at Hasselsven and surface water at Goorven are dominated by SO_4 . Surface waters in all pools differ strongly from interstitial bottom waters in having a lower mean pH value as well as lower SiO_2 , Fe, NH_4 , HCO_3 and H_2PO_4 concentrations and higher SO_4 concentrations. The variability is small for pH ($\text{CV} < 15\%$), generally moderate ($\text{CV} < 100\%$) for most solutes and generally high ($\text{CV} > 100\%$) for NO_3 , H_2PO_4 and HCO_3 , due to their low concentrations. For the solutes that form the bulk of the dissolved matter, the analytical precision is good.

Specific conductivity. The mean specific conductivity (EC) is highest in the Goorven pool (110 to 199 $\mu\text{S}\cdot\text{cm}^{-1}$) and lower in the other pools (61 to 108 $\mu\text{S}\cdot\text{cm}^{-1}$; Table 6.14). Total solute concentrations increase from surface to bottom water, reaching highest values in the lower part of the organic debris layer. The increase is most pronounced for Kliplo, intermediate for Tongbersven and relatively small for Gerritsfles and Hasselsven. The variation in EC and total solute concentrations is generally low. A seasonal variation in EC occurs to some extent in all pools with highs in autumn and lows in spring, but is most pronounced in Gerritsfles. Peak values are generally more distinct in autumn 1983 than in autumn 1984 (Microfiche).

Table 6.14. Electric conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$) and total cationic charge ($\text{mmol}_c\cdot\text{m}^{-3}$) in poolwater. Values are means and coefficients of variation. Number of observations as in Table 6.10. S = surface water, I1 = upper interstitial water, I2 = lower interstitial water.

Site	Depth	EC		Charge	
		mean	CV	mean	CV
HV	S	108	22	597	33
	I1	102	23	656	18
	I2	107	23	717	19
TV	S	66	19	550	21
	I1	67	12	571	15
	I2	81	36	686	34
GV	S	145	21	1024	15
GF	S	72	15	546	17
	I1	71	18	574	21
	I2	72	21	603	22
KL	S	61	9	510	12
	I1	77	15	728	15
	I2	93	14	983	9

pH. The pH values measured in the laboratory decrease in the order Kliplo ($5.3 < \text{pH} < 5.9$), Tongbersven ($4.9 < \text{pH} < 5.6$), Gerritsfles ($4.8 < \text{pH} < 5.0$), Goorven ($4.1 < \text{pH} < 5.7$) and Hasselsven ($3.9 < \text{pH} < 4.0$). The variation in pH is generally small, but highest at Gerritsfles. Temporal variation has a distinct seasonal pattern at Gerritsfles, Tongbersven and Kliplo, with lows in spring and highs in autumn. In most pools the (lab) H^+ activity shows a significant positive correlation (95% confidence) with SO_4 , and a negative correlation with NH_4 , Fe and HCO_3 concentrations (Table 6.15).

Organic carbon. The dissolved organic carbon (DOC) concentration is highest in the pools at Tongbersven and Hasselsven (466 to 3259 $\text{mmol} \cdot \text{m}^{-3}$). In general, DOC concentrations increase somewhat from surface water to interstitial water. This is most pronounced in Hasselsven, where the variation in concentration is also highest. DOC levels are highest in summer and lowest in winter, particularly in the interstitial water. DOC is significantly positively correlated at the 95% confidence level with Fe at Gerritsfles ($r = 0.52$, $n = 91$), Hasselsven ($r = 0.69$, $n = 83$) and Goorven ($r = 0.89$, $n = 8$) (Table 6.16).

Table 6.15. Correlation of the moorland pool H^+ activity, as measured in the laboratory, with SO_4 , NH_4 , Fe and HCO_3 . Values are correlation coefficients significant at the 95% confidence level, and numbers of observations (in brackets).

	SO_4	NH_4	Fe	HCO_3
HV	0.18 (90)	n.s.	-0.29 (84)	n.s.
TV	n.s.	-0.53 (68)	n.s.	-0.39 (67)
GV	n.s.	n.s.	n.s.	-0.79 (8)
GF	0.40 (99)	-0.36 (98)	-0.28 (95)	-0.33 (90)
KL	0.52 (97)	-0.39 (97)	-0.34 (90)	-0.40 (96)

Table 6.16. Correlation of dissolved Fe concentrations with DOC, SO_4 and HCO_3 in moorland pool water. Values are correlation coefficients significant at the 95% confidence level and numbers of observations (in brackets). Data for Goorven (GV) are for surface water only.

	DOC	SO_4	HCO_3
HV	0.69 (83)	-0.48 (86)	0.37 (84)
TV	n.s.	n.s.	0.40 (62)
GV	0.89 (8)	n.s.	0.83 (8)
GF	0.52 (91)	-0.37 (94)	0.85 (86)
KL	0.27 (89)	-0.60 (90)	0.71 (89)

Silica. The Si concentrations in poolwater are highest at Tongbersven (27 to 144 $\text{mmol} \cdot \text{m}^{-3}$), slightly lower at Kliplo and Hasselsven (2 to 112 $\text{mmol} \cdot \text{m}^{-3}$) and lowest at Gerritsfles (5 to 9 $\text{mmol} \cdot \text{m}^{-3}$). The mean Si concentration in the surface water of Goorven (46 $\text{mmol} \cdot \text{m}^{-3}$) is relatively high. The low Si concentrations illustrate that the pool at Gerritsfles is almost exclusively rainwater fed and that the interaction of the pool water with Si containing minerals in the sediment is limited. Because the influx of significant amounts of Si-rich soil solution and groundwater into the other three pools is small (chapter 5), the relatively high Si concentrations in these pools must originate largely from interactions with the mineral sediment. This is also suggested by the distinctly higher Si concentrations in the interstitial water compared to the surface water. The variation in concentration is particularly high in the case of low Si levels (GF), probably due to analytical inaccuracy. The concentrations of dissolved Si are generally highest in autumn and lowest in winter.

Potassium. The K concentrations are highest in the Tongbersven pool (52 to 101 $\text{mmol} \cdot \text{m}^{-3}$), intermediate in the pools at Goorven, Hasselsven and Kliplo (27 to 67 $\text{mmol} \cdot \text{m}^{-3}$) and lowest at Gerritsfles (27 to 29 $\text{mmol} \cdot \text{m}^{-3}$). Only at Kliplo and Tongbersven mean K concentrations show a distinct increase from surface to interstitial water. The variation in K concentration is small in all pools at all depths. Only at Tongbersven and Hasselsven a seasonal variation in K concentration was observed with highest values in summer and lowest in winter.

Sodium. The Na concentrations are highest in the Goorven and Kliplo pools (253 to 310 $\text{mmol} \cdot \text{m}^{-3}$), lowest in the Hasselsven pool (133 to 173 $\text{mmol} \cdot \text{m}^{-3}$) and intermediate in the Gerritsfles and Tongbersven pools (171 to 212 $\text{mmol} \cdot \text{m}^{-3}$). The mean concentrations of Na do not vary with depth in the pools, with the exception of the pools at Kliplo and Hasselsven. Our data suggest that the organic sediment does not supply or sorb significant amounts of Na. Dissolved sea salt in precipitation is probably the major source of Na in these pools, as is also indicated by the significant positive correlation (at the 95% confidence level) of Na with Cl at Gerritsfles ($r = 0.68$, $n = 94$), Tongbersven ($r = 0.59$, $n = 62$) and Hasselsven ($r = 0.61$, $n = 87$). A significant correlation between Na and Cl was not observed at Kliplo, possibly due to (1) an additional Na source in the sediment and (2) an extremely low temporal variation in these components at Kliplo, relative to the variation observed in the other pools (CV 5 to 11% vs. 12 to 40%). Also in the surface water of the Goorven pool Na and Cl were not significantly correlated. Seasonal variation in dissolved Na concentrations was distinct in all pools with the exception of Kliplo, with highs in summer and lows in winter.

Calcium. The Ca concentrations are highest in the Goorven pool (310 $\text{mmol}_c \cdot \text{m}^{-3}$), and lowest in the Gerritsfles pool (37 to 43 $\text{mmol}_c \cdot \text{m}^{-3}$). Only at Kliplo a gradient of increasing mean Ca concentrations with depth was observed. In general Ca concentrations show peak values in summer and lowest values in winter. Concentrations are

significantly correlated with Mg in all pools (Kliplo: $r = 0.59$, $n = 97$; Gerritsfles: $r = 0.58$, $n = 100$; Tongbersven: $r = 0.68$, $n = 68$; Hasselsven: $r = 0.95$, $n = 92$; Goorven: $r = 0.71$, $n = 8$).

Magnesium. The magnesium concentration is somewhat lower than the Ca concentration at Tongbersven (43 to 46 $\text{mmol}_c \cdot \text{m}^{-3}$, Hasselsven (48 to 64 $\text{mmol}_c \cdot \text{m}^{-3}$) and Goorven (120 $\text{mmol}_c \cdot \text{m}^{-3}$), and somewhat higher than Ca at Kliplo (66 to 97 $\text{mmol}_c \cdot \text{m}^{-3}$) and Gerritsfles (43 to 46 $\text{mmol}_c \cdot \text{m}^{-3}$). Like Ca, Mg only shows a distinct gradient of increasing concentration from surface to interstitial water in Kliplo. In most pools CV values for Mg are considerably lower than those for Ca.

Aluminium. The Al concentrations in pool waters are low compared to those found in soil solutions and groundwater. Highest concentrations occur at Goorven (61 $\text{mmol}_c \cdot \text{m}^{-3}$). Mean concentrations in interstitial water are highest in the most acidic pool Hasselsven.

Iron. The Fe concentrations, assumed to be present as Fe^{2+} , are highest at Kliplo (37 to 184 $\text{mmol}_c \cdot \text{m}^{-3}$) and Hasselsven (12 to 153 $\text{mmol}_c \cdot \text{m}^{-3}$), intermediate at Gerritsfles (33 to 84 $\text{mmol}_c \cdot \text{m}^{-3}$) and Goorven (52 $\text{mmol}_c \cdot \text{m}^{-3}$), and lowest at Tongbersven (27 to 39 $\text{mmol}_c \cdot \text{m}^{-3}$). In all pools Fe concentrations increase from surface to interstitial water. No clear seasonal variation in Fe concentrations was observed in any of the pools. As indicated in Table 6.16 Fe is positively correlated with DOC and HCO_3 , and negatively with SO_4 concentrations in most pools. Our data indicate that reduction of SO_4 and Fe^{3+} and simultaneous production of HCO_3 occurs to some extent in all pools.

Manganese. The Mn concentrations are generally low in all pools: mean 1 to 2 $\text{mmol}_c \cdot \text{m}^{-3}$ at Gerritsfles, Goorven and Tongbersven and 4 to 6 $\text{mmol}_c \cdot \text{m}^{-3}$ at Kliplo and Hasselsven.

Ammonium. Like Si and Fe, mean NH_4 concentrations increase from surface to interstitial water in all pools with the exception of the Gerritsfles pool. In the Goorven pool mean NH_4 concentration in surface water is 267 $\text{mmol} \cdot \text{m}^{-3}$. At Gerritsfles mean NH_4 is about 190 $\text{mmol} \cdot \text{m}^{-3}$ in both surface and interstitial water, and in the other pools concentrations increase with depth from 45 to 260 $\text{mmol} \cdot \text{m}^{-3}$ (Kliplo), from 124 to 192 $\text{mmol} \cdot \text{m}^{-3}$ (Tongbersven) and from 46 to 74 $\text{mmol} \cdot \text{m}^{-3}$ (Hasselsven).

Whether these differences in concentration are related to different atmospheric NH_4 inputs or to differences in N-transformations in the respective pools will be discussed in Chapter 9. In general CV values for NH_4 are low. Seasonal variation in NH_4 concentration, with elevated concentrations in autumn and decreased concentrations in spring, were observed in both surface and interstitial water of Gerritsfles and Hasselsven. In Kliplo and Tongbersven a seasonal variation in NH_4 was only observed in surface water, with highs in winter and lows in summer.

Chloride. The Cl concentrations are highest in the Goorven pool ($455 \text{ mmol} \cdot \text{m}^{-3}$) and lower in the other pools (214 to $320 \text{ mmol} \cdot \text{m}^{-3}$). Mean Cl concentrations do not change considerably with depth in any of the pools. The CV values for Cl are low, but nevertheless Cl concentrations show some seasonal variation with highs in autumn and lows in winter and spring, in all pools. As was noted before Cl is well correlated with Na in all pools, with the exception of Kliplo and Goorven.

Nitrate. Nitrate is virtually absent from all pools, presumably due to denitrification and/or NO_3 assimilation. The observed low values are in strong contrast with the high NO_3 concentrations in soil solutions and groundwater.

Sulphate. The SO_4 concentrations decrease in the order Goorven ($552 \text{ mmol} \cdot \text{m}^{-3}$), Hasselsven (321 to $398 \text{ mmol} \cdot \text{m}^{-3}$), Gerritsfles (211 to $231 \text{ mmol} \cdot \text{m}^{-3}$), Tongbersven (157 to $183 \text{ mmol} \cdot \text{m}^{-3}$) and Kliplo (20 to $96 \text{ mmol} \cdot \text{m}^{-3}$). In contrast to all other solutes, SO_4 concentrations tend to decrease from surface to interstitial water, indicating that SO_4 is removed in the sediment, probably as a result of reduction. The concentration gradient from surface water to interstitial water is strongest at Kliplo and far less in the other pools. As SO_4 concentrations were measured in oxidized samples values indicate total dissolved inorganic S rather than SO_4 alone. As mentioned earlier, SO_4 is negatively correlated to DOC, Fe and HCO_3 .

In August 1984 the chemical changes of the moorland pool water were recorded in Tongbersven and Hasselsven during a one day period, with special reference to sulphide. Twenty ml water samples were directly collected in 50 ml polyethylene syringes with 5 ml of a buffer solution containing 32 g NaOH and 29 g ascorbic acid per liter (Van Breemen 1976), to prevent volatilization of H_2S and rapid oxidation of the sample. Sulphide was measured in these samples using an Orion specific electrode (model 94-16) and an Orion double junction reference electrode (model 90-2), filled

Table 6.17. Dissolved sulphate ($\text{SO}_4(1)$), sulphide ($\text{S}(1)$) and total sulphur ($\text{S}_{\text{tot}}(1)$) in Tongbersven (21 and 22 August 1984) and Hasselsven (7 and 8 August 1984) and dissolved sulphate ($\text{SO}_4(2)$) in Tongbersven and Hasselsven (March 1983 to March 1985). Values are means ($\text{mmol} \cdot \text{m}^{-3}$) for the one-day period (indicated with (1)) and for two years of monitoring (indicated with (2)), respectively.

Site	Depth	$\text{SO}_4(1)$	$\text{S}(1)$	$\text{S}_{\text{tot}}(1)$	$\text{SO}_4(2)$
TV	S	136	7	143	183
	11	62	126	188	157
	12	54	131	185	167
HV	S	274	3	277	398
	11	273	7	280	321
	12	164	95	259	353

with 10% KNO_3 solution. In a second sample the field pH was recorded and a third sample, stored in tightly capped glass containers, was analysed for all major components within a week of collection (Pek 1984). Total S concentrations during this day were similar to the mean SO_4 concentrations of the two year monitoring (Table 6.17) at Tongbersven, but considerably lower at Hasselsven. However, dissolved SO_4 concentrations in Hasselsven found in the regular monitoring samples during this summer period were also lower than the mean concentrations (Microfiche).

The data in Table 6.17 indicate that part of the dissolved SO_4 , as determined in the regular monitoring programme, is probably formed by oxidation of reduced S compounds. Reduced inorganic S compounds are of little importance in the surface water, making up only 1% (Hasselsven) to 5% (Tongbersven) of total dissolved S. By contrast, the contribution of reduced inorganic S to total S in interstitial water may be as high as 37% (Hasselsven) and 71% (Tongbersven). In Gerritsfles and Kliplo no sulphide determinations were carried out, but the occurrence of sulphide in the interstitial water of these pools is likely. Therefore alkalinity concentrations calculated from the regular (oxidized) samples of the monitoring project are underestimated due to acidification caused by sulphide oxidation, especially in interstitial water.

Phosphate. Phosphate is presumably present in poolwater as H_2PO_4^- . The CV values are high, partly due to analytical errors. However, reported mean values can be considered as reasonable estimates of dissolved P concentrations. Phosphate concentrations are highest at Hasselsven and low at Kliplo and Gerritsfles. With the exception of Gerritsfles, phosphate concentrations are distinctly higher in the interstitial water than in the the surface water.

Organic anions. Organic anion concentrations (A^-) were estimated from charge balance discrepancies and therefore have high CV values. Nevertheless, the data were used as a first estimate of the contribution of organic anions to the total sum of anions. A significant positive correlation exists between DOC and A^- at Kliplo ($r = 0.45$, $n = 87$), Gerritsfles (0.62 , $n = 79$), Tongbersven ($r = 0.27$, $n = 59$) and Hasselsven ($r = 0.85$, $n = 81$). The concentrations of organic anions are highest in the Kliplo interstitial water (up to $241 \text{ mmol}_c \cdot \text{m}^{-3}$), where they make up more than 40% of the anionic charge in solution. At Tongbersven mean A^- concentrations are about $100 \text{ mmol}_c \cdot \text{m}^{-3}$ at all depths, and at Gerritsfles about $50 \text{ mmol}_c \cdot \text{m}^{-3}$. At Hasselsven appreciable amounts of organic anions were only found in the interstitial water (about $100 \text{ mmol}_c \cdot \text{m}^{-3}$). As a consequence of sulphide oxidation during transport of the interstitial water samples, part of the organic anions may become protonated. Therefore organic anion concentrations may be underestimated in interstitial water samples that are high in dissolved sulphide (Tongbersven, Hasselsven and probably Gerritsfles).

Bicarbonate and alkalinity. Bicarbonate concentrations are highest in the interstitial water at Kliplo (up to $400 \text{ mmol} \cdot \text{m}^{-3}$) and lower in the interstitial water at Tong-

Table 6.18. Alkalinity at different depths in the moorland pools. Values (in $\text{mmol}_c \cdot \text{m}^{-3}$) are mean alkalinities, calculated as the difference between strong base cations (Na, NH_4 , Ca, Mg) and strong acid anions (SO_4 , NO_3 , Cl).

Site	Depth	Alk
HV	S	-168
	I1	-195
	I2	-200
TV	S	67
	I1	146
	I2	217
GV	S	-146
GF	S	-2
	I1	94
	I2	26
KL	S	34
	I1	384
	I2	445

bersven (up to $160 \text{ mmol} \cdot \text{m}^{-1}$) and Gerritsfles (up to $60 \text{ mmol} \cdot \text{m}^{-3}$). In the interstitial water at Hasselsven HCO_3 is virtually absent. Like organic anions, HCO_3 concentrations in the interstitial water of Tongbersven, Hasselsven and Gerritsfles may be underestimated due to the oxidation of sulphide.

The alkalinity, calculated as the difference of strong base cations (Na, NH_4 , Ca, Mg) and strong acid anions (SO_4 , NO_3 , Cl) (Shaffer et al. 1988), in surface water is highest in Tongbersven, somewhat lower in Kliplo, about zero in Gerritsfles, and strongly negative in the acidic Hasselsven and Goorven (Table 6.18). The interstitial water has significantly higher alkalinity concentrations than the surface water in Gerritsfles and particularly in Tongbersven and Kliplo due to higher bicarbonate concentrations.

6.4.2 Medium-term changes in poolwater composition at GV, GF and KL

Monthly sampling of surface water in the pools at Goorven (stations A, B and E) and Gerritsfles started in July 1979. As temporal changes were not extremely large, the sampling frequency was reduced to four times a year in July 1980. Because the differences between the three stations in Goorven were small the full set of analyses was

continued only at station E. At the stations A and B only pH, EC, O₂, Ca and Cl were monitored from August 1980 onwards. In August 1984 complete ionic balances were made for stations A and B (Microfiche). Graphical analysis and Friedman two-way analysis of variance by ranks of each of the investigated parameters revealed differences in the concentrations of SiO₂ ($P < 0.001$, minimal at station A and maximal at E) and the field measured conductivity ($P < 0.02$, maximal at B). Quarterly sampling of Kliplo was started in May 1981. From all pools occasional samples were available from other sources since c. 1975.

The individual results are presented on Microfiche. The pools are compared with each other in Table 6.21. Nitrite is left out of the tables, because it was always below the detection limit ($0.2 \text{ mmol} \cdot \text{m}^{-3}$). To assess trends Spearman rank correlation coefficients were calculated over the observation period. The trends were also assessed from visual inspection of the plots of each of the parameters against time, because many of the parameters were not monotonously increasing or decreasing but had a minimum of maximum within the period of observation.

On some of the sampling dates the pools were ice-covered. In the presence of an ice layer the surface water generally had higher ion concentrations (and lower pH values) than without ice cover (Microfiche, Fig. 5.3). These interruptions do not seriously disturb the medium-term pattern of concentration changes.

At Kliplo the changes in solute concentration are small. Most striking are the decrease in colour (Fig. 5.3) and other parameters associated with humus (e.g. Fe³⁺ and H₂PO₄⁻ since 1981). Also pH/l is decreasing since 1983, but it is doubtful whether this drop is persistent. pH/f did not change within the same period. Sodium and Cl had a maximum in the summer of 1976, when the water level in Kliplo was extremely low (see section 5.4.5). Sulphate and other parameters associated with acidification (e.g. aluminium and calcium) have been constantly low over the period of observation.

Although differing in some details the changes at Goorven and Gerritsfles are very similar. In these two pools, particularly at Gerritsfles, elevated levels of SO₄, Al, Ca, Mg, CO₂, EC, and even Na and K were present in 1977-1978. High concentrations of these solutes are associated with the acidification of the moorland pools (e.g. Van Dam et al. 1981), and are probably the result of the dry summer of 1976. In the Gerritsfles pool the concentrations of all solutes except Na are lower than in Goorven. Since 1978 these concentrations have dropped. This decrease was most rapid in the few years after 1977-1978 and much slower from c. 1981 onwards. Several solutes, e.g. Al and Ca no longer decreased in concentration after 1981, particularly in Gerritsfles. Since c. 1981 pH/f, pH/l and alkalinity increase in this pool (Fig. 5.3).

Changes in the pool at Kliplo are of minor importance when compared to those in the other pools. This supports our hypothesis regarding the importance of oxidation and reduction processes in the acid-base chemistry of the studied pools. In dry summers only a small fraction of the bottom of Kliplo is exposed to the atmosphere (section 5.4.5). Therefore the sediment is not aerated in such years and the reduction of SO₄ can continue. Oxidation of iron sulphides and reduced nitrogen compounds

is unlikely and hence no strong acids are formed. As a result no reduced levels of humic and fulvic acids, which is often seen in acidifying lakes (e.g. Almer et al. 1978, Dillon et al. 1984), occur and the pool is permanently brown coloured. The SO_4 concentration in the Kliplo pool is presumably kept low by reduction, which is a common

Table 6.19. Comparison of pH (measured in the field) in four different periods. Differences between the first and last period on all but the first sampling stations are significant at the 98% confidence level (Wilcoxon two-sample test, two-tailed). Also significant are the differences in Gerritsfles between the first and second period and in Kliplo between first and third period. GVA, GVB, GVE = Goorven stations A, B and E, respectively. — = no data.

		GVA	GVB	GVE	GF	KL
1919-1930	median	—	6.0	5.7	5.5	6.0
	range	—	5.5-6.6	5.4-6.0	5.5-6.5	6.0-6.5
	n	—	—	3 3	2	9
1950-1960	median	5.2	—	—	4.1 ^a	5.2
	range	—	—	—	4.0-4.1 ^a	5.2-5.2
	n	1	—	—	2 ^a	1
1970-1976	median	—	3.5	—	3.9	5.6
	range	—	—	—	—	3.9-8.8
	n	—	1	—	1	10
1978-1985	median	4.1	3.9	3.9	4.3	5.2
	range	3-5.0	3.3-4.9	3.4-5.6	3.9-5.5	4.1-7.8
	n	18	19	19	17	24

^a 1 measurement (1950) in field, 1 measurement (1960) in laboratory.

Table 6.20. Long-term changes in mean values of selected chemical parameters of Gerritsfles. Ionic concentrations in $\text{mmol} \cdot \text{m}^{-3}$, n = number of observations, — = no data.

	pH-field	pH-lab.	NH_4	Cl	SO_4	n
1925	—	4.4	0	395	354	1
1928	5.5	—	—	—	—	1
1930	5.8 ^a	6.5	21	468	396	1
1950	4.0	—	—	395	—	1
1960	—	4.1	111	429	800 ^c	1
1974	3.9	4.1	47	282	541	1
1977	—	4.0	89	339	916	1
1978	4.1	4.1	50	353	625	1
1979-85	4.4 ^b	4.7	99	267	277	23

^a n = 8, ^b n = 17, ^c inferred from correlation with Ca^{2+} and Mg^{2+} .

Table 6.21. Trends in chemical data from Goorven, Gerritsfles and Kliplo. For Kliplo no measurements of H_3PO_4 , Mn, COLOUR, SiO_2 and CO_2 are available from before 1981. I = increase, C = constant, D = decrease, Min = minimum, Max = maximum. Parentheses indicate that trend is not very clear.

Parameter ^a	Goorven E (GV)			Gerritsfles (GF)			Kliplo (KL)			Order of stations
	mean ^b	corr. ^c	trend ^d	mean ^b	corr. ^c	trend ^d	mean ^b	corr. ^c	trend ^d	
ALK	13	50	I since 82	24	37	I since 81	66	-42	(Max 81)	GV < GF < KL
pH/f	4.1	39	I since 82	4.4	10	I since 81	5.3	-18	C	GV < GF < KL
pH/l	4.2	77	I since 81	4.7	42	I since 80	5.5	-39	D since 83	GV < GF < KL
H_3PO_4	0.19	15	C	0.27	-31	D since 81	0.40	-69	D since 81	GV \leq GF < KL
t- PO_4 /f	0.87	-3	C	1.0	-29	Max 80-83	1.2	-76	D since 81	GV \leq GF \leq KL
Mn	3.0	-72	D	3.1	-72	D	3.8	-43	D since 81	GV = GF \leq KL
NO_3	4.4	-14	C	7.5	13	(I)	7.1	-33	C	GV < KL \leq GF
$O_2\%$	87	-36	(D)	102	-21	C	89	-46	(D since 82)	GV = KL < GF
COLOUR	12.8	-35	Max 82-83	8.6	36	Max 83-84	30	-65	D since 81	GF < GV < KL
KMnO ₄ u	32	33	(I)	21	16	(I since 80)	51	-4	C	GF < GV < KL
NH ₄ -org	22.2	-33	C	20.2	-15	C	28.8	-52	Max 82	GF \leq GV < KL
Na	323	-39	D	210	-26	D	260	14	C	GF < KL < GV
Cl	423	8	C	267	-15	C	323	19	C	GF < KL < GV
Fe	53	14	Max 83	17	18	C	51	-53	D	GF < KL < GV
SiO_2	31	69	I	8.9	-26	C	10	40	I since 81	GF \leq KL < GV
CO_2	386	-40	D	154	-56	D	163	51	I since 81	GF \leq KL < GV
CO_3	13	36	C	0	0	C	0	0	C	GF = KL < GV
EC/f	16.9	-51	D	8.7	-9	D	6.4	38	C	KL < GF < GV
EC/l	15.6	-42	D	8.1	-28	D	6.1	11	C	KL < GF < GV
SO ₄	620	-58	D	277	-45	D	130	-22	C	KL < GF < GV
Al	89	-46	D	24	-57	D until 82	2.7	-32	Max 82	KL < GF < GV
Ca	158	-58	D	82	-68	D until 82	70	10	C	KL < GF < GV
K	50	-69	D	41	-17	D	35	-49	Max 80-82	KL < GF < GV
NH ₄	173	67	I since 82	99	78	I since 82	41	19	C	KL < GF < GV

NH ₄ /(NH ₄ + NO ₃)	0.97	54	I	0.88	56	Min 81	0.97	40	Min 80-82	KL > GF < GV
Mg	143	-64	D	67	-85	D	69	-14	C	KL = GF < GV

^a Classified according to ranking of sampling stations in last column.

^b Calculated from quarterly observations from 790815-850212 in Goorven and Gerritsfles and from 810506-850212 in Kliplo.

^c Spearman rank correlation coefficient (x 100) with time, calculated over the same period as the mean.

^d Trend since 1979.

process in the humic moorland pools in the province of Drenthe (Baas Becking & Nicolai 1934).

