Time series analysis of changes in the soil solution: Evidence for approach to nitrogen saturation in Dutch forest soils

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Abstract

In the Netherlands, high atmospheric inputs of ammonium N followed by microbial oxidation of ammonium N to nitric acid and low N uptake from poor tree growth, has resulted in high levels of dissolved nitrate and strong soil acidification in forest soils. So-called nitrogen saturated soils where the supply of atmospheric N plus mineralised soil organic N exceeds the capacity of the ecosystem (vegetation plus soil biota) to assimilate N have been observed occasionally. At high levels of N availability, N saturation leads to enhanced soil acidification and groundwater pollution.

To test if nitrate saturation is being approached elsewhere, temporal trends in concentrations of dissolved nitrate and some other elements in a number of acidic forest soils were analysed statistically. A procedure was developed to account simultaneously for short-term, mainly seasonal variability plus any longer-term trend on a time scale of 4–7 years. Although results should be interpreted with care, because of the limited period of data collection, strong evidence for a long-term increase in nitrate concentrations has been found in all plots considered. These trends could not be accounted for by trends in atmospheric deposition or soil hydrology in general, suggesting the approach to nitrogen saturation. The procedures used in this study to analyse the monitored data focus on the estimation of trends and calculation of its significance. They can be applied to similar studies dealing with temporally varying data, sampled at irregular intervals and exhibiting missing values.

Introduction

Acid atmospheric deposition, or 'acid rain', is the result of strong acidity (H_2SO_4 and HNO_3) of rain or snow, plus dry-deposited potentially acid gases (SO_2 and NH_3) or aerosols (e.g. $(NH_4)_2SO_4$) which collect on the soil surface and vegetation cover. The potentially acid substances may eventually be oxidised to sulphuric and nitric acids in the soil. High inputs of acid deposition in Western Europe, derived from emissions by industry, automobiles and agriculture, have strongly acidified many soils under forests and woodlands (Ulrich et al., 1979; Hallbäcken and Tamm, 1986; Van Breemen et al., 1987).

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In the Netherlands, a combination of the following three factors has resulted in high levels of dissolved nitrate in soil solutions and shallow groundwater under forests in the Netherlands (Booltink et al., 1988):

(1) continued high atmospheric inputs of N (30–60 kg ha^{-1} year^{-1}) mainly caused by ammonia emissions from animal husbandry;

(2) microbial oxidation of ammonium N to nitric acid (nitrification) even under acid soil conditions;

(3) relatively low, and locally declining, tree growth.

Acidity from nitrification now equals or exceeds this, because of the formation of sulphuric acids. Because aluminium compounds are the main buffering substance in the generally base-poor sandy soils, this leads to a predominance of dissolved Al and NO_3 ion concentrations in soil solutions and drainage waters.

Out of 17 woodlands monitored for atmospheric inputs and drainage outputs of inorganic N, five showed nitrate leaching that equalled or exceeded N inputs in throughfall (Van Breemen and Verstraten, 1990). This so-called state of nitrogen saturation implies that the supply of atmospheric N plus mineralised soil organic N exceeds the capacity of the ecosystem (vegetation plus soil biota) to assimilate N. Nitrogen saturation leads to enhanced soil acidification and groundwater pollution. It may result from a combination of increased availability of soil organic N (as a result of accumulated inputs of inorganic N) and decreased capacity of biota to take up N (e.g. as a result of impaired functioning of biota, caused by acid deposition or resulting from other causes). To test whether nitrate saturation is being approached in woodlands that are not (yet) N-saturated, temporal trends in dissolved nitrate concentrations in acidic forest soils from seven sites with 4–6 years of monthly monitoring of the soil chemical state were analysed statistically. One of these seven plots was N-saturated, as indicated by the fact that atmospheric inputs were lower than leaching rates of N below the root zone.

The monitored variables, which included pH and the concentrations of Al, NO_3, SO_4 and Cl in the soil solution, vary on different scales in space and in time (Stein et al., 1988). Spatial variation includes variation with depth and variation between plots at various distances. Temporal variability includes seasonal, largely cyclic, variations, mainly resulting from seasonal variations in plant uptake of nutrients, evapotranspiration and leaching. The aim of this study was to detect any long-term trends superimposed on the seasonal variations, taking spatial variation into account. Because these may indicate long-term trends in atmospheric deposition, as well as changes in the soil–vegetation system itself, trends in deposition have also been considered. This research is linked with current research topics on space–time methods (Bennett, 1979; Bottcher and Strebel, 1988; Loader and Switzer, 1989; Rouhani and Wackernagel, 1990).

