

# Chapter 16

## Changes in Soil Solution Chemistry, Seepage Losses, and Input–Output Budgets at Three Beech Forests in Response to Atmospheric Depositions

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### 16.1 Introduction

Atmospheric depositions have increased substantially since industrialisation and have affected many forest properties. Forest soils of low buffering to the acid load as those of sandy or silty texture significantly declined in soil pH and some essential nutrients during the last decades (see Chap. 21) causing a controversial discussion about the stability of such forest ecosystems (Ulrich 1981, 1987, 1992, 1994b). Of 1,700 soils studied in the forest soil survey programme of Germany, 60% of all soils have  $\text{pH}(\text{H}_2\text{O}) < 4.2$  (Wolff and Riek 1997a, b). N deficiency, which has been a common feature of forest stands in the temperate region (Tamm 1991), does not occur any more due to high N deposition rates in Europe (except of north and east Europe). On the contrary, the N supply has increased as indicated by high N contents of the tree foliage and surface organic layer samples (Tietema and Beier 1995; Alewell et al. 2000b; McNulty et al. 1991; Wolff and Riek 1997a). Nitrate losses with seepage water have increased at some locations (Dise and Wright 1995; Bredemeier et al. 1998; Matzner et al. 2004; Borken and Matzner 2004), which led to a discussion about the saturation of forests with nitrogen (e.g. Ågren and Bosatta 1988; Tamm 1991; Gundersen et al. 1998; Aber et al. 1998). However, political actions by European countries have led to a noticeable decline in atmospheric depositions of sulphur and nitrogen in the 1980s and 1990s (Ferrier et al. 2001) raising questions about the recovery of forest ecosystems from soil acidification. A general recovery of alkalinity of lakes and streams was observed in all regions of Europe in the 1990s (Stoddard et al. 1999) except at many sites in central Europe where a significant delay in aquatic recovery from acidification (Alewell et al. 2000a) was observed. Recovery of water acidification can take decades, because of the release of previously stored sulphate from soils with a high storage capacity for sulphate continues leading to acidification of aquatic systems (Matzner 2004). Moreover, many of the European forest stands are experiencing changes due to the so-called “climate change” phenomenon. For example, significant changes in the climate at the Solling site with

increased air temperature and precipitation have been recorded since the Solling project was established in 1966 (see Chap. 2). All these impacts on forest ecosystems constitute the basis for extensive research for which the most promising tool is the long-term monitoring of element budgets of representative ecosystems. This allows one to follow forest development under changing environmental conditions.

Three beech forests covering a range of soil properties were considered in this study to evaluate the effects of acid and nitrogen depositions, especially on carbon and nutrient turnover and pools. Soil solution chemistry was studied at different depths to observe the reactions of deposited elements with soil matrix. For quantifying the element fluxes with seepage, water output was estimated by modelling the water balance on each site. The response of soil solution to decreasing atmospheric deposition was studied by trend analysis. Input–output (I/O) budgets were used to assess the overall increase or loss of elements for the stands. The annual I/O budgets were established for three periods of roughly a decade each: (1) from 1969 to 1980, when the atmospheric deposition of  $\text{SO}_x$  and  $\text{NO}_x$  increased to peak emissions in Europe, (2) from 1981 to 1989, when deposition started to decline, and (3) from 1990 to 2002 when deposition further declined (Ferrier et al. 2001) as a result of an international agreement in Europe under the Convention on Long Range Transboundary Air Pollution (CLRTAP) of the United Nations Economic Council for Europe (UN–ECE). The selected beech forests were intensively studied during the observational periods and the results have been previously presented in many publications. An update of the results will be presented here. For the most extensive publications on input–output analysis of preceding periods refer to Matzner (1989), Ulrich (1994a), Meesenburg et al. (1995) and Eichhorn (1994, 1999).

Our intention was to address the following questions in this chapter. (1) How do these ecosystems with different soil properties respond to acid depositions? (2) Do these ecosystems accumulate or lose N, and are they linked to the soil chemical status? (3) How do these ecosystems respond to decreasing atmospheric depositions of sulphuric acid and base cations? (4) Are there any indications of recovery from high depositions of acid and N?

## 16.2 Soil Solution Collection and Statistical Analysis

Monitoring of soil solution (measurement of ion concentrations) started at the Solling site in 1969 at the interface of the organic layer and mineral soil (depth 0 cm) and in the subsoil (–90 cm depth). From 1981 onwards, the monitoring was extended with soil solution sampling at several other soil depths, e.g. –20 cm depth. At the Göttinger Wald site, soil solution monitoring started in 1981, and at the Zierenberg site, in 1989 at several soil depths. The monitoring is still being continued.

Soil solution is collected by suction plates and suction cups (tension lysimeters) which sample soil solution at the same place producing a time series with short sampling intervals during several years. A detailed description of the technique applied is given by Meiwes et al. (1984), and Meesenburg et al. (1997) for the Solling and Göttinger Wald sites and by Jochheim (1992) and Eichhorn (1995) for Zierenberg site. The lysimeters were installed with three to ten replicates at fixed soil depths of 0, 20 and 90 cm at Solling, 5, 20 and 100 cm at Göttinger Wald, and 20, 60 and 100 cm at Zierenberg. Soil solution is collected at weekly or biweekly intervals. Combined samples of two to three lysimeters of each depth are sampled weekly at Solling and Göttinger Wald, which are pooled to monthly samples for chemical analysis. Biweekly samples from Zierenberg are analysed for each lysimeter separately. Analytical methods are described by Fassbender and Ahrens (1977) and König and Fortmann (1996a–d).

Linear regression analyses were used to describe the temporal variability of solute concentrations and to detect trends. Analyses have been performed for annual mean concentrations or solute fluxes for the period 1981–2002 for Solling and Göttinger Wald and for 1990–2002 for Zierenberg. Statistical analyses have been performed with the software package SPSS 11.5 (SPSS).

### 16.3 Modelling of Water Fluxes

We used the hydrology model SIMPEL for the estimation of evapotranspiration and water fluxes beneath the rooting zone (Hörmann 1997). Although other hydrology models are available (Hörmann and Schmidt 1995; Tiktak and van Grinsven 1995), we chose SIMPEL because it has been successfully calibrated to various forest ecosystems including beech stands (Hörmann and Meesenburg 2000), and because of its limited requirement for input data.

SIMPEL is a very simple hydrologic model. A detailed description of SIMPEL is given by Hörmann (1997, 1998). Thus, only a short overview of the basic principles is given here. SIMPEL uses a capacity approach for the simulation of water fluxes. Three consecutive storages (ecosystem layers) are defined: the canopy of the stand, the litter layer and the soil layer. Potential evapotranspiration within SIMPEL can be calculated with different methods ranging from simple (e.g. Thornthwaite 1948) to more physically based equations (e.g. Penman 1948/Monteith 1965). Interception is simulated as a simple bucket model with canopy water storage capacity as the only parameter. Canopy water storage capacity can be estimated by using leaf area index (LAI) which is considered to change in time according to phenological phases. The soil water storage is defined by field capacity, permanent wilting point and maximum rooting depth. Outflow from the soil water storage above field capacity is the difference between infiltration and transpiration. Below field capacity, seepage is simulated according to Glugla (1969). The reduction from potential to actual evapotranspiration is calculated using a linear reduction function where

**Table 16.1** Input parameters and parameter values for the soil module of SIMPEL

| SIMPEL input parameter  | Unit  | Göttinger Wald | Zierenberg | Solling |
|-------------------------|-------|----------------|------------|---------|
| Field capacity          | Vol.% | 25             | 25         | 25      |
| Permanent wilting point | Vol.% | 12             | 12         | 12      |
| Reduction limit         | Vol.% | 20             | 19         | 24      |
| Maximum rooting depth   | Cm    | 180            | 180        | 180     |

transpiration starts to be restrained at the reduction limit and ceases at the permanent wilting point.

In the present case, the canopy layer and the litter layer have been omitted from the model. Measured values of stand precipitation were used as infiltration data into the soil storage. For the estimation of potential evapotranspiration, a derivation of the Penman/Monteith formula with constant values for albedo, aerodynamic and canopy resistance has been used. Global radiation, air temperature and relative humidity are required as site-specific input parameters for the calculation of potential evapotranspiration. No site-specific climatic data are available for the whole simulation period of the study sites. Thus, data from nearby climate stations of the German Weather Service (DWD) have been used for the simulations. Site-specific transfer functions for the extrapolation of the DWD data were derived from short-term measurements at the study sites. Global radiation has been calculated from sunshine duration using the Angström formula (DVWK 1996). A common set of parameter values for the three study sites was used for the soil module (Table 16.1). Only the reduction limit served as a calibration parameter. The model has been run on a daily time step.

## 16.4 Calculation of Input–Output Balances of Various Elements and Acid Production

Element fluxes at 100 cm soil depth (soil output) were obtained by multiplying the element concentrations in soil solution with the respective water flux for that period. For periods with missing values of soil solution concentrations (no soil solution sample), a linear interpolation between the preceding and the following periods was applied.

Element budgets of the ecosystems and the production of acidity were calculated using the approach suggested by Ulrich (1994a). The budget of any solute is the difference between total deposition and seepage output. Additional input of base cations by mineral weathering was estimated by using the PROFILE model (Sverdrup and Warfvinge 1992) (Table 16.2). The mineral composition of the soils used for weathering estimates is described in Chap. 3. The weathering rates for Ca and Mg are similar to the rates obtained by the so-called “historical” method which was applied for the Solling site (Wesselink et al. 1994). ZrO was used as an

**Table 16.2** Net element retention for annual increment by trees (from Chap. 8) and element weathering ( $\text{mmol}_c \text{m}^{-2}$  per year) on the three beech sites. H is the negative equivalent of the sum of base cations (Na, K, Mg, Ca)

|                | Flux                | Na | K      | Mg     | Ca    | H          | $N_{\text{tot}}$ |
|----------------|---------------------|----|--------|--------|-------|------------|------------------|
| Solling        | Uptake              | 0  | 8.2    | 6.8    | 21    | -36        | 43               |
|                | Weathering          | 26 | 52     | 27     | 8     | -113       | 0                |
| Göttinger Wald | Uptake              | 0  | 22     | 18     | 151   | -190       | 126              |
|                | Weathering          | 7  | 20     | 27     | 1,179 | -1,233     | 0                |
| Zierenberg     | Uptake <sup>a</sup> | 0  | 7.5–12 | 4.6–13 | 33–55 | -45 to -79 | 38–63            |
|                | Weathering          | 5  | 56     | 202    | 67    | -331       | 0                |

<sup>a</sup>Uptake is given as  $x - \text{SD}$  and  $x + \text{SD}$  ( $x$  mean, SD standard deviation). The mean was calculated based on the measured breast diameter and height at Zierenberg site (Chap. 8), regression analysis for the different biomass compartments and the basal areas from the Göttinger Wald and Solling sites (Peter Rademacher, personal communication), and element concentrations (mean  $\pm$  SD) of a literature review by Jacobsen et al. (2003) of which the concentrations for noncalcareous soils were taken

internal standard to calculate historical weathering rates by comparing the mineral pools at 60 cm depth with the composition in the reference C horizon at 180 cm depth. Unfortunately, the Solling soil does not contain loess material in the C horizon, so a loess profile southeast of Solling was used which has a mineralogical composition similar to that of the Solling site in the topsoil. While the historical weathering rates for Ca ( $8 \text{ mmol}_c \text{m}^{-2}$  per year) and Mg ( $30 \text{ mmol}_c \text{m}^{-2}$  per year) were identical, the rates for Na ( $5 \text{ mmol}_c \text{m}^{-2}$  per year) and K ( $6 \text{ mmol}_c \text{m}^{-2}$  per year) were much lower than the estimates obtained with the PROFILE model indicating methodological problems in estimating realistic weathering rates. N release by weathering was assumed to be negligible. Export of cations by biomass was estimated as net accumulation in plant biomass by Rademacher et al. and included an aboveground increment ( $>7$  cm diameter) and coarse roots ( $>2$  mm) (Chap. 8).