The chemistry of both Goorven and Gerritsfles is strongly influenced by the occurrence of extremely dry years like 1976 when respectively c. 75 and 50% of the bottom area of these pools was exposed to the atmosphere. The reduced S compounds, that were accumulated in the bottom because of the high S load in the decades before, oxidized and H_2SO_4 was formed, which gave rise to high SO_4 concentrations during refilling. After the drought-induced peaks the SO_4 concentrations gradually declined due to dilution with precipitation water and SO_4 reduction, generating alkalinity. The SO_4 concentrations may be higher at Goorven than at Gerritsfles because of the larger proportion of desiccated bottom. After a drop from 1977 onwards the SO_4 concentration stabilized in 1980 in the Gerritsfles and as late as 1982 in the Goorven pool. The cations Al, Ca, Mg, Na and K have a similar pattern through time as SO_4 and are known to be weathered at increasing rates from watersheds exposed to acidification (see Schnoor & Stumm 1985 for a review) and released from sediments of acidifying lakes by cation exchange (Oliver & Kelso 1983, Baker et al. 1985). Vangenechten et al. (1981) observed a similar pattern in the changes of major solutes in Belgian moorland pools during refilling after the drought of 1976. Also in 1960, after the drought of 1959, the Ca and Mg levels in Gerritsfles were as high as in 1977 (Microfiche) and the inferred SO_4 concentration was also similar to that of 1977 (Table 6.20).

Both colour and potassium permanganate consumption, associated with the presence of dissolved organic matter, were very low during the first years after the drought of 1976, but increased after c. 1981, indicating an increasing decomposition of organic material from the sediment with increasing pH (Fig. 5.3).

The NH_4 concentration increased in the pools at Gerritsfles and Goorven since 1982 (Fig. 5.3). Nevertheless the concentration of inorganic N (NO_3 and NH_4) in the pools is still considerably lower than would be expected from the composition of the precipitation (Table 6.1). Moreover nearly all N is present as NH_4 (97% in Goorven and 88% in Gerritsfles, Table 6.21), while in the precipitation c. 65% is present as NH_4 (Table 6.1). Removal of nitrogen may occur through assimilation or through nitrification of NH_4 and subsequent denitrification. Like SO_4 reduction, nitrification proceeds optimally in neutral or alkaline environments. Nevertheless, nitrification has been reported to occur in very acid (pH < 4) environments (Focht & Verstraete 1977, Van Breemen et al. 1982). Also denitrification is possible at low pH values when enough organic material is present (Focht & Verstraete 1977, Hemond 1983).

The aquatic macrophytes probably play an important role in the nitrogen economy of moorland pools. As has been described in section 2.5.4 peat mosses and particularly *Juncus bulbosus* developed explosively in Goorven and Gerritsfles after the drought of 1976 and gradually declined again after 1978. As *J. bulbosus* and some *Sphagnum* species are able to metabolize ammonium (Schuurkes et al. 1986), the increase of ammonium in Goorven and Gerritsfles may partly be due to the decline of *J. bulbosus*.

6.4.3 Long-term changes in poolwater composition

Chemical data for the Goorven, Gerritsfles and Kliplo pools for the period 1919-1985 are presented on Microfiche. Only for pH sufficient data are available for a statistical comparison of the different periods. The results, given in Table 6.19 show that for all four stations in the Goorven pool, pH dropped significantly from 1930-1939 to 1978-1985. A significant decrease in pH also occurred between the periods 1919-1930 and 1950-1960 at Gerritsfles and 1919-1930 and 1970-1976 at Kliplo. The pH-drop is largest at Goorven (2.1 and 1.8 at stations B and E, respectively) and smallest at Kliplo (0.8). Gerritsfles is intermediate with a decline of 1.2 units. The presented data indicate acidification of the Goorven, Gerritsfles and Kliplo pools over the last sixty years, although the absolute pH decrease is uncertain because pH measurement before 1965 were made with colorimetric methods.

For other chemical parameters too few data are available for statistical analysis. From Goorven station B (Microfiche) a sample is available from November 1919 (taken under a thin layer of ice). Iron, Mn, NH_4 and P are present in much lower concentrations than in any of the recent samples. However, these differences may be caused by less sensitive detection methods in the past, especially for the latter two solutes. Alkalinity was $149 \text{ mmol}_c \cdot \text{m}^{-3}$ in the old sample and zero in each of the recent samples. Sulphate increased considerably from $208 \text{ mmol}_c \cdot \text{m}^{-3}$ in 1919, to $458 \text{ mmol}_c \cdot \text{m}^{-3}$ in 1975 and $729\text{-}1645 \text{ mmol}_c \cdot \text{m}^{-3}$ in 1979-85.

Table 6.20 summarizes selected chemical parameters of Gerritsfles. Field pH decreased significantly over the last 60 years but in contrast lab pH has not changed significantly. The single measurements of NH_4 in 1925 and 1930 were much lower than the average value in 1979-85, but in the latter period single measurements with similar low values as in 1925 and 1930 commonly occurred (Microfiche). Therefore the occurrence of a significant change in the concentration of NH_4 cannot be assessed. The Cl concentration decreased significantly ($P < 0.01$, Wilcoxon two-sample test) between the periods 1925-1950 and 1960-1985 at Gerritsfles. This may be caused by the change of the brackish Zuiderzee into the freshwater lake IJsselmeer in 1932, which probably caused a decline of the Cl concentration in precipitation at Gerritsfles. The SO_4 concentration in 1979-1985 is similar to that in 1925 and 1930. The peaks in 1960 and 1977-1978 are due to the extremely dry years 1959 and 1976.

Apart from the changes in field pH (Table 6.19) no long-term changes are apparent at Kliplo (Microfiche). The peaks of total P and H_2PO_4 are probably caused by differences in analytical methods. The high values of Cl (max. $818 \text{ mmol} \cdot \text{m}^{-3}$) in the extremely dry summer of 1976 (mean 1981-1985: $323 \text{ mmol} \cdot \text{m}^{-3}$) are due to concentration by evaporation.

7 Atmospheric deposition: Variation and origin

The following section consists of two parts: a descriptive part which focuses on the spatial and temporal variation in precipitation amount and composition, and an analytical part which focuses on the origin of solutes in precipitation and the relative importance of wet deposition, dry deposition and canopy leaching. Only data collected before March 1985 were used; for the starting dates at the various sites, see Table 3.4.

7.1 Comparison of bulk and throughfall plus stemflow fluxes

Annual bulk and throughfall plus stemflow fluxes, as well as their four-year means are given in Table 7.1. For all solutes throughfall plus stemflow fluxes are considerably higher than bulk deposition fluxes, except for H. Table 7.2 gives the deposition ratios (DR) of throughfall plus stemflow deposition relative to bulk deposition (Parker 1983). DR values range from c. 2 to 5 for most solutes but are 0.97 for H and 14 for K. The high DR values may be a result of leaching or of additional dry deposition in the forest canopy.

Deposition ratios were compared to literature values for *Pinus sylvestris* stands (Table 7.2; Parker 1983). Values for Na, Mg, Cl and Ca are well within the range found in literature. For NO_3 the DR is near the maximum value found in literature, and for K it is somewhat above this value. For SO_4 and NH_4 DR is appreciably higher than the maximum value reported in the literature (4.2 vs. 3.1 and 5.0 vs. 3.0, respectively). The literature maximum of 3.0 for NH_4 is due to a single value attributed to nearby cattle grazing (Horntvedt & Joranger 1974); excluding this values gives a maximum of 0.7. The high DR value for NH_4 is undoubtedly due to high NH_4 deposition, which in turn is related to the high ammonia emission in The Netherlands (Buijsman et al. 1985). The high value for SO_4 is probably caused by a combination of high atmospheric SO_2 concentrations and a high deposition velocity as a result of $(\text{NH}_4)_2\text{SO}_4$ formation (see 7.3.5). In contrast to what is generally observed (cf. Parker 1983), throughfall pH values at our sites are higher than those in bulk precipitation. Acid neutralization in tree canopies at our sites is probably related to the high deposition of NH_3 , which is converted to NH_4^+ on the leaf surface.

Table 7.1. Mean annual bulk and throughfall + stemflow pH and water and solute fluxes for the four research sites. pH values are corrected and flux weighted means. Water in $\text{mm} \cdot \text{y}^{-1}$, ions in $\text{kmol}_c \cdot \text{ha} \cdot \text{y}^{-1}$, — = no data.

Site	Year	Water	pH	H	K	Na	Ca	Mg	Zn	NH ₄	Cl	NO ₃	SO ₄	F
Bulk deposition fluxes														
TV	81	826	4.33	0.47	0.029	0.49	0.16	0.11	0.009	0.75	0.59	0.39	0.98	0.025
	82	687	4.41	0.32	0.036	0.31	0.20	0.08	0.007	0.85	0.41	0.37	0.94	0.016
	83	777	4.59	0.23	0.038	0.53	0.22	0.12	0.006	0.78	0.64	0.34	0.93	0.016
	84	843	4.48	0.31	0.036	0.43	0.12	0.11	0.005	0.85	0.54	0.39	0.91	0.015
	mean	783	4.44	0.33	0.035	0.44	0.17	0.11	0.006	0.81	0.54	0.37	0.94	0.018
GF	81	—	—	—	—	—	—	—	—	—	—	—	—	—
	82	557	4.49	0.24	0.026	0.43	0.17	0.11	0.005	0.67	0.55	0.34	0.74	0.011
	83	986	4.56	0.30	0.035	0.72	0.18	0.17	0.004	0.88	0.86	0.45	0.97	0.013
	84	878	4.44	0.37	0.034	0.50	0.13	0.12	0.006	0.74	0.63	0.44	0.84	0.015
	mean	814	4.50	0.31	0.032	0.55	0.16	0.13	0.005	0.77	0.68	0.41	0.85	0.013
KL	81	—	—	—	—	—	—	—	—	—	—	—	—	—
	82	659	4.43	0.31	0.025	0.48	0.16	0.11	0.004	0.71	0.61	0.40	0.77	0.007
	83	945	4.56	0.27	0.034	0.72	0.16	0.16	0.004	0.75	0.86	0.41	0.82	0.010
	84	854	4.50	0.31	0.039	0.61	0.15	0.14	0.004	0.69	0.73	0.39	0.82	0.011
	mean	824	4.50	0.29	0.033	0.60	0.16	0.14	0.004	0.71	0.74	0.40	0.81	0.009
Canopy generated fluxes														
TVA	81	—	—	—	—	—	—	—	—	—	—	—	—	—
	82	—	—	—	—	—	—	—	—	—	—	—	—	—
	83	458	4.47	0.19	1.058	0.99	0.52	0.31	0.010	4.77	1.50	0.83	4.34	0.067
	84	560	4.96	0.12	0.639	0.93	0.41	0.31	0.018	4.15	1.27	0.40	3.69	0.050
	mean	513	4.68	0.15	0.839	0.96	0.46	0.31	0.014	4.45	1.38	0.61	4.00	0.058
TVB	81	804	4.42	0.43	0.389	1.35	0.49	0.39	0.023	3.72	1.68	0.91	3.91	0.085
	82	674	4.68	0.22	0.341	0.90	0.47	0.26	0.023	3.94	1.14	0.91	3.72	0.072
	83	773	4.84	0.15	0.421	1.44	0.49	0.36	0.015	3.74	1.79	0.92	3.53	0.068
	84	895	4.57	0.33	0.290	3.65	0.58	0.86	0.020	3.74	4.70	0.50	4.15	0.062
	mean	754	4.60	0.27	0.380	1.29	0.49	0.35	0.020	3.80	1.62	0.90	3.73	0.075
GF	81	—	—	—	—	—	—	—	—	—	—	—	—	—
	82	441	4.43	0.33	0.425	1.28	0.51	0.37	0.010	3.85	1.75	1.08	3.67	0.062
	83	719	4.47	0.40	0.606	2.16	0.54	0.54	0.009	4.58	2.81	1.40	4.16	0.089
	84	659	4.48	0.35	0.446	1.75	0.51	0.49	0.009	3.76	2.24	0.87	3.57	0.065
	mean	611	4.46	0.36	0.494	1.74	0.52	0.47	0.009	4.07	2.28	1.12	3.81	0.072
KL	81	—	—	—	—	—	—	—	—	—	—	—	—	—
	82	458	4.56	0.28	0.374	1.33	0.38	0.36	0.006	3.53	1.76	1.01	3.10	0.033
	83	759	4.60	0.33	0.459	2.35	0.37	0.49	0.006	3.98	2.99	1.27	3.48	0.047
	84	715	4.64	0.30	0.464	2.13	0.51	0.58	0.006	3.81	2.47	0.71	3.85	0.046
	mean	650	4.61	0.30	0.434	1.96	0.42	0.48	0.006	3.78	2.42	1.00	3.48	0.042

Table 7.2. Mean deposition ratios (DR = throughfall plus stemflow flux divided by bulk deposition flux) over the period January 1981 (Tongbersven B) or February 1982 (Gerritsfles and Kliplo) up to February 1985, compared to the range found in literature for *Pinus sylvestris*.

Component	DR	DR (lit)
water	0.83	
H	0.97	
K	14.3	0.9-13.6
Na	3.2	1.7-6.1
Ca	2.9	1.6-5.4
Mg	3.6	1.3-7.7
Zn	2.2	
NH ₄	5.0	0.2-0.7 (3.0 ^a)
Cl	3.3	1.7-5.8
NO ₃	2.6	0.4-2.9
SO ₄	4.2	1.0-3.1
F	4.5	

^a High value attributed to contamination.

7.2 Spatial and temporal variation

Solute fluxes found in throughfall plus stemflow are generally 20-100% higher in this study compared to those reported over the same period for two deciduous forest stands in the Netherlands: oak/beechn forest at 'Tenkink' (Duysings et al. 1989), and oak/birch forest at 'Oude Maat' (Van Breemen et al. 1988). For K, however, fluxes found at 'Tenkink' and 'Oude Maat' are slightly higher than those reported here, and for NO₃ and Ca there is little difference. The differences can be explained from a higher aerosol capture efficiency of coniferous forest (for NH₄ and SO₄), and a smaller distance to the coast of our sites (for Na, Mg and Cl).

Bulk deposition and throughfall fluxes measured by Houdijk & Roelofs (1988) in mixed stands of *Pinus sylvestris*, *P. nigra* and *Pseudotsuga mensiesii* are c. 10-30% higher than those reported here for Ca, NH₄ and SO₄. For K in throughfall and for H, Na, Mg and NO₃ in both bulk flux and throughfall there is no systematic difference, but for K the bulk flux reported by Houdijk is c. 7 times the value reported here. The latter difference is probably due to a different sampling or analytical procedure, while the other differences are due to differences in tree species, position of the samplers or measuring period.

7.2.1 Comparison of samplers at Kliplo

At Kliplo samplers KL2 and KL3 were located close to a tree stem, KL4 under a canopy of intermediate density and KL5 in a more or less 'open' space between trees. KL6 collected stemflow of a slender tree (d.b.h. 15 cm) and KL7 of a thick tree (d.b.h. 34 cm; KL2 and KL3 were close to this tree; Fig. 3.4).

The throughfall samplers yield a lower water flux than the bulk deposition samplers due to interception and evaporation (Table 7.3), but there is a significant ($P < 0.05$) linear correlation between throughfall flux and bulk precipitation flux (Fig. 7.1). The largest interception is found for the 'open space' sampler KL5, which may be due to windshelter. Stemflow starts at a monthly precipitation intensity of c. 40 mm·month⁻¹, and is also significantly correlated with bulk precipitation flux, although with a lower correlation coefficient (Fig. 7.1). The stemflow amount (in mm·month⁻¹) is only c. 1% of the bulk precipitation amount.

Concentrations vary strongly among the samplers. The mean ratio of throughfall or stemflow concentration relative to bulk concentration (Parker 1983) for SO₄ over the complete measuring period varies from 1.6 to 15.2 in throughfall and from 17 to 22 in stemflow. The 'openspace' sampler KL5 yields values nearest to those in bulk precipitation and the 'near-stem' sampler KL3 yields the highest concentrations. There is no clear relationship between water flux and solute concentration (Fig. 7.2). Like concentration ratio, deposition ratios also show a considerable variation among the samplers (Table 7.3). For SO₄ DR values vary from 1.0 to 12.5 in throughfall and from 0.13 to 0.32 in stemflow.

The relative importance of throughfall and stemflow fluxes compared to bulk depo-

Table 7.3. Mean bulk precipitation amount (mm·y⁻¹) over the period February 1982 to February 1985 at Kliplo, together with concentration (mmol_c·m⁻³) and flux (kmol_c·ha·y⁻¹) of SO₄, K and Cl in bulk deposition. In addition, deposition (DR) and concentration ratios (CR) relative to bulk deposition are given for the individual throughfall and stemflow samplers.

		Water	SO ₄		K		Cl	
			conc	flux	conc	flux	conc	flux
KL1	bulk	804	98	0.79	4	0.03	89	0.72
		DR	CR	DR	CR	DR	CR	DR
KL2	throughfall	0.75	4.5	3.3	16.5	12.3	4.2	3.2
KL3	throughfall	0.82	15.2	12.5	30.8	25.3	8.7	7.2
KL4	throughfall	0.90	3.0	2.7	15.6	14.0	2.7	2.4
KL5	throughfall	0.65	1.6	1.0	7.0	4.5	1.6	1.0
KL6	stemflow	0.01	21.9	0.3	46.4	0.7	14.1	0.2
KL7	stemflow	0.01	16.5	0.1	32.9	0.3	7.4	0.1

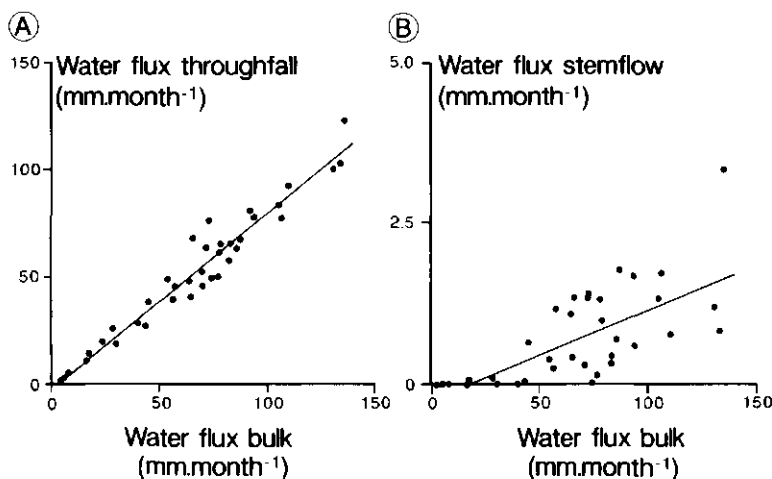


Figure 7.1. Kliplo, relation between throughfall (a) and stemflow (b) flux, and bulk precipitation flux.

Regression equations:

throughfall = $-2.9 + 0.82 \cdot \text{bulk}$, $r = 0.97$; $P < 0.05$

stemflow = $-0.26 + 0.014 \cdot \text{bulk}$, $r = 0.67$; $P < 0.05$.

Data are from February 1982 to Februari 1985.

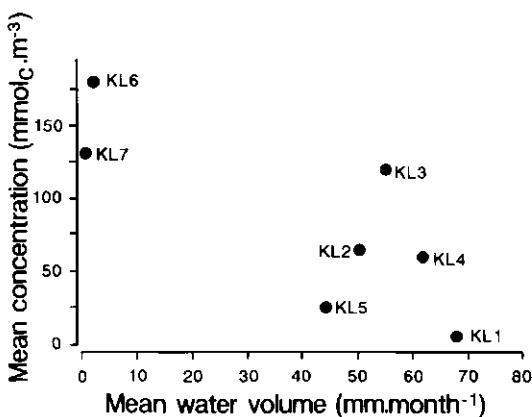


Figure 7.2. Kliplo, mean concentration of K vs. mean water flux:

KL1: bulk sampler

KL2 to KL5: throughfall samplers

KL6 and KL7: stemflow samplers

Data from February 1982 to Februari 1985.

sition fluxes is indicated for the major solutes in Table 7.4. In spite of the high concentrations, solute fluxes in stemflow are low because of the small water flux, so that the contribution of stemflow to total input flux into the soil is small. Throughfall fluxes are several times higher than bulk deposition fluxes for all major solutes except H and

Table 7.4. Mean water ($\text{mm} \cdot \text{y}^{-1}$) and solute ($\text{kmol}_e \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$) fluxes in bulk deposition at Kliplo over the period February 1982 to February 1985 at Kliplo, together with deposition ratios (DR) in stemflow and throughfall.

	Water	H	K	Na	Ca	Mg	Zn	NH ₄	Cl	NO ₃	SO ₄	PO ₄	F
bulk	804.5	0.28	0.032	0.59	0.15	0.13	0.004	0.70	0.72	0.39	0.79	0.006	0.010
DR thr	0.8	1.1	14.1	3.5	3.0	3.8	1.7	5.7	3.4	2.5	4.8	0.7	4.8
DR stem	0.01	0.09	0.03	0.04	0.03	0.02	0.02	0.04	0.04	0.03	0.05	0.01	0.04

PO₄. Because solute fluxes in throughfall vary over a short distance depending on the position relative to the trees, reliable estimates of throughfall fluxes can only be obtained from a large number of samplers, certainly more than the 2-6 used in this project. Therefore the calculated meteoric solute fluxes should be considered as first estimates. The mean coefficient of variation over the four throughfall samplers for the monthly flux of SO₄ is 76%. When the values from the four samplers are considered as random samples the estimated CV of the mean is $76/(\sqrt{4}) = 38\%$. To bring this CV back to an acceptable level of 10%, 58 samplers would be needed. With the gutter samplers the variation is probably less. Comparable results were obtained by Duysings et al. (1986) in oak/beechn forest.

For most solutes throughfall plus stemflow fluxes appear to be significantly ($P < 0.05$) correlated with the corresponding bulk fluxes. The correlation is strongest for the throughfall sampler KL5, which yields concentrations closest to those in bulk deposition, and for the biologically inactive Cl.

7.2.2 Comparison of funnel and gutter samplers at Gerritsfles

At Gerritsfles the gutter samplers GF5 and GF6 were placed c. 5 m from the funnel samplers GF2 and GF3, respectively. For none of the solutes the fluxes estimated with funnel and gutter samplers differ significantly at the 95% confidence level, although for most solutes the gutters yield somewhat lower values than the funnels (Table 7.5).

For Zn and PO₄ the fluxes found in the gutters are appreciably higher than in the funnels, which may attributed to contamination from the PVC material and from biotic sources, respectively. The water capture efficiency is almost equal for the two sampler types.

Table 7.5. Mean gutter/funnel ratios for throughfall at Gerritsfles, for two gutter/funnel pairs. Numbers of observations are 15 (pair 1) and 8 (pair 2).

	Water	pH	H	K	Na	Ca	Mg	Zn	NH ₄	Cl	NO ₃	SO ₄	PO ₄	F
pair 1	0.95	0.98	0.88	0.66	0.68	0.79	0.70	2.82	0.76	0.70	0.78	0.73	4.03	0.79
pair 2	1.03	1.02	0.30	1.02	0.97	0.99	0.94	2.07	0.90	0.96	0.89	0.87	3.64	0.96

7.2.3 Spatial and temporal variation of mean fluxes

In this and the following sections canopy generated fluxes refer to net fluxes generated in the canopy, i.e. throughfall plus stemflow fluxes minus the fluxes in bulk precipitation. Spatial and temporal variation in bulk and canopy generated fluxes of all solutes at Tongbersven B, Gerritsfles and Kliplo were analysed by means of analysis of variance. Data from March 1982 to February 1984 were used to detect seasonal variation, spatial variation and their interaction. Data from January 1981 to December 1983 (for Tongbersven B) and from March 1982 to February 1985 (for Gerritsfles and Kliplo) were used to detect year-to-year variation. Results are summarized in Tables 7.6 and 7.7.

In bulk flux spatial variation between TVB, GF and KL is small; significant ($P < 0.05$) differences were only found for Zn and F. In canopy generated fluxes there are also significant differences for Zn and F, and in addition for the sea-spray ions Na, Cl and Mg. No significant differences were found for NH_4 , SO_4 and NO_3 .

The differences in Zn and F are probably caused by industrial emissions in the Southern part of The Netherlands (Budel), Belgium and Germany, causing a decrease in flux from South to North. Differences in the sea-spray ions Na, Cl and Mg are probably related to differences in distance to the coast, causing a decrease in the order KL, GF, TVB (from north-west to south-east). Differences in NH_4 flux, though too small to be significant, may be caused by differences in local ammonia emission. This may also be the case with SO_4 , of which the deposition is enhanced by atmospheric ammonia as a result of formation of $(\text{NH}_4)_2\text{SO}_4$ (see section 7.3.5).

In bulk flux a significant ($P < 0.05$) seasonal variation exists for the sea-spray ions,

Table 7.6. Mean bulk and canopy generated fluxes over the period March 1982 to February 1985 for the Tongbersven B (TVB), Gerritsfles (GF) and Kliplo (KL) sites, in $\text{mm} \cdot \text{y}^{-1}$ (water) and $\text{kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ (solute). Canopy generated fluxes are (throughfall + stemflow - bulk deposition) except for water which is (throughfall + stemflow). Different letters indicate significant differences between the stations according to the standard errors of difference ($P < 0.05$). In brackets: effect close to significance ($0.05 < P < 0.1$)

Site	water	H	K	Na	Ca	Mg	Zn	NH_4	Cl	NO_3	SO_4	F
Bulk deposition fluxes												
TVB	754.5a	0.24a	0.038a	0.49a	0.21a	0.12a	0.006a	0.81a	0.61a	0.36a	0.94a	0.016a
GF	812.2a	0.23a	0.032a	0.64a	0.17a	0.15a	0.005ab	0.79a	0.79a	0.40a	0.87a	0.012ab
KL	842.8a	0.26a	0.031a	0.69a	0.16a	0.15a	0.004b	0.73a	0.86a	0.41a	0.81a	0.009b
Canopy generated fluxes												
TVB	730.4a	0.12a	0.374a	1.26(a)	0.48a	0.32a	0.017a	3.74a	1.59(a)	0.91a	3.50a	0.069a
GF	619.7a	0.22a	0.521a	1.95(b)	0.54b	0.50b	0.010b	4.28a	2.57(b)	1.23a	4.01a	0.077a
KL	652.9a	0.16a	0.416a	2.03(b)	0.38a	0.47b	0.006c	3.72a	2.61(b)	1.12a	3.29a	0.040b

Table 7.7. Summer (April through September) and winter (October through March) fluxes over the period March 1982 to February 1985; mean of Tongbersven B, Gerritsfles and Kliplo, in $\text{mm} \cdot \text{y}^{-1}$ (water) and $\text{kmol}_e \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ (solutes). Different letters indicate significant differences ($P < 0.05$).

Season	water	H	K	Na	Ca	Mg	Zn	NH ₄	Cl	NO ₃	SO ₄	F
Bulk deposition fluxes												
winter	893.9a	0.20a	0.033a	0.88a	0.16a	0.20a	0.005a	0.80a	1.09a	0.36a	0.90a	0.013a
summer	712.4a	0.29a	0.035a	0.34b	0.20a	0.08b	0.005a	0.75a	0.41b	0.42a	0.85a	0.011a
Canopy generated fluxes												
winter	725.8a	0.23a	0.386a	2.56a	0.53a	0.61a	0.012a	4.78a	3.29a	0.93a	4.77a	0.076a
summer	609.4a	0.10b	0.489a	0.96b	0.41b	0.27b	0.010b	3.07b	1.27b	1.25b	2.47b	0.048b

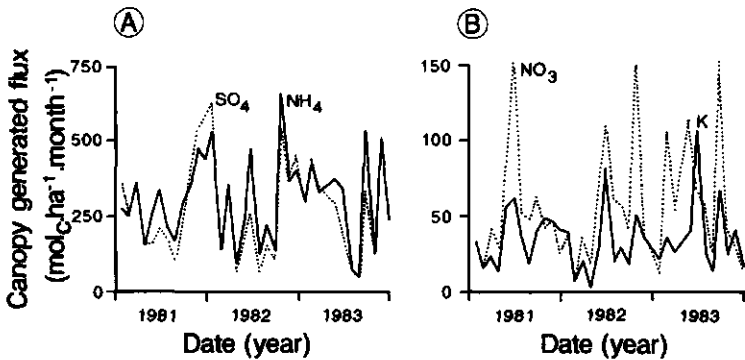


Figure 7.3. Temporal variation in canopy generated flux of (a) SO₄ and NH₄, and (b) NO₃ and K at Tongbersven B.

in canopy generated flux for all solutes except K. All solutes with a significant seasonal variation show a higher flux in winter than in summer both in bulk and canopy generated flux, with the exception of the canopy generated NO₃ flux where the reverse is true. The canopy generated flux of K is also higher in summer than in winter but the difference is not significant.

Higher fluxes in winter may be caused by (a) a higher rate of sea-spray formation in winter due to often strong westerly winds (Na, Mg, Cl), and (b) higher emission rates of NH₄ and SO₄ in winter. In summer the canopy generated flux of NO₃ may increase due to a higher oxidation rate of NH₄ in summer (see 7.3.6), whereas the canopy generated K flux may increase due to a higher rate of leaching during the growing season. There are no obvious explanations for the seasonal differences in canopy generated flux of H, Zn and F.

Significant year-to-year differences in flux were found in a few cases only, and these

were invariably caused by an extreme value in one year: precipitation amount, very low at Gerritsfles in 1982; H, very high at Tongbersven B (canopy generated) in 1981; and F, very high at Tongbersven (bulk) in 1981. In the relatively short observation period annual trends in fluxes could not be detected. As an example, Fig. 7.3 shows temporal variation in canopy generated flux of SO₄, NH₄, NO₃ and K at Tongbersven B.