Methods

Study sites and soil solution

The statistical analysis deals with a time series analysis of soil solution data from four different sites in the Netherlands. Seven different plots have been monitored between 1981 and 1987: three plots in De Oude Maat (Plots A, B and C), two plots near Gerritsfles (Plots Y and W), one plot near Tongbersven and one near Hasselsven. The main characteristics of the site are given in Table 1. Except for De Oude Maat, where Plot A has a calcareous subsoil, soils are invariably sandy and acidic (pH 3–4). The calcareous subsoil of Plot A at De Oude Maat was not considered in the analysis for pH and Al. Vegetation consists of oak–birch woodland at De Oude Maat, Scots pine at Gerritsfles (Plot W) and Tongbersven and heather (*Calluna*) at Hasselsven; Plot Y at Gerritsfles is unvegetated (inland) dune sand. Atmospheric deposition, mainly dry-deposited ammonium sulphate derived from intensive animal husbandry (NH_3) and fossil fuel burning (SO_2) is generally high (2–5 kmol ha^{-1} $year^{-1}$ of ammonium sulphate) on forests and lower (1–2 kmol ha^{-1} $year^{-1}$ of ammonium sulphate) on heathland and unvegetated land. For further details on sites and the stand and soil characteristics, see Van Breemen et al. (1988) and Van Dobben et al. (1992).

At De Oude Maat, the soil solution was sampled monthly from February 1981 until April 1987 at 10, 20, 40, 60 and 90 cm below the surface and analysed chemically. Usually two or sometimes four replicated samplers were used for each depth. In the current analysis, data from any one depth per plot were averaged, or, if only one sample was available, that one was used. The repli-

Table 1
Characteristics of the sites used in this study. Data for De Oude Maat are from Van Breemen et al. (1988) and Booltink et al. (1988) and for other sites, from Van Dobben et al. (1992)

Site/plot	Soil type[1]	Vegetation	Tree age (years)	N_{in}[2]	N_{out}[2]
De Oude Maat	A Haplaquept	*Quercus robur* *Betula pendula*	45	3.9	4.9
	B Dystrochrept	*Quercus robur*	45	4.1	2.7
	C Udipsamment	*Quercus robur*	45	3.2	1.8
Gerritsfles	W Udipsamment	*Pinus sylvestris*	>60	3.8	2.0
	Y Udipsamment	Bare	–	2.2	1.0
Tongbersven	Haplorthod	*Pinus sylvestris*	40	4.2	1.8
Hasselsven	Haplorthod	*Calluna vulgaris/ Erica tetralix*		3.3	0.3

[1]Classification according to USDA, 1975.
[2]Throughfall input and drainage output (kmol ha^{-1} $year^{-1}$) of total inorganic (nitrate plus ammonium). N: annual average for 6 years (De Oude Maat) and 4 years (other sites).

cated data showed only little variation. At the other sites, soil solution samples were collected monthly for 4 years at depths corresponding to soil horizons or in and below the rooting zone as follows: 40 and 100 cm (Gerritsfles, Plot W); 0, 40 and 100 cm (Gerritsfles, Plot Y); 7, 22, 70 and 110 cm (Hasselsven); 12, 35, 57 and 100 cm (Tongbersven). Atmospheric inputs of nitrogen and sulphur were estimated from throughfall samples collected fortnightly and analysed monthly in six (De Oude Maat) or two (other sites) replicated funnel collectors under forest, and from bulk deposition in the case of heathland and bare soil. For discussions on these estimates of atmospheric deposition under conditions in the Netherlands, see Van Breemen et al. (1988), Van Breemen and Verstraten (1990) and Van Dobben et al. (1992).

While samples of soil solutions and throughfall water were analysed for all major solutes, the measurements used include only pH, Al, NO_3, SO_4 and Cl in the soil solution, and inorganic nitrogen ($NH_4 + NO_3$) and SO_4 in throughfall.