The acid load of the ecosystems by deposition and system-internal H production was calculated (see Sect. 16.10) according to Ulrich (1994a) and is the sum of following values:

- (1) Acid input: positive budget values (input  $>$  output) of Ma cations (H, Mn, Al, Fe) (input =total deposition + the negative equivalent of the sum of cations taken up for plant increment; output =leaching losses).
- (2) N transformation:  $\text{NH}_4$  input  $-\text{NH}_4$  output  $-\text{NO}_3$  input  $+\text{NO}_3$  output.
- (3) S release: negative budget values of  $\text{SO}_4$ . Dissolution of aluminum sulphate represents the mobilisation of previously stored  $\text{H}_2\text{SO}_4$  from atmospheric deposition in the solid soil phase (Prenzel 1983).
- (4) Weak acidity (carbonic and organic acids) is calculated as the charge balance difference. Cl is only taken into account in the calculation if a negative budget cannot be attributed to the loss of neutral salts, i.e. if the budget is not balanced by Mb cations.
- (5) Mb retention: positive budgets of Mb cations (Na, K, Mg, Ca) corrected for neutral salt accumulation. Mb cations are bound to acidic groups releasing Ma cations (e.g. protons).

## 16.5 Solution Composition From Soils of Different Buffer Systems

Sulphate is the dominant anion in the soil solution at the Solling site (Table 16.3) which is related to its high atmospheric depositions. For this highly acid soil Al and H occur in all soil layers. A strong relation between Al and sulphate and nitrate in soil solution was found to be typical for soils with base saturation values of <25% and pH values of <4.5 for 192 sites spread over 12 European countries (de Vries et al. 2003). In soils with base saturation values of >25% and pH values of >4.5, there was a strong relationship between Ca and strong acid anions, indicating that the acidity in these soils is mainly neutralised by the release of base cations. Soils of Göttinger Wald and Zierenberg fall in this group with mean base saturation values of >93% (Chap. 3). High H concentration in soil solution below the surface organic layer at Solling (Table 16.3) has atmospheric deposition and nitrification processes as primary sources (Chaps. 13 and 15). Since buffer substances are absent in the surface organic layer most of H is leached and buffered in the mineral soil as indicated by low pH values of soil solution (pH 4.1–4.5). Owing to the low content of silicates such as feldspars and illites in the Solling soil and the advanced level of acidification in this soil, silicate weathering does not buffer all the protons completely. Therefore, Al occurs in considerable concentrations making up more than 50% of the sum of cations in solution of the mineral soil layers. However, at >80 cm soil depth proton buffering capacity increases due to a higher content of illites causing slightly lower concentrations of H and Al in the soil solution. Al occurs predominantly in monomeric form in the soil solution collected at >20 cm depth which is supposed to be toxic for tree roots whereas less toxic soluble organic Al complexes occur in solutions from below the surface organic layer (Dietze and Ulrich 1992).

At the less acid Göttinger Wald and Zierenberg sites, acidity generated by the system internal processes or added through atmospheric depositions is buffered by easily weatherable silicates or carbonates, as indicated by solution pH values of 6.1–8.0 and high concentrations of Ca and Mg in soil solution. Buffering of protons by Al silicates occurs only in the acidified surface mineral soil where carbonate is absent as indicated by Al concentration in soil solution. Increased concentrations of Ca and Mg indicate buffer reactions with carbonates at >5 cm soil depth (Göttinger Wald) and at >60 cm soil depth (Zierenberg).  $\text{HCO}_3^-$  is the accompanying anion of Ca and Mg.  $\text{HCO}_3^-$  was not measured but could be calculated as the excess of cations over anions in soil solutions where organic anions are negligible ( $\Sigma^+ - \Sigma^-$ , Table 16.3). High Mg concentration in the soil solution from Zierenberg originates from dissolved Mg-rich minerals like olivine, pyroxene or hornblende of the basaltic debris (Chap. 3).

Concentrations of  $\text{SO}_4$  and Cl increased with soil depth due to their discrimination by plant roots during water uptake. However, increase in the concentration of  $\text{SO}_4$  with depth was smaller than that of Cl during the period of 1969–1980 at Solling (Table 16.3) which was explained by the  $\text{SO}_4$  retention in this highly acidic

**Table 16.3** Mean concentrations (unweighted) standard deviation of spatial replicates of major ions ( $\mu\text{mol}_e \text{L}^{-1}$ ) in soil solution at different sampling depths and for different sampling periods at the study sites ( $\Sigma+ - \Sigma- =$  sum of cations  $-$  sum of anions)

| Depth                              | Period | Na  | K   | Mg   | Ca   | Al  | Mn   | H    | NH <sub>4</sub> | NO <sub>3</sub> | SO <sub>4</sub> | Cl    | $\Sigma+ - \Sigma-$ |
|------------------------------------|--------|-----|-----|------|------|-----|------|------|-----------------|-----------------|-----------------|-------|---------------------|
| <b>Mean, Solling</b>               |        |     |     |      |      |     |      |      |                 |                 |                 |       |                     |
| 0 cm                               | 69-80  | 81  | 95  | 68   | 222  | 176 | 50   | 178  | 84              | 221             | 411             | 116   | 218                 |
|                                    | 81-89  | 80  | 86  | 58   | 187  | 130 | 42   | 211  | 51              | 280             | 329             | 106   | 130                 |
|                                    | 90-02  | 90  | 47  | 34   | 72   | 93  | 15   | 146  | 18              | 95              | 141             | 90    | 189                 |
| 20 cm                              | 81-89  | 95  | 12  | 37   | 60   | 452 | 29   | 60   | 7               | 125             | 410             | 134   | 82                  |
|                                    | 90-02  | 102 | 4   | 21   | 25   | 228 | 14   | 40   | 8               | 29              | 213             | 113   | 87                  |
| 90 cm                              | 69-80  | 104 | 17  | 47   | 88   | 314 | 36   | 78   | 9               | 18              | 426             | 163   | 87                  |
|                                    | 81-89  | 75  | 14  | 35   | 39   | 361 | 21   | 49   | 7               | 18              | 437             | 110   | 38                  |
|                                    | 90-02  | 85  | 7   | 24   | 21   | 191 | 10   | 35   | 6               | 12              | 252             | 91    | 24                  |
| <b>Mean, Göttinger Wald</b>        |        |     |     |      |      |     |      |      |                 |                 |                 |       |                     |
| 5 cm                               | 81-89  | 69  | 52  | 74   | 1131 | 20  | 1.2  | 0.53 | 7               | 313             | 593             | 124   | 324                 |
|                                    | 90-02  | 79  | 20  | 41   | 560  | 41  | 0.3  | 0.49 | 7               | 51              | 244             | 101   | 353                 |
|                                    | 81-89  | 80  | 9   | 86   | 2396 | 6   | 0.5  | 0.05 | 6               | 298             | 634             | 152   | 1,501               |
| 20 cm                              | 90-02  | 91  | 5   | 69   | 2132 | 3   | 0.4  | 0.04 | 6               | 190             | 276             | 104   | 1,736               |
|                                    | 81-89  | 222 | 20  | 126  | 5004 | 7   | 0.4  | 0.02 | 13              | 286             | 771             | 218   | 4,117               |
| 90-02                              | 187    | 14  | 108 | 5095 | 3    | 0.3 | 0.01 | 17   | 99              | 431             | 148             | 4,746 |                     |
| <b>Mean, Zierenberg</b>            |        |     |     |      |      |     |      |      |                 |                 |                 |       |                     |
| 20 cm                              | 90-02  | 166 | 29  | 745  | 604  | 40  | 0.3  | 1.02 | 6               | 683             | 408             | 185   | 316                 |
|                                    | 90-02  | 202 | 13  | 844  | 729  | 7   | 0.3  | 0.21 | 3               | 739             | 486             | 219   | 355                 |
|                                    | 90-02  | 250 | 14  | 711  | 1378 | 4   | 0.3  | 0.07 | 2               | 536             | 511             | 217   | 1,096               |
| <b>Standard deviation, Solling</b> |        |     |     |      |      |     |      |      |                 |                 |                 |       |                     |
| 0 cm                               | 69-80  | 3   | 17  | 5    | 40   | 27  | 10   | 14   | 36              | 89              | 19              | 7     |                     |
|                                    | 81-89  | 5   | 14  | 4    | 26   | 80  | 9    | 57   | 33              | 57              | 23              | 3     |                     |
|                                    | 90-02  | 9   | 20  | 4    | 21   | 42  | 5    | 62   | 5               | 64              | 9               | 8     |                     |

(continued)

Table 16.3 (continued)

| Depth                              | Period | Na | K  | Mg  | Ca  | Al | Mn | H   | NH <sub>4</sub> | NO <sub>3</sub> | SO <sub>4</sub> | Cl | $\Sigma+ - \Sigma-$ |
|------------------------------------|--------|----|----|-----|-----|----|----|-----|-----------------|-----------------|-----------------|----|---------------------|
| 20 cm                              | 81-89  | 6  | 1  | 3   | 7   | 40 | 3  | 2   | 1               | 38              | 19              | 2  |                     |
|                                    | 90-02  | 3  | 0  | 3   | 2   | 5  | 2  | 3   | 0               | 2               | 16              | 1  |                     |
| 90 cm                              | 69-80  | 4  | 5  | 2   | 2   | 5  | 1  | 2   | 1               | 1               | 14              | 17 |                     |
|                                    | 81-89  | 7  | 5  | 3   | 3   | 25 | 0  | 2   | 0               | 3               | 19              | 12 |                     |
|                                    | 90-02  | 6  | 1  | 2   | 1   | 22 | 0  | 2   | 0               | 3               | 23              | 8  |                     |
| Standard deviation, Göttinger Wald |        |    |    |     |     |    |    |     |                 |                 |                 |    |                     |
| 5 cm                               | 81-89  | 7  | 51 | 15  | 280 | 5  | 0  | 2   | 2               | 121             | 135             | 23 |                     |
|                                    | 90-02  | 7  | 10 | 4   | 74  | 12 | 0  | 1   | 2               | 14              | 24              | 11 |                     |
| 20 cm                              | 81-89  | 6  | 4  | 13  | 240 | 1  | 0  | 0   | 7               | 88              | 78              | 15 |                     |
|                                    | 90-02  | 4  | 2  | 12  | 520 | 1  | 0  | 0   | 1               | 78              | 46              | 8  |                     |
| 100 cm                             | 81-89  | 27 | 4  | 24  | 377 | 1  | 0  | 0   | 6               | 58              | 26              | 19 |                     |
|                                    | 90-02  | 22 | 2  | 25  | 578 | 1  | 0  | 0   | 4               | 52              | 84              | 16 |                     |
| Standard deviation, Zierenberg     |        |    |    |     |     |    |    |     |                 |                 |                 |    |                     |
| 20 cm                              | 90-02  | 38 | 20 | 306 | 194 | 18 | 0  | 1.1 | 8               | 1,798           | 235             | 44 |                     |
| 60 cm                              | 90-02  | 60 | 10 | 390 | 268 | 6  | 0  | 0.1 | 3               | 2,204           | 246             | 58 |                     |
| 100 cm                             | 90-02  | 33 | 11 | 212 | 861 | 3  | 0  | 0.1 | 1               | 785             | 178             | 49 |                     |