7.3 Origin of solutes in bulk and canopy generated fluxes

Generally solute fluxes are not determined by one simple process. Solute may have several sources, and may be transported and deposited in various ways and in various forms. Sulphate, for instance, may originate from sea-spray, from SO₂, or from SO₄ taken up from the soil by the vegetation and subsequently leached from the canopy. Sulphate can be transported as dissolved SO₄, as particulate SO₄ or as gaseous SO₂ or H₂S. Therefore calculation of simple relations between solute concentrations, solute fluxes and water flux (e.g. Ulrich et al. 1979) is generally insufficient to reach conclusions on the origin of the solutes. This is even more so where data, as in the present case, have been collected on a monthly basis. The time-scale of changes in the atmosphere is much shorter than one month, so the data reflect the overall result of deposition under different atmospheric conditions. Therefore the present dataset can only be used to test some simple hypotheses on the origin of solutes. In this section the general relationships between solute and water fluxes are discussed first (7.3.1, 7.3.2 and 7.3.3), followed by a discussion on the origin of a number of individual solutes (7.3.4 to 7.3.6). In 7.3.7 the most likely origins of the solutes in bulk deposition and throughfall plus stemflow deposition are summarized.

7.3.1 Relationship between solute and water fluxes

The flux of nearly all solutes increases with increasing water flux. This relation was described using the following equations

$$S = a + b \cdot W \quad (7.1)$$

and

$$S = a + b \cdot W + c \cdot W^2 \quad (7.2)$$

with:

S solute flux in kmol_c·ha⁻¹·y⁻¹

W water flux in mm·y⁻¹

a, b and c are constants

Results are summarized in Table 7.8, which is based on the minimal model: equation (7.2) when c differs significantly ($P < 0.05$) from zero, else equation (7.1). In the bulk

flux linear relations are satisfactory for all solutes, and in a number of cases the straight line goes through the origin. In canopy generated flux there is a relative decrease at high water flux (c negative) except in the cases of NO_3 (linear), Zn (linear through the origin) and H (no correlation).

For an interpretation of these relations three principal sources of solutes can be considered: wet deposition, dry deposition and leaching. In bulk flux the presence of dry deposition is a possible explanation for the non-zero intercept. However, in the cases where the intercept does not differ significantly from zero dry deposition may also occur if its magnitude is correlated to the magnitude of wet deposition. This can be the case when the atmospheric conditions that give rise to a high level of wet deposition also give rise to a high level of dry deposition. The sea-spray ions Na, Cl and Mg probably have a zero intercept because 'oceanic' weather conditions with strong westerly winds give rise to high levels of both wet and dry deposition. Therefore estimation of dry deposition from the magnitude of the intercept (Miller et al. 1976) may lead to inaccurate results and will not be attempted here.

For canopy generated fluxes second-order relations with water fluxes generally give the best fit (Table 7.8). The relative decrease in deposition at high water flux indicates that depletion of a finite source takes place. Because the wet deposition component has been removed from the canopy generated flux by subtraction, its source either consists of dry deposition, or of easily leachable solutes of biological origin. It is probably not possible to distinguish between these sources on the basis of the relation with water flux. Note that Cl, which is biologically inactive, shows the same type of relationship with water flux as K, which is easily leached from plants.

Table 7.8. Regression coefficients (a, b and c) and percentage variance accounted for (var), for the regression of solute flux on water flux and squared water flux, calculated for the Tongbersven B, Gerritsfles and Kliplo sites over the period March 1982 to February 1985. Values are significant at the 95% confidence level. For details see text. Var = percentage variance accounted for, n.s. = not significant.

	H	K	Na	Ca	Mg	Zn	NH_4	Cl	NO_3	SO_4	F
Bulk deposition fluxes											
$a \cdot 10^2$	n.s.	1.69	n.s.	10.81	n.s.	n.s.	38.12	n.s.	14.44	31.89	0.70
$b \cdot 10^4$	3.63	0.20	6.22	0.66	1.33	0.03	4.74	7.79	3.03	6.83	0.09
$c \cdot 10^7$	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
var	49	18	29	7	31	17	44	30	42	65	22
Canopy generated fluxes											
$a \cdot 10^2$	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	29.15	n.s.	n.s.
$b \cdot 10^4$	n.s.	8.78	28.06	7.14	7.22	0.08	75.72	35.40	4.75	80.43	1.13
$c \cdot 10^7$	n.s.	-3.44	-9.82	-2.78	-2.75	n.s.	-31.37	-12.60	n.s.	-35.95	-0.40
var	0	36	33	29	32	9	40	32	15	35	44

7.3.2 Relationship between solutes in bulk and canopy generated fluxes

Theoretically the relation between bulk and canopy generated flux can be used to distinguish between dry deposition and leaching. A strong correlation between the fluxes of a given solute in bulk and canopy generated deposition indicates a common origin, which is probably the atmosphere. On the other hand, if leaching is an important source for a solute in canopy generated flux, no correlation with bulk flux is expected. However, the fluxes should be corrected for the effect of water flux, which may cause apparent correlations as both bulk and canopy generated flux are correlated with water flux. This was done by using the difference between the actual fluxes, and the values predicted by equations (7.1) and (7.2) (the residual values), instead of the actual fluxes themselves.

The equation

$$\text{canopy generated flux} = a + b \cdot \text{bulk flux} \quad (7.3)$$

with a and b constants

was fitted using values corrected for water flux. Table 7.9 gives the result, and shows that strong positive correlations between the corrected bulk and canopy generated fluxes exist for the sea-spray ions Na, Mg and Cl, and a weaker correlation for NO_3 . Negative correlations are found for Ca and free acid. A negative correlation indicates that buffering takes place in the canopy: when bulk flux is relatively high, canopy generated flux relatively low, and vice versa. For H there is even a net decrease in the canopy due to a strong buffering. A further explanation of these relationships is given in 7.3.7.

7.3.3 Relationship between fluxes of various solutes

Relationships between solute fluxes can be used to gain information on their sources. A strong correlation may indicate that two solutes have the same or related sources, and the spatial and temporal variation in their fluxes may yield some insight into the

Table 7.9. Regression coefficients (b) for the linear regression of canopy generated flux on bulk flux, for the Tongbersven B, Gerritsfle and Kliplo sites over the period March 1982 to February 1985, corrected for the effect of water flux (for details see text). Values for a are never significantly different from zero, values given for b are significant at the 95% confidence level. Var = percentage variance accounted for, n.s. = not significant.

	H	K	Na	Ca	Mg	Zn	NH_4	Cl	NO_3	SO_4	F
$b \cdot 10^2$	-0.7	n.s.	1.1	-0.8	0.9	n.s.	n.s.	1.3	0.9	n.s.	n.s.
var	25	0	38	12	15	0	1	44	7	2	1

nature of that source.

In considering these relations, two major problems arise: (1) all solute fluxes are strongly correlated to water flux, so that corrected fluxes should be used (as in 7.3.2), and (2) the number of two-by-two combinations of solutes is very large, and therefore a simple presentation of the results (e.g. as a correlation matrix) is difficult to interpret. In this study principal component analysis (PCA, based on the correlation matrix) was used to arrive at a more legible presentation of the results. In Figs. 7.4 and 7.5 the loadings of the solute fluxes on the first three axes are plotted against each other, resulting in a diagram in which solutes that are highly correlated are grouped close together.

From the diagrams a strong correlation between the sea-spray ions Na, Mg and Cl

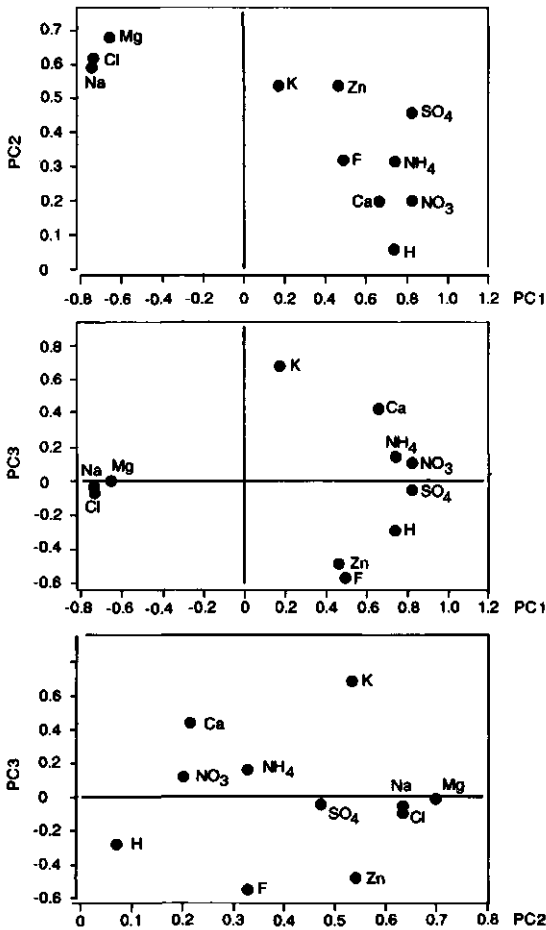


Figure 7.4. PCA of bulk solute fluxes: loadings of the solute fluxes on the first three axes plotted against each other. Percentages variance accounted for by the first three axes: PC1, 43%; PC2, 21 %; PC3, 12%.

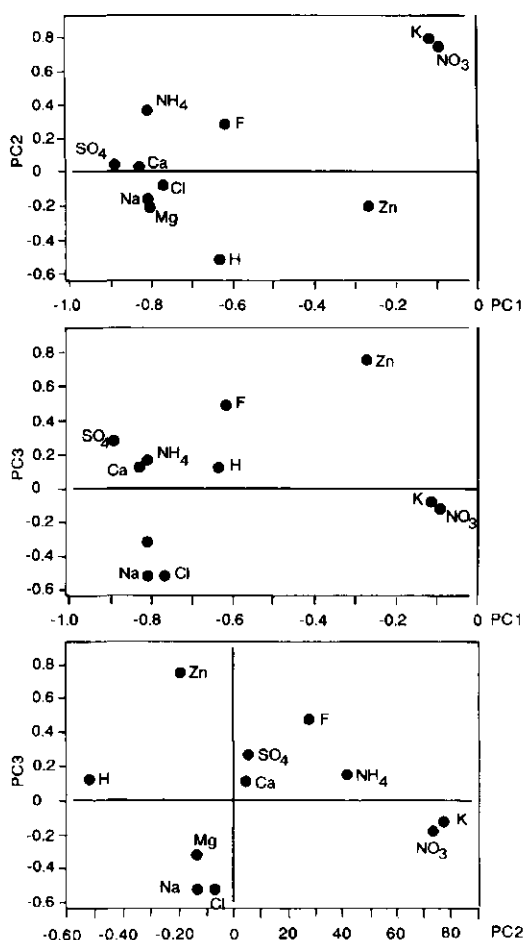


Figure 7.5. PCA of canopy generated solute fluxes: loadings of the solute fluxes on the first three axes plotted against each other Percentages variance accounted for by the first three axes: PC1, 46%; PC2, 17%; PC3, 15%.

becomes evident. In both bulk and canopy generated fluxes their loadings on the first three axes are close to each other. In canopy generated fluxes two more clusters of correlated solutes emerge: (a) NH₄, SO₄ and Ca, and (b) K and NO₃. In bulk flux the correlation between K and NO₃ is absent, whereas a weak correlation exists between NH₄, SO₄ and Ca. In bulk flux, NO₃ is also close to the cluster NH₄, SO₄ and Ca.

To obtain some insight in the cause of these correlations, analysis of variance was used to detect seasonal and geographical variation in the scores of all samples on the first three PCA axes (Table 7.10). The results obtained for canopy generated fluxes are easiest to interpret. PC1 (Fig. 7.5) is related to temporal variation; scores on this axis are low in winter and high in summer. Because the solutes with a strong negative loading on this axis (sea-spray ions) have a higher mean flux near the sea, scores on

Table 7.10. Mean scores on the first three PCA axes of bulk and canopy generated solute fluxes at Tongbersven B, Gerritsfles and Kliplo sites over the period March 1982 to February 1985. Summer is April through September, winter is October through March. For further explanation see text.

Bulk deposition fluxes			
axis	TVB	GF	KL
PC1	0.027	-0.008	-0.029
PC2	(no significant difference)		
PC3	-0.029	0.004	0.033
axis	winter	summer	
PC1	-0.032	0.033	
PC2	0.025	-0.026	
PC3	-0.022	0.023	
Canopy generated fluxes			
axis	TVB	GF	KL
PC1	0.028	-0.032	0.002
PC2	-0.024	0.032	-0.009
PC3	0.075	-0.008	-0.067
axis	winter	summer	
PC1	-0.045	0.049	
PC2	-0.048	0.047	
PC3	(no significant difference)		

this axis also have a significant ($P < 0.05$) geographical variation. Scores on PC2 are high in summer and for Gerritsfles samples, low in winter and for Tongbersven and Kliplo samples. This axis may be related to solute fluxes regulated by biological activity: potassium, which is easily leached from plants (Tukey 1970) has a strong positive loading on this axis, and free acid, which is partly neutralized (taken up) by the trees, has a strong negative loading. The Gerritsfles site differs from the other sites in that the stand is more open, and the trees are older and less vital. This may cause a higher rate of leaching and neutralization. PC3 is related to geographical variation; scores on this axis have no significant temporal variation. Tongbersven samples have

high, Gerritsfles samples intermediate and Kliplo samples low PC3 scores, corresponding to positive loadings of Zn and F and negative loadings of sea-spray ions.

For bulk fluxes the axes results are not so easy to interpret. Scores on PC2 have significant seasonal, but no geographical variation. Scores on PC1 have both geographical and seasonal variation. However, in spite of the significant correlations, scores on the first three axes are probably not primarily determined by geographical variation. Geographical variation would result in high loadings of Zn and F in one direction and high loadings of sea-spray ions in the opposite direction (compare Table 7.6), which is not the case. PC2 is probably related to season (winter high, summer low). The sea-spray ions have high positive loadings on this axis and the loading of free acid (with highest flux in summer) is about zero. PC1 may be related to weather conditions. Solutes with a high negative loading on this axis are of sea-spray origin, whereas ions with a high positive loading are of continental (Ca) or anthropogenic (NH_4 , SO_4) origin. An interpretation of PC3 could not be found.

7.3.4 Sea-spray origin of Na, Mg, Cl, K, Ca, and SO_4

If sea-spray is a major source of solutes, solute flux ratios are expected to be similar to the concentration ratios in seawater. For Cl a pure sea-spray origin was assumed. Although Cl may be partly of anthropogenic origin, it was used as a tracer for sea-spray rather than Na because Cl is biologically and chemically more conservative. If Cl completely originates from sea-spray, the flux of any solute that partly originates from sea-spray should be positively correlated with Cl flux, with a regression coefficient equal to the concentration ratio in sea-water. Parameters for the regression equation

$$\text{FLUX}(\text{component}) = a + b \cdot \text{FLUX}(\text{Chloride}) \quad (7.4)$$

with a and b constants

were calculated, and the results are given in Table 7.11. For Na and Mg in both bulk and canopy generated fluxes the percentage of variance accounted for is high and the regression coefficients are nearly equal to the concentration ratios in sea-water. For Na the intercept does not differ significantly from zero, for Mg it does but its contribution is small compared to that of the second term. For most other solutes, however, there are larger discrepancies. Only for SO_4 in bulk flux the sea-water concentration ratio is within the 95% confidence limit of the regression coefficient; for canopy-generated K this is nearly the case.

For Ca in bulk flux the regression coefficient is negative. This suggests soil-dust as an additional source for Ca, assuming that continental weather conditions give rise to a high flux of Ca, whereas oceanic conditions give rise to a high flux of Cl. Soil dust was also assumed as a source for Ca by Duysings et al. (1989). The low value of the regression coefficient for K (c. 25% of the value expected on the basis of a sea-spray

Table 7.11. Intercept (a), regression coefficient (b) and percentage of variance accounted for (var), for equation (7.4).

ratio = ratio between b and (concentration of component in seawater divided by concentration of chloride in seawater)

contr = estimated mean contribution of sea-spray to total deposition (in %), calculated as $b \cdot (\text{mean deposition of chloride}) / (\text{mean deposition of component})$

For a, b and ratio 95% confidence limits are given. Data used are from the Tongbersven B, Gerritsfles and Kliplo sites over the period March 1982 to February 1985.

Component	a · 10 ²	b	var	ratio	contr
Bulk deposition fluxes					
Na	-0.37-1.43	0.80-0.82	99	0.93-0.95	99
Mg	1.30-2.69	0.15-0.17	93	0.79-0.87	84
K	2.12-3.06	0.00-0.02	9	0.12-0.41	20
Ca	15.08-20.16	-0.06-0.00	2	-2.92-0.15	0
SO ₄	64.99-83.03	0.08-0.29	8	0.76-2.77	14
Canopy generated fluxes					
Na	-3.99-5.89	0.75-0.80	97	0.87-0.93	99
Mg	4.72-12.64	0.13-0.18	66	0.69-0.91	72
K	21.26-35.50	0.05-0.12	6	1.19-3.20	30
Ca	7.53-17.85	0.10-0.16	45	5.43-8.35	60
SO ₄	74.40-169.60	0.90-1.41	43	8.74-13.71	58

origin) can probably be explained from a partial soil-dust origin as well. Remarkable are the extremely high values found for the regression coefficients of Ca and SO₄ in canopy generated flux (c. 7 and c. 11 times the expected value, respectively).

These ions are less soluble than Na, Mg and Cl, especially when SO₄ concentrations are high as a result of anthropogenic emission, and a fractioning of sea-spray aerosol after its formation might take place, resulting in a longer residence time in the atmosphere for Ca and SO₄.

7.3.5 Sulphate from (NH₄)₂SO₄, SO₂ and sea-spray

To obtain more information about the origin of SO₄, its bulk and canopy generated fluxes were compared to (1) atmospheric SO₂ concentration, (2) fluxes of NH₄, and (3) fluxes of two indicators for sea-spray, Ca and Cl. Sulphur dioxide concentrations used are monthly mean values from the nearest measuring sites of the Dutch National Air Pollution Survey: Hoogersmilde (8 km from Kliplo), Loenen (14 km from Gerritsfles) and Helvoirt (8 km from Tongbersven). Parameters were estimated for the regression of SO₄ flux on SO₂ concentration, water flux, squared water flux, fluxes of

NH₄, Cl and Ca, and the product of SO₂ concentration and NH₄ flux. For each parameter the significance was tested by means of Student's t-test. Terms with no significant ($P < 0.05$) contribution were omitted and the regression equations were recalculated. It was checked whether this did not lead to a strong decrease in percentage of variance accounted for, which indicates that low t-values are a result of mutually correlated variables. The resulting regression equations are:

bulk flux:

$$\text{SO}_4 = 0.0168 + 0.56 \cdot \text{NH}_4 + 0.78 \cdot \text{Ca} + 0.0004 \cdot W \quad (7.5)$$

(87% variance accounted for)

canopy generated flux:

$$\text{SO}_4 = -0.66 + 0.75 \cdot \text{NH}_4 + 1.87 \cdot \text{Ca} + 0.0328 \cdot \text{SO}_2 \quad (7.6)$$

(91% of variance accounted for)

or

$$\text{SO}_4 = -0.19 + 0.61 \cdot \text{NH}_4 + 1.74 \cdot \text{Ca} + 0.01 \cdot (\text{NH}_4 \cdot \text{SO}_2) \quad (7.7)$$

(92% of variance accounted for)

with:

SO₄, NH₄, Ca fluxes in kmol_c·ha⁻¹·y⁻¹

SO₂ concentration in μg·m⁻³

W water flux in mm·y⁻¹

For all parameters $P < 0.001$. Addition of variables previously deleted did not improve the fit significantly.

A significant ($P < 0.05$) correlation existed between atmospheric SO₂ concentration and SO₄ flux in canopy generated flux. In bulk flux no such correlation was found. Moreover, the significant contribution of water flux to SO₄ flux found in bulk flux was absent in canopy generated flux. This indicates that canopy generated SO₄ fluxes are primarily derived from dry-deposited SO₂, whereas SO₄ in bulk flux primarily originates from wet deposition. In bulk flux and in canopy generated flux there was a positive correlation between SO₄ and NH₄, indicating an enhanced deposition of SO₂ in the presence of NH₃. A significant contribution of the Ca term was also found in both cases. The parameter estimates for the Ca term are near to one for all equations (bulk flux: 0.78 ± 0.29 , canopy generated flux: 1.86 ± 0.87 or 1.74 ± 0.82). There are two possible explanations for this CaSO₄ deposition: (a) CaSO₄ originates from soil-dust and SO₂; dry deposition of SO₂ may be enhanced by a neutralizing effect of soil-dust (like for NH₃); and (b) CaSO₄ originates from sea-spray; because of its

lower solubility it is transported over longer distances than Na, Mg and Cl (see 7.3.4). If the latter is the case, the contribution of sea-spray to SO_4 deposition (estimated as the contribution of the Ca-term using the overall mean values for the variables) can be calculated as 15% for bulk and 19 to 21% for canopy generated flux. For bulk flux this is nearly the same value as calculated in 7.3.4 (Table 7.11) but for canopy generated flux there is an unexplained discrepancy.

In canopy generated flux there is a strong interaction between SO_2 and NH_4 , indicating a dependence of the deposition velocity of SO_2 on the concentration of NH_3 , a phenomenon that has also been noted by Buijsman et al. (1984) and Adema et al. (1986). Assuming sea-spray as the source for CaSO_4 , the sum of the terms for NH_4 , SO_2 and their interaction in equations (7.5) to (7.7) can be considered as an estimate for the contribution of SO_2 to total SO_4 deposition, and thus the deposition velocity of SO_2 in the forest can be calculated. From equation (7.6) the following estimate for the deposition velocity (SO_4 -flux/ SO_2 -conc) can be derived:

$$v_d = 0.75 \cdot (\text{NH}_4/\text{SO}_2) + 0.0328 \quad (7.8)$$

and from equation (7.7):

$$v_d = 0.61 \cdot (\text{NH}_4/\text{SO}_2) + 0.01 \cdot \text{NH}_4 \quad (7.9)$$

with:

v_d deposition velocity on forest in $\text{kmol}_c \cdot \text{ha}^{-1} \cdot \mu\text{g}^{-1} \cdot \text{m}^3 \cdot \text{y}^{-1}$

NH_4 and SO_2 as in equation (7.7)

for SO_2 $1 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \mu\text{g}^{-1} \cdot \text{m}^3 \cdot \text{y}^{-1} = 10.2 \text{ cm} \cdot \text{sec}^{-1}$

Using the overall mean values for SO_2 and NH_4 , the deposition velocity of SO_2 on the forest can be estimated as $1.66 \text{ cm} \cdot \text{sec}^{-1}$ (equation (7.8)) or $1.39 \text{ cm} \cdot \text{sec}^{-1}$ (equation (7.9)). These values are c. 1.5-2 times higher than the value of $0.8\text{-}1 \text{ cm} \cdot \text{sec}^{-1}$ that is usually cited for SO_2 deposition velocity over bare soil or grassland (McMahon & Denison 1979). This discrepancy may be caused by (1) differences in roughness length between forest and grassland; (2) edge effects in the forest stands; and (3) biological leaching of SO_4 (see also Duysings et al. 1989).

As models for the description of SO_2 deposition, equations (7.8) and (7.9) are unrealistic because both imply a very high deposition velocity at low SO_2 concentration. Moreover, equation (7.9) implies that no SO_2 is deposited in the absence of NH_4 . Therefore a more realistic model was tested, which assumes (1) a non-zero deposition velocity for SO_2 in the absence of NH_3 and (2) a linear increase in SO_2 deposition with increasing NH_3 concentration. The same assumptions were made for the deposition velocity of NH_3 in relation to the concentration of SO_2 :

$$\text{SO}_4 = a \cdot (1 + b \cdot \text{NH}_3) \cdot \text{SO}_2 + e \cdot \text{Ca} \quad (7.10)$$

$$\text{NH}_4 = c \cdot (1 + d \cdot \text{SO}_2) \cdot \text{NH}_3 \quad (7.11)$$

with:

SO_2 , SO_4 , NH_4 , Ca as in equation (7.7)

NH_3 concentration of NH_3 in the atmosphere in $\mu\text{g} \cdot \text{m}^{-3}$

a to e constants

Eliminating NH_3 (for which no data are available), the equations can be combined to:

$$\text{SO}_4 = a \cdot \text{SO}_2 + z \cdot \text{NH}_4 \cdot \text{SO}_2 / (1 + d \cdot \text{SO}_2) + e \cdot \text{Ca} \quad (7.12)$$

with:

$$z = a \cdot b / c$$

The magnitude of the non-linear parameter d was estimated by iterative Newton optimization, the other parameters by multiple regression. Again the equation was recalculated after the omission of the nonsignificant linear term a, resulting in:

$$\text{SO}_4 = 0.14 \cdot \text{NH}_4 \cdot \text{SO}_2 / (1 + 0.126 \cdot \text{SO}_2) + 1.75 \cdot \text{Ca} \quad (7.13)$$

(93% of variance accounted for)

The deposition velocity of SO_2 can be estimated as follows:

$$v_d = 0.14 \cdot \text{NH}_4 / (1 + 0.126 \cdot \text{SO}_2) \quad (7.14)$$

At mean SO_2 concentration and NH_4 flux v_d is $1.33 \text{ cm} \cdot \text{sec}^{-1}$, which is similar to the value estimated from equation (7.9). These results suggest that the interaction between SO_2 and NH_3 is so strong that a deposition velocity for SO_2 in the absence of NH_3 cannot be estimated by this method.

7.3.6 Sources of NO_3

Nitrate may originate from many different sources, e.g. deposition of atmospheric gases, plant leaching or oxidation of NH_4 . Nitrogen monoxide has a very low solubility in water and a low reactivity and its contribution to NO_3 deposition is probably negligible. For nitric acid no atmospheric concentration data are available. Therefore nitrogen dioxide is the only gaseous N compound that could be taken into account. Atmospheric NO_2 concentrations were obtained from the same measuring sites that were used for the SO_2 data (see 7.3.5). As an indicator of canopy leaching the flux of

K was used. Because the oxidation rate of NH_4 to NO_3 is expected to be higher in summer than in winter, the season was also taken into account.

To gain some insight into the importance of the various NO_3 sources a multiple regression was performed of NO_3 flux on water flux, squared water flux, fluxes of K and NH_4 , a season-factor (1 from April to September, else 0) and the product of season factor and NH_4 flux. The short-cut method described in 7.3.5 was used: calculation of the complete regression equation, omission of non-significant terms, recalculation of the simplified equation and check of the percentage of variance accounted for. The results are given below:

bulk flux:

$$\text{NO}_3 = -0.066 + 0.000096 \cdot W + 0.42 \cdot \text{NH}_4 - 0.29 \cdot \text{NO}_2 + 0.081 \cdot \text{SF} \quad (7.15)$$

(73% variance accounted for)

canopy generated flux:

$$\text{NO}_3 = -0.078 + 0.15 \cdot \text{NH}_4 + 0.451 \cdot \text{SF} \quad (7.16)$$

(43% variance accounted for)

with:

NO_3, NH_4 fluxes in $\text{kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$

NO_2 concentration in $\mu\text{g} \cdot \text{m}^{-3}$

W water flux in $\text{mm} \cdot \text{y}^{-1}$

SF season-factor, 1 from April to September, 0 from October to March

There is a significant ($P < 0.05$) positive correlation between NO_3 and NH_4 fluxes, and a significant seasonal effect (more NO_3 in summer than in winter), both in bulk and canopy generated flux. Assuming completely independent atmospheric sources for NH_4 and NO_3 this indicates that NO_3 partly originates from oxidation of NH_4 . However, it is not possible to decide whether the oxidation takes place in the atmosphere, in the canopy or in the sample collectors. Because the relationship exists both in bulk and in canopy generated flux, leaching of NO_3 may be unimportant. This is corroborated by the absence of a significant correlation between NO_3 and K in canopy generated flux. Also, dry deposition of atmospheric NO_2 is probably unimportant as a source for NO_3 . In bulk flux there is even a significant negative relationship between NO_2 and NO_3 . Omission of the NO_2 term from equation (7.15) results in a higher parameter estimate for the season term and hardly any change in the percentage of variance accounted for:

$$\text{NO}_3 = -0.066 + 0.000099 \cdot W + 0.43 \cdot \text{NH}_4 + 0.104 \cdot \text{SF} \quad (7.17)$$

(72% variance accounted for)

Therefore, the negative relationship may simply be caused by an opposite seasonal variation of these components (NO_2 high in winter because of a high rate of emission, NO_3 high in summer because of a high rate of NH_4 oxidation).

7.3.7 Summary of probable origin of solutes

The origins hypothesized for the various solutes, summarized in Table 7.12, can be tested using the relationship between water-flux corrected bulk and canopy generated fluxes calculated in 7.3.2. Solute with highly correlated bulk and canopy generated fluxes are likely to have dry deposition or a combination of wet and dry deposition as a common origin. This is the case with Na, Mg and Cl. These ions are probably deposited in both wet and dry form under 'oceanic' weather conditions. For Ca the corrected bulk and canopy generated fluxes are negatively related, which can be explained from a different origin of this solute in bulk and forest: soil-dust and sea-spray, respectively, which are connected to mutually exclusive weather conditions. The negative correlation between bulk and canopy generated flux for H can only be explained from a biological buffering (e.g. excretion or exchange against K). The weak but significant positive correlation between corrected bulk and canopy generated fluxes of NO_3 may be due to the oxidation of NH_4 which probably takes place at high temperatures in both bulk and throughfall samples.