In the soil solution, NO_3 and SO_4 were selected because these anions reflect the acidifying substances, Al and pH were chosen because they reflect the degree of soil acidification, while Cl was chosen to check for trends in an inert component. In throughfall, ammonium was considered in addition to NO_3 and SO_4 for its potential acidity, and its contribution to the atmospheric nitrogen load on the soil.

Soil temperature was measured monthly throughout the monitoring period at De Oude Maat, and for 1 year at the other sites. At De Oude Maat, moisture contents have been simulated for every depth separately using the SWATRE simulation model (Belmans et al., 1983). SWATRE calculates the changes in moisture content and hence water fluxes in depth and time for compartments of a soil profile of 10 cm thickness. Moisture contents have been calibrated on pressure-head values measured weekly for the first 3 years.

Statistical methods

The main question in the current analysis concerns the presence, size and significance of the time trend. Frequent missing observations, the presence of a trend, irregularity in sampling intervals and possible influence of external factors prohibited the use of standard software for spectral analysis or Box-Jenkins analysis. Typically, the concentration of any ion is subject to the influence of various external factors, including seasonal trends and long-term changes. Based upon these considerations, attention was focused on the regression approach for time series analysis (Kendall et al., 1983; Harvey, 1984; Chatfield, 1989), also called the two-step full transform method. Different explanatory variables are used in the statistical model, including time. More specifically, the following model was used:

$$\left.\begin{array}{l} \text{pH} \\ \text{Al} \\ \text{NO}_3 \\ \text{SO}_4 \\ \text{Cl} \end{array}\right\} = C + \text{time} + st_0 + st_1 + st_2 + st_3 + st_4 + \text{Moist} \qquad (1)$$

where pH is the pH of the soil solution, and Al, NO_3, SO_4 and Cl stand for the respective solute concentrations at each depth considered, C is a constant, time is expressed in months, st_0 represents the soil temperature at a depth of 10 cm at the time of measurement, st_1 the soil temperature at a depth of 10 cm 1 month before measurement, st_2 the temperature at a depth of 10 cm 2 months before measurement, etc. Moist is the moisture content at the time of measurement, simulated by the SWATRE model (see Study sites and soil solution section).

Although fluxes are quantitatively more significant in characterising (rates of) soil acidification, we have focused here on concentrations. The reasons for this are that fluxes show much greater temporal (seasonal) variation than concentrations, so the chance of detecting significant trends in fluxes is quite small, and in addition, soil solution concentrations are ecologically more relevant than fluxes.

By including soil temperature and moisture content, which vary seasonally and which strongly influence nitrification, the main soil acidifying process involved, the seasonality in soil acidification was at least partly accounted for. Because atmospherically derived ammonium is nitrified mainly in the surface soil, the temperature of the top soil at several different times during and before measurement, not the soil temperature at the depth and time of measurement, was incorporated in the model.

As soil temperatures were available for 12 months only for the sites Gerritsfles, Hasselsven and Tongbersven, predicted values based on a regression model which links these 12 month measurements with measurements at De Oude Maat ($R' = 0.70–0.83$, 10 d.f.) were used instead.

At Plot A (De Oude Maat) and at Gerritsfles, Hasselsven and Tongbersven, the moisture content was not determined, and hence not included in the model. This model was applied at all depths at which the soil solution composition was monitored.

Equation (1) may be abbreviated to

$$\underline{y} = X\beta + \underline{\epsilon} \qquad (2)$$

where y (underlined to indicate its stochasticity), contains the values of the concentrations, the matrix X contains the values of the explanatory variables at the different times, while the vector β contains the parameters for the explanatory variables. The vector $\underline{\epsilon}$ contains the error terms. The model, with-

out the factors st_x and Moist, was also used to estimate trends in throughfall and rainfall.