soil (Ulrich et al. 1980; Meiwes et al. 1980; Khanna et al. 1987; Alewell et al. 2000b). The retained  $\text{SO}_4$  was released into the soil solution after 1985 as indicated by the higher increase in concentration of  $\text{SO}_4$  than that of Cl during 1990–2002. This also resulted in a negative sulphur budget (Sect. 16.9). Retention or loss of  $\text{SO}_4$  in acid soils is explained by the formation and dissolution of aluminum hydroxyl sulphate ( $\text{AlOHSO}_4$ , e.g. Jurbanite) (Meiwes et al. 1980; Prenzel 1983), by adsorption processes (Alewell et al. 2000b) and by retention in biomass.  $\text{AlOHSO}_4$  may exist as an intermediate product on the surface of other minerals in soils, and is dissolved when pH values increase to produce Al and  $\text{SO}_4$  in soil solution.

The nitrate concentration in soil solution of the three sites followed the order: Solling < Göttinger Wald < Zierenberg (Table 16.3). High concentrations of nitrate in the solution collected below the litter layer indicated high mineralisation rates in the surface organic layer at the Solling site. But relatively high concentrations of  $\text{NH}_4$  suggested that N was only partly nitrified in the acid surface organic layer. Controlled incubation studies showed that nitrification rate was low in the F horizon of the surface organic layer which was explained by the absence of autotrophic nitrifiers and low activity of heterotrophic nitrifiers (Chap. 13). A decrease in the concentrations of ammonium and nitrate with soil depth at the Solling site suggested their transformation or uptake at deeper depths. Ammonium concentrations are generally low due to high nitrification rates in the less acid soils of Zierenberg and Göttinger Wald (Chap. 13). In these soils, mineralisation processes occurred in the mineral soil and were maintained by bioturbation of organic matter by earthworms that resulted in high nitrate concentrations in the Ah horizon. Very high nitrate concentrations below 100 cm depth at Zierenberg indicated high N losses with seepage water.

Concentrations of dissolved organic nitrogen (DON) were high, its values lying between those of ammonium and nitrate concentrations (Tables 16.3 and 16.4). DON and dissolved organic carbon (DOC) values decreased with increasing soil depth as has been observed in several studies (Kaiser and Zech 2000; Michalzik et al. 2001). The ratios between DOC and DON slightly decreased with depth at the Göttinger Wald and Zierenberg sites and increased at the Solling site. However, the values of these ratios (13–56), when calculated from long-term mean concentrations in Table 16.4 were in the range as reported by Michalzik et al. (2001) who compiled such data for temperate forests.

## 16.6 Temporal Trends in Soil Solution Chemistry

Stricter emission control measures in Europe and structural changes in the industry, i.e. reduction in the size of heavy industry and changes in the energy consumption and fuel mixtures used for energy production, significantly reduced atmospheric deposition since mid 1980s in Europe (Ferrier et al. 2001). Atmospheric depositions peaked around 1985 across Europe. The long-term observations at the Solling and Göttinger Wald sites showed a decrease for sulphur (–60% at Solling and Göttinger

**Table 16.4** Mean pH, mean concentrations and standard deviation of spatial replicates ( $\mu\text{mol L}^{-1}$ ) of total nitrogen ( $N_{\text{tot}}$ ), dissolved organic N (DON), and dissolved organic C (DOC) in soil solutions collected from different sampling depths and for different sampling periods at the three study sites (n.d., not determined)

| Depth                              | Period | pH   | $N_{\text{tot}}$ | DON | DOC   |
|------------------------------------|--------|------|------------------|-----|-------|
| Mean, Solling                      |        |      |                  |     |       |
| 0 cm                               | 69–80  | 3.8  | 406              | 98  | n.d.  |
|                                    | 81–89  | 3.7  | 433              | 103 | n.d.  |
|                                    | 90–02  | 3.8  | 188              | 78  | 3,490 |
| 20 cm                              | 81–89  | 4.2  | 168              | 34  | n.d.  |
|                                    | 90–02  | 4.4  | 49               | 13  | 729   |
| 90 cm                              | 69–80  | 4.1  | 44               | 19  | n.d.  |
|                                    | 81–89  | 4.3  | 24               | 0   | n.d.  |
|                                    | 90–02  | 4.5  | 17               | 0   | 182   |
| Mean, Göttinger Wald               |        |      |                  |     |       |
| 5 cm                               | 81–89  | 6.4  | 403              | 84  | 1,427 |
|                                    | 90–02  | 6.3  | 120              | 62  | 1,886 |
| 20 cm                              | 81–89  | 7.3  | 375              | 69  | 983   |
|                                    | 90–02  | 7.5  | 243              | 52  | 1,053 |
| 100 cm                             | 81–89  | 7.8  | 369              | 68  | 863   |
|                                    | 90–02  | 8.0  | 152              | 36  | 827   |
| Mean, Zierenberg                   |        |      |                  |     |       |
| 20 cm                              | 90–02  | 6.1  | 813              | 83  | 1,879 |
| 60 cm                              | 90–02  | 6.7  | 821              | 66  | 954   |
| 100 cm                             | 90–02  | 7.2  | 590              | 37  | 747   |
| Standard deviation, Solling        |        |      |                  |     |       |
| 0 cm                               | 69–80  | n.d. | 122              | 23  | n.d.  |
|                                    | 81–89  | n.d. | 75               | 18  | n.d.  |
|                                    | 90–02  | n.d. | 72               | 23  | 1,012 |
| 20 cm                              | 81–89  | n.d. | 34               | 0   | n.d.  |
|                                    | 90–02  | n.d. | 3                | 3   | 121   |
| 90 cm                              | 69–80  | n.d. | 25               | 26  | n.d.  |
|                                    | 81–89  | n.d. | 2                | 3   | n.d.  |
|                                    | 90–02  | n.d. | 4                | 2   | 34    |
| Standard deviation, Göttinger Wald |        |      |                  |     |       |
| 5 cm                               | 81–89  | n.d. | 120              | 11  | 262   |
|                                    | 90–02  | n.d. | 11               | 2   | 84    |
| 20 cm                              | 81–89  | n.d. | 100              | 12  | 217   |
|                                    | 90–02  | n.d. | 93               | 25  | 294   |
| 100 cm                             | 81–89  | n.d. | 62               | 8   | 142   |
|                                    | 90–02  | n.d. | 65               | 10  | 164   |
| Standard deviation, Zierenberg     |        |      |                  |     |       |
| 20 cm                              | 90–02  | n.d. | 432              | 35  | 639   |
| 60 cm                              | 90–02  | n.d. | 519              | 32  | 408   |
| 100 cm                             | 90–02  | n.d. | 195              | 23  | 196   |

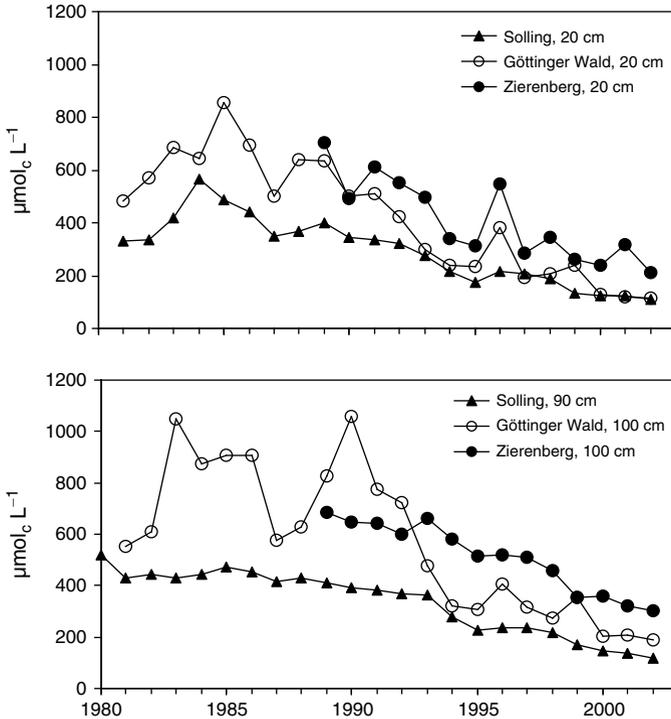
Wald), H (–72% at Solling and Göttinger Wald), and nitrogen depositions (–38% for Solling and –20% for Göttinger Wald) for the periods 1981–1989 and 1990–2002 (Chap. 15). Emission control measures such as air filtration on large combustion plants have led to the reduction in depositions of other essential nutrients such as base cations which have decreased by about 60% at the Solling and Göttinger Wald sites (Chap. 15). These reductions in the atmospheric deposition have changed the soil solution chemistry significantly as indicated by long-term monitoring data of the Solling and Göttinger Wald sites. However, these trends are less distinct at the Zierenberg site due to the short observational period. Trend analysis of soil solution concentrations performed by linear regression analysis showed declining trends for several elements (Table 16.5) which is most consistent for sulphate at all the three beech sites (Fig. 16.1). The effect of reduced atmospheric depositions on soil solution chemistry was most pronounced at Solling where a significant reduction in the concentrations of most elements was observed. Mb cations (Na +K +Mg +Ca) also showed a dramatic decrease in soil solutions collected at 90 cm depth (Fig. 16.2). The amount of exchangeable base cations have decreased from 35 to <20 kmol<sub>c</sub> ha<sup>-1</sup> during 1969 to 2001 (Chap. 3).

At the Göttinger Wald and Zierenberg sites, this reduction in atmospheric depositions had only a small effect on soil solution chemistry. There was a decreasing trend in base cations and an increasing Al content indicating still ongoing acidification of the surface soil at the Göttinger Wald site (Table 16.5) despite the decrease in acid depositions. There was a higher reduction of nitrate concentration in soil solution than in total atmospheric depositions pointing to a reduction in mineralisation, which was probably induced by the increased acidification in the topsoil at the Göttinger Wald site. The Zierenberg site did not show any effect in the surface 20 cm soil except for K and Mn. However, an increase in Al and H at a depth of below 20 cm pointed to acidification in relation to high net nitrification. Fluxes of Al, H and nitrate increased with time at 100 cm soil depth (Table 16.7).