If atmospheric HCl is a (minor) source for Cl besides sea-spray, the quotients of deposition ratio (ion/Cl) and concentration ratio (ion/Cl) in seawater calculated in 7.3.4 (Table 7.11) are all somewhat too low. Correction would bring the values for Na and Mg closer to the expected value of one. The low calculated sea-spray contribution of Mg in the canopy generated flux compared to Na indicates that some leaching of Mg may take place. However, sea-spray must be by far the largest source for both Na, Mg and Cl.

Table 7.12. Summary of probable origin of solutes in bulk and canopy generated flux.

Solute	Bulk flux	Canopy generated flux
SO_4	SO_2 (wet dep.), sea-spray	SO_2 (dry dep.), sea-spray, (leaching?)
NO_3	NO_2 , HNO_3 , oxidation of NH_4	oxidation of NH_4
NH_4	NH_3	NH_3
Na	sea-spray	sea-spray
Mg	sea-spray, (soil-dust?)	sea-spray, (leaching?)
Cl	sea-spray, (HCl?)	sea-spray
K	sea-spray, soil-dust	leaching
Ca	soil-dust, (sea-spray?)	sea-spray, (soil-dust?)
Zn, F	anthropogenic?	anthropogenic?
H	SO_2 , NO_x , partly neutralized by soil-dust and NH_3	SO_2 , neutralized by NH_3 and cation leaching

The large quantity of canopy generated CaSO_4 is probably only deposited in dry form and not (as with Na, Mg and Cl) in both wet and dry form, as this compound is not found in bulk flux. Soil dust, which is a likely source for Ca only in bulk flux, is probably filtered off at forest edges.

8 Input-output budgets of terrestrial ecosystems

8.1 Net atmospheric input

Input-output budgets of the major solutes in the four terrestrial ecosystems were calculated for four hydrological years (April 1, 1983 to March 31, 1984; April 1, 1984 to March 31, 1985; April 1, 1985 to March 31, 1986; April 1, 1986 to March 31, 1987).

The atmospheric inputs of Si, Al, Fe, Mn, F and H_2PO_4 at the research sites were assumed to equal bulk deposition. The total atmospheric inputs of the major components present in seaspray aerosol (K, Na, Ca, Mg, Cl) were assumed to be equal to the flux in bulk precipitation plus an additional dry deposition term. The additional dry deposition of Cl was calculated by subtracting bulk flux from throughfall flux. Dry deposition of the other seasalt components was calculated from the dry deposition of Cl, using K/Cl, Na/Cl, Ca/Cl, Mg/Cl and SO_4/Cl ratios as in seawater. The dry deposition of seaspray aerosol only appears to be of quantitative importance at the two forested sites (TV and GFF). Chloride fluxes in throughfall (HV) and soil solutions (HV and GFB, see below) suggest that the dry deposition of seasalt components is relatively unimportant at these sites and was therefore not considered.

Total atmospheric input of SO_4 was assumed to equal the throughfall flux, or in the case of the non-forested HV and GF sites the soil solution flux at 0 and 2 cm depth, respectively. At the HV site the 0 cm soil solution flux was used rather than the throughfall flux as an estimate of the atmospheric input, because the SO_4 flux in the soil was significantly higher than in throughfall. Possibly stemflow accounts for a relatively large proportion of the total S input at the *Calluna* covered HV site (see 5.1.2). The non-seasalt derived SO_4 in the atmospheric input was assumed to originate from atmospheric precursors of H_2SO_4 .

Only in the forests (TV and GFF), where deposition of N compounds is high, total atmospheric inputs of NO_3 and NH_4 were assumed to equal throughfall fluxes. At the other sites (HV and GFB) the throughfall or 0 cm soil solution flux of N compounds probably underestimates the total deposition of N, due to foliar uptake (HV) or uptake by mosses and algae (GFB). Therefore, the dry deposition of NO_3 and NH_4 at these non-forested sites was estimated by multiplying the total atmospheric input of non-seasalt derived SO_4 with the ($\text{NO}_3/\text{non-seasalt SO}_4$) and ($\text{NH}_4/\text{non-seasalt SO}_4$) ratios in bulk deposition.

The dry deposition input of free H^+ was estimated according to

$$(H)_{\text{dry}} = (SO_4)_{\text{in,nss}} - (SO_4)_{\text{bu,nss}} + (NO_3)_{\text{in}} - (NO_3)_{\text{bu}} + (NH_4)_{\text{bu}} - (NH_4)_{\text{in}} \quad (8.1)$$

where 'in' indicates the estimated total atmospheric input, 'bu' bulk deposition, and 'nss' the non-seasalt component of SO_4 . All units are in $\text{kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$.

The water and solute fluxes in bulk deposition and throughfall, together with the estimated atmospheric inputs are given in Table 8.1. The total deposition of NH_4 and SO_4 is highest in the forest stands and lowest in the bare driftsand (GFB). The deposition of NH_4 and SO_4 in the heathland is also surprisingly high. Similar high deposition rates for these compounds for non-forest vegetation were earlier discussed by Heil et al. (1988). Due to the high deposition rate of NH_3 and the formation of NH_4^+ , most of the acidity associated with the input of SO_4 and NO_3 is neutralized. Only at HV the deposition of H^+ is somewhat elevated, whereas at the forest sites the net input of free H^+ even becomes negative, i.e. more HCO_3^- than free H^+ enters the ecosystem. The input of HCO_3^- occurs in the form of NH_4HCO_3 .

8.2 Leaf litter fluxes

The amounts of litterfall and its chemical composition in the two pine stands are given in Table 8.2. The annual amounts of litterfall in both stands are similar to the amounts reported for the oak-birch woodland plots at 'Oude Maat', The Netherlands (Van Breemen et al. 1988). However, the concentrations of all major nutrients are considerably lower in the pine than in the oak-birch litter. The contents of Ca, N, S and P are significantly higher in the Tongbersven than in the Gerritsfles litter. In contrast, Si, Na and Cl concentrations are significantly lower in the litter at TV. The higher Na and Cl concentration in *Pinus* litter at GFF reflect the significantly higher Na and Cl inputs at this site (Tables 7.6 and 8.1). The lower N and S contents in the litterfall at GFF coincide with a somewhat lower $(NH_4)_2SO_4$ deposition (Table 8.1), although this difference was not significant at the 95% level between 1982 and 1985 (Table 7.6). The difference in chemical composition between Gerritsfles and Tongbersven may be partly due to differences in contribution of needles, twigs and cones to the litter samples. This variation in sample composition is illustrated in Table 8.3.

Chemical fluxes associated with biocycling are given in Table 8.4. As in oak-birch systems (Van Breemen et al. 1988) the major part of the annual nutrient uptake by pine is returned to the soil by leaf leaching or litterfall. As can be expected, the nutrient fluxes in the heathland are small compared to those in the pine and oak-birch forests. However, in contrast to the forested sites, a considerable part of the total annual nutrient uptake by *Calluna* is stored in the living biomass and not returned to the soil.

8.3 Soil solution fluxes

The chemical fluxes at various depths in the unsaturated soil zone of the four research sites are given in Table 8.5. The solute fluxes at 100 (TV) and 110 (HV) cm depth are

Table 8.1. Four year (April 1, 1983 - March 31, 1987) mean annual fluxes of water and major solutes in bulk precipitation (bulk), throughfall plus stemflow (thr.), as well as estimated atmospheric input (inp.) at the research sites. DOC = dissolved organic carbon ($\text{kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$), A^- = organic anions. Ionic fluxes in $\text{kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$, water fluxes in $\text{mm} \cdot \text{y}^{-1}$.

Site	Water	H	DOC	A^-	Si	K	Na	Ca	Mg	Al	Fe	Mn	NH_4	F	Cl	NO_3	SO_4	H_2PO_4
HV	bulk	785.1	0.18	2.34	0.76	0.05	0.05	0.55	0.13	0.03	0.02	0.00	0.87	0.01	0.60	0.40	0.98	0.03
	thr.	623.1	0.11	3.28	0.82	0.04	0.13	0.58	0.37	0.18	0.03	0.01	0.91	0.01	0.63	0.35	1.07	0.02
	inp.	-	0.98	-	0.05	0.05	0.55	0.27	0.13	0.03	0.02	0.00	2.27	0.01	0.60	1.08	2.49	0.03
TV	bulk	800.0	0.16	3.05	0.88	0.07	0.05	0.69	0.25	0.15	0.03	0.02	0.93	0.01	0.72	0.38	1.01	0.03
	thr.	499.6	-0.04	11.23	1.53	0.04	0.58	0.93	0.43	0.28	0.05	0.01	3.68	0.04	1.20	0.55	3.21	0.02
	inp.	-	-0.24	-	0.07	0.06	1.10	0.27	0.25	0.03	0.02	0.00	3.68	0.01	1.20	0.55	3.21	0.03
GFB	bulk	839.2	0.18	2.61	0.95	0.06	0.04	0.70	0.23	0.16	0.02	0.01	0.89	0.01	0.77	0.42	0.93	0.01
	thr.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	inp.	-	0.46	-	0.06	0.04	0.70	0.23	0.16	0.02	0.01	0.00	1.45	0.01	0.77	0.70	1.48	0.01
GFF	bulk	839.2	0.18	2.61	0.95	0.06	0.04	0.70	0.23	0.16	0.02	0.01	0.89	0.01	0.77	0.42	0.93	0.01
	thr.	618.1	-0.11	9.02	1.28	0.03	0.37	1.35	0.48	0.37	0.07	0.01	3.02	0.04	1.66	0.80	2.60	0.02
	inp.	-	-0.02	-	0.06	0.06	0.06	1.47	0.26	0.34	0.02	0.01	3.02	0.01	1.66	0.80	2.60	0.01

Table 8.2. Litterfall amount and its chemical composition at the two *Pinus sylvestris* research sites. Values are means and standard deviations of five replicates; amounts are from May 17, 1984 to May 14, 1985, whereas concentrations are three-year means from May 17, 1984 to May 15, 1987. Weight in $\text{t} \cdot \text{ha}^{-1}$, concentration in $\text{mmol} \cdot \text{kg}^{-1}$.

Site		Weight	Concentration											
			Si	K	Na	Ca	Mg	Al	Fe	Mn	Cl	N _{tot}	S _{tot}	P _{tot}
TV	mean	5.09	110	55	9	85	20	17	12	4	13	1128	44	22
	s.d.	1.22	23	9	4	11	2	3	4	0	1	99	5	3
GFF	mean	6.17	199	45	21	49	20	19	13	4	19	829	36	16
	s.d.	1.00	29	11	7	6	3	3	3	0	3	116	3	3

Table 8.3. Contribution of needles, twigs and cones to the litterfall in the two *Pinus sylvestris* stands. Values are percentages of total mean litterfall.

Site	Needles	Twigs	Cones
TV	77.5	8.9	13.6
GFF	61.6	7.9	30.5

Table 8.4. Cycling of the major elements at the two *Pinus sylvestris* stands (GFF and TV) and in the *Calluna vulgaris* plot (HV). Values are fluxes in $\text{kmol}_e \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$, where N has a valency of 1 (NH_4 or NO_3). ? indicates an unknown value that is probably negligible. Other unknown values are indicated as -. Data on net nutrient uptake at GFF and TV were taken from De Visser (1987), for HV literature values for litterfall and net nutrient uptake were used (see Nieuwenhuyse 1986).

Site		Si	K	Na	Ca	Mg	Al	Fe	Mn	Cl	N	S	P
HV	litter	-	0.02	0.00	0.07	0.02	-	-	-	-	0.62	-	-
	leaf leach	-0.01	0.08	0.03	0.10	0.05	0.00	-0.01	0.01	0.03	?	-	0.01
	net uptake	-	0.07	0.01	0.11	0.08	-	-	-	-	0.09	-	-
	tot uptake	-	0.17	0.04	0.28	0.15	-	-	-	-	0.71	-	-
TV	litter	0.56	0.28	0.05	0.87	0.20	0.26	0.12	0.04	0.07	5.74	0.45	0.11
	leaf leach	-0.03	0.52	-0.17	0.16	0.03	0.02	-0.01	0.01	?	?	?	-0.01
	net uptake	-	0.12	?	0.25	0.09	-	-	-	-	0.40	-	-
	tot uptake	-	0.92	-0.12	1.28	0.32	-	-	-	-	6.14	-	-
GFF	litter	1.23	0.28	0.13	0.60	0.25	0.35	0.16	0.05	0.12	5.11	0.44	0.10
	leaf leach	-0.03	0.31	-0.12	0.22	0.03	0.05	0.00	0.02	?	?	?	0.01
	net uptake	-	0.10	?	0.21	0.08	-	-	-	-	0.34	-	-
	tot uptake	-	0.69	0.01	1.03	0.36	-	-	-	-	5.45	-	-

Table 8.5. Fluxes major solutes in soil solutions at the four research sites between April 1, 1983 and March 31, 1987. Values are mean annual fluxes in $\text{kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ (DOC and Si) and $\text{kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$. Al is assumed to have a valency of 3 and Fe and Mn of 2. Negative values for H^+ indicate net HCO_3^- input. 'inp.' stands for the atmospheric input, according to Table 8.1. '0*' stands for '0 cm' fluxes calculated from mean annual throughfall plus stemflow plus complete mineralization of the mean annual leaf litter inputs; NH_4 and NO_3 fluxes in '0*' were calculated by adding total N in atmospheric input and annual litterfall, and partitioning this total N input between NH_4 and NO_3 according to their distribution in the measured forest floor leachate. '-' are unknown values.

Site	Depth	Water	H	DOC	A ⁻	Si	K	Na	Ca	Mg	Al	Fe	Mn	NH ₄	F	Cl	NO ₃	SO ₄	H ₂ PO ₄
HV	inp	78.51	0.98	-	-	0.05	0.05	0.55	0.27	0.13	0.03	0.02	0.00	2.27	-	0.60	1.08	2.49	0.03
	0*	62.31	-	-	-	-	0.15	0.58	0.44	0.20	-	-	-	2.69	-	-	1.28	-	-
	0	53.27	0.76	21.15	0.60	0.46	0.57	0.41	0.45	0.31	0.23	0.05	0.02	2.71	0.01	0.71	1.29	2.49	0.08
	7	47.96	1.43	15.81	0.48	0.53	0.44	1.01	1.07	0.55	1.74	0.06	0.01	0.75	0.03	1.27	0.23	5.38	0.01
	22	38.49	0.24	2.79	0.35	0.24	0.22	0.61	0.29	0.23	2.18	0.01	0.00	0.33	0.01	0.74	0.23	2.95	0.00
	70	36.61	0.21	3.53	0.34	0.26	0.09	0.48	0.28	0.26	2.05	0.00	0.00	0.01	0.01	0.59	0.54	2.20	0.00
TV	inp	80.00	-0.24	-	-	0.07	0.06	1.10	0.27	0.25	0.03	0.02	0.00	3.68	-	1.20	0.55	3.21	0.03
	0*	49.96	-	-	-	0.60	0.86	0.98	1.30	0.48	0.31	0.13	0.05	6.89	-	1.27	3.08	3.66	0.13
	0	41.68	0.42	19.57	0.79	0.12	0.91	0.80	0.75	0.31	0.14	0.02	0.03	5.06	0.03	1.23	2.26	4.09	0.08
	12	30.92	1.19	20.43	0.20	0.32	0.43	0.60	0.39	0.23	0.30	0.04	0.01	3.10	0.01	1.05	1.58	3.28	0.03
	35	24.39	0.23	4.00	0.28	0.42	0.13	0.65	0.14	0.19	3.74	0.01	0.00	1.21	0.02	0.99	1.76	3.36	0.00
	57	23.77	0.22	3.72	0.15	0.46	0.14	0.78	0.15	0.27	5.32	0.00	0.00	0.69	0.02	1.18	2.05	4.35	0.00
GFB	inp	83.92	0.46	-	-	0.06	0.04	0.70	0.23	0.16	0.02	0.01	0.00	1.45	-	0.77	0.70	1.48	0.01
	0*	83.92	-	-	-	0.06	0.04	0.70	0.23	0.16	0.02	0.01	0.00	1.45	-	0.77	0.70	1.48	0.01
	0	66.69	0.25	4.62	0.77	0.20	0.05	0.62	0.25	0.21	1.00	0.01	0.01	0.46	0.02	0.81	0.58	1.48	0.00
	40	67.58	0.27	3.51	0.49	0.35	0.06	0.50	0.20	0.17	1.70	0.01	0.01	0.03	0.02	0.68	0.83	1.47	0.00
	100	67.71	0.22	5.35	0.64	0.48	0.05	1.44	0.21	0.18	1.44	0.02	0.01	0.03	0.01	0.75	0.98	1.96	0.00
GFF	inp	83.92	-0.02	-	-	0.06	0.06	1.47	0.26	0.34	0.02	0.01	0.00	3.02	-	1.66	0.80	2.60	0.01
	0*	61.81	-	-	-	1.26	0.65	1.48	1.08	0.62	0.42	0.17	0.07	6.05	-	1.78	2.88	3.04	0.12
	0	46.47	0.33	26.78	0.72	0.17	0.67	1.51	0.36	0.37	0.18	0.05	0.02	4.93	0.04	2.13	2.35	2.91	0.07
	10	40.97	0.38	24.61	0.58	0.46	0.28	1.67	0.45	0.45	2.09	0.09	0.01	3.08	0.00	2.28	2.13	2.92	0.01
	40	31.58	0.31	6.55	0.32	0.65	0.14	1.74	0.36	0.56	5.64	0.01	0.02	0.15	0.04	2.58	2.75	3.35	0.00
	100	28.29	0.20	2.52	0.28	0.42	0.13	1.37	0.24	0.39	4.65	0.01	0.01	0.04	0.03	1.98	1.93	3.16	0.00

based on a few observations only (Microfiche), and should be viewed with caution. Solute fluxes at 0 cm depth (leachate of 0 horizons, in which rooting and therefore nutrient uptake is prevented) were compared with throughfall plus leaf litter fluxes, assuming a complete mineralization of the annual litterfall (0*). The estimated atmospheric inputs are also given (inp.).

For K, Na, Cl and SO_4 the throughfall plus leaf litter fluxes (0*) in the forest soils (TV and GFF) were only slightly different from the soil solution (0) fluxes. In contrast, the total inputs of Ca, Mg, N, P, Al, Fe, Mn and Si to the forest floors were significantly higher than the measured 0 cm fluxes leaving the forest floor. Probably a net storage of these elements in the organic matter of the forest floor takes place, because nutrient uptake by roots is prevented in the 0 cm lysimeters.

Dissolved organic carbon (DOC) has the highest fluxes (on a molar basis) in all soils. Only in the forest subsoils the Al fluxes reach similar high values. The fluxes of DOC in the surface layers of the forest soils are considerably higher than those in the non-forested soils.

The Si flux values do not differ significantly between forested and non-forested soils, all reaching a maximum below 40 cm depth. Only at the HV site the Si flux reaches its maximum at shallower depths (E horizon). However, not only the Si fluxes are exceptionally high in the HV E horizon, also the fluxes of Na, Ca, Mg, Cl and SO_4 are higher in this horizon than in both the horizon above (0) and below (Bhs).

The Hasselsven data suggest that the production of Na, Ca, Mg, Cl and SO_4 (due to mineralization) in the E horizon exceeds uptake of these elements. The E horizon at Hasselsven is relatively rich in organic matter, which may be due to mechanical input of organic matter from the 0 horizon during heathland management, e.g. mowing, burning, etc. The Si fluxes observed in our soils (coversands and driftsands) are considerably lower than those reported for other acidic soils developed in alluvial deposits in The Netherlands. Van Breemen et al. (1988) found a mean annual Si mobilization of 1.5 to $2.2 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ between 0 and 10 cm soil depth. The difference in Si flux may partly be due to the higher biocycling of Si in deciduous relative to coniferous forest (Bartoli 1983).

The cation fluxes are dominated by Al in all soils and at all depths, except for the 0 horizons, where NH_4 dominates. The fluxes of Al are highest in the forest soils, reaching maximum values of $5.6 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$, and considerably lower in the non-forested plots (maximum $2.2 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$). The Al fluxes distinctly increase in the upper 20 to 40 cm of all mineral soils and decrease slightly below this depth. In the forested Spodosol at Tongbersven, the mobilization of Al is highest in the Bhs horizon ($3.44 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$). In contrast, the Al mobilization in the heathland Spodosol is highest in the E horizon. Where the Al mobilization occurs in the two Spodosols is primarily determined by the N transformation patterns, which are different for the two soils, as will be discussed in 8.4.

The NH_4 fluxes are highest in the 0 horizons (2.7 to $5.1 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ in the heathland and forested soils, respectively) and decrease rapidly with depth in the mineral soils to negligible values in the subsoils. The strongest decrease in NH_4 flux is found

in the Hasselsven Spodosol, where the NH_4 (and also NO_3) fluxes are already small in the E horizon. However, this strong gradient in soil solution NH_4 at HV changed significantly during the last hydrological year, when NH_4 also increased in the subsoil.

The fluxes of K and P in the vegetated systems clearly demonstrate the importance of nutrient cycling, with highest values in the surface soil layers. The bare driftsand does not show this phenomenon.

In all soils the anion flux is dominated by SO_4 at all depths. Fluxes of SO_4 and NO_3 are generally higher in the forest soils than in their non-forested counterparts, due to the higher $(\text{NH}_4)_2\text{SO}_4$ inputs in forests. The NO_3 fluxes below the root zone in the two forest soils are significantly higher than the atmospheric NO_3 input, indicating a net nitrification.

In Fig. 8.1 the fate (drainage or retention) of the total atmospheric N input for the four research sites is given. In the forest soils most of the deposited NH_4 is nitrified and leached as NO_3 . In the bare driftsand a continuous decrease in atmospherically derived N over the four-year monitoring period resulted in a decrease in N retention. By contrast, the NO_3 drainage increased steadily. At Hasselsven the total N input increased over the years, and in the last hydrological year the deposited N was no longer fully retained in the soil-vegetation system. In this hydrological year (1986-1987) a considerable fraction of the deposited N (primarily NH_4) left the soil as NO_3 .

In general SO_4 and NO_3 are the mobile anions in the soil solutions associated with

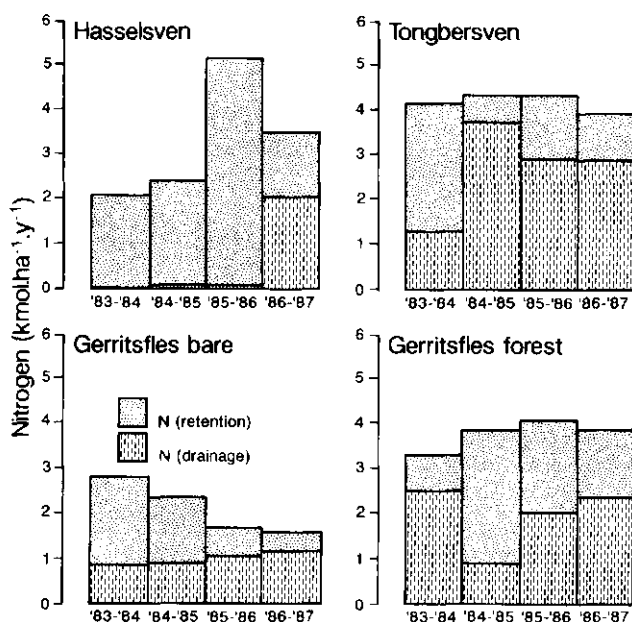


Figure 8.1. Nitrogen budgets ($\text{NH}_4 + \text{NO}_3$) for the four research sites. For drainage fluxes calculated values at 100 cm depth (GFB and GFF), 70 cm depth (HV) and 57 cm depth (TV) were used. It was assumed that for each hydrological year $\text{N}(\text{input}) = \text{N}(\text{drainage}) + \text{N}(\text{retention})$.

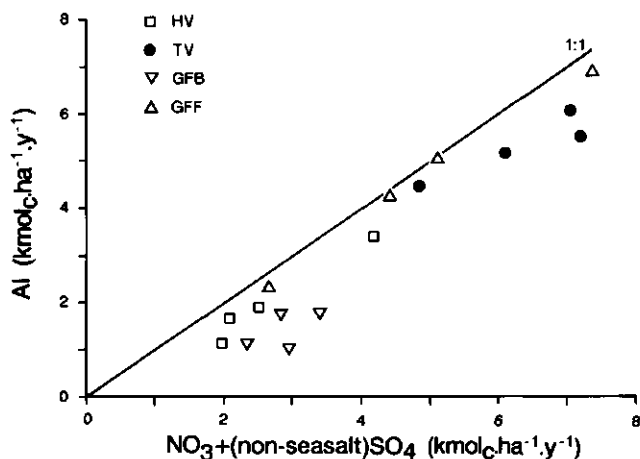


Figure 8.2. Aluminium fluxes as a function of the summed NO_3 and non-seasalt derived SO_4 fluxes at the four research sites. Drainage fluxes were taken from the same soil depths as in Fig. 8.1.

the acid (H) or potential acid (NH_4) input. Fig. 8.2 shows that most of the SO_4 and NO_3 below the rooting zones is counterbalanced by dissolved Al. This indicates that most of the anthropogenically derived acidity is neutralized by Al dissolution. Only at the bare driftsand (GFB) a considerable fraction of the atmospheric acidity is neutralized by Na.

Ionic charge discrepancies in soil solutions are small and reach highest values in the 0 horizons, never exceeding 20% of the total anionic charge in solution.

8.4 Proton budgets of terrestrial systems

Proton budgets can be used to summarize and quantify the various sources and sinks of acidity in ecosystems. To make a proton budget input and output fluxes of the major solutes and gases of the system must be known. Proton budgets are discussed in detail by Driscoll and Likens (1982) and by Van Breemen et al. (1983). Sources of acidity which need to be considered are free acid input from the atmosphere, net N transformations (e.g. NH_4 assimilation, nitrification), weak acid inputs (CO_2 and organic acids), assimilation of base cations by vegetation, and anion weathering. Sinks of acidity include weathering of base cations and aluminium, assimilation or sorption of anions and the export of free acidity.

Table 8.6 summarizes the mean annual proton budgets for the four research sites over a four-year period. The total acid load is highest in the two forest soils and lower in the non-forested plots. Although the total deposition of NH_4 in the pine forests is slightly higher than in many oak-birch woodlands in The Netherlands (e.g. Van Breemen et al. 1988), their total acid load is somewhat lower, due to a lower net nitrification rate. Apparently the pine ecosystems assimilate more of the nitrogen input than the oak-birch systems. The higher N retention in the pine forests relative to the hard-

Table 8.6. Mean annual proton budgets for the four soil-vegetation systems between April 1, 1983 and March 31, 1987. Values are in $\text{kmol}_e \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$. As input, data from Tables 8.1, 8.4 and 8.5 were used. Ntr = nitrification. As lower boundaries for the soil profiles were used 100 cm (GFF and GFB), 70 cm (HV) and 57 cm (TV).

	H^+ sources					H^+ sinks			
	external		internal						SUM
	inp.	Ntr.	Org. Acids	Biom. assim.	Anion weath.	Al weath.	base cat. weath.	H+ exp.	
HV	1.0	1.7	0.0	0.3	- 0.3	2.7	2.1	0.4	0.2
TV	-0.2	4.5	-0.2	0.5	1.1	5.7	5.3	0.1	0.2
GFF	0.0	4.1	-0.2	0.4	0.9	5.2	4.7	0.4	0.2
GFB	0.5	1.7	-0.2	0.0	0.5	2.5	1.4	0.7	0.2

wood systems at 'Oude Maat' may be due to (1) a younger vegetation (Tongbersven) and (2) younger soils that are still building up pools of organic matter (Gerritsfles). Although there was a significant year-to-year variation the efficiency of N retention seemed to decrease during the monitoring period resulting in higher outputs of NO_3 with drainage water. Therefore stronger acidification rates of the soil may occur in the near future.

Most of the acidity formed is caused by assimilation of NH_4 (production of one mol H^+ per mol NH_4^+ assimilated). At the non-forested plots the input of free acidity is considerable, but significantly lower than H production by N transformations. In contrast, the atmospheric input of free H^+ is quantitatively unimportant for the total acid load of the forest soils.

The assimilation of base cations by the living biomass and anion mobilization in the soil are relatively unimportant acid sources at all sites. However, cation assimilation may have been underestimated, because only uptake in the living biomass was included and not a possible storage of nutrients in dead organic matter (build-up of the forest floor). A maximum estimate of nutrient assimilation at the three vegetated sites would be the sum of 'litter' and 'net uptake' in Table 8.4. But even this maximum estimate of cation assimilation would not account for more than 30% of the total acid input. The biomass assimilation (net uptake) in the forest plots equals (GFF) or exceeds (HV) the base cation weathering rate. This implies that the forest stands satisfy part of their nutrient demand through atmospheric inputs (largely from sea-spray origin).