Because ordinary linear regression is likely to yield results which are overly optimistic, i.e. significance is reached too soon, the autocorrelation of the data is taken into account. It is assumed that the error term $\underline{\epsilon}$ can be described satisfactorily by an autoregressive process of order 2. This process was considered sufficient as it accounts for short time dependencies (i.e. 1 month) and periodical dependencies (i.e. 12 months) and was selected among several other processes. Hence, for the error term the following model was imposed

$$\epsilon_t = \underline{e}_t - \alpha_1 \epsilon_{t-1} - \alpha_{12} \epsilon_{t-12}$$

where e_t are independent normal error terms with zero mean and variance σ^2, ϵ_{t-1} and ϵ_{t-12} are the errors 1 month and 12 months, respectively, before t, and α_1 and α_{12} are the parameters which link those errors with the errors at time t. Based upon ordinary least squares estimation, the model parameters and the autoregressive terms are estimated, which in turn are used to re-estimate the parameters, using one iteration step. All analyses were carried out using the Autoreg procedure of the Statistical Analysis Systems Institute (SAS, 1985).

Results and discussion

Figure 1 shows the time series of Al concentrations in Plot B (De Oude Maat). This series was selected as it includes several interesting features; however, other time series would have served the same purpose. Decreasing concentrations for the depth of 10 cm, and increasing concentrations for the depths of 40, 60 and 90 cm are observed. Also, strong seasonality is observed, with high peaks in Al concentration in the autumn of each year, which are particularly clear at the larger depths.

The gaps in the graphs correspond with missing observations. Linear interpolation or substitution of the average value into these gaps would have provided unrealistic values. This was particularly the case because missing observations frequently occurred in blocks of several months in dry periods where no soil solution was available. Predictions by means of kriging or cokriging are considered to be more appropriate, using for instance atmospheric parameters like temperature and precipitation as covariables (Stein and Corsten, 1991). However, the procedure followed in this study is not hampered by missing observations.

The quality of the models is evaluated using the Yule–Walker estimate of the total percentage of explained variance (Table 2). In general, these values are not very large, and rarely exceed 0.8, while some are as low as 0.2. Also included are the degrees of freedom; in general these are sufficiently large to allow inference based on these models. However, care should be taken when attention is focused on the larger depths at Hasselsven and Tongbersven.
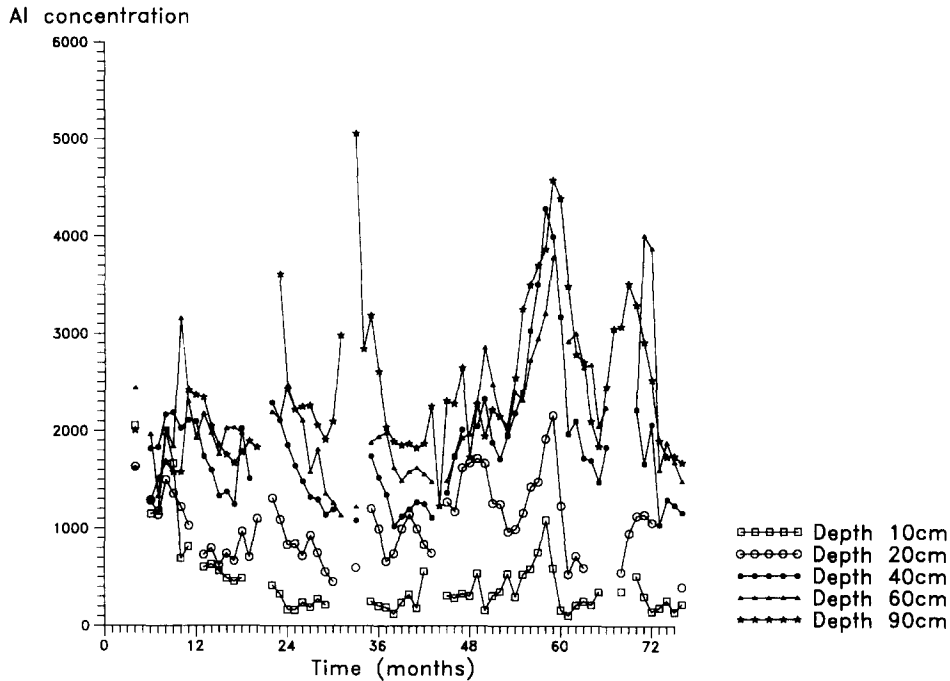
Al concentration

Fig. 1. Concentration of Al ions in Plot B (De Oude Maat) at several depths during 6 years.