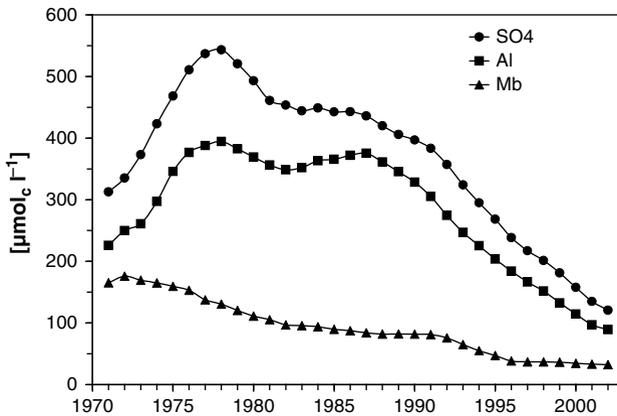
**Table 16.5** Temporal trends of concentrations in soil solution at different depths (cm) of the Solling (SO) and Göttinger Wald (GW) sites from 1981 to 2002 and of the Zierenberg (ZB) site from 1990 to 2002

| Site | Depth | Na | K  | Mg | Ca | H  | Mn | Al | TIC | NO <sub>3</sub> | N <sub>tot</sub> | DON | SO <sub>4</sub> | Cl |
|------|-------|----|----|----|----|----|----|----|-----|-----------------|------------------|-----|-----------------|----|
| SO   | 0     | o  | -- | -- | -- | o  | -- | -- |     | --              | --               | --  | --              | -- |
|      | 20    | o  | -- | -- | -- | -- | -- | -- |     | --              | --               | --  | --              | -- |
|      | 90    | o  | -- | -- | -- | -- | -- | -- |     | o               | o                | o   | --              | -- |
| GW   | 5     | o  | -- | -- | -- | o  | o  | ++ | o   | --              | --               | o   | --              | -- |
|      | 20    | o  | -  | -- | o  | o  | o  | -  | ++  | o               | -                | --  | --              | -- |
|      | 100   | o  | o  | -  | o  | -- | -- | -- | ++  | -               | -                | o   | --              | -- |
| ZB   | 20    | o  | -- | o  | o  | o  | -- | o  |     | o               | o                | -   | --              | o  |
|      | 60    | o  | -- | o  | o  | o  | -- | ++ |     | o               | o                | o   | --              | o  |
|      | 100   | o  | o  | o  | o  | ++ | -- | ++ |     | o               | o                | o   | --              | o  |

Test of trend with correlation coefficient after Pearson; o no trend, + significant increasing trend  $p \leq 0.05$ , ++ highly significant increasing trend  $p \leq 0.01$ , - significant decreasing trend  $p \leq 0.05$ , -- highly significant decreasing trend  $p \leq 0.01$



**Fig. 16.1** Time series of sulphate concentrations ( $\mu\text{mol}_c \text{L}^{-1}$ ) in soil solutions from 20 cm and 90 or 100 cm depths at three beech sites

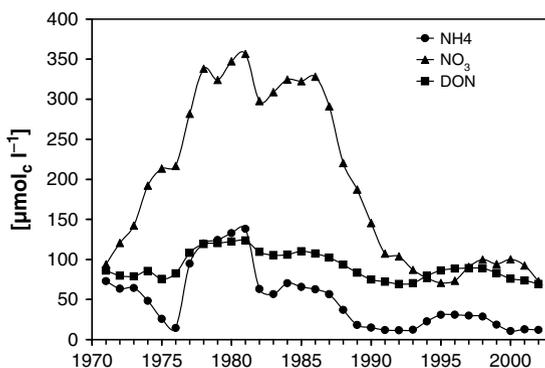


**Fig. 16.2** Five-year moving average of  $\text{SO}_4^{2-}$ , Al and Mb cations (Na, K, Mg, Ca) concentrations in soil solution (90 cm depth) at the Solling site

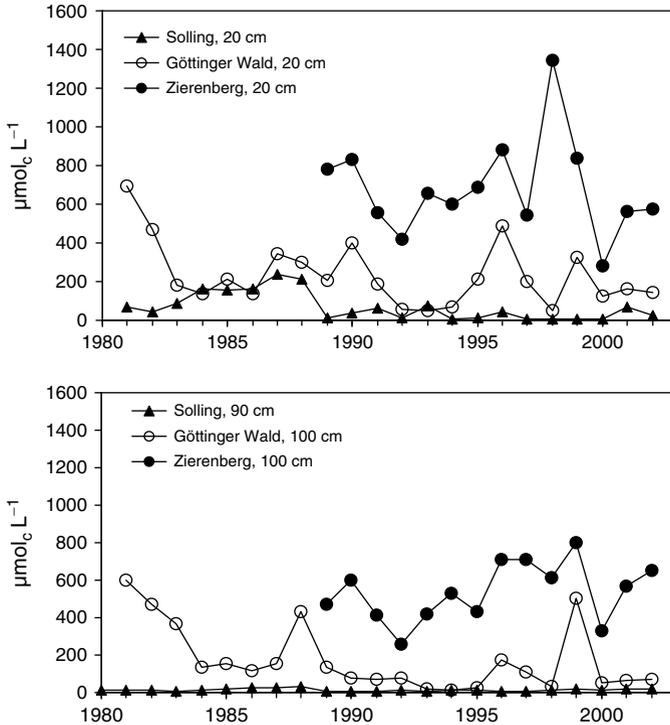
There was a decrease in nitrate concentration in soil solution which could be observed clearly below the surface organic layer and this decrease followed the declining trend in N depositions (Chap. 15). Nitrate concentrations increased during 1970s, stayed constant during 1980s, and then declined to values observed at the beginning of the 1970s (Fig. 16.3). The magnitude of changes in nitrate concentration decreased with increasing soil depth (Fig. 16.4; Table 16.5) at the Solling and Göttinger Wald sites but no temporal trend was observed at the Zierenberg site probably because of the short observation period. Since deposited ammonium is either immobilised in the surface organic layer as was indicated by  $^{15}\text{N}$  studies (Chap. 14) or is nitrified, ammonium concentration in the solutions did not show any temporal pattern.

Toxic effects of monomeric Al on roots and soil fauna are commonly expressed through molar ratios of base cations (BC) to Al (Sverdrup and Warfvinge 1992; Cronan and Grigal 1995; de Vries et al. 2003).  $(\text{Mg}+\text{Ca})/\text{Al}$  ratio of less than 1.0–3.0 in soils with low BC concentrations as proposed by Sverdrup and Warfvinge (1992) indicated a high degree of stress on plant roots which was the case for the Solling site (Fig. 16.5). In such situations, the rhizosphere activity may mitigate the adverse effects of Al (Högberg and Jensén 1994).

The alkalinity of the solution is used as a measure of the recovery of lakes, streams or soils from acidification (Reuss and Johnson 1986; Alewell 2001) and was calculated for the Solling site as  $(\text{Na} + \text{K} + \text{Ca} + \text{Mg} + \text{NH}_4) - (\text{Cl} + \text{NO}_3 + \text{SO}_4)$ . The alkalinity was negative when soil solution sampling started at Solling in 1969 (Fig. 16.5). The temporal pattern of alkalinity inversely followed the concentrations of sulphate, for example from 1975 to 1989 at the Solling site concentration of sulphate was high but alkalinity was very low. Since the beginning of the 1990s, the alkalinity has increased to values which are slightly higher than those at the beginning of the 1970s though still negative. A similar increase in alkalinity of soil solution was reported by Matzner et al. (2004) who interpreted it as a slight but significant recovery of soil solution from acidification.



**Fig. 16.3** Five-year moving average of  $\text{NH}_4$ ,  $\text{NO}_3$  and DON concentrations in soil solution beneath the surface organic layer at the Solling site

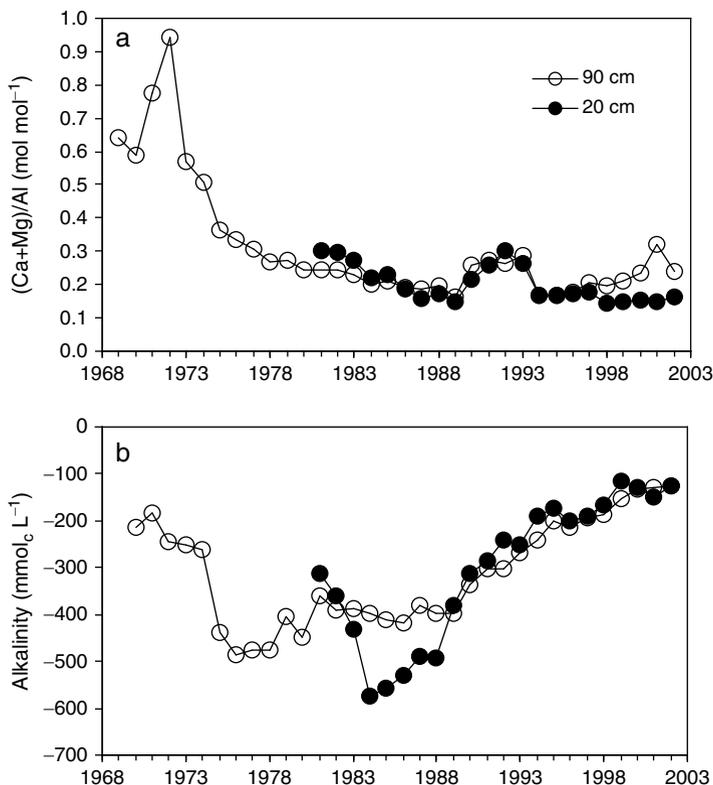


**Fig. 16.4** Time series of nitrate concentrations ( $\mu\text{mol}_c \text{L}^{-1}$ ) at 20 cm and 90 or 100 cm depths of the three beech sites

### 16.7 Hydrologic Regime

For the determination of solute outputs, estimates of soil water fluxes have to be coupled with nutrient concentrations obtained by the sampling of soil solution. For none of the study sites, direct measures of all water fluxes, especially the drainage (e.g. by the use of calibrated watersheds) are available. Thus, a number of water fluxes were estimated by using simulation model (see Sect. 16.3).