Neutralization of the acidity is primarily accomplished by weathering of Al at all sites. Weathering of base cations (particularly Na) is only of significance in the bare driftsand, where Na-containing minerals are apparently more abundant than at the other sites.

Soil acidification, defined as a decrease in the acid neutralizing capacity (ANC;

Table 8.7. Mean annual changes in the pools of various soil chemical compounds and the soil ANC between April 1, 1983 and March 31, 1987. Values are in $\text{kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$. Positive values indicate increasing pools, negative values decreasing pools.

	K	Na	Ca	Mg	Al	Cl	SO ₄	ΔANC
HV	-0.11	+0.06	-0.12	-0.21	-2.02	+0.01	+0.29	-2.70
TV	-0.20	+0.32	-0.13	-0.11	-4.78	+0.02	-1.14	-3.78
GFF	-0.17	0.10	-0.19	-0.13	-4.63	-0.32	-0.56	-4.14
GFB	-0.01	-0.74	+0.02	-0.02	-1.42	+0.02	-0.48	-1.71

Van Breemen et al. 1983) in the four soils is given in Table 8.7. The changes in base cation pools are generally small and the leaching of Al is the most important factor causing the strong decrease in ANC in all soils. The low weathering rate of base cations is in strong contrast to the rates reported for the acidic soils at 'Oude Maat', where mobilization rate of base cations due to weathering ranges from 1.5 to 2.1 $\text{kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ for K, Ca plus Mg (Van Breemen et al. 1988). This difference in base cation weathering between the loamy sands at 'Oude Maat' and the coversands and driftsands in this study must be due to the difference in mineral assemblage, the loamy sands being richest in weatherable minerals.

The low mobilization rates of Si and base cations in both forested and non-forested sandy soils suggests that at our sites the weathering rates of primary minerals are not much affected by the total acid load. This would also mean that 'free' Al (consisting of exchangeable, organically complexed and amorphous solid phase Al) rather than Al-silicate is the dominant source of the solubilized Al. Indeed, Mulder et al. (1989a) demonstrated that dissolved Al largely originates in the solid phase organically bound fraction. At the current leaching rate the Dutch spodic horizons may become Al depleted within a few hundred years. With a concomitant decline in soil pH, Fe may eventually take over the role of major acid neutralizing compound. The depletion of secondary Al may also induce an enhanced mineralization or leaching of soil organic matter, thus resulting in a reduction in CEC and pools of organic N.

The sites' potential for plant growth may be weakened by the elevated concentrations of Al (Andersson & Kelly 1984) and NH_4 (Roelofs et al. 1985). Unfortunately historic data on forest productivity are lacking for our sites, so that it is not possible to judge whether changes in tree vitality have occurred. However, in the long run increased concentration of Al and possibly Fe in conjunction with (hypothesized) decreased pools of soil organic C (CEC) and N are expected to cause a decline in forest productivity.

9 Input-output budgets of aquatic ecosystems

Input-output budgets and residence time of major solutes and water were calculated for two hydrological years (April 1, 1983 to March 31, 1984, and April 1, 1984 to March 31, 1985), for the moorland pools at Hasselsven (HV), Tongbersven (TV), Gerritsfles (GF) and Kliplo (KL), using the model BUDGET (section 4.2.5). For the Gerritsfles and Kliplo pools the budgets GF* and KL* for the hydrological years 1982 to 1986 and 1982 to 1987, respectively, were also calculated. The sources of the data used for the budgets are presented in Table 9.1.

The mean fluxes and residence times for GF* and KL* are given in Table 9.2, and those for HV, TV, GF and KL are presented in Table 9.3. The annual output of water and solutes in GF* and KL* is presented in Figs 9.1 and 9.2. The annual bulk precipitation balances the sum of the output components (including storage change) and is not given.

Table 9.1. Sources of data for BUDGET cases and corresponding VENSIM cases. E_o = evaporation, P = precipitation, C_p = Cl concentration in precipitation, C_v = Cl concentration in poolwater. Precipitation quantity for Leende (and Dwingeloo) from KNMI (1980-87), evaporation for Eindhoven, Andel, Eelde and Deelen from KNMI (1982-1988), evaporation data for Eelde from KNMI (pers. comm.), C_p for Eindhoven and Witteveen from KNMI/RIVM (1978-1987). L = local bulk precipitation sampler (Microfiche). Incidentally missing values of local bulk samplers were completed with data from nearest meteorological station. Measurements at Gerritsfles from April 1985 to April 1987 did not match calendar months and were recalculated using daily precipitation amounts from the nearby meteorological station Kootwijk (KNMI 1980-1987). LUW = monthly samples analysed by Agricultural University Wageningen (Microfiche), WMN = quarterly samples analysed by Waterleidingbedrijf Midden-Nederland (Microfiche). Incidentally missing values of LUW data set were completed with values from WMN data set (when available) and vice versa. Extreme values, occurring during periods of ice-cover, were disregarded.

Variable	HV	TV	GF	GF*	KL	KL*
Hydrological years	83-84 ^a	83-84	83-84	82-86	83-84	82-87
E_o (VENSIM)	Eindhoven	Eindh./Andel ^b	Deelen	Deelen	Eelde	Eelde
P (BUDGET)	Leende	L	L	L	L	L ^c
C_p (VENSIM)	Eindhoven	L	L	L	L	L ^d
C_p (BUDGET)	Eindhoven	L	L	L	L	Witteveen
C_v (BUDGET)	LUW	LUW	LUW	WMN	LUW	WMN

^a 83-84 is April 1, 1983 to April 1, 1985.

^b mean value of stations Eindhoven and Andel.

^c Dwingeloo in 85-87.

^d Witteveen in 85-87.

GERRITSFLES

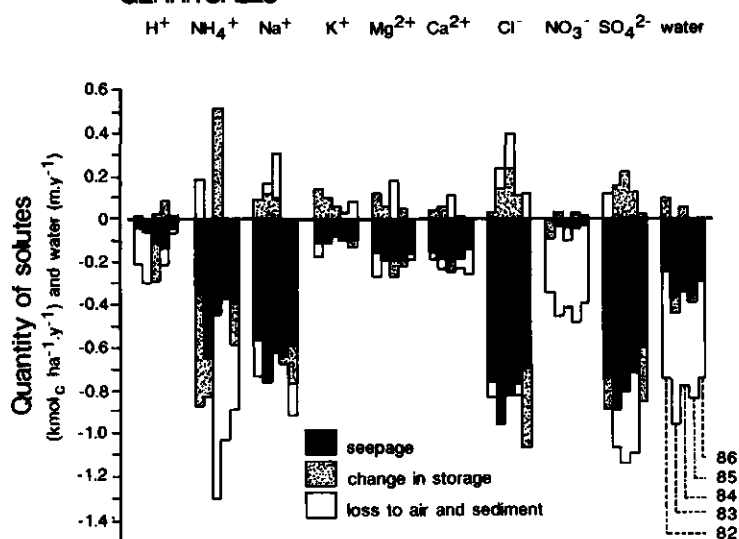


Figure 9.1. Gerritsfles, solute and water balances during hydrological years 1982-1986. Each bar represents one year as indicated below the diagram for water.

KLIPO

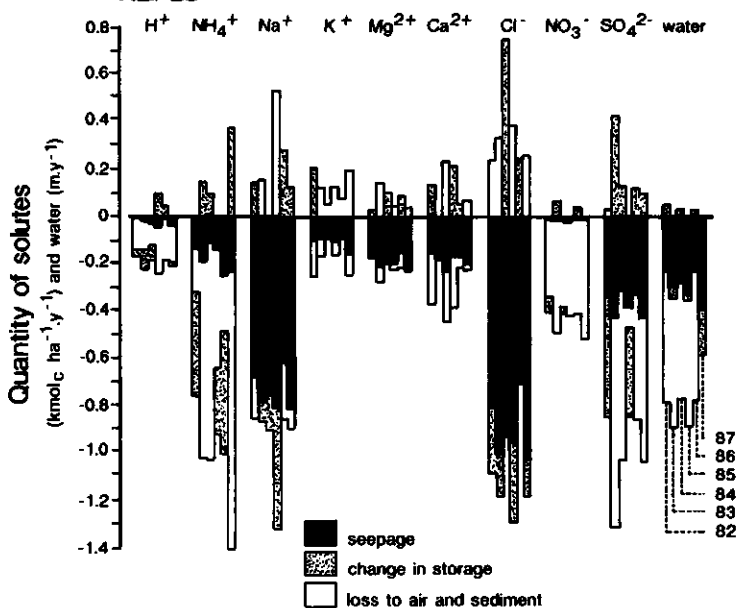


Figure 9.2. Klipto, solute and water balances during hydrological years 1982-1987. Each bar represents one year as indicated below the diagram for water.

Table 9.2. Residence time, relative losses, and mean fluxes of major solutes and water in Gerritsies pool from April 1, 1982 to April 1, 1987 (GF*) and Kliplo pool from April 1, 1982 to April 1, 1988 (KL*) (input and storage decrease are positive). Cl* = values for chloride calculated by VENSIM. Alk = alkalinity, Sumcat = sum of cations, Suman = sum of anions. Values for water are in $\text{mm} \cdot \text{y}^{-1}$, solutes in $\text{kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$, residence time in year.

Budget	Variable	Water	H	K	Na	Ca	Mg	NH ₄	Cl	NO ₃	SO ₄	Cl*	Alk	Sumcat	Suman
GF*	bulk precipitation	794	0.19	0.04	0.64	0.19	0.15	0.84	0.73	0.40	0.87	0.73	-0.14	2.05	2.00
	seepage	-330	-0.08	-0.10	-0.64	-0.17	-0.18	-0.44	-0.81	-0.03	-0.76	-0.78	0.09	-1.60	-1.61
	volatilization and sedimentation	-473	-0.09	-0.03	0.01	0.03	0.01	-0.33	-0.05	-0.35	-0.15	0.00	0.11	-0.44	-0.45
	change in storage	8	-0.01	-0.03	0.02	0.01	0.02	0.08	0.03	-0.01	0.04	0.05	-0.06	-0.02	0.06
	relative loss	-0.60	-0.51	-0.72	0.02	0.18	0.04	-0.39	-0.07	-0.88	-0.17	0.00	-0.82	-	-
	residence time	0.85	1.26	5.66	2.31	2.03	2.56	1.08	2.47	0.16	1.84	2.37	-	-	-
KL*	bulk precipitation	857	0.18	0.04	0.65	0.18	0.14	0.89	0.78	0.43	0.87	0.78	-0.17	2.09	2.08
	seepage	-302	-0.02	-0.10	-0.75	-0.18	-0.19	-0.17	-0.91	-0.02	-0.38	-0.85	-0.09	-1.41	-1.31
	volatilization and sedimentation	-526	-0.16	-0.06	0.02	0.02	0.03	-0.62	0.13	-0.42	-0.47	-0.01	0.24	-0.68	-0.76
	change in storage	-28	-0.01	-0.00	0.07	0.03	0.02	0.10	0.01	0.00	-0.02	0.08	0.02	0.01	-0.01
	relative loss	-0.61	-0.87	-1.77	0.04	0.12	0.20	-0.69	0.17	-0.97	-0.54	-0.01	-1.41	-	-
	residence time	1.13	0.30	9.28	3.91	3.45	4.38	0.60	4.02	0.12	1.37	3.79	-	-	-

The budgets GF and KL use data for bulk deposition and pool water chemistry that were collected monthly. GF* uses pool water chemistry data that were collected quarterly. The results for GF and GF* for the hydrological years 1983 and 1984 are very similar. In the KL and KL* budgets seepage and storage change are very similar for the hydrological years 1983 and 1984, but in these years bulk deposition values for NH_4 and SO_4 in the local sampler that was used in KL were c. 15% lower than those at the meteorological station Witteveen, which were used in KL*. Wet deposition of other components is similar in the local and the Witteveen samplers.

The loss of solutes to sediments and air could not be measured directly, and had to be calculated as a balance term in the budgets. Consequently this term includes all errors and uncertainties of the other terms. The largest source of uncertainty is probably the estimation of dry deposition, especially for NH_4 and SO_4 . Although dry deposition of NH_4 and SO_4 on open water is similar to bulk deposition, dry deposition on emergent littoral plants, e.g. *Molinia caerulea* may be twice that value (Buskens 1990). Therefore losses to sediment and air may have been underestimated, at least for NH_4 and SO_4 . A comparison of budgets with measured and modelled concentration of Cl (Cl and Cl* in Tables 9.2 and 9.3) may yield some insight in the reliability of the calculations. For GF* these budgets are nearly equal, but in most other cases there are discrepancies, particularly for HV. The results should therefore be viewed with caution.

The mean annual seepage of Na, Mg, Ca, and Cl in GF* and KL* is about equal to the mean annual bulk deposition (relative loss, i.e. quotient of 'volatilization and sedimentation' and 'bulk precipitation', between -0.2 and $+0.2$). This indicates that no important leaching of Mg and Ca occurred from 1982 to 1986, as was observed after the drought of 1976 (section 6.4.2).

For SO_4 the mean annual seepage is only slightly lower than the mean annual bulk deposition in GF*, and therefore the mean relative loss is comparatively small (-0.17). However, in KL* the mean relative loss of SO_4 amounts to -0.54 (Table 9.2). This large loss of SO_4 may be due to bacterial reduction, which is a common process in moorland pools (Schuurkes 1987). The higher rate at Kliplo, compared to Gerritsfles is probably due to the higher pH in the sediment interstitial water of the former pool (Table 6.12).

Feijtel et al. (1989) made monthly measurements of the SO_4 concentration gradient in the sediment at one station in the Gerritsfles pool during the calendar year 1987 and calculated the SO_4 reduction rate by a kinetic transport model. The loss of SO_4 to air and sediment was estimated as $1.2 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$, which differs from the value of $0.15 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ given in Table 9.2. Seepage was estimated as $0.4 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ by Feijtel et al. (1989) and $0.76 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ by our model (Table 9.2). At least part of the difference may be caused by a difference in the estimated dry deposition, as Feijtel et al. (1989) included a dry deposition of $0.4 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ in their budget.

Mean annual loss is lower than mean annual input for H, NH_4 and NO_3 in GF* and KL* (relative loss below -0.2 ; Table 9.2). The relative loss of NO_3 is -0.88 in

Table 9.3. Residence time, relative losses, and mean yearly fluxes of major solutes in moorland pools from April 1, 1983 to April 1, 1985 (input and storage decrease are positive). Cl* = values for chloride calculated by VENSIM. Alk = alkalinity, Sumcat = sum of cations, Suman = sum of anions. Values for Water are in $\text{mm} \cdot \text{y}^{-1}$, solutes in $\text{kmol} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$, residence time in year.

Budget	Variable	Water	H	K	Na	Ca	Mg	NH ₄	Cl	NO ₃	SO ₄	Cl*	Alk	Sumcat	Suman
GF	bulk precipitation	855	0.28	0.03	0.47	0.15	0.12	0.81	0.58	0.43	0.87	0.58	-0.30	1.86	1.88
	seepage	-364	-0.06	-0.09	-0.66	-0.13	-0.16	-0.66	-0.91	-0.02	-0.80	-0.87	0.02	-1.77	-1.73
	volatilization and sedimentation	-478	-0.22	0.06	0.10	-0.01	-0.01	-0.32	0.11	-0.43	-0.28	0.00	0.43	-0.40	-0.60
	change in storage	-12	0.00	0.00	0.10	-0.01	0.05	0.18	0.22	0.02	0.22	0.29	-0.14	0.31	0.46
	relative loss	-0.56	-0.80	2.06	0.21	-0.05	-0.07	-0.40	0.19	-1.00	-0.31	0.00	-1.37	-	-
	residence time	0.83	0.42	5.97	2.98	1.88	2.82	1.57	3.23	0.07	1.80	3.06	-	-	-
KL	bulk precipitation	828	0.25	0.04	0.48	0.17	0.12	0.80	0.58	0.42	0.87	0.58	-0.25	1.86	1.86
	seepage	-303	-0.02	-0.08	-0.75	-0.19	-0.20	-0.16	-0.97	-0.01	-0.31	-0.90	-0.10	-1.40	-1.28
	volatilization and sedimentation	-524	-0.21	0.08	0.18	0.18	0.08	-0.95	0.27	-0.43	-0.69	0.03	0.41	-0.65	-0.85
	change in storage	-1	-0.02	0.03	0.09	-0.17	0.00	0.31	0.11	0.01	0.14	0.29	-0.06	0.19	0.27
	relative loss	-0.63	-0.87	2.20	0.37	1.07	0.67	-1.18	0.47	-1.01	-0.80	0.06	-1.63	-	-
	residence time	1.17	0.22	7.88	5.22	3.49	5.53	0.60	5.66	0.04	1.15	5.27	-	-	-
TV	bulk precipitation	768	0.24	0.04	0.42	0.16	0.10	0.81	0.51	0.35	0.89	0.51	-0.24	1.76	1.76
	seepage	-253	-0.02	-0.13	-0.53	-0.17	-0.11	-0.32	-0.62	0.00	-0.46	-0.64	-0.17	-1.28	-1.09
	volatilization and sedimentation	-489	-0.22	0.11	0.24	0.07	0.00	-0.48	0.17	-0.36	-0.44	0.00	0.57	-0.28	-0.63
	change in storage	-26	0.00	0.01	-0.14	-0.06	0.01	0.00	-0.06	0.01	0.02	0.12	-0.16	-0.20	-0.04
	relative loss	-0.64	-0.91	3.10	-0.58	0.43	-0.03	-0.60	0.32	-1.01	-0.50	0.01	-2.42	-	-
	residence time	0.44	0.12	5.05	1.95	1.42	1.55	0.55	1.84	0.02	0.70	1.77	-	-	-
HV	bulk precipitation	836	0.24	0.03	0.46	0.23	0.11	1.00	0.51	0.44	1.10	0.51	-0.21	2.08	2.05
	seepage	-320	-0.33	-0.22	-0.60	-0.38	-0.22	-0.18	-0.78	-0.03	-1.36	-0.71	0.55	-1.95	-2.16
	volatilization and sedimentation	-471	-0.04	0.28	0.31	0.16	0.09	0.92	0.47	-0.41	-0.17	0.00	0.02	-0.12	-0.10
	change in storage	-44	0.14	0.09	-0.17	0.00	-0.02	0.10	-0.20	0.00	0.43	0.20	-0.36	-0.01	0.22
	relative loss	-0.56	-0.18	8.33	0.68	0.69	0.86	0.92	0.92	-0.93	0.50	-0.01	-0.11	-	-
	residence time	0.59	2.39	8.76	1.89	2.17	2.74	0.19	2.17	0.07	1.67	1.96	-	-	-

GF* and -0.97 in KL*. These high values are probably due to denitrification (see Section 6.4.2). The removal of NH_4 , presumably by nitrification and subsequent denitrification, is also more efficient in KL* (relative loss -0.69) than in GF* (relative loss -0.39). As a consequence of the more efficient removal of SO_4 and NO_3 from the Kliplo pool than from the Gerritsfles pool, the removal of H is also most efficient in Kliplo (Table 9.2).

Mean annual loss is higher than mean annual input for K in GF* (relative loss 0.72) and KL* (relative loss 1.77). The loss of K must be compensated by release of K from the sediment. The high output of K is related to high concentrations in poolwater at Gerritsfles and Kliplo, which is 2.4-3.2 times higher than what might be expected on the basis of the composition of precipitation (assuming that Cl is conservative). The mean concentration of K in 188 acidified moorland pools in The Netherlands, sampled between 1983 and 1986 (Maenen 1987), is 3.8 times higher than expected on the basis of the K/Cl ratio in bulk precipitation data from KNMI/RIVM (1983-1986) stations in moorland pool districts.

The net loss of K from moorland pools is apparently a general phenomenon in The Netherlands and is probably caused by the high NH_4 deposition. High K concentrations were also observed in experiments with addition of $(\text{NH}_4)_2\text{SO}_4$ to small-scale soft water model ecosystems (Schuurkes 1987). The depletion of K found in moorland pools is in contrast to findings for terrestrial ecosystems (Section 8).

As the oldest data of K concentrations in moorland pools are from 1968 and abundant data are present only from c. 1975 onwards (Kersten 1985), it is impossible to reconstruct the presumably simultaneous increase of NH_4 and K concentrations from historical time series. If the K output continues to exceed the input, exhaustion of the K pool could be expected in the long run. The K pool in the upper 10 cm of the sediment of the Gerritsfles and Kliplo pools is roughly equal to 1000-2000 times the present annual release (E.C.L. Marnette, pers. comm.).

The rate of internal alkalinity generation is an important measure for comparison of pools with regard to their sensitivity to acidification. Unfortunately the alkalinity of precipitation has not been measured or has been measured by a method different from the one used for poolwater. Therefore the alkalinity was calculated as in Section 6.4.1, p. 136-137. The average yearly alkalinity production (Table 9.2) is in GF* $0.11 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ for 1982-1986; in KL* $0.24 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ for the period 1982-1987 and $0.30 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ for the period 1982-1986. These values are in the same order of magnitude as the values of 0.22 - $0.46 \text{ kmol}_c \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$ reported by Shaffer et al. (1988) for four precipitation dominated seepage lakes in the U.S.A. The higher rate of alkalinity generation in the Kliplo pool is probably due to the higher pH in the sediment interstitial water compared to Gerritsfles (mean pH 5.9 and 5.0, respectively). The rate of alkalinity producing biochemical processes in moorland pools, like denitrification and SO_4 reduction is positively related to pH in the range pH 3 to pH 7 (Schuurkes 1987). The production of alkalinity by weathering is considered to be of minor importance in moorland pools.

As there is a considerable annual variation, particularly in storage change and in

volatilization and sedimentation of the Gerritsfles and Kliplo pools (Figs. 9.1 and 9.2), it is not possible to extrapolate the results of the measurements in 1983 and 1984 (Table 9.3) to other years. This also becomes apparent from a comparison of the budgets GF* and KL* (Table 9.2) with GF and KL (Table 9.3). Because of the large uncertainties in the annual budgets, an analysis of the causes of the annual variation will not be attempted here and is a topic of further research.

The budgets GF, KL, TV, and HV (Table 9.3) probably contain larger errors than GF* and KL* (Table 9.2), as appears from the high relative losses of the conservative Cl ion, which varies from 0.24 (in TV) to 0.92 (in HV). The bad performance of HV is not surprising, as also the hydrological model for Hasselsven (Section 5.3.2) also did not perform well. The calculated average yearly alkalinity production, according to Shaffer et al. (1988), for GF, KL, TV, and HV is 0.43, 0.41, 0.57 and 0.02 $\text{kmol}_e \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$, respectively. Gerritsfles and Kliplo have about equal values in the models GF and KL, while they have different values in the more reliable models GF* and KL*. The calculated alkalinity production in the Tongbersven pool is even higher than in Kliplo, probably due to high levels of both SO_4 reduction (relative loss of SO_4 -0.50) and denitrification (relative loss of NO_3 -1.01) in the Tongbersven pool. Both processes are stimulated by the relatively high pH of 5.1 in the surface water and 5.5 in the sediment interstitial water of this pool (Table 6.12).

10 Diatoms

The studied slides and results of the counts are given on Microfiche. Table 10.1 gives the average relative abundance of the most important taxa in three periods, together with data on diatom-inferred pH and diversity measures. See Van Dam (1987) for a detailed presentation and discussion of the results.

10.1 Hasselsven

The diatom flora of the Hasselsven pool (Microfiche, Table 10.1) is characteristic for extremely acid waters, with a very high abundance of *Eunotia exigua*. Rare taxa (e.g. *Brachysira* species, *Neidium densestriatum*, *Navicula leptostriata*, *Nitzschia perminuta*) were found occasionally. The mean total number of taxa (11) and mean number of taxa in the count (4) are very low. The dominance (relative abundance of the most abundant taxon in the count) is very high (Table 10.1). Although no old samples are available for comparison, this pool has probably been acidified strongly during the last decades.

10.2 Goorven

The diatom flora of the Goorven pool at the three sampling stations A, B and E (Fig. 2.8) is given on Microfiche. Station E was studied most intensively, because from this station several samples taken before and after the extremely dry year 1921 were available, and the biological effects of a drought in the past could be assessed. The diatom assemblages from the three sampling stations are rather different, particularly during the years 1919-1929. After 1953 the diatom assemblages of the three stations became more similar (Table 10.1). As a whole the diatom assemblages in the years 1919-1953 were typical for oligo- to mesotrophic, weakly to strongly acid pools. Species like *Brachysira brebissonii*, *Cymbella gracilis*, *Eunotia elegans*, *Peronia fibula* and *Navicula leptostriata* are rather common in most of the old samples and are rare elsewhere in The Netherlands and adjacent areas.

In the period 1919-1929 station A was dominated by *Achnanthes minutissima*, *Cymbella microcephala* and *Brachysira vitrea* fo. *lanceolata*. *Nitzschia perminuta* and *Cymbella gracilis* were subdominants. Station B was dominated by *Navicula leptostriata* and *Fragilaria virescens*, with *Frustulia rhomboides* var. *saxonica*, *Brachysira exilis* fo. *lanceolata* and *Nitzschia perminuta* as other important taxa. At station E *Frustulia rhomboides* var. *saxonica*, *Tabellaria quadrisepata*, *Eunotia incisa*

Table 10.1. Average relative abundance of diatom taxa with a mean relative abundance of at least four valves in at least one sampling period in the Hasselven, Goorven, Gerritsfles and Kliplo, pools, together with pH spectra, diatom-inferred pH and diversity indices. From (19. . .) to (19. . .) indicates period of sampling. 0 = taxon present outside the count, - = taxon not found.

POOL	HV	GV	st.	A	GV	st.	B	GV st.	E	TV	GF	KL				
FROM 19...	83	19	52	78	25	50	75	19	75	83	16	50	64	24	48	72
TO 19...	84	29	53	84	29	53	84	28	84	84	18	60	84	29	64	84
Number of samples	5	3	2	11	5	3	12	12	12	5	7	4	21	2	4	11
Eunotia exigua	379	3	3	252	0	3	334	0	357	93	9	34	317	0	5	9
E. paludosa	0	-	-	-	0	-	0	0	0	10	1	2	0	-	1	0
Frustulia rhomboides var. saxonica	8	7	34	18	38	55	7	106	4	60	30	101	40	41	30	104
Navicula 'hoefleri'	-	-	0	3	0	-	1	5	0	4	0	0	-	12	2	18
N. subtilissima	1	2	4	4	4	5	1	24	0	1	33	2	0	31	13	66
Tabellaria quadrisepata	-	0	17	10	1	35	9	60	13	134	5	8	20	17	4	5
others	0	0	6	1	0	0	0	0	2	4	3	1	1	-	1	1
Acidobiontic taxa (subtotals)	308	12	64	288	43	98	52	195	376	304	81	149	378	101	56	203
Brachysira brebissonii	1	-	6	13	6	20	2	1	2	4	0	0	-	-	-	0
B. brebissonii f. thermalis	-	1	6	0	0	-	0	1	0	-	0	0	-	-	-	-
Cymbella gracilis	1	11	3	2	9	3	0	0	-	0	1	-	-	2	7	0
Eunotia elegans	-	1	6	3	9	4	0	2	-	-	1	-	-	-	-	-
E. incisa	0	2	88	5	6	107	3	70	1	1	103	43	2	65	37	25
E. pectinalis var. minor	-	0	9	0	0	0	0	-	-	0	0	-	-	0	0	-
E. pect. var. minor f. impressa	-	2	0	1	4	-	0	0	-	-	0	-	-	-	-	-
E. rhomboidea (asymmetrical forms)	0	1	54	10	2	17	15	1	10	3	26	112	12	14	13	60
E. rhomboidea (symmetrical forms)	0	0	2	1	0	-	0	1	1	0	25	35	2	4	5	3
Navicula leptostriata	0	3	3	1	83	8	1	66	0	0	2	1	-	45	55	26
N. mediocris	-	1	2	3	7	5	2	0	0	-	2	1	-	-	0	0
Peronia fibula	-	0	3	0	5	3	0	3	0	-	-	0	-	-	-	-
Pinnularia appendiculata	-	-	2	-	0	-	-	0	-	-	13	0	0	0	-	0
P. irrorata	-	-	6	0	-	-	-	-	-	0	0	1	-	-	-	-
Stauroneis anceps fo. gracilis	-	0	0	-	0	0	0	0	-	0	2	0	0	0	4	1

[illegible]

and *Navicula leptostriata* were dominant taxa. The latter diatom assemblage is quite similar to the present assemblage of Kliplo, which is a humic pool. Particularly *Frustulia rhomboides* var. *saxonica* is known as an indicator of humic acid waters. Presumably Goorven was, at least near station E, more humic in the past than presently.

In the period 1975-1984 the similarity between the three stations is much greater than in 1919-1929. *Eunotia exigua*, an acidobiontic species, is the dominant species on all stations and its abundance is larger than that of any of the dominant species sixty years ago. The relative abundance of *Eunotia exigua* increases from station A to E. In contrast, circumneutral diatoms like *Eunotia bilunaris* and *Fragilaria virescens* decrease from station A to E in the most recent period.