First, temporal trends in the chemistry of the atmospheric input are discussed, i.e. throughfall water and bulk open field precipitation. R^2 values for throughfall data are particularly low (often lower than 0.1), despite the large number of degrees of freedom: the model poorly describes the data, which predominantly exhibited variation undeclared by the model. There is no significant pattern here except in the throughfall at Gerritsfles (Plot W), where concentrations of NH_4, Cl and SO_4 (as well as $NH_4 + NO_3$, not shown here) increase with time. The throughfall trends in Gerritsfles are difficult to explain and may be caused by local circumstances. The distance of this site from the sea is too great to yield an explanation of the Cl trend in terms of changing seasonal conditions, and in addition, no particular pattern in the rainfall which would have accounted for this trend was observed during the monitored years. This implies that, except for the Gerritsfles site, explanations for any trend in soil solution concentration should be sought in processes in the soil, rather than in changes in deposition.

Second, trends in Cl, a predominantly inert solute, are considered to test whether long-term changes in soil hydrology could explain any trends in NO_3, SO_4, Al and pH (Table 3). Over time, Cl concentrations tend to decrease, but only in four of 27 cases is the trend significant at the $\alpha = 0.1$ or 0.05 level. In the absence of trends in atmospheric input concentrations, decreasing Cl con-

Table 2
R^2 values in the seven plots for throughfall data (Thr) and measurements at several depths. The numbers of degrees of freedom are included in parentheses

Site/plot	Depth (cm)	pH	Al	NO$_3$	Cl	SO$_4$	NH$_4$
De Oude Maat							
Plot A	Thr	0.08(82)	–	0.04(82)	0.11(82)	0.10(82)	0.54(82)
	10	0.58(46)	0.50(42)	0.58(43)	0.53(42)	0.39(43)	
	20	0.37(34)	0.41(32)	0.56(34)	0.39(33)	0.40(34)	
	40	0.24(49)	0.64(44)	0.66(48)	0.21(47)	0.57(48)	
	60			0.86(34)	0.71(34)	0.54(35)	
	90			0.82(40)	0.68(39)	0.54(40)	
Plot B	Thr	0.02(81)	–	0.06(81)	0.07(81)	0.02(81)	0.01(81)
	10	0.46(37)	0.79(34)	0.74(36)	0.38(35)	0.21(36)	
	20	0.36(47)	0.65(45)	0.53(46)	0.56(45)	0.50(47)	
	40	0.38(39)	0.83(39)	0.70(39)	0.51(38)	0.38(39)	
	60	0.26(49)	0.64(45)	0.62(48)	0.47(47)	0.20(48)	
	90	0.17(53)	0.67(52)	0.72(52)	0.33(51)	0.61(52)	
Plot C	Thr	0.25(82)	–	0.02(82)	0.09(82)	0.04(82)	0.02(82)
	10	0.41(35)	0.12(34)	0.54(34)	0.64(33)	0.29(34)	
	20	0.34(48)	0.35(46)	0.55(47)	0.46(47)	0.38(47)	
	40	0.25(35)	0.58(35)	0.58(33)	0.35(34)	0.28(34)	
	60	0.18(40)	0.79(39)	0.72(39)	0.53(39)	0.53(39)	
	90	0.29(52)	0.52(52)	0.80(52)	0.32(52)	0.47(52)	
Gerritsfles							
Plot W	Thr	0.21(46)	–	0.20(46)	0.30(45)	0.09(46)	0.24(46)
	40	0.42(23)	0.75(23)	0.65(23)	0.50(22)	0.74(23)	
	100	0.27(21)	0.69(18)	0.60(21)	0.53(20)	0.89(21)	
Plot Y	0	0.45(23)	0.55(23)	0.24(24)	0.16(23)	0.21(24)	
	40	0.21(23)	0.38(21)	0.10(22)	0.54(21)	0.51(22)	
	100	0.22(22)	0.25(18)	0.60(19)	0.48(18)	0.49(19)	
Hasselsven							
	Thr	0.60(24)	–	0.02(24)	0.06(24)	0.04(24)	0.08(24)
	7	0.33(15)	0.33(12)	0.47(12)	0.43(11)	0.40(12)	
	22	0.78(17)	0.79(13)	0.43(14)	0.49(13)	0.60(14)	
	70	0.37(15)	0.44 (7)	0.47 (8)	0.28 (8)	0.26 (8)	
	110	0.54(13)	0.52 (4)	0.80 (4)	0.77 (4)	0.62 (4)	
Tongbersven							
	Thr	0.21(46)	–	0.05(46)	0.03(46)	0.12(46)	0.12(46)
	12	0.28(21)	0.20(16)	0.50(17)	0.35(17)	0.52(20)	
	35	0.44(21)	0.61(20)	0.82(21)	0.53(20)	0.31(22)	
	57	0.11(18)	0.62 (9)	0.85 (8)	0.62 (8)	0.51(13)	
	100	0.32 (8)	–	–	–	–	