During 1990 to 2002, simulated mean potential evapotranspiration (interception not included) was highest for the Göttinger Wald site and lowest for the Solling site (Table 16.6). Differences in actual evapotranspiration among the three sites followed the same order but were smaller in magnitude. The highest evapotranspiration at the Göttinger Wald site is related to higher air temperatures at this site (Chap. 2). Due to very different precipitation and interception values on these sites, the outflow flux from soils is also very different with Solling having the highest value. Mean output water flux of 638 mm for the Solling site was similar to the value of 588 mm given by Benecke (1984) for 1969 to 1975 and of 572 mm by Ellenberg et al. (1986) for 1976–1981. The present simulation with the SIMPEL model yielded an average



**Fig. 16.5** Time series of (a) the ratio between concentrations of base cations (Ca + Mg) and Al in soil solution ( $\text{mol}_c \text{mol}_c \text{L}^{-1}$ ) and (b) the soil solution alkalinity ( $(\text{Na} + \text{K} + \text{Ca} + \text{Mg} + \text{NH}_4) - (\text{Cl} + \text{NO}_3 + \text{SO}_4)$ ) at 20 and 90 cm depths at the Solling site

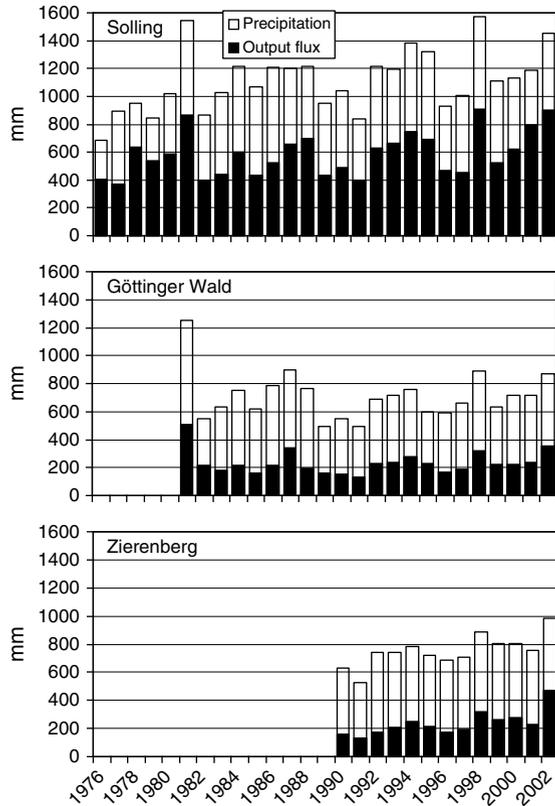
**Table 16.6** Mean annual values of measured (precipitation, interception) and simulated water balance components (mm) for the study sites for the period 1990–2002 (evapotranspiration does not include crown interception)

|                              | Göttinger Wald  | Zierenberg | Solling |
|------------------------------|-----------------|------------|---------|
| Precipitation                | 684             | 752        | 1,184   |
| Interception                 | 68 <sup>a</sup> | 148        | 253     |
| Potential evapotranspiration | 616             | 553        | 457     |
| Actual evapotranspiration    | 387             | 368        | 293     |
| Output water flux            | 229             | 236        | 638     |

<sup>a</sup>Low interception probably relate to an underestimation of precipitation

output flux of 568 mm for 1976–1981. Mean annual soil water fluxes for the Zierenberg and Göttinger Wald sites were calculated to be lower than those observed for the Solling site with large year to year variation in the values

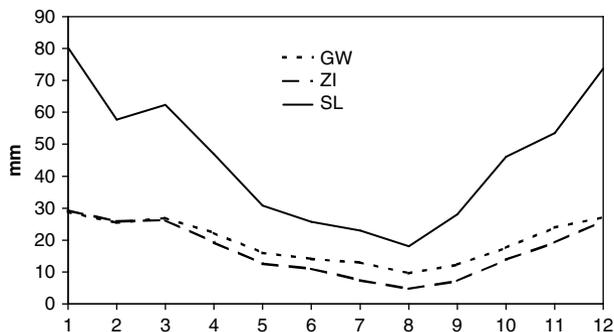
**Fig. 16.6** Annual precipitation rates and output water fluxes (mm) at the three beech sites



(Fig. 16.6). At Solling, the lowest and highest values of annual output fluxes occurred in 1977 with 370 and in 1998 with 908 mm. At Göttinger Wald, the highest annual values of output flux (505 mm) occurred in 1981, and the lowest value of 134 was calculated for 1991. The driest year at Zierenberg was also 1991 with 134 mm of output fluxes and the highest flux during the 1990–2002 observation period for Zierenberg occurred in 2002 with 471 mm.

Seasonal pattern of monthly output fluxes for water during the 1990–2002 (Fig. 16.7) indicated that the highest values occurred in January and the lowest values in August. Simulation with the SIMPEL model indicates that the outflow from these soils occurred during the whole year, though at low rates during the summer months.

The long-term observation at the Solling site revealed an increase in precipitation and temperature (Chap. 2) and raised the question about future changes in the hydrologic regime. However, energy input from global radiation remained more or less constant and evapotranspiration did not change, so any surplus water from increased precipitation will increase output water fluxes.



**Fig. 16.7** Simulated values of mean monthly output water fluxes (1990–2002) at Göttinger Wald (GW), Zierenberg (ZI), and Solling (SL) sites

## 16.8 Element Seepage Losses

Among the cations, the amount of Al loss was the highest at the Solling site (Table 16.7). Losses of sulphate exceeded those of Al and caused losses of base cations such as Mg and Ca. At the Göttinger Wald and Zierenberg sites, Ca is the main cation in the soil solution (also Mg at the Zierenberg site) which is lost in large amounts. Sulphate and  $\text{HCO}_3$  are the main anions accompanying Ca and Mg with seepage water. Nitrogen losses are low or moderate at Solling ( $12 \text{ mmol m}^{-2}$  per year) and Göttinger Wald ( $32 \text{ mmol m}^{-2}$  per year) in contrast to very high losses of  $148 \text{ mmol m}^{-2}$  per year at Zierenberg.

Linear trend analysis of the mean solute fluxes indicated that flux trends were somewhat different from those obtained for concentrations at the three beech sites (Table 16.8). The negative trends indicated a decrease in solute fluxes and thus in groundwater contamination and followed the pattern of emission reduction in the 1990s at the Solling and Göttinger Wald sites (the Zierenberg site was an exception). Decreasing trends in the fluxes of sulphate (highly prominent) and of Al, Ca, Mg, Mn and K (significant) were observed at the Solling site, whereas the negative trend of nitrogen at the Göttinger Wald site was not very clear because of very high water fluxes at the beginning of the project in 1981 (see Fig. 16.5). Losses of nitrate and DOC at the Zierenberg site increased in association with high output water fluxes and this also led to higher losses of Mg, Na, K, Cl and DON.

## 16.9 Element Budgets

Annual mean values of total deposition, drainage losses and plant uptake for increment were used to develop input–output budgets for a number of elements for the three sites, which are presented as mean values of different periods in Table 16.9.

**Table 16.7** Mean seepage losses at 90 cm (Solling) and 100 cm depth (Göttinger Wald and Zierenberg). Values are given in  $\text{mmol}_e \text{m}^{-2}$  per year except  $\text{mmol m}^{-2}$  per year for  $\text{DON}$ ,  $N_{\text{tot}}$ , and  $\text{DOC}$

| Period         | mm  | $\text{NO}_3$ | DON | $N_{\text{tot}}$ | DOC  | Cl | $\text{SO}_4$ | Ca   | Mg  | K | Na | Al  | Mn | H  |
|----------------|-----|---------------|-----|------------------|------|----|---------------|------|-----|---|----|-----|----|----|
| Solling        |     |               |     |                  |      |    |               |      |     |   |    |     |    |    |
| 76–80          | 508 | 10            | 7   | 19               | n.d. | 66 | 276           | 32   | 24  | 9 | 48 | 204 | 17 | 50 |
| 81–89          | 560 | 12            | 3   | 14               | n.d. | 60 | 248           | 22   | 20  | 7 | 42 | 205 | 12 | 29 |
| 90–02          | 638 | 8             | 1   | 12               | 101  | 54 | 154           | 12   | 14  | 4 | 51 | 117 | 6  | 22 |
| Göttinger Wald |     |               |     |                  |      |    |               |      |     |   |    |     |    |    |
| 81–89          | 244 | 80            | 13  | 97               | 164  | 50 | 181           | 1251 | 32  | 5 | 50 | 1   | 0  | 0  |
| 90–02          | 229 | 23            | 6   | 32               | 157  | 31 | 89            | 1130 | 23  | 3 | 39 | 1   | 0  | 0  |
| Zierenberg     |     |               |     |                  |      |    |               |      |     |   |    |     |    |    |
| 90–02          | 236 | 140           | 8   | 148              | 181  | 52 | 112           | 314  | 167 | 4 | 60 | 1   | 0  | 0  |

**Table 16.8** Mean solute fluxes (90 cm depth (Solling) or 100 cm depth (Göttinger Wald and Zierenberg)) and linear trends (slope of the regression functions) for the study sites for the periods 1981–2002 (Solling and Göttinger Wald) and 1990–2002 (Zierenberg)

|                  | Unit                                       | Solling |       | Göttinger Wald |         | Zierenberg |       |
|------------------|--|---------|-------|----------------|---------|------------|-------|
|                  |  | Mean    | Trend | Mean           | Trend   | Mean       | Trend |
| H <sub>2</sub> O | mm   | 588     |       | 235            |         | 236        | 16.74 |
| H                | mmol <sub>c</sub> m <sup>-2</sup> per year | 29      |       | 0.003          | -0.0001 | 0.03       | 0.005 |
| Ca               | mmol <sub>c</sub> m <sup>-2</sup> per year | 19      | -1.0  | 1,179          |         | 314        |       |
| Mg               | mmol <sub>c</sub> m <sup>-2</sup> per year | 18      | -0.6  | 27             |         | 167        | 10.9  |
| Na               | mmol <sub>c</sub> m <sup>-2</sup> per year | 47      |       | 43             |         | 60         | 4.73  |
| K                | mmol <sub>c</sub> m <sup>-2</sup> per year | 6       | -0.2  | 4              |         | 4          | 0.36  |
| Al               | mmol <sub>c</sub> m <sup>-2</sup> per year | 162     | -7.6  | 1              | -0.07   | 1.2        | 0.24  |
| Mn               | mmol <sub>c</sub> m <sup>-2</sup> per year | 10      | -0.5  | 0.1            | -0.004  | 0.06       |       |
| Cl               | mmol <sub>c</sub> m <sup>-2</sup> per year | 58      |       | 39             | -1.8    | 52         | 2.65  |
| SO <sub>4</sub>  | mmol <sub>c</sub> m <sup>-2</sup> per year | 208     | -8.6  | 126            | -8.4    | 112        |       |
| NO <sub>3</sub>  | mmol <sub>c</sub> m <sup>-2</sup> per year | 10      |       | 46             | -4.6    | 140        | 14.31 |
| DON              | mmol m <sup>-2</sup> per year              | 1       |       | 9              | -0.5    | 8          | 0.71  |
| N <sub>tot</sub> | mmol m <sup>-2</sup> per year              | 14      |       | 59             | -5.4    | 148        | 15.03 |
| DOC              | mmol m <sup>-2</sup> per year              | 93      |       | 160            |         | 181        | 19.16 |

Only values for significant trends  $p \leq 0.05$  are given

### 16.9.1 Solling Site

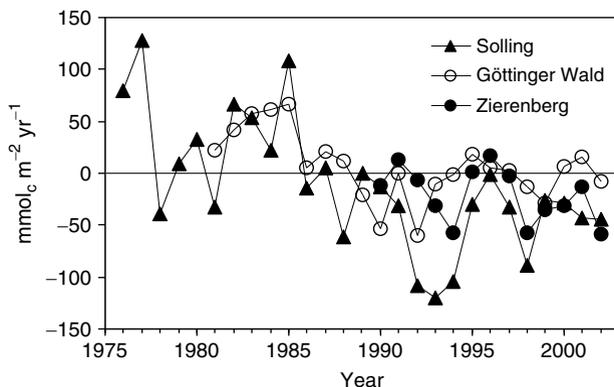
The input–output budgets of this ecosystem (TD–SL) are positive for most of the elements except aluminum and manganese in the first two decades, indicating their retention within the ecosystem (Table 16.9). Losses of Al and Mn are due to high acidity levels in this soil. I/O budgets for S and Mg indicate their losses during the recent periods.