The period 1950-1953 was only investigated at stations A and B. The majority of the species of the earliest period was still present, although the relative abundance of alkaliphilous species, like *Nitzschia perminuta* and *Cymbella microcephala*, was much lower than in 1919-1929. The same is true for circumneutral taxa such as *Achnanthes minutissima* and *Brachysira exilis* fo. *lanceolata*. Species which are characteristic for acid waters, e.g. *Tabellaria quadrisepata*, *Eunotia rhomboidea* and especially *Eunotia incisa* are more abundant in 1950-1953 than in 1919-1929. Particularly the latter species was most abundant in the middle period.

The diatom-inferred pH (Table 10.1) within the period 1919-1929 gradually decreased from 6.9 at station A, via 5.8 at station B to 4.9 at station E. In 1975-1984 these values are 4.3, 4.1 and 4.1, respectively. The values during the period 1950-1953 at stations A and B are intermediate. Thus the decrease of diatom-inferred pH over time was largest at station A (1.6 units), and smallest at station E (0.8 units). These changes are statistically significant (Table 10.2). The pH gradient, which was present sixty years ago, apparently still exists, although the extremes are closer together and the diatom-inferred pH indicates acidification at all sampling stations. The present gradient is not detectable by direct pH measurement (Van Dam 1987).

The average total number of species in the sample and the number of species in the count significantly decreased between the periods 1919-1929 and 1975-1984. The dominance significantly increased over the same period (Tables 10.1 and 10.2). Thus over the last sixty years both the diversity within the whole pool and the diversity at each sampling station decreased. The dissimilarity between the three sample stations also decreased.

10.3 Tongbersven

The diatom flora of the Tongbersven pool (Microfiche, Table 10.1) is characteristic for humic acid waters. The most abundant taxa (*Eunotia exigua*, *E. bilunaris* and *Frustulia rhomboides* var. *saxonica*) are rather common in The Netherlands and adjacent areas, but a number of rare taxa is fairly common in this pool, such as *Brachysira brebissonii*, *Cymbella gracilis* and *Navicula hoefleri*.

The mean diatom-inferred pH in 1983-1984 was 4.4 (Table 10.1). The mean total

Table 10.2. Goorven stations A, B, E, Gerritsfles and Kliplo, two-tailed significance levels of Wilcoxon two-sample tests applied to Renberg-inferred pH (pH-RENBE), total number of taxa (NRSPTOTA), number of taxa in count (NRSPCOUN) and dominance (DOMINANC) between different periods; - = too few samples for test, n.s. = not significant.

Period 1		1916-1929	1916-1929	1948-1964
Period 2		1948-1964	1964-1984	1964-1984
GVA	pH-RENBE	-	<0.01	-
	NRSPTOTA	-	0.02	-
	NRSPTOTA	-	n.s.	-
	DOMINANC	-	n.s.	-
GVB	pH-RENBE	<0.05	<0.002	<0.01
	NRSPTOTA	n.s.	<0.01	n.s.
	NRSPCOUN	n.s.	<0.002	<0.01
	DOMINANC	n.s.	<0.002	<0.01
GVE	pH-RENBE	-	<0.002	-
	NRSPTOTA	-	<0.01	-
	NRSPCOUN	-	<0.002	-
	DOMINANC	-	<0.002	-
GF	pH-RENBE	n.s.	<0.001	<0.01
	NRSPTOTA	n.s.	<0.01	<0.01
	NRSPCOUN	n.s.	<0.001	<0.001
	DOMINANC	n.s.	<0.01	<0.01
KL	PH-RENBE	-	-	<0.002
	NRSPTOTA	-	-	n.s.
	NRSPCOUN	-	-	n.s.
	DOMINANC	-	-	n.s.

number of taxa, mean number of taxa in the count, and the dominance are about the same as in the humic pool Kliplo (see 10.5 and Table 10.1). No historic diatom samples are available for the investigated basin of Tongbersven.

10.4 Gerritsfles

The diatom flora of the Gerritsfles pool (Microfiche, Table 10.1) is typical for strongly to extremely acid waters. Taxa like *Brachysira vitrea* and *Navicula subtilissima* are rather common in the earliest samples and are rare elsewhere in The Netherlands and adjacent areas. In the period 1916-1918 *Eunotia incisa* and *E. bilunaris* were dominant taxa, while *Brachysira vitrea* fo. *lanceolata*, *E. rhomboidea* (asymmetrical and

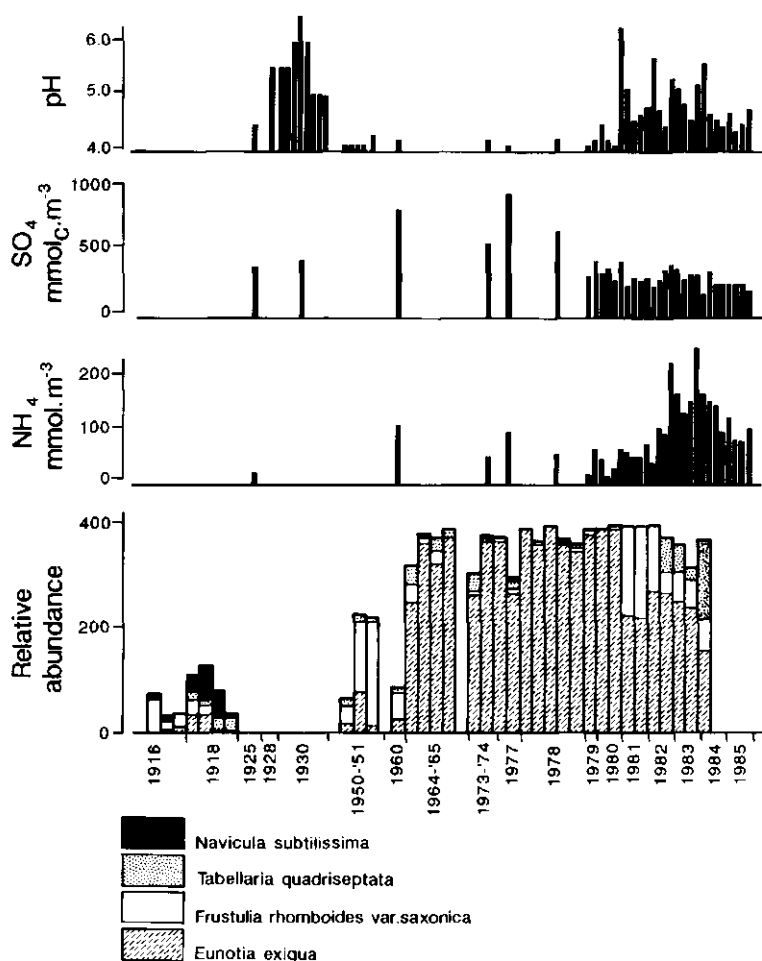


Figure 10.1. Gerritsfles: changes in some chemical parameters and relative abundance of acidobiontic diatoms.

symmetrical forms), *Frustulia rhomboides* var. *saxonica* and *Navicula subtilissima* where subdominant. From 1950 to 1960 *E. rhomboidea* (predominantly asymmetrical forms) and *F. rhomboides* var. *saxonica* were dominant taxa, while *E. incisa* was subdominant. In the period 1964-1984 *E. exigua* became dominant and *F. rhomboides* var. *saxonica* was the only subdominant taxon.

The diatom-inferred pH (Tables 10.1 and 10.2) decreased significantly from 4.8 to 4.1 over the last 70 years. The mean total number of taxa per sample is 23-24 before 1960 and only 12 in the most recent period. The mean number of taxa in the count also decreased, while the dominance increased. As a whole, the diversity of diatom taxa in Gerritsfles in the period 1964-1984 is significantly lower than before (Tables 10.1, 10.2).

The major break in the long-term development of the diatom assemblages is between 1960 and 1964. In that period the constantly low relative abundance of c. 20 valves of *Eunotia exigua* changed to a constantly high relative abundance of c. 317 valves (Fig. 10.1). At the same time other taxa (e.g. *E. rhomboides*, *E. incisa*, *Tabellaria flocculosa*) suddenly declined. *Pinnularia microstauron* was most abundant in this transition period. Presumably these changes were induced by the extremely dry summer of 1959 (Schuurmans 1977), when probably a large part of the bottom of the pool dried up. The concomitant release of sulphate from the sediment after refilling (Vangenechten et al. 1981, Van Dam et al. 1981) may have induced the enormous increase of *Eunotia exigua* and the decrease of other species with a time lag of a few years.

10.5 Kliplo

The diatom flora of the Kliplo pool (Microfiche, Table 10.1) is typical for moderately acid, oligo-mesotrophic waters. Taxa like *Navicula leptostriata*, *N. hoefleri* and *N. subtilissima* are rather common in most of the samples and are rare elsewhere in The Netherlands and adjacent areas.

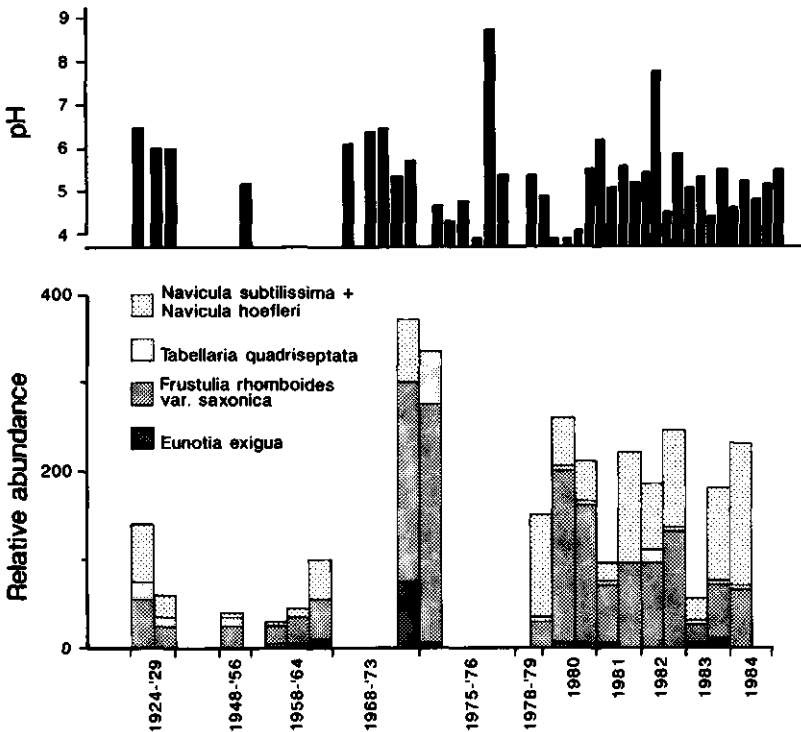


Figure 10.2. Kliplo: changes in pH and relative abundance of acidobiontic diatoms.

The differences between the periods 1924-1920, 1948-1964 and 1972-1984 are far less obvious than in Goorven and Gerritsfles. In the first period *Tabellaria flocculosa* was the dominant species. Other abundant taxa were *Frustulia rhomboides* var. *saxonica*, *Navicula subtilissima*, *N. leptostriata*, *Eunotia incisa* and *E. bilunaris*. In the second period *Brachysira vitrea* fo. *lanceolata*, with *F. rhomboides* var. *saxonica*, *E. incisa*, *E. bilunaris*, *T. flocculosa*, *N. leptostriata* and *Nitzschia gracilis* as other important taxa. In the last period *F. rhomboides* var. *saxonica* dominated the assemblages, while *N. subtilissima*, *N. leptostriata*, *E. rhomboidea* (asymmetrical forms), *E. incisa*, *E. bilunaris* and *T. flocculosa* were other abundant species.

The mean total number of taxa per sample and the mean number of taxa in the count are relatively constant with c. 29 and 18 taxa respectively (Table 10.1). In contrast, the dominance increased over the last 60 years (Table 10.1), indicating a decrease of the diversity of the diatom assemblages. The diatom-inferred pH (Table 10.1) changed significantly from 5.0 via 5.5 to 4.7 over the last 60 years (Table 10.2). In contrast to Gerritsfles and Goorven no significant changes are found after the extremely dry year 1976 (Fig. 10.2).

11 Conclusions

1. For most solutes concentrations in throughfall are c. 2-5 times their concentrations in bulk deposition. This difference is caused by a higher capture efficiency for atmospheric gases and aerosols of tree canopies compared to open samplers, and by the leaching of solutes from the trees.
2. Sodium, Mg and Cl are largely sea-salt derived in both bulk flux and in throughfall. Leaching of these solutes is probably unimportant.
3. Most NH_4 and SO_4 in throughfall originate from deposition of atmospheric NH_3 and SO_2 . Their deposition is probably enhanced by co-deposition as $(\text{NH}_4)_2\text{SO}_4$. The estimated mean deposition velocity of SO_2 over pine forest at the studied sites is $1.33 \text{ cm} \cdot \text{sec}^{-1}$.
4. Transformation of nitrogen (i.e. assimilation or nitrification of NH_4) is the most important source of soil acidity at all sites.
5. Acid neutralization is primarily accomplished by the dissolution of secondary Al. In podzolic soils this results in a rapid depletion of Al in the spodic (Bhs) horizon. Concomitantly an increase in the mineralization rate or an increased dissolution of organic matter (both suggested in literature) may be expected. Because organic matter is by far the most important contributor to the CEC this decrease may have severe implications for future forest productivity on these soils.
6. The base cation weathering rates are extremely low in the studied soils and barely produce enough nutrient cations to support the net assimilation by the vegetation.
7. In the studied soils the mobilization of Si and base cations does not increase as a result of increased acid loads.
8. All pools are mainly fed by precipitation. At two sites the groundwater table is far below the pool bottom; at the other two sites the bottom is occasionally below the groundwater table, but inflow of groundwater is not likely to occur. In addition, no evidence was found for inflow of water over the spodic horizon into the pool. This means that none of the studied pools have a significant terrestrial

catchment area. Therefore a coupling of the processes and the rates of acidification in the terrestrial and adjacent aquatic ecosystems is unlikely.

9. The internal rate of alkalinity production due to denitrification and sulphate reduction is lowest in the pool with the lowest average pH of sediment interstitial water and highest in the pool with the highest average pH. It is not clear whether a high pH is the cause or a consequence of a high rate of alkalinity production.
10. Diatom analysis of herbarium samples (1916-1973) and recent samples (1977-1984) demonstrated a long-term acidification of the moorland pools. The largest pH decrease was found in pools where the largest part of the bottom desiccates in extremely dry years.
11. The acidification reduced the diversity of both diatom assemblages and macrophytic vegetation. *Eunotia exigua*, a diatom characteristic for waters loaded with mineral acids, became the dominant species, replacing taxa which are characteristic for humic acid waters, e.g. *Navicula subtilissima* and *Frustulia rhomboides* var. *saxonica*. Among the macrophytes *Juncus bulbosus* and *Sphagnum* became the dominant taxa. The growth of isoetid taxa, e.g. *Lobelia dortmanna*, was suppressed.
12. After the extreme drought of 1921 no acidification occurred. The acidification that occurred after the drought periods of 1959 and 1976 in the pools where a large part of the bottom dried up is probably due to re-oxidation of reduced sulphur compounds that had accumulated in the sediment during the preceding period of high atmospheric deposition.

Appendix 1

Description and classification of the four soils studied

All soils were described using the 'Guidelines for soil description' (FAO 1977). Soils were classified according to de Bakker and Schelling (1966) and Soil Survey Staff (1975).

Gerritsfles Forest (GFF)

I) Information on the site sampled

Date of examination: 09-15-1982 Description: J. Mulder and N. van Breemen

Location: ca. 0.5 km SW of the moorlandpool 'Gerritsfles', near Kootwijk, the Netherlands.

Elevation: ca. 40 m above sea level

Land-form: drift sand with a rolling topography (slopes up to 40%, but the range in elevation less than 10 m)

Physiographic position of the site: at the lower part of an eastfacing slope of a 4 m high sanddune

Slope: concave, moderately steep (13-25%)

Vegetation: *Pinus sylvestris* (ca. 60 yr); Undergrowth: *Deschampsia flexuosa*

Climate: humid, with a well-distributed rainfall (ca. 800 mm annually)

II) General information on the soil

Soil name (Dutch classification system): Duinvaag

Soil moisture regime: udic

Soil temperature regime: mesic

Soil Taxonomy: Typic Udipsamment

Parent material: driftsand (105-300 μm) of local origin

Drainage class 5: somewhat excessively drained

Moisture condition soil, prevailing at moment of examination: dry throughout

Stoniness class 0: no stones

Rock outcrop class 0: no rocks

III) Description of individual soil horizons

O1	+10/+7-0 cm	little decomposed <i>Pinus</i> litter with abundant very fine and fine roots and common medium roots, having a clear, smooth boundary
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C 0 > 200 cm well sorted fine driftsand (median 157 μm). Throughout the profile 0.5 to 30 mm thick wavy bands occur, that differ in organic matter content. Particularly the top 40-cm is evenly darkened (10YR 5.5/3.5; light yellowish brown to brown) presumably due to transported organic matter from the forest floor. Colour > the 40-cm: 10YR 6/4 (light yellowish brown). In the upper 0.5-cm some bleached sandgrains are present. No colour mottles. Structure grade 0: Structureless (single grain). Consistency when dry: soft. No cutans. Very few large pores, very few coarse pores and few very fine pores. Many fine roots (up to the 60-cm), common coarse roots to below the 120-cm; most very coarse roots (4 to 5 cm diameter) grow horizontally between the 40- and 70-cm depth.

Gerritsfles bare (GFB)

I) Information on the site sampled

Date of examination: 09-30-1982

Description: J. Mulder

Location: 40 m south of profile GFF

Elevation: 40 m above sea level

Land-form: drift sand with a rolling topography (slopes up to 40%, but the range in elevation less than 10 m)

Physiographic position of the site: at the lower part of a Southwest facing slope of an 8 m high sanddune

Slope: concave, moderately steep (13-25%)

Vegetation: a few mm thick layer of algae

Climate: humid, with a well distributed rainfall (ca. 800 mm annually)

II) General information on the soil

Soil name (Dutch soil classification system): Duinvaag

Soil Taxonomy: Typic Udipsamment

Soil moisture regime: udic

Soil temperature regime: mesic

Parent material: driftsand (105-300 μm), of local origin

Drainage class 5: somewhat excessively drained

Moisture condition soil, prevailing at moment of examination: dry from 0 to the 20-cm, moist below the 20-cm depth

Stoniness class 0: no stones

Rock outcrop class 0: no rocks

III) Description of individual soil horizons

C 0 > 200 cm well sorted fine driftsand (median 169 μm) with 1 to 2 mm thick layers, which differ in organic matter content. The top 25 to 35-cm has a more even and darker colour (10YR 5/4; dull yellowish brown) than the soil below this depth (consisting of a few mm to 10 cm thick bands of lighter (10YR 7/6; bright yellowish brown) and darker (10YR 5/4; dull yellowish brown) material). No colour mottles. Structure class 1: very weak, medium subangular blocky from 0 to 3 cm (probably due to the influence of the algae); structureless, single grain below the 3-cm depth. Consistency when dry: soft between the 0 and 3-cm and loose at greater depth. No cutans. Very few fine pores. Few very fine roots in the upper 25-cm; no roots at greater depth.

Tongbersven (TV)

I) Information on the site sampled

Date of examination: 10-11-1982 Description: J. Mulder

Location: 10 m Southeast of moorlandpool Tongbersven near Oisterwijk, the Netherlands

Elevation: 10 m above sea level

Land-form: coversands with a rolling topography (slopes up to 30%, but the range in elevation less than 10 m)

Physiographic position of the site: summit of a dune with a 30% Northwest and a 5% Southeast facing slope

Slope: almost flat

Vegetation: *Pinus sylvestris* (ca. 35 years old); no undergrowth

Climate: humid with a well distributed rainfall (ca. 800 mm annually)

II) General information on the soil

Soil name (Dutch soil classification system): Haarpodzol

Soil taxonomy: Typic Haplorthod

Soil moisture regime: udic

Soil temperature regime: mesic

Parent material: well sorted coversand (75-300 μm)

Drainage class 4: well drained

Moisture condition soil, prevailing at moment of examination: moist throughout

Depth of groundwater table, between October 1982 - April 1985: minimum -354 cm, maximum -479 cm

Stoniness class 0: no stones

Rock outcrop class 0: no rocks

III) Description of individual soil horizons

O1	+5/3–0 cm	partly decomposed <i>Pinus</i> litter; many very fine roots. An abrupt smooth boundary
E	0–17/23 cm	well sorted fine sand (median 147 μm); colour 5YR 4/2 (grayish brown) with prominent coarse patches of 10YR 4/3 (brown); no colour mottles present. Structure grade 0: Structureless (single grain); consistency when moist: loose. Few fine pores; common coarse, medium and fine roots. An abrupt wavy boundary
Bhs	17/23–38/40 cm	well sorted fine sand (median 150 μm); colour 5YR 2.5/1 (brownish black) with some very thin lighter coloured fibers; no colour mottles present. Structure grade 1: weak; thin platy structure; consistency when moist is firm. Few fine pores; very few medium and few fine roots, which are limited to the upper portion of this horizon. A gradual broken boundary
Bs	38/40–54/58 cm	well sorted fine sand (median 142 μm); colour 7.5YR 4/4 (brown); a few 5 to 10 mm thick wavy fibers are present; common coarse distinct mottles (2.5 Y 7/4; light yellow). Structure grade 0: structureless (single grain); consistency when moist: loose. Few fine pores; very few fine roots. A clear wavy boundary
BC1	54/58–87/88 cm	well sorted fine sand (median 15 μm); colour 10 YR 5/6 (yellowish brown); few coarse distinct sharp mottles (2.5 Y 7/4; light yellow) containing very loosely packed sand. Few fibers (10 YR 4/4; brown). Structure grade 0: structureless (single grain); consistency when moist: loose. Few fine pores; very few fine roots. A diffuse boundary
BC2	> 87/88 cm	well sorted fine sand (median 147 μm); colour 10 YR 6/6 (bright yellowish brown) with irregular shaped patches of 10 YR 6/8 (bright yellowish brown). To a depth of 250 cm still few fibers present. Structure grade 0: structureless (single grain); consistency when moist: loose. very few fine pores; no roots.

Hasselsven (HV)

I) Information on the site sampled

Date of examination: 10-25-1982

Author of description: J. Mulder

Location: ca. 75 m SE of moorlandpool Groot Hasselsven, near Leende, the Netherlands

Elevation: 28 m above sea level

Land-form: coversand with undulating topography

Physiographic position of the site: lower part of a slope

Slope: > 100 m long, 3‰, NW facing

Vegetation: *Calluna vulgaris* with some mosses and lichens. Climate: humid with a well distributed rainfall (ca. 800 mm annually)

II) General information on the soil

Soil name (Dutch soil classification system): Haarpodzol

Soil taxonomy: Typic Haplorthod

Soil moisture regime: udic

Soil temperature regime: mesic

Parent material: coversand (75-300 μm)

Drainage class 4: well drained

Moisture condition soil, prevailing at moment of examination: moist throughout

Depth of groundwater table between October 1982 - April 1985: minimum -128 cm,
maximum -282 cm

Stoniness class 0: no stones

Rock outcrop class 0: no rocks

III) Description of individual soil horizons

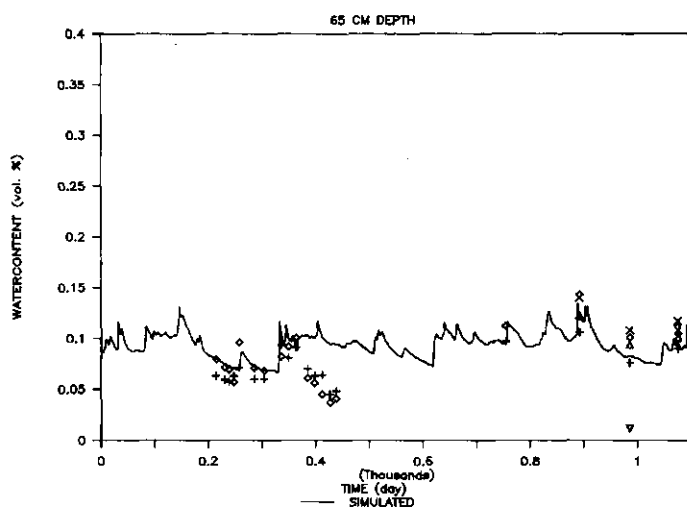
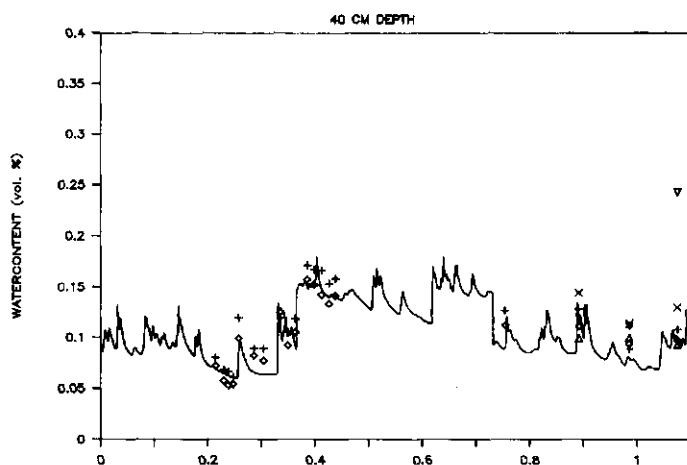
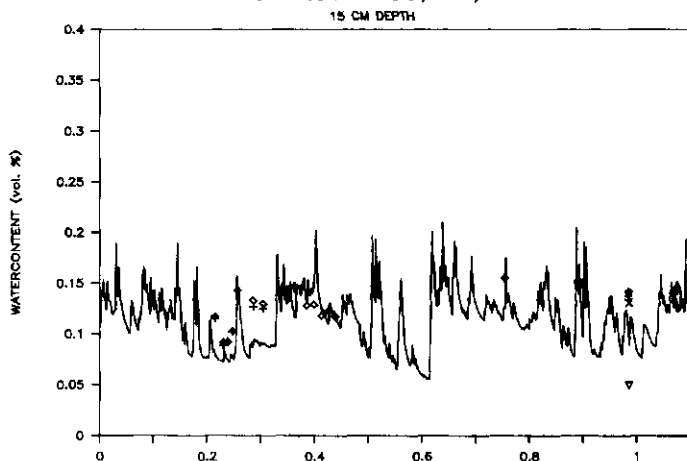
O1	+3- 0 cm	<i>Calluna vulgaris</i> residues in various stages of decomposition. Many very fine roots, common medium and fine roots. An abrupt smooth boundary
E	0 -10/11 cm	fairly well sorted sand (median 146 μm), containing a few gravels (up to 1 cm in diameter). Colour 5 YR 3/1, at the lower end changing to 5 YR 2.5/1 (both brownish black); no colour mottles. Structure grade 0: structureless (single grain); consistency when moist: loose. Common very fine pores; few very fine roots and common fine and medium roots. A clear wavy boundary
Bhs1	10/11-13/16 cm	fairly well sorted sand (median 147 μm), containing a few gravels (up to 1 cm in diameter). Colour 5 YR 3/2 (dark reddish brown); few faint medium mottles of lighter coloured material present. Structure grade 0: structureless (massive); consistency when moist is very friable. Few very fine pores; common fine and very fine roots. A clear wavy boundary
Bhs2	13/16-29/31 cm	fairly well sorted sand (median 149 μm), containing a few gravels (up to 1 cm in diameter). Colour 5 YR 3/3 (dark reddish brown) changing with depth to 10 YR 5/8 (yellowish brown) plus fibers (7.5 YR 4/4; brown); no colour

		mottles. Structure grade 0: structureless (massive); consistency when moist is very friable. Few very fine pores; few fine and medium roots. A clear wavy boundary
Bs	29/31-81/85 cm	fairly well sorted sand (median 141 μm), containing a few gravels (up to 1 cm in diameter). Colour 10 YR 7/8 (yellow orange) with few coarse diffuse faint mottles of darker (more black) material; no fibers. Structure grade 0: structureless (single grain); consistency when moist: loose.
C	> 81/85 cm	Many micropores; no roots. A gradual boundary fairly well sorted sand (median 125 μm), containing a few gravels (up to 1 cm in diameter). Colour: irregularly shaped patches of 10 YR 8/2 (light gray) and 10 YR 6/8 (bright yellowish brown); no fibers. Structure grade 0: structureless (single grain); consistency when moist is loose (light gray patches) or friable (bright yellowish brown patches). Many micropores and few very fine pores; no roots.

Appendix 2

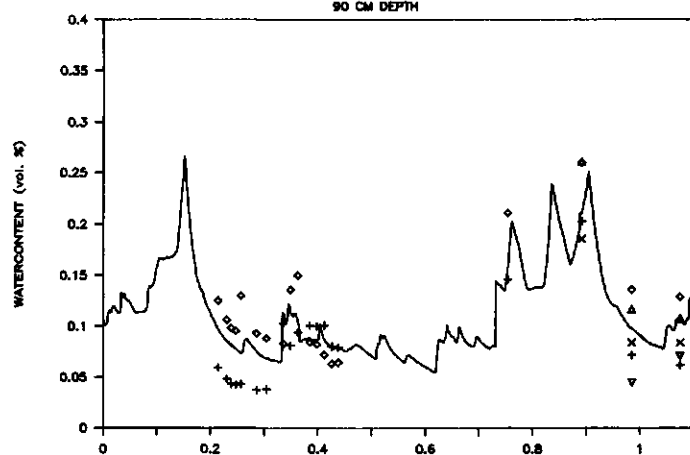
Simulated and measured soil water contents for the period 1983-1985 at Hasselsven (HV), Tongbersven (TV), Gerritsfles forest (GFF) and Gerritsfles bare (GFB). Different symbols denote different sample points (neutron probe access tubes).