The long-term sulphate budget is driven by strongly decreasing input rates of atmospheric deposition from 264 to 102 mmol<sub>c</sub> m<sup>-2</sup> per year (Table 16.9), accompanied by seepage rates which have decreased from 248 to 154 mmol<sub>c</sub> m<sup>-2</sup> per year during the last two decades (Table 16.7). Thus, a delay in response of seepage outputs to strongly decreased deposition results in negative values of balance in the budget for sulphur. The temporal variation is high (Fig. 16.8) due to large fluctuations of seepage water fluxes. Source of sulphate is the amount of S which has accumulated in the soil during high atmospheric input conditions (Meiwes et al. 1980; Khanna et al. 1987; Alewell et al. 2000b). A net release of sulphate from acid forest soils after emission reduction has recently been reported from other sites in Germany (Matzner et al. 2004). Studies at the Fichtelgebirge mountains and the Steigerwald hillside in South Germany indicated a net release of 4 kg in the period of 1995–2001 and 19 kg S ha<sup>-1</sup> per year for 1993–2001 similar to the Solling site with losses of 8 kg S ha<sup>-1</sup> per year in the period 1990–2002. Catchments studies conducted in Europe showed a similar reduction in sulphate output. However, they differed in their response to reduced sulphur depositions. Whereas catchments in

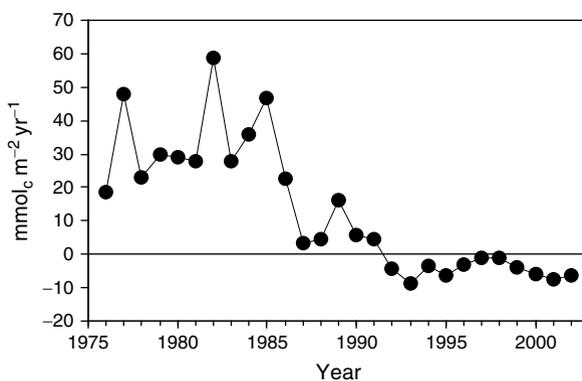
**Table 16.9** Total deposition (TD) and element budgets (TD-SL and TD-SL-PI) in  $\text{mmol}_e \text{m}^{-2}$  per year for DON,  $N_{tot}$ , DOC where SL is seepage losses and PI plant increment (from Table 16.2) for consecutive periods for the Solling, Göttinger Wald, and Zierenberg sites

|                           | Na  | K        | Mg           | Ca           | $N_{tot}$  | DON | DOC  | SO <sub>4</sub> | Cl | H       | Mn  | AL   | $\Sigma+ - \Sigma-$ |
|---------------------------|-----|----------|--------------|--------------|------------|-----|------|-----------------|----|---------|-----|------|---------------------|
| Solling, 1976–1980        |     |          |              |              |            |     |      |                 |    |         |     |      |                     |
| TD                        | 60  | 17       | 25           | 75           | 311        | 66  | n.d. | 318             | 91 | 205     | 2   | n.d. | 46                  |
| TD-SL                     | 12  | 8        | 1            | 43           | 292        | 60  | n.d. | 42              | 25 | 155     | -15 | -204 | -17                 |
| TD-SL-PI                  | 12  | 0        | -6           | 22           | 249        | 60  | n.d. | 42              | 25 | 191     | -15 | -204 | -17                 |
| Solling, 1981–1989        |     |          |              |              |            |     |      |                 |    |         |     |      |                     |
| TD                        | 61  | 15       | 19           | 62           | 289        | 47  | n.d. | 264             | 88 | 204     | 2   | n.d. | 37                  |
| TD-SL                     | 20  | 8        | -2           | 40           | 275        | 49  | n.d. | 16              | 28 | 175     | -10 | -205 | 16                  |
| TD-SL-PI                  | 20  | -1       | -8           | 19           | 232        | 49  | n.d. | 16              | 28 | 211     | -10 | -205 | 16                  |
| Solling, 1990–2002        |     |          |              |              |            |     |      |                 |    |         |     |      |                     |
| TD                        | 55  | 8        | 10           | 22           | 186        | 17  | n.d. | 102             | 59 | 55      | 1   | n.d. | 9                   |
| TD-SL                     | 4   | 3        | -4           | 10           | 174        | 17  | -101 | -52             | 5  | 32      | -5  | -117 | -6                  |
| TD-SL-PI                  | 4   | -5       | -11          | -11          | 131        | 17  | -101 | -52             | 5  | 68      | -5  | -117 | -6                  |
| Göttinger Wald, 1981–1989 |     |          |              |              |            |     |      |                 |    |         |     |      |                     |
| TD                        | 36  | 12       | 16           | 75           | 196        | 31  | 36   | 210             | 58 | 132     | 1   | n.d. | 8                   |
| TD-SL                     | -14 | 6        | -16          | -1,176       | 99         | 18  | -133 | 29              | 9  | 132     | 1   | -1   | -1,027              |
| TD-SL-PI                  | -14 | -15      | -34          | -1,326       | -28        | 18  | -133 | 29              | 9  | 322     | 1   | -1   | -1,027              |
| Göttinger Wald, 1990–2002 |     |          |              |              |            |     |      |                 |    |         |     |      |                     |
| TD                        | 35  | 5        | 9            | 27           | 158        | 13  | 173  | 79              | 41 | 37      | 0   | n.d. | 2                   |
| TD-SL                     | -4  | 2        | -14          | -1,102       | 126        | 7   | 16   | -10             | 10 | 37      | 0   | -1   | -1,054              |
| TD-SL-PI                  | -4  | -20      | -32          | -1,253       | 0          | 7   | 16   | -10             | 10 | 227     | 0   | -1   | -1,054              |
| Zierenberg 1990–2002      |     |          |              |              |            |     |      |                 |    |         |     |      |                     |
| TD                        | 53  | 14       | 39           | 77           | 171        | 19  | n.d. | 91              | 63 | 61      | 0   | n.d. | 96                  |
| TD-SL                     | -7  | 11       | -128         | -237         | 23         | 18  | -181 | -21             | 11 | 61      | 0   | -1   | -147                |
| TD-SL-PI                  | -7  | -1 to -3 | -132 to -140 | -271 to -292 | -15 to -40 | 18  | -181 | -21             | 11 | 106-140 | 0   | -1   | -147                |

Positive numbers of TD-SL and TD-SL-PI indicate net retention of a component, negative numbers net release.  $\Sigma+ - \Sigma-$  is the difference between the sum of cations and anions (n.d., not determined)



**Fig. 16.8** Long-term annual budgets of sulphate (total deposition – leaching losses) at the three beech sites at Solling, Göttinger Wald and Zierenberg



**Fig. 16.9** Long-term values of annual ecosystem budget of Ca (total deposition + weathering – seepage output – plant increment) at the Solling beech site

Scandinavia and the Czech Republic/Slovakia with shallow soils and relatively small sulphate storage capacity responded quickly to decreased S input, the deeply weathered soils in Germany with high sulphate storage capacity responded more slowly to decreased deposition and this response was considered to be the results of the release of stored sulphate (Alewell 2001; Prechtel et al. 2001).

When the amount of elements retained by plant increments (PI) is included in the output value (TD-SO-PI) then the obtained budgets indicated that the Solling soil which was a sink for Ca became a net source during the three decades of observation period (Table 16.9). The net source amounted to  $11 \text{ mmol}_c \text{ m}^{-2}$  per year and is higher than that calculated for mineral weathering ( $8 \text{ mmol}_c \text{ m}^{-2}$  per year; Sect. 16.4). When the amount of Ca released by mineral weathering is included in the input, most of the Ca values remained under the zero line since 1992 (Fig. 16.9) indicating a net loss of Ca. Both atmospheric depositions (TD) and seepage outputs

of Ca have decreased during this period. However, decrease in TD was higher than the decrease in seepage losses. This pattern is hence quite similar to the one observed for sulphate. Under these conditions, sustainable forest utilisation seems to be no longer possible with respect to forest nutrition.

The long-term observation at Solling site indicated that exchangeable Ca decreased from about  $14 \text{ kmol}_c \text{ ha}^{-1}$  in 1966 to  $7 \text{ kmol}_c \text{ ha}^{-1}$  in 1983 (0–50 cm, Chap. 3), and since then had stayed at this low level indicating a significant decline of plant available Ca. This may partially be due to the retention of Ca in the surface organic layer for which the amount increased from 4.5 to  $8.8 \text{ kmol}_c \text{ ha}^{-1}$  from 1966 to 2001 (Chap. 4). As the mass of surface organic layer at the Solling site increased, it retained C, N, Ca and other elements. Foliage Ca levels showed Ca deficiency (Chap. 5) without any prospect of recovery since input by weathering and TD did not cover the plant demand for growth increment. The recent decrease in TD and exchangeable Ca and its retention in the surface organic layer will have some long-term consequences on the nutrition and vitality of trees in future.

Mg showed similar decreasing trends in total deposition and leaching losses as Ca. The decrease in TD of Mg (from 19 to  $10 \text{ mmol}_c \text{ m}^{-2}$  per year, Table 16.9) exceeded the decline in leaching losses during the last observation decades (from 20 to  $14 \text{ mmol}_c \text{ m}^{-2}$  per year, Table 16.7), thus TD did not cover the amount of leaching losses. Considering the additional amount of Mg retained in plant increment ( $7 \text{ mmol}_c \text{ m}^{-2}$  per year) the total amount required annually in addition to that received through TD at the Solling site, was about  $11 \text{ mmol}_c \text{ Mg m}^{-2}$  per year (Table 16.9). Through mineral weathering about  $27 \text{ mmol}_c \text{ Mg m}^{-2}$  per year would be released (Table 16.2) which may cover the requirements at the Solling site of  $11 \text{ mmol}_c \text{ Mg m}^{-2}$  per year as well as the additional amount required for humus accumulation in surface organic layer ( $6 \text{ mmol}_c \text{ m}^{-2}$  per year). Even though the overall ecosystem budget is positive the content of Mg in leaves pointed to its deficiency (Chap. 11). Weathering rates might be realistic because two independent methods estimated similar values for Mg (and Ca, see Sect. 16.4). Thus, a reduction in Mg availability through interactions with Al in the apoplast of roots (Godbold and Jentschke 1998) might be a plausible explanation for Mg deficiency at this acid soil.

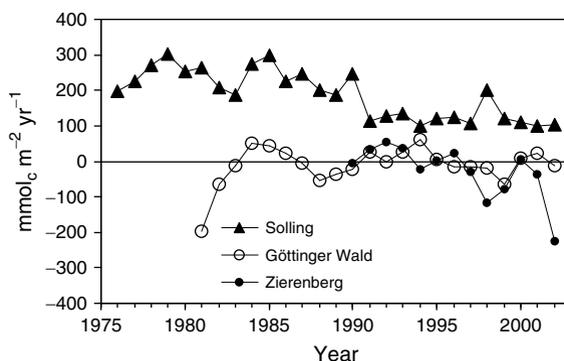
A negative K budget (TD-SL-PI,  $-5 \text{ mmol}_c \text{ m}^{-2}$  per year, Table 16.9) and high weathering rates of  $52 \text{ mmol}_c \text{ m}^{-2}$  per year as calculated by PROFILE model of Sverdrup and Warfvinge (1992) (Table 16.2) suggested that the overall budget was balanced. The main assumption is that the weathering rate for K is realistic. This may not be the case because the amount of exchangeable K did not show any increase during the observational period of more than three decades at the Solling site (Chap. 3). A much lower weathering rate of  $6 \text{ mmol}_c \text{ K m}^{-2}$  per year was calculated by the ZrO method (see Sect. 16.4) which would just cover the negative budget. However, K content in beech leaves revealed an increasing trend of K deficiency during the last decade (Chap. 11). Thus, there was an overestimation of K weathering by the PROFIL model. The same result is revealed for Na. The ecosystem budget of  $+4 \text{ mmol}_c \text{ m}^{-2}$  per year is just balanced by the weathering rate calculated by the ZrO method ( $5 \text{ mmol}_c \text{ m}^{-2}$  per year) whereas a much higher value was estimated by the PROFILE model ( $26 \text{ mmol}_c \text{ m}^{-2}$  per year). Losses of Al and

Mn decreased in time (Table 16.9) which indicated that, due to low inputs of H through atmospheric depositions, the amount of protons buffered through the release of Al was also reduced.

High amount of nitrogen inputs from atmospheric depositions was retained at the Solling site, which was more than  $281 \text{ mmol}_c \text{ m}^{-2}$  per year (about  $39 \text{ kg N ha}^{-1}$  per year) during the first two observation periods (Table 16.9). During the last decade, N retention decreased markedly to  $174 \text{ mmol}_c \text{ m}^{-2}$  per year ( $24 \text{ kg N ha}^{-1}$  per year). As the amount of N lost by leaching is low at this site and the annual amount retained by plant increment is constant and low ( $43 \text{ mmol}_c \text{ m}^{-2}$  per year or  $6 \text{ kg N ha}^{-1}$  per year), the main reduction in N retention occurred in the soil which has decreased from about  $33$  to  $18 \text{ kg N ha}^{-1}$  per year (Fig. 16.10). Most important for N retention at the Solling site is the surface organic layer where on average  $21 \text{ kg N ha}^{-1}$  per year were accumulated during the 36-year period (Chap. 3). This increase was assigned to the increase in mass of surface organic layer, though the C/N ratio did not change. According to the extensive studies by Berg and McLaugherty (2003), high N content in freshly fallen litter would decrease its decomposition in the long-term and would thus increase the amount of organic matter remaining in the surface organic layer. Berg (2003) calculated from the data on humus accumulation at Solling site and decomposition studies of litter from another 26 European beech forests that incomplete litter decomposition may sequester about  $27 \text{ kg N ha}^{-1}$  per year at the Solling site which is in the range of the value obtained for other sites.

## 16.9.2 Göttinger Wald Site

Temporal changes in the input–output (I/O) budgets at Göttinger Wald site do not indicate any clear trends for most of the elements (Table 16.9). However, for some individual years, the N budget values was negative (Fig. 16.10). At this site, N is not



**Fig. 16.10** Long-term annual budgets (total deposition – plant uptake – leaching losses) of total N at the three beech sites at Solling, Göttinger Wald and Zierenberg (for Zierenberg, the mean uptake for increment was used)

retained by the soil because of the low amount of organic matter in the surface organic layer and high biological activity. The amount of N retained by plant increment is about three times higher than at the Solling site (Table 16.2). I/O budgets of Ca, Mg, K and Na are negative indicating high amount of outputs by seepage water and plant increment. Weathering rates of Mg and K would just meet the demand for considering the relationship TD-SL-PI, by assuming weathering rates were correctly estimated by the PROFIL model. Foliage nutrient levels indicated sufficient levels for Mg, an optimal level of nutrition for K and a luxuriant nutrient level for Ca. Budgets for aluminum and sulphur generally exhibited small values when compared to the Solling site. However, a shift from sulphur retention (period 1981 to 1989) to a release of stored sulphur from the soil (1990–2002, Table 16.9) was observed which is expected to cause an increased acid load for the soil.

### 16.9.3 Zierenberg Site

At the Zierenberg site, where the observation period was the shortest of the three, a general trend towards more negative values of I/O budgets for nutrients was observed, despite a strong seasonal character of the values. The unique feature of the Zierenberg site is the continuing high leaching loss of N. The amount of N in seepage output and sequestration by growth increment was 15–40 mmol<sub>c</sub> m<sup>-2</sup> per year more than total N deposition at this site indicating an annual loss of 2–6 kg N ha<sup>-1</sup> per year from the soil (Table 16.9). Figure 16.10 indicates an increasing trend of nitrate fluxes which was positively correlated with precipitation rates ( $r^2 = 0.73$ ) and water output rates ( $r^2 = 0.82$ ), though the amount of N deposition did not change much. The negative I/O budgets for N suggested a decrease of organic N pools in the soil (Eichhorn 1995; Eichhorn and Hüttermann 1994, 1999; Fried 2001). This loss of N through humus degradation would assume high level of acidity or the presence of aluminum in soil solution. OH-groups of phenolic substances could be masked by Al-cation forming stable Al-complexes which is assumed to prevent further polymerisation processes to larger organic molecules as proposed by Ulrich (1981). In general, organo-metallic complexes are regarded to be stabilising soil humus (Blaser and Klemmedson 1987); however, dissolved organic carbon as a precursor of humus showed a similar reaction with Al. Using lignin as a model, the enzymatically catalysed polymerisation of phenols was clearly inhibited in the presence of Al-ions (Jentschke 1984; Haars et al. 1989; Hüttermann et al. 1989). Aluminum and nitrates were released into seepage water through acidification for which increasing positive trends (Table 16.8) were observed. In addition to Al, other elements as K, Ca and Mg were released by silicate weathering and carbonate dissolution, of which Ca and Mg occurred in appreciable amounts in the output fluxes. Increased precipitation rates and temperatures during the nonvegetation period of recent decades were observed as a general trend (Chap. 2). This would increase the leaching losses of nitrates at high nitrifying sites similar to Zierenberg during the nonvegetation period, especially those with additional litter input from N-rich herbaceous vegetation like *Urtica dioica*.

## 16.10 Acid Loading: Atmospheric Depositions and System-Internal H Production

Production and consumption of H ions in ecosystems are determined by the input and output of other ions as the electro-neutrality has to be maintained at any macroscopic scale in soil solutions. During their uptake and losses electro-neutrality is preserved through transfer of protons among different components of a system (Ulrich 1981, 1994a). Thus, the total ecosystem proton production rates can be inferred from the input-output budgets of major ions (Bredemeier et al. 1990; Ulrich 1994a).

N transformation processes may play an important role for consumption and production of protons. For each mole of  $\text{NH}_4$  input, one mole of H is released if taken up or 2 moles of H will be produced if completely nitrified (according to the overall stoichiometric equation  $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$ ). Thus, depending upon the sources and fate of N, the total proton production can be calculated. For the methodology to calculate acid budgets refer to Sect. 16.4.

The overall total acid production rates were highest at Göttinger Wald ( $>1 \text{ mol m}^{-2}$  per year in both decades, where a significant part of the total protons was weak acidity from carbonic acid dissociation (73% and 81% of the total protons produced in the two consecutive periods) (Table 16.10). This acidity is primary buffered through dissolution of limestone (carbonate buffer range) and the release of Ca into the solution phase. This process is therefore related to the amount of precipitation as indicated by positive correlation between water output and production of weak acidity ( $r^2 = 0.94$ ) and losses of Ca ( $r^2 = 0.94$ ) and Mg ( $r^2 = 0.77$ ) with seepage water. The contribution of atmospheric deposition and uptake of base cations for plant increment to the total production of acidity has decreased from 23 to 18% (of which plant increment contributed to about 14%) reflecting the decline in atmospheric depositions.

**Table 16.10** Mean annual acid production rates in  $\text{mmol m}^{-2}$  per year calculated from input/output balances (considering total deposition, plant increment, and leaching losses), given separately for the consecutive decades, and relative contributions of four different processes to the total at the Solling, Göttinger Wald and Zierenberg sites, calculated according to Ulrich 1994a

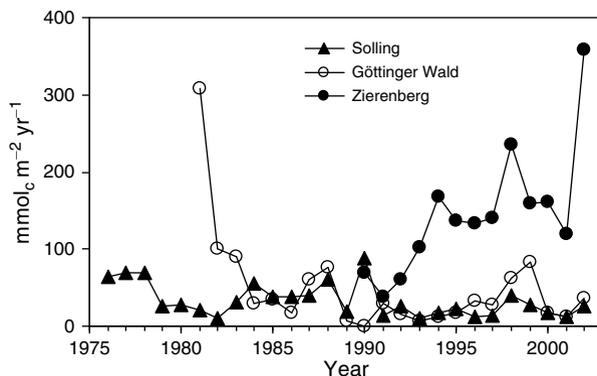
| Site           | Period | Total $\text{H}^+$ production ( $\text{mmol m}^{-2}$ per year) | S release (% of total) | N transformation (% of total) | Acid input (% of total) | Weak acidity release (% of total) |
|----------------|--------|--|------------------------|-------------------------------|-------------------------|-----------------------------------|
| Solling        | 76–80  | 284  | 3                      | 18                            | 67                      | 8                                 |
|                | 81–89  | 280  | 4                      | 12                            | 75                      | 4                                 |
|                | 90–02  | 150  | 34                     | 17                            | 46                      | 8                                 |
| Göttinger Wald | 81–89  | 1,400  | 0                      | 6                             | 23                      | 73                                |
|                | 90–02  | 1,300  | 1                      | 2                             | 18                      | 81                                |
| Zierenberg     | 90–02  | 407–416  | 6                      | 35–36                         | 23–26                   | 35–36                             |

H production by Mb retention is not shown. Acid input refers to the sum of positive budgets of H, Mn, Al and Fe. Weak acidity refers to carbonic and organic acids

At Zierenberg, the weak acids contributed 35–36% to the total proton load which occurred in deeper soil layers close to the boundary of tertiary basaltic debris overlying Triassic limestone. The proportion of protons produced from N transformation processes was 35–36% of the total proton load at the Zierenberg site, where nitrification was highest among the three sites. The input of acid contributed to 23–26% of the total load of which plant increment added 19%. Proton buffering occurred through consumption of protons for weathering of primary silicates or carbonates causing the release of Mb cations of which Ca and Mg dominated the soil solution.

Due to the acid conditions at the Solling site the production of weak acidity was low and consisted almost exclusively of organic acid deprotonation (4–8% of the total load). The primary sources of acidity in this ecosystem were the inputs by H deposition and the negative equivalent of base cations taken up for plant increment. The total amount of proton load decreased from 280 to 150 mmol m<sup>-2</sup> per year during the last two decades. The relative proportion of acid input to the total load decreased from 75 to 46% (Table 16.10), of which 14–24% were contributed by cation retention by plants. Contribution of N transformations to acid load at the Solling site was primarily related to the retention of deposited ammonium whose relative proportion to total acid load increased from 12 to 17% during the last two decades, despite a decrease in acidity produced by N transformation from 35 to 25 mmol m<sup>-2</sup> per year. The most important component of the current acid load at Solling is the release of stored sulphate increasing from 12 to 52 mmol m<sup>-2</sup> per year and contributing about 4% and 34% to the total acid load during the last two decades. This resulted in delaying the recovery from soil acidification. A delay in recovery from soil acidification due to release of sulphate present in the deep weathered acid soils has been shown to be widespread in central Europe (Alewell et al. 2000a). Total acid load at Solling would have been higher than 150 mmol m<sup>-2</sup> per year if the acid production for the uptake and accumulation of base cations in the surface organic layer were included in the calculation. Assuming that Na, K, and Mg were retained in the same proportion as Ca, an additional potential of H load of 30 mmol m<sup>-2</sup> per year has to be considered. Buffering of acidity at Solling occurred predominantly by the leaching of Al which contributed about 54% of the sum of cations in the output flux.