HASSELSVEN 83, 84, 85

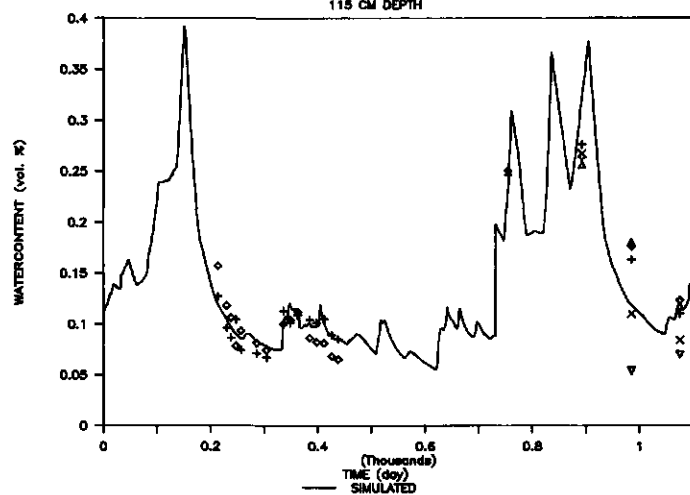


HASSELSVEN 83, 84, 85

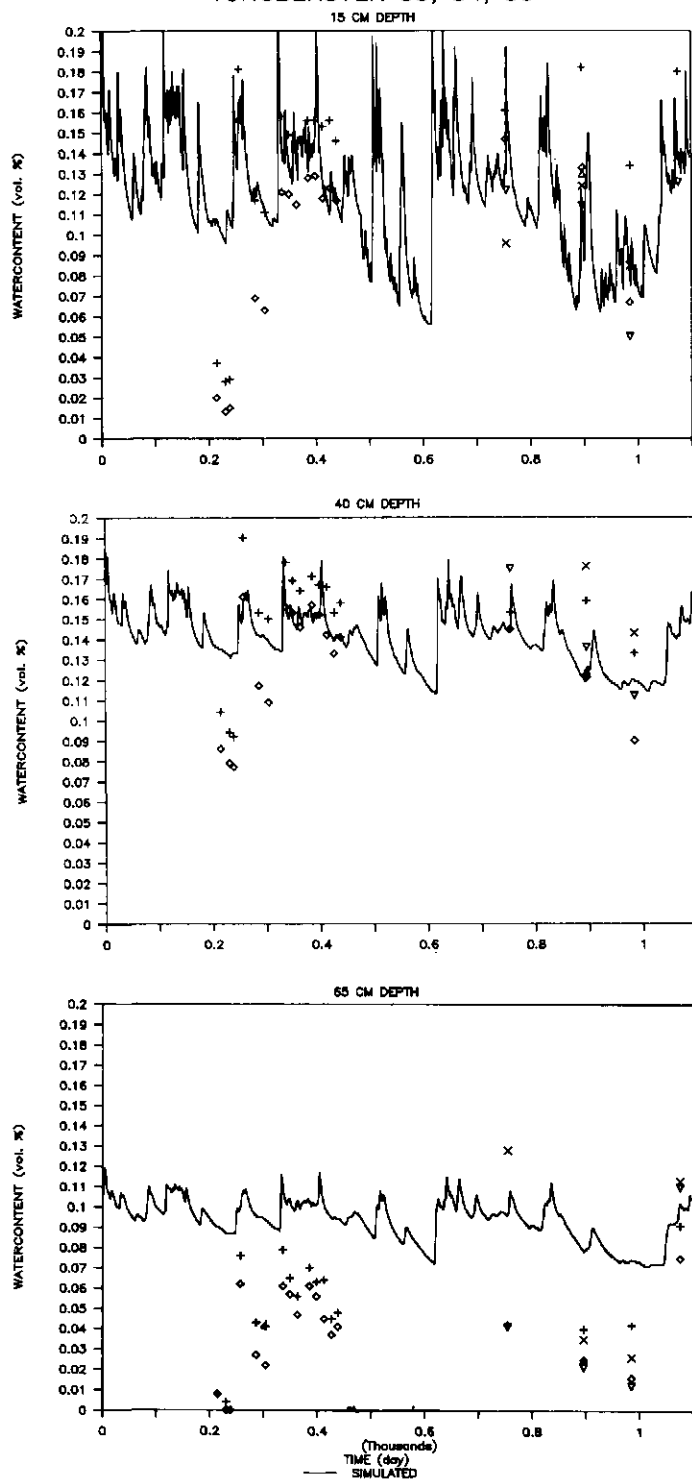
90 CM DEPTH



115 CM DEPTH

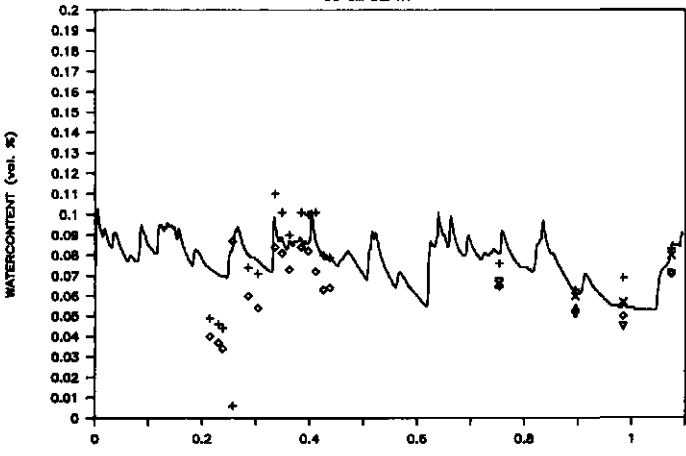


TONGBERSVEN 83, 84, 85

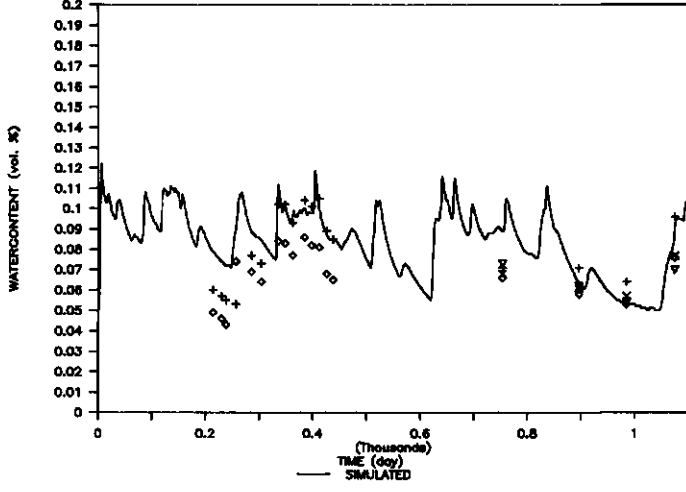


TONGBERSVEN 83, 84, 85

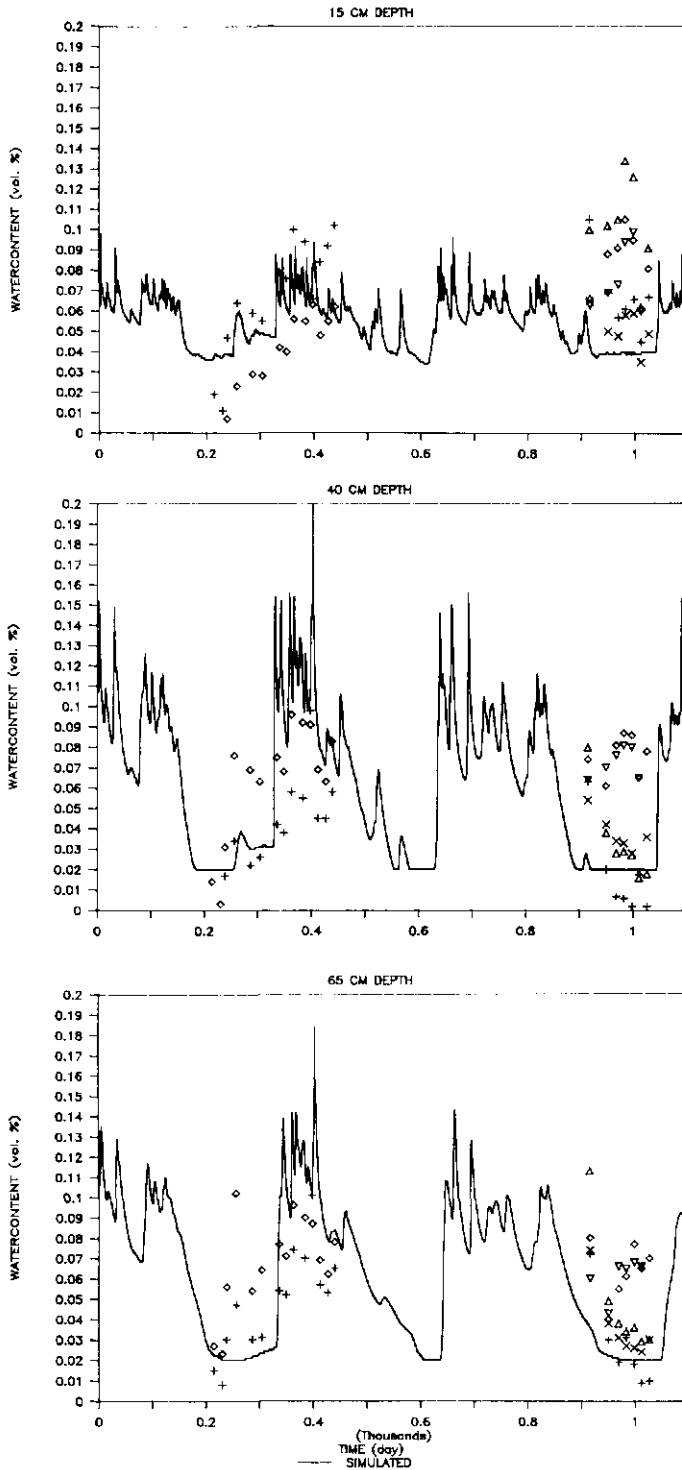
90 CM DEPTH



115 CM DEPTH

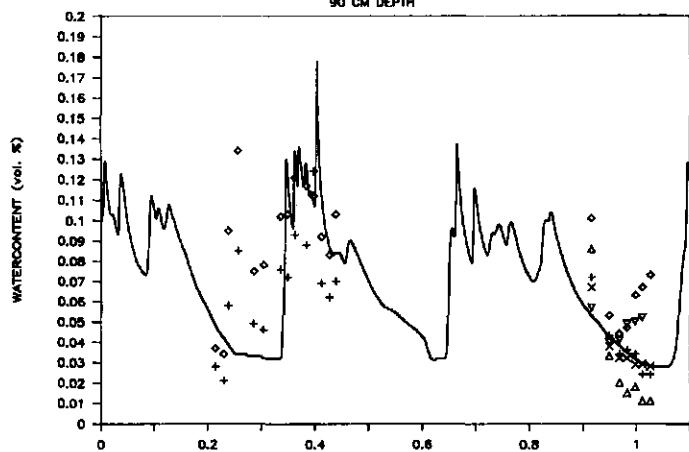


GERRITSFLES FOREST 83, 84, 85

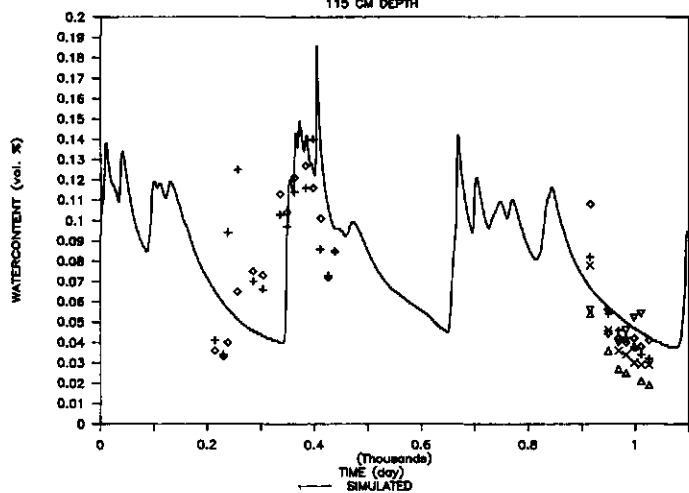


GERRITSFLES FOREST 83, 84, 85

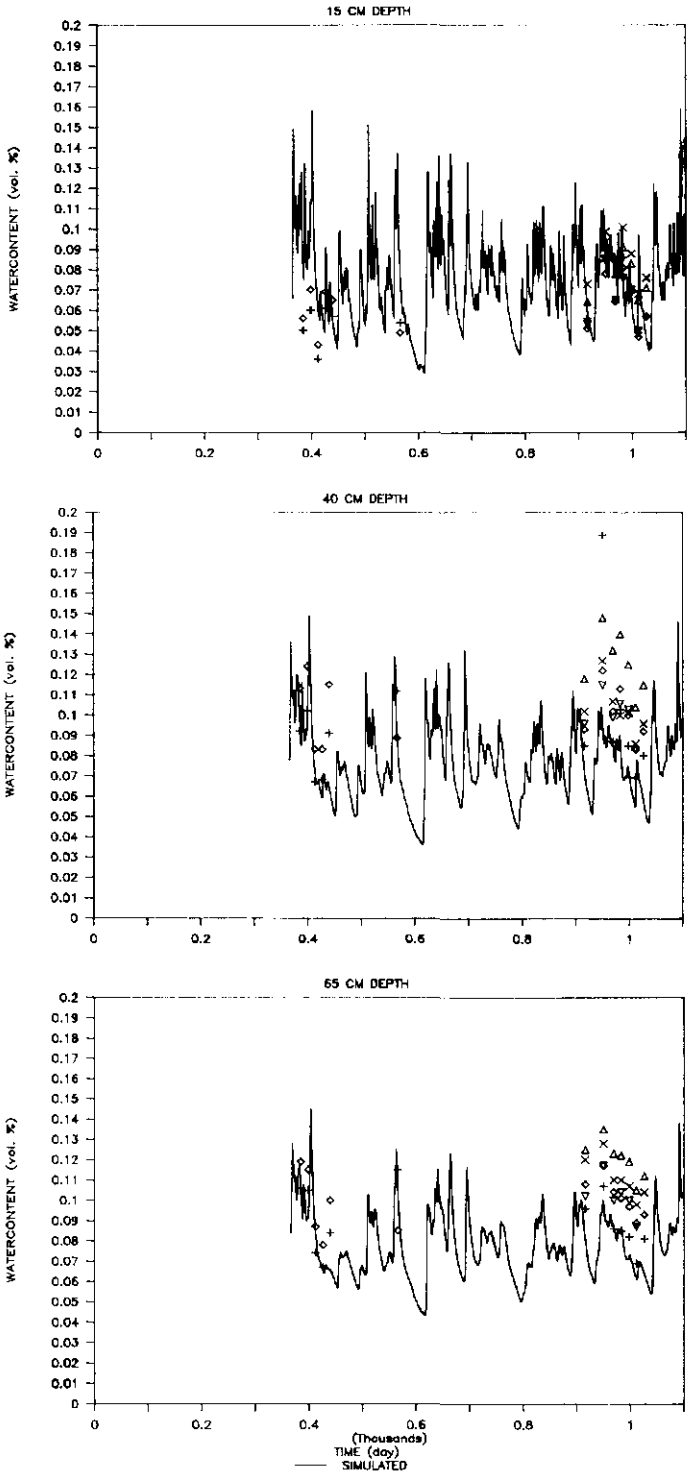
90 CM DEPTH



115 CM DEPTH

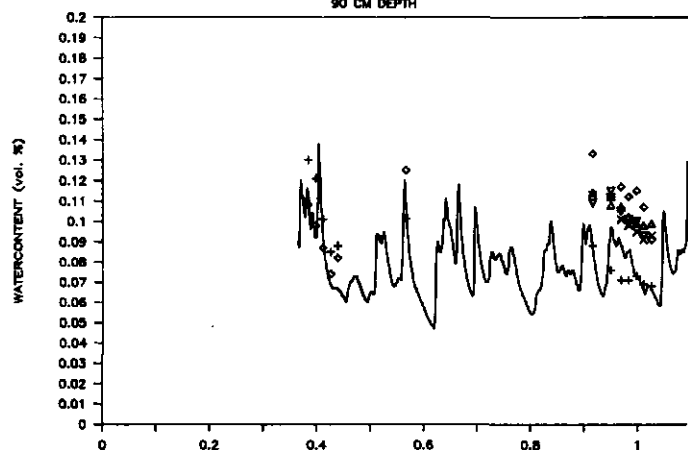


GERRITSFLES BARE 83, 84, 85

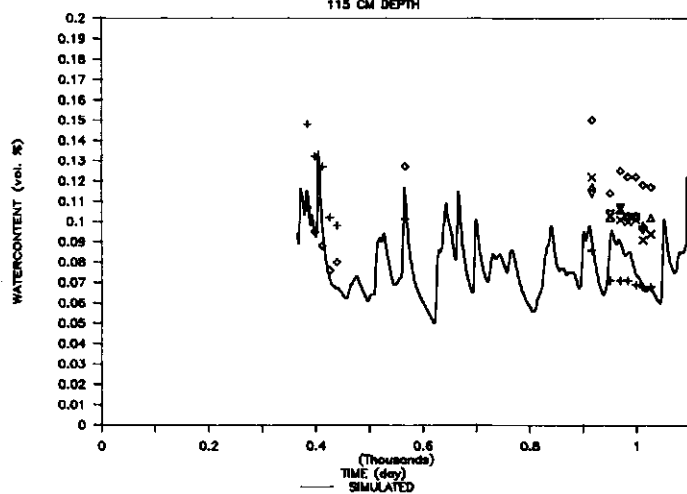


GERRITSFLES BARE 83, 84, 85

90 CM DEPTH



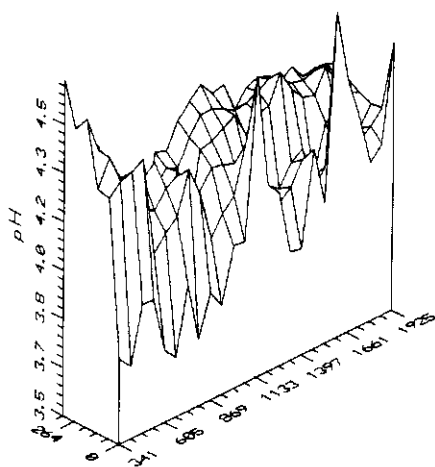
115 CM DEPTH



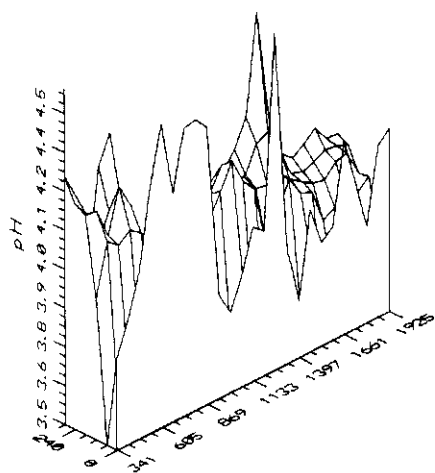
Appendix 3

Solute concentrations as a function of time (day number after January 1, 1982) and depth (in cm) in the four soil investigated. Values are means of duplicates lysimeters. Extreme values have been smoothed by the method of plotting.

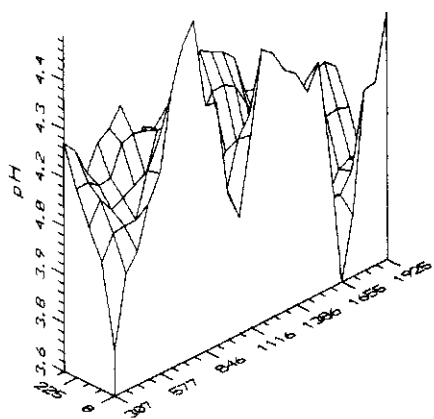
HASELSVEN pH



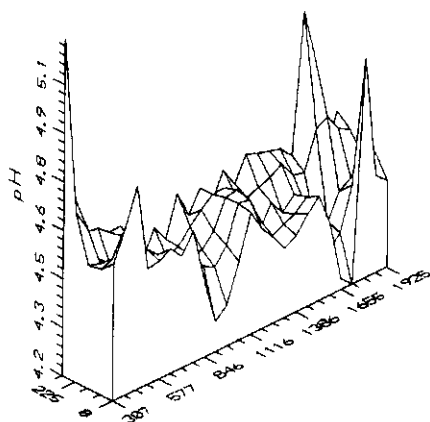
TONGBERSVEN pH



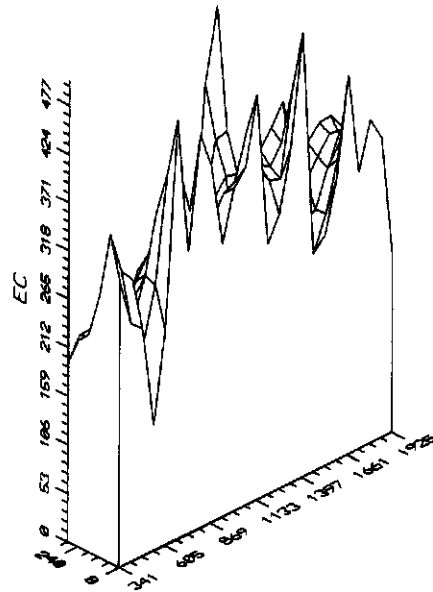
GERRITSFLES-FOREST pH



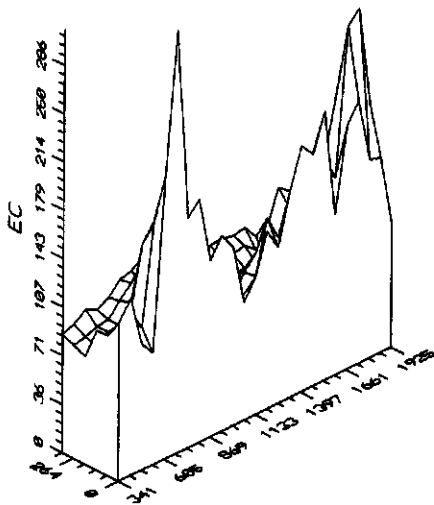
GERRITSFLES-BARE pH



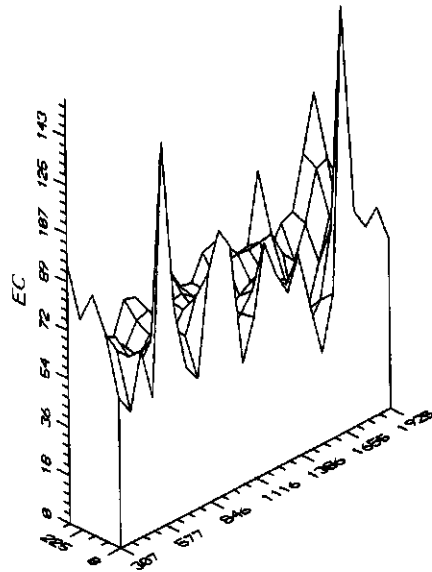
TONGBERSVEN EC



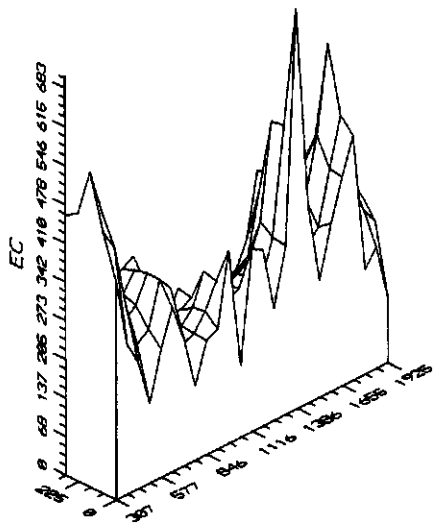
HASSELSVEN EC



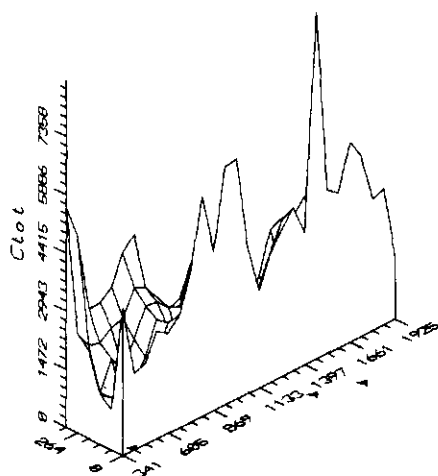
GERRITSFLES-BARE EC



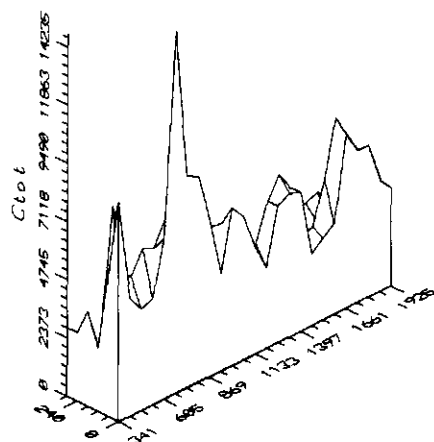
GERRITSFLES-FOREST EC



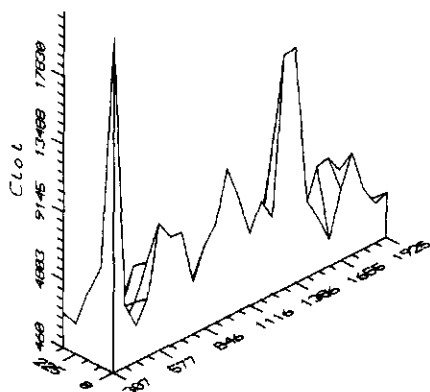
HASSELSVEN Ctot



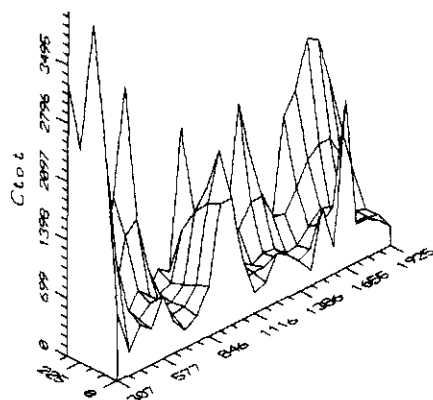
TONGBERSVEN Ctot



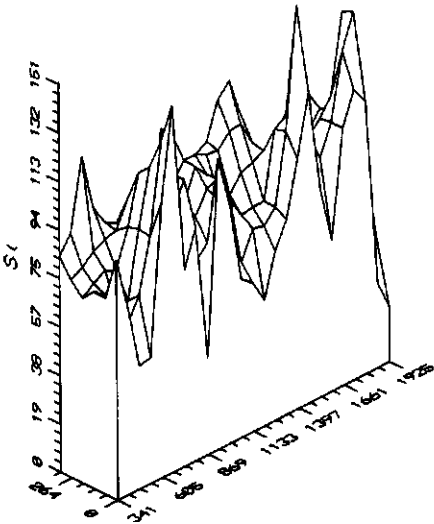
GERRITSFLES-FOREST Ctot



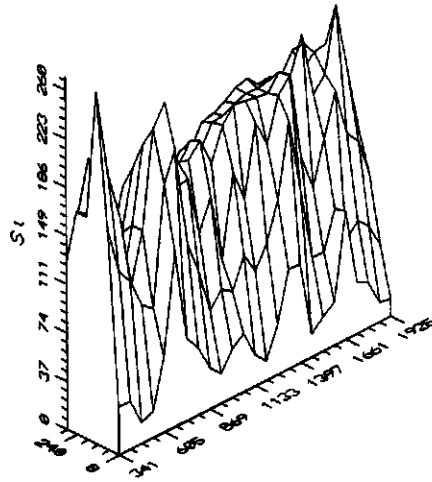
GERRITSFLES-BARE Ctot



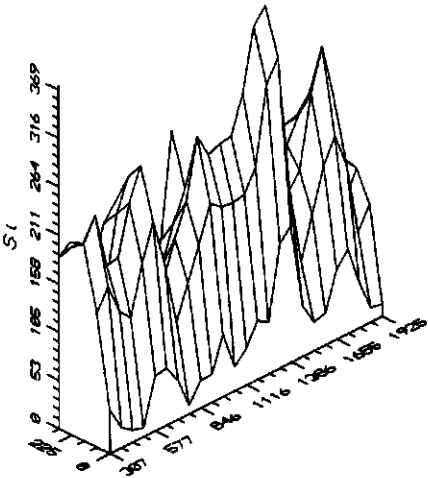
HASSELSVEN SL



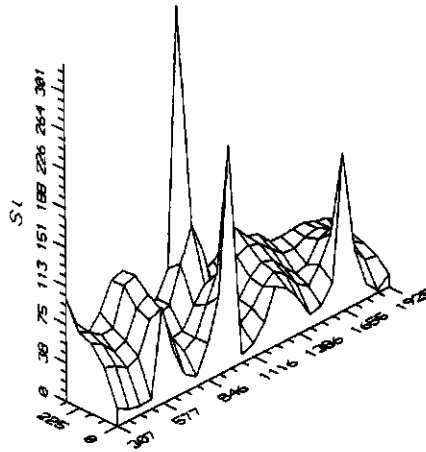
TONGBERSVEN SL



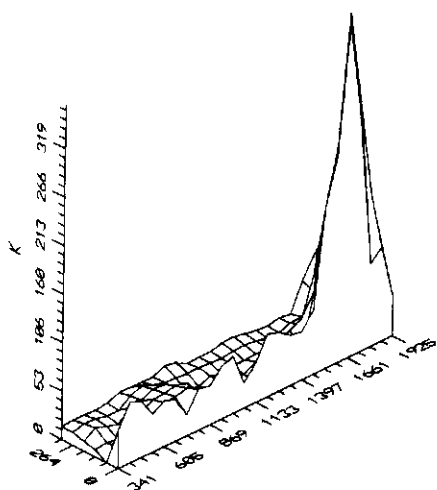
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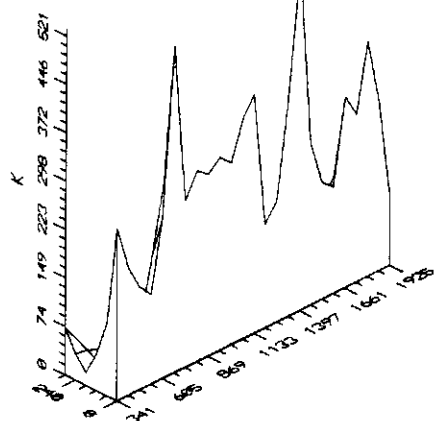
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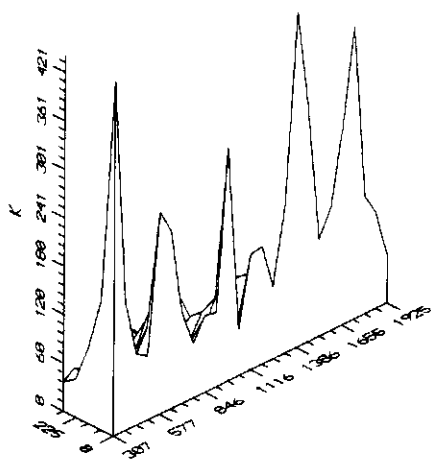
HASSELSVEN K