Declining N depositions suggested a decreasing trend in acidity production. H generation by transformation of N at Solling decreased from 51, 35, to 25 mmol m<sup>-2</sup> per year during the three decades (Fig. 16.11). The Göttinger Wald site showed a small decreasing trend in protons, if the initial value was considered as an outlier in the data. The H production by N transformations at Zierenberg, however, showed an increasing trend which is driven by increased precipitation and water output during the observation period. A higher loss of N with increased precipitation might occur at sites where an excess of nitrates exist in the soil which is leached at higher rates of water flow before N is retained by plants or microorganisms. The highest value of acid production was observed in 2002 and corresponded to an acidification rate of 360 mmol Hm<sup>-2</sup> per year by N transformation alone, and this in turn makes up 47% of total proton production in that year.



**Fig. 16.11** Comparison among the three sites of time series of acidity production by transformation of deposited N compounds

## 16.11 Final Discussion

The long-term observation at the Solling and Göttinger Wald sites indicated that total depositions had decreased for sulphur (−60% at Solling and Göttinger Wald), H (−72% at Solling and Göttinger Wald), and nitrogen (−38% at Solling, −20% at Göttinger Wald) and base cations (−60% at Solling and Göttinger Wald) between two periods of 1981–1989 and 1990–2002. Emissions of SO<sub>2</sub> have significantly decreased since the mid-1980s in Europe (Ferrier et al. 2001). Deposition measurements from other studies in Europe confirmed a decline by 38–82% for sulphate and approximately 20% for inorganic nitrogen during the 1990s (Prechtel et al. 2001; Wright et al. 2001). This poses the question as to what were the effects of these changes on soils of different soil chemical states? The soil chemical properties determine biochemical and biological properties and thus contribute to the stability of an ecosystem (Ulrich 1994b). The three beech forests, Solling, Göttinger Wald and Zierenberg, represent the range of soil properties in Europe, with calcareous, intermediate and very acid soils, and thus could be regarded as typical representatives of three contrasting forest ecosystem types with respect to element budgets. Owing to differences in soil properties the response of these ecosystems to decreasing atmospheric depositions differed widely.

### 16.11.1 *Response of Acid–Base Soil Properties to Decreasing Atmospheric Deposition*

The decreasing sulphate depositions caused a decrease in sulphate export from all three beech sites. Owing to the small contribution of deposited acidity to the total H production at the carbonate-rich Göttinger Wald site, the response of soil solution chemistry to decreasing atmospheric deposition was small. Solute concentration of

sulphate, N and base cations in the surface 5 cm soil decreased, but that of Al increased suggesting that soil acidification may have continued in this layer despite the reduction in acid load. Similarly, it was not possible to assess if this decrease in acid deposition has changed soil solution chemistry in the surface soil at the Zierenberg site due to lack of solution sampling within 0–20 cm layer. At lower depths at the Zierenberg site there was an increase in the concentration of Al and H suggesting that soil processes significantly modified the concentration of solute in atmospheric depositions. In addition, high precipitation and soil water drainage during 1990–2002 increased nitrate losses at Zierenberg and thus contributed further to increased soil acidification.

In the highly acid Solling soil, a decrease in leaching losses of almost all ions in soil solution was observed indicating the importance of decreasing atmospheric acid load for soil solution chemistry on similar sites. Though the total production of acidity decreased during the last 10 years at the Solling site, changes in soil solution composition were still of a minor nature. For example, the base-cations/Al ratio remained low and the alkalinity of soil solution increased only slightly indicating that the recovery of soil solution acidity was a very slow process in such soils. One of the main reasons is desorption and the release of previously stored sulphate from the solid phases (Stoddard et al. 1999; Alewell et al. 2000a). The net release of sulphate from the soil profile amounted to about  $8 \text{ kg ha}^{-1}$  per year and contributed to 34% of total acidity production at the Solling site during the last decade. The soil capacity to adsorb sulphate is large, the modelled adsorbed pool in 2003 down to 100 cm was  $1,030 \text{ kg S ha}^{-1}$  for a “clean-rain” treatment in the Solling roof project adjacent to the Solling beech forest (Martinson et al. 2005). Model prediction shows no recovery, based on the criteria of Bc/Al ratio above 1 in the rooting zone, before the year 2050, independent of future deposition cuts. Another reason for the delayed recovery is related to low levels of base cations in the atmospheric depositions. The decrease in calcium fluxes in total deposition exceeded the decrease in leaching losses. The Ca budget clearly indicated that the ecosystem at the Solling site has changed from being a sink to a net source. Foliage chemistry also showed deficiency of Ca and Mg in the leaves (see Chap. 11). Thus, a further significant recovery in acidity of soil solution is expected in future depending on the amount of sulphur stored in the soil. Similar studies by Matzner et al. (2004) reported an annual net release of S from the soil profile of 4 and  $19 \text{ kg ha}^{-1}$  as an average between 1993–1995 and 2001 at two sites. Long-term trends in sulphate concentrations and fluxes in throughfall and streamwater of 20 European catchments revealed a similar trend (Prechtel et al. 2001). However, it is highly unlikely that the Ca supply of the trees will improve without liming.

### ***16.11.2 Response of N and C Budgets of Soils to Decreasing Atmospheric Depositions***

N depositions have also decreased at all sites but the decrease was only detectable at sites where long time series (Solling and Göttinger Wald) were available. The 13-year observation period at Zierenberg was too short to detect such changes. A significant

decreasing trend in nitrate concentrations was detectable only in the surface soil layers of the Solling and Göttinger Wald sites. Most of the  $21 \text{ kg ha}^{-1}$  per year N atmospheric inputs at Göttinger Wald were retained for annual increment by plants ( $18 \text{ kg ha}^{-1}$  per year, considering above ground biomass and coarse roots) and the remaining amount leached with seepage water ( $4.5 \text{ kg N ha}^{-1}$ ) while the soil N pool was constant during 1990–2002. Thus, N deposition at this site meets the demand for the annual growth and any excess amount is leached with seepage water indicating that this forest is near (quasi-) steady state. Such systems are defined by organic matter production in the soil that equals the respiration, a closed nutrient cycle, and amount of organic matter stored in the soil being at a maximum level under given environmental conditions (Odum 1969, 1983; Ulrich 1992).

The Zierenberg site showed two interesting features. Firstly, nitrate concentrations showed no clear trends in time and the annual seepage fluxes were significantly increasing during the 13 years of observation period mainly due to increasing water fluxes. This pattern was not observed on the other two sites. Secondly, an interesting feature of N dynamics at the Zierenberg site was a negative N budget. Output by seepage water ( $21 \text{ kg N ha}^{-1}$ ) and retention by plant increment ( $5\text{--}9 \text{ kg N ha}^{-1}$ ) exceeded the input by total deposition ( $24 \text{ kg N ha}^{-1}$ ) by about  $2\text{--}6 \text{ kg N ha}^{-1}$  annually. This may be attributed to a process described as humus degradation (Ulrich 1981; Eichhorn 1994, 1995). The theory of humus degradation assumes the presence of aluminum in the soil solution causing inhibition of the repolymerisation of organic components to form humus. High nitrification leads to the production of acidity and free Al in the soil triggering an amplifying effect where organic N in the soil is further nitrified and lost. In this soil, organic matter production and respiration processes are not balanced. According to the ecosystem theory by Ulrich (1992), such a forest is in a transient state and will continue losing carbon, nitrogen and other nutrients from the mineral soil until a new (quasi-) steady state with lower C and N contents in the mineral soil under high soil acidity is achieved.

At the Solling site, most of the N received from atmospheric depositions was retained in the soil. However, this retention decreased to about  $18 \text{ kg N ha}^{-1}$  per year during the last 10 years following a similar decrease in N inputs. Leaching losses of N were low and only a small amount was retained for growth increment, which did not change with the decrease in N depositions. Most of the N was retained in the surface organic layer in association with an accumulation of organic matter. C/N ratio of the soil did not change. C/N ratios of  $>25$  in the surface organic layer have been found as critical values for the ability of forest ecosystems to retain N (Matzner and Grosholz 1997; McDonald et al. 2002). But in the surface organic layer at the Solling site this value was much lower than that critical value. An annual increase in mass of surface organic layer of  $350 \text{ kg C}$  and  $21 \text{ kg N ha}^{-1}$  occurred during the last 36-year period (see Chap. 4 for more details). Whether organic matter accumulation is controlled by high N depositions as suggested by Berg and McLaugherty (2003) and/or by acid depositions as suggested by Persson and Wirén (1993) is not clear from the data. Matzner et al. (2004) reported a relatively low N retention in a spruce forest at the Fichtelgebirge (Coulissenhieb site) with an acid podzolic soil and mor humus type litter layer. At this site, an average 80% of the mineral N in throughfall was leached as nitrate with seepage water.

## 16.12 Conclusions

Political action by European countries has led to a noticeable decline in atmospheric depositions of sulphuric acid and to a lesser extent of nitrogen since the end of the 1980s. This decline has raised the question: how do forest ecosystems with different soil properties respond and recover? Data presented from the three sites provided the following conclusions:

- In the highly acid Solling soil, a decrease in leaching losses of almost all ions in soil solution was observed, although base cations/Al ratio and alkalinity still remained low or increased only slightly. This was related to desorption and release of previously stored sulphate from the solid phases which contributed to one-third of total acidity produced or added to the system. A decline in atmospheric deposition of base cations changed this ecosystem from a sink to a net source of Ca. To improve Ca supply of the trees, liming will be needed.
- Solute concentrations in the carbonate-rich Göttinger Wald soil decreased in the carbonate-free surface soil layer whereas solute concentrations in deeper soil layers which were rich in carbonates and silicates were not affected. Highly significant increases of Al in solution samples from 5 cm depth suggested that soil acidification may have continued despite the reduction in acid load.
- In the base-rich and carbonate-free Zierenberg soil, high values of Al and H concentrations were observed in solutions collected from 20 cm soil depths. This was not related to atmospheric depositions but to degradation of soil organic matter, probably initiated by formerly high levels of acid load.
- A significant decrease in nitrate concentrations was observed in soil solutions of the surface mineral soils of the Göttinger Wald and Solling sites. At the Göttinger Wald site, high annual increment meets N deposition and excess amounts are leached indicating that this forest is near (quasi-) steady state with respect to nutrients (a closed nutrient cycle) and constant C and N pools in the soil.
- At the Zierenberg site, a net loss of N from soil organic matter was observed, where acidification of the mineral soil promoted humus degradation suggesting a transient ecosystem state. The acid Solling soil retained most of the N received from atmospheric deposition by increasing the surface organic layer. This moder humus soils has probably a high potential for N retention in future.

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