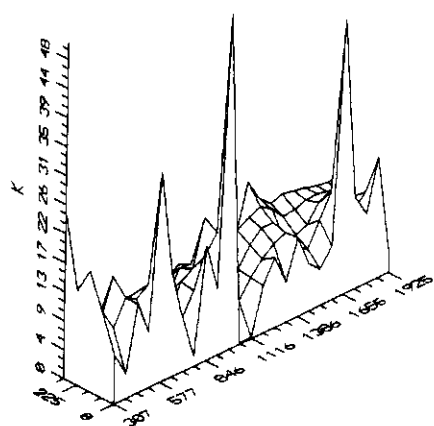
TONGBERSVEN K



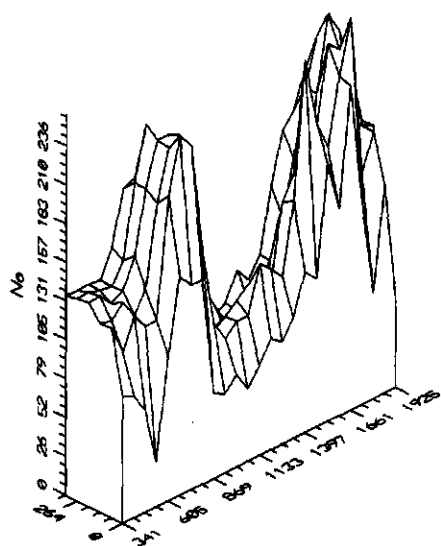
GERRITSFLES-FOREST K



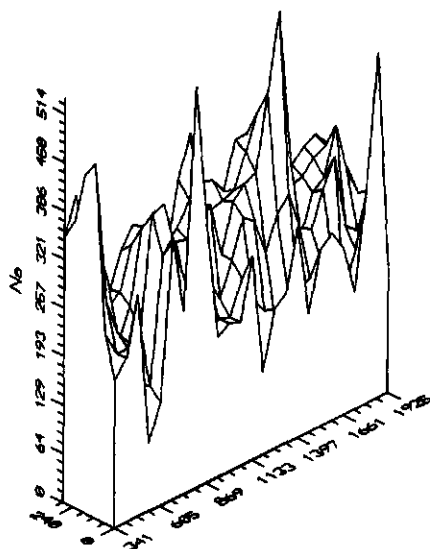
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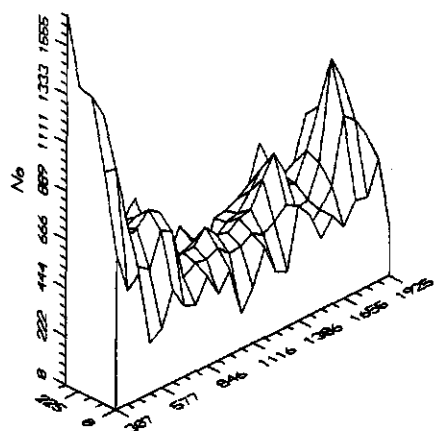
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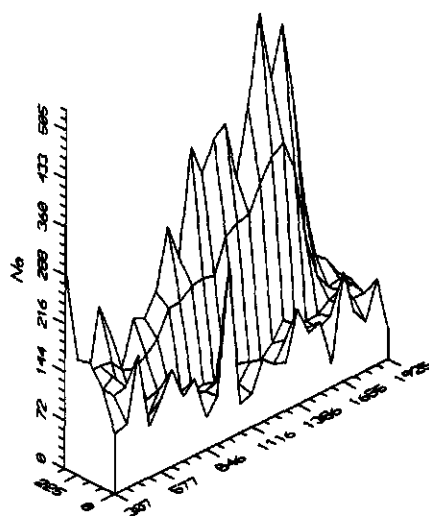
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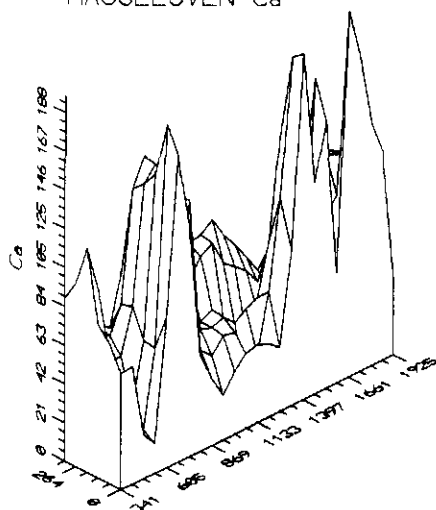
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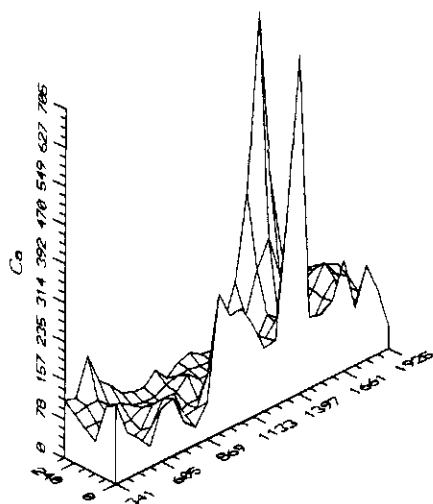
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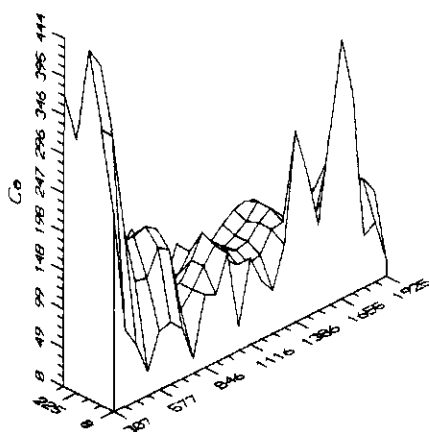
HASSELSVEN C₀



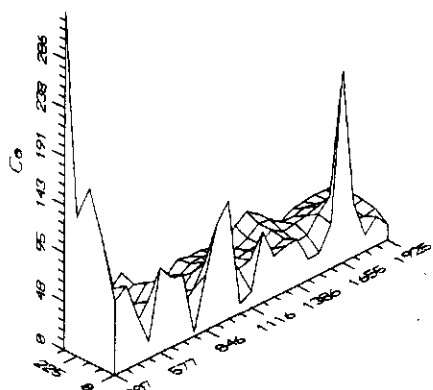
TONGBERSVEN C₀



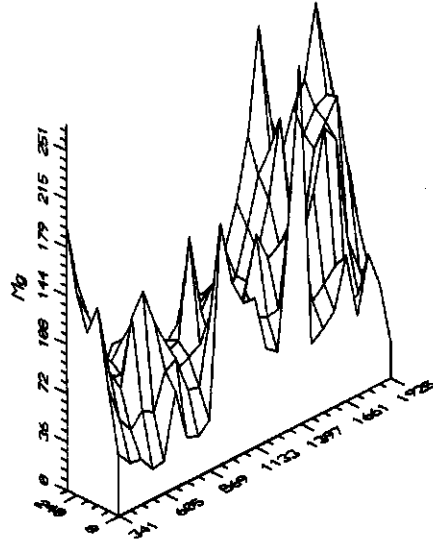
GERRITSFLES-FOREST C₀



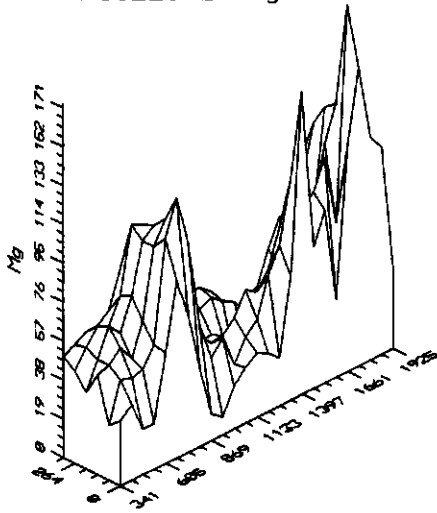
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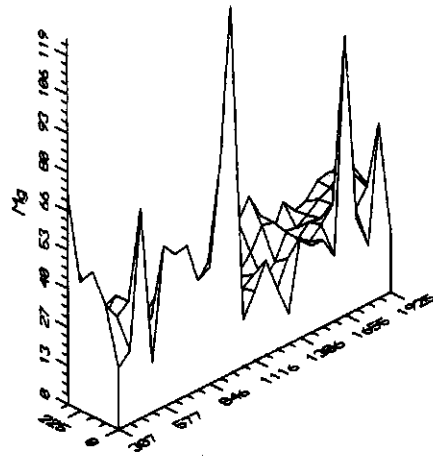
TONGBERSVEN M_g



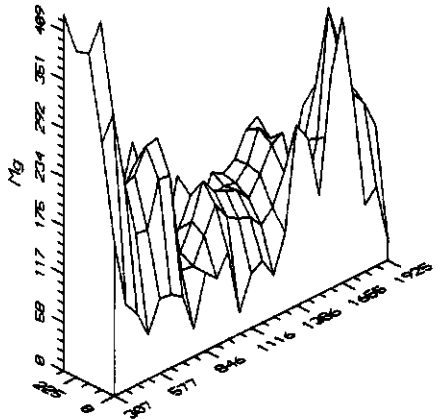
HASELSVEN M_g



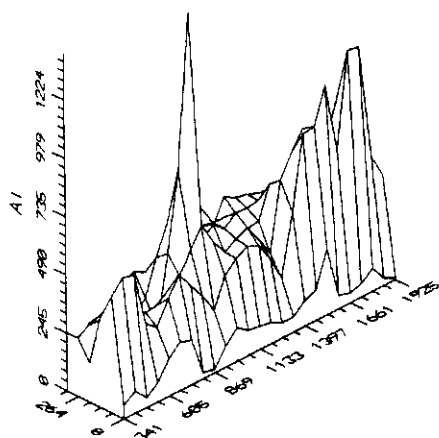
GERRITSFLES-BARE M_g



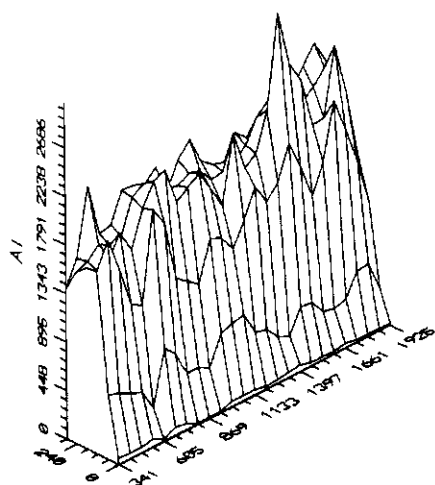
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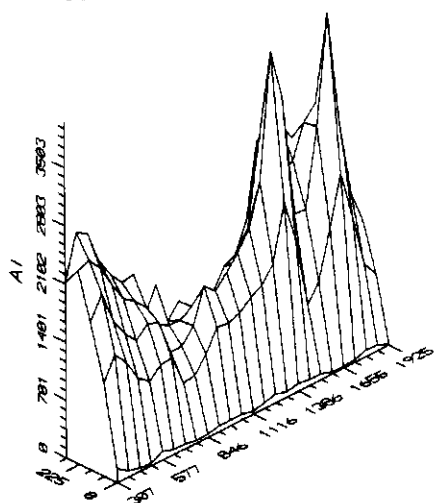
HASSELSVEN AI



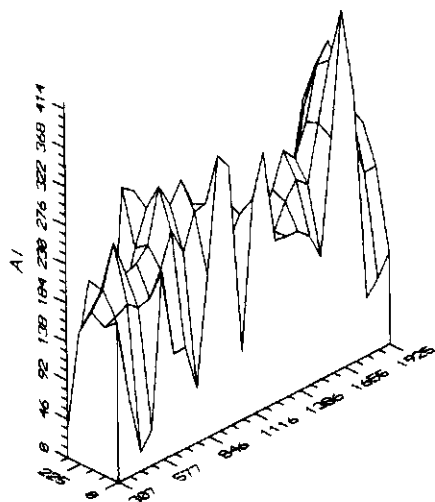
TONGBERSVEN AI



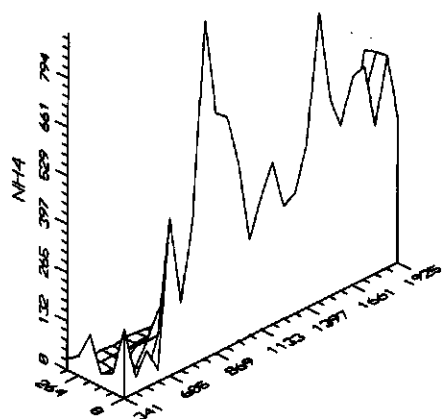
GERRITSFLES-FOREST AI



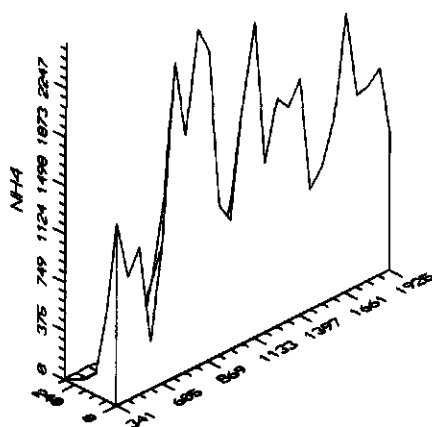
GERRITSFLES-BARE AI



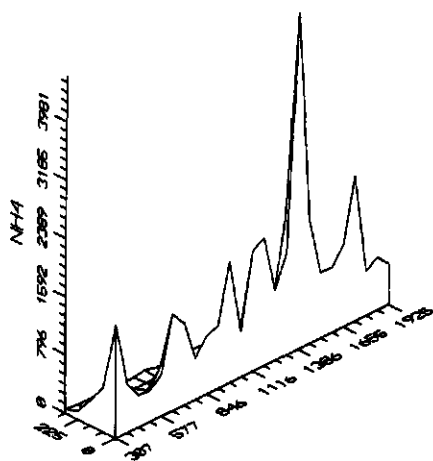
HASSELSVEN NH4



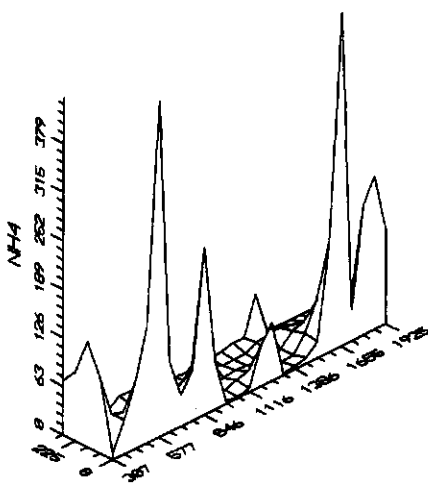
TONGBERSVEN NH4



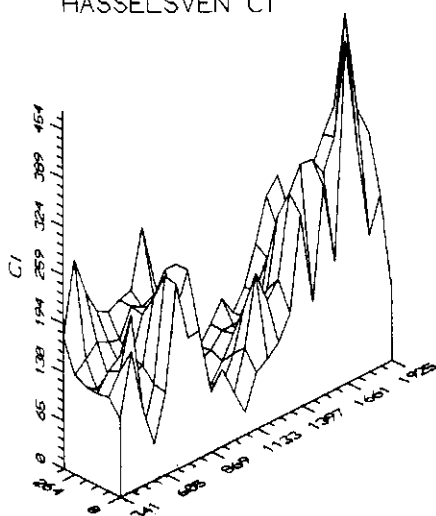
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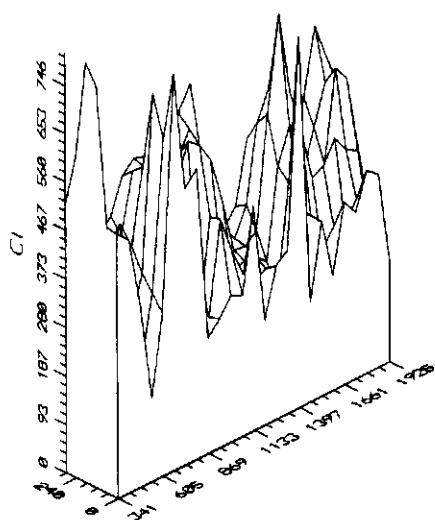
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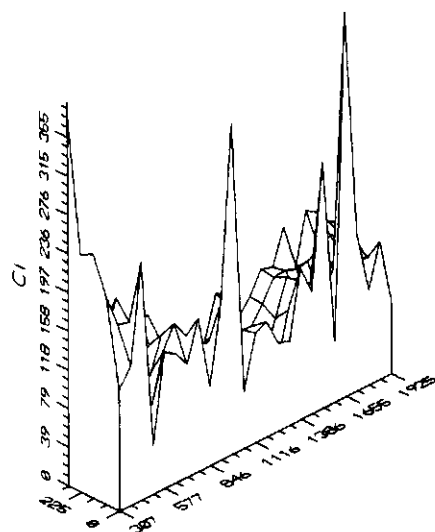
HASSELSVEN CI



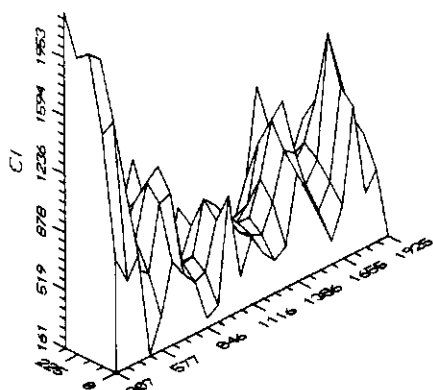
TONGBERSVEN CI



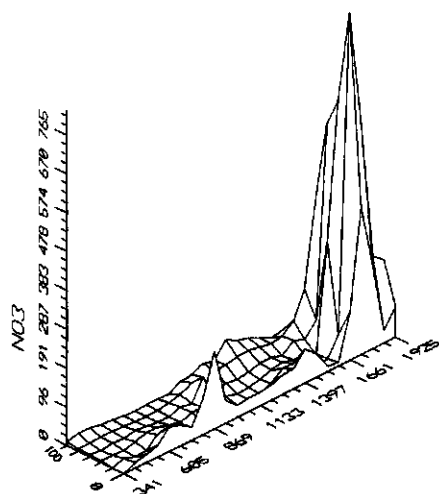
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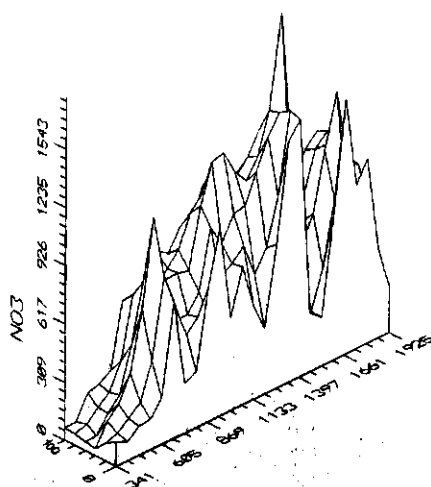
GERRITSFLES-FOREST CI



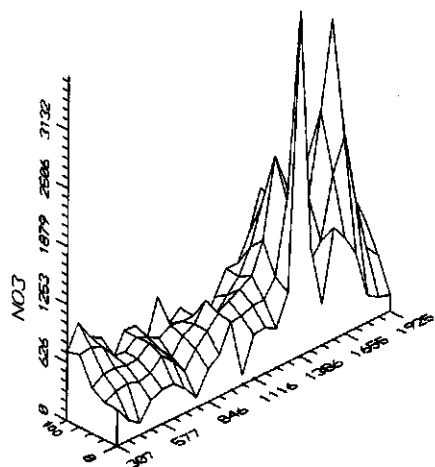
HASSELSVEN N03



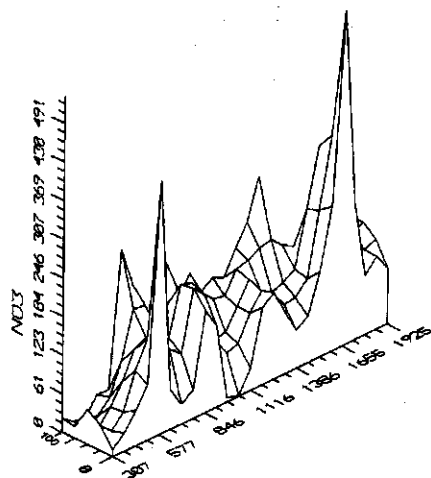
TONGBERSVEN N03



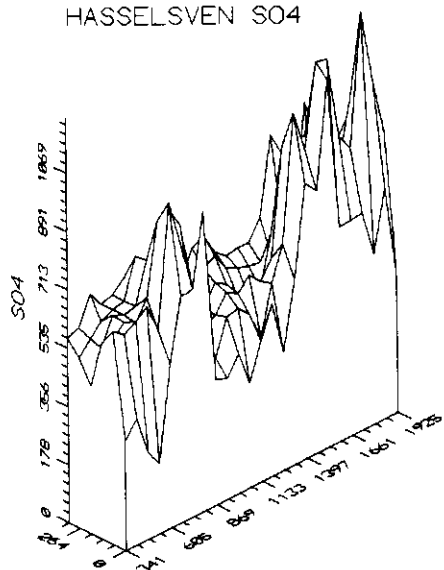
GERRITSFLES-FOREST N03



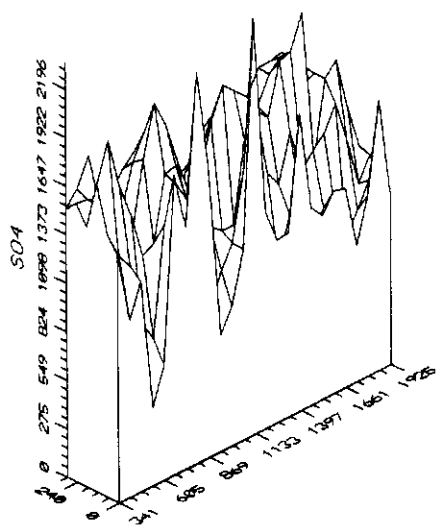
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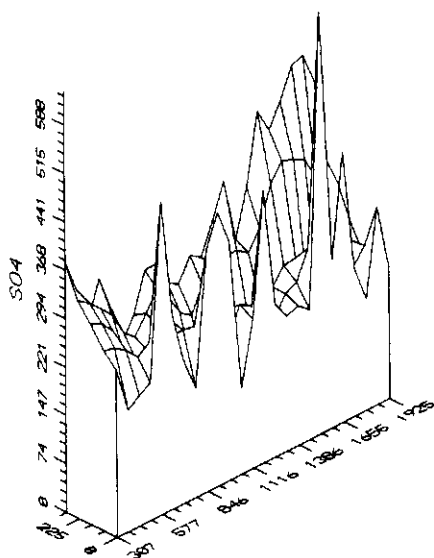
HASSELSVEN SO4



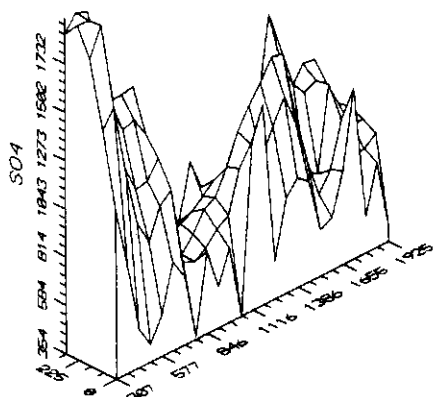
TONGBERSVEN SO4



GERRITSFLES-BARE SO4



GERRITSFLES-FOREST SO4



Appendix 4

List of publications originating from this project.

- Breemen, N. van & Mulder, J., 1986. Atmospheric acid deposition: Effects on the chemistry of forest soils. In: T. Schneider (ed): *Acidification and its policy implications*, pp. 141-152. Elsevier, Amsterdam, the Netherlands.
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- Dam, H. van, 1990. Monitoring of chemistry and diatoms in shallow moorland pools in The Netherlands, pp. 66-70 in: R. Merz (ed.): *Convention on Long-Range Transboundary Air-Pollution, International Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes, Fifth Meeting of The Programme Task Force, Freiburg, Federal Republic of Germany, October 17-19, 1989*. Umweltbundesamt, Berlin.
- Dam, H. van, Geel, B. van, Wijk, A. van der & Dickman, M.D., 1988. pH changes over two centuries in three Dutch moorland pools. In: P. Mathy (ed.): *Air pollution and ecosystems*, pp. 954-959. Reidel, Dordrecht.
- Dam, H. van, Geel, B. van, Wijk, A. van der, Geelen, J.F.M., Heijden, R. van der & Dickman, M.D., 1988. Palaeolimnological and documented evidence for alkalization and acidification of two moorland pools (The Netherlands). *Review of Palaeobotany and Palynology* 55: 273-316.
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- Grinsven, J.J.M. van, Breemen, N. van, Riemsdijk, W.H. van & Mulder, J., 1987. The sensitivity of acid forest soils to acid deposition. In: *Proc. UNESCO-IHP Symp. Acidification and Water Pathways, Vol. II*, pp. 365-374. Norw. Nat. Comm. Hydrol., Oslo, Norway.
- Mulder, J., 1987. The aluminum chemistry of Spodosols, impacted by strong acid inputs. In: B. Moldan & T. Paces (eds.): *Proc. GEOMON Int. Workshop Geochemistry and Monitoring of Representative Basins*, pp. 95-98. Geological Survey Prague, Czechoslovakia.
- Mulder, J. & Breemen, N. van, 1987. Differences in aluminum mobilization in Spodosols in New Hampshire (USA) and the Netherlands as a result of acid deposition. In: T.C. Hutchinson & K.M. Meema (eds.): *Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Ecosystems*, pp. 361-376. Springer-Verlag, Berlin, Heidelberg, FRG.
- Mulder, J., Dobben, H.F. van, Visser, P.H.B. de, Booltink, H.W.G. & Breemen, N. van, 1987. Effect of vegetation cover (pine forest vs. no vegetation) on atmospheric deposition and soil acidification. In: *Proc. UNESCO-IHP Symp. Acidification and Water Pathways, Vol. I*, pp. 79-89. Norw. Nat. Comm. Hydrol., Oslo, Norway.
- Mulder, J., 1988. Impact of acid atmospheric deposition on soils: Field monitoring and aluminum chemistry. PhD thesis, Agric. Univ., Wageningen, the Netherlands.
- Mulder, J., Breemen, N. van & Eijck, H.C., 1989. Depletion of soil aluminium by acid deposition and implications for acid neutralization. *Nature* 337: 247-249.

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