centrations may be related to decreasing values of evapotranspiration minus precipitation in the growing season. Such a trend would also contribute to decreasing trends in the concentration of all other solutes. Indeed, sulphate concentrations also tend to decrease with time in most cases. The contrary, however, appears to be true for NO$_3$ and Al: these increase in 24 out of 27 cases (NO$_3$) and 20 out of 27 cases (Al), with highly significant values in

Table 3
Time trends (mmol m^3 year^{-1} or pH unit year^{-1}) for throughfall data (Thr) and measurements at various depths in the seven different plots

Site/plot	Depth (cm)	pH	Al	NO$_3$	Cl	SO$_4$	NH$_4$
De Oude Maat							
Plot A	Thr	0.040	–	12	3	–18	–36
	10	–0.032	–15	–15	–5	–36	
	20	–0.016	91	64	–12	–45	
	40	0.023	126	133	–22**	–83***	
	60			338**	–57*	–151***	
	90			–77	–35	–55*	
Plot B	Thr	0.076	–	10	16	–1	–23
	10	–0.028	–81**	36	11	–45	
	20	–0.015	19	78	–4	–4	
	40	0.023	158**	88	–21*	–43	
	60	0.031*	122*	–4	–14	–12	
	90	0.033*	251***	216**	–10	–36	
Plot C	Thr	0.070	–	6	1	–15	–21
	10	–0.070***	88	62	–14	–39	
	20	–0.043**	–13	51	0	23	
	40	–0.031	112**	30	–13	–13	
	60	–0.005	141***	91	13	–25	
	90	–0.005	147*	205*	–15	–108	
Gerritsfles							
Plot W	Thr	0.134	–	23	56***	67**	104***
	10	–	–	–	–	–	–
	40	–0.069***	994***	660***	38	160**	
	100	–0.009	–26	188**	–122	–210**	
Plot Y	0	–0.091***	–	3	–16	–2	45**
	40	0.014	–16	5	–18*	–9	
	100	0.016	–4	39**	1	24**	
Hasselsven							
	Thr	–0.034	–	2	18	–6	75
	7	0.066	24	24	43	–3	
	22	–0.086***	130***	92**	31	67	
	70	0.058*	53	68	–5	9	
	110	0.117**	23	6	16	99	
Tongbersven							
	Thr	0.011	–	–23	–40	–144	–110
	12	0.053*	–23	57	–50	–145	
	35	–0.025	124	162*	–32	37	
	57	0.010	135	242***	–16	67	
	100	0.080	–	–	–	–	

*$\alpha=0.1$; **$\alpha=0.05$; ***$\alpha=0.01$.

each of the plots. The fact that the explained variance is generally much higher in the case of Al and NO$_3$ (R^2 mostly above 0.5) than in the case of the other solutes lends further credence to the analysis. Given the relatively constant atmospheric input concentrations of NH$_4$ in most locations and the otherwise

decreasing trends in solute (Cl, SO_4) concentrations, the increases in the soil solution of nitrate and aluminium support the hypothesis that the studied ecosystems are losing their ability to retain atmospheric N and that they are experiencing increasing soil acidification. This is caused by the increasing formation of nitric acid as a result of the increased net mineralisation of organic N, followed by nitrification. At Gerritsfles (Plot W), the increasing soil acidification can probably be attributed in part to the increasing loads of atmospheric ammonium sulphate over the 4 year study period. Increasing soil acidification is further supported by decreasing pH values in most cases. As could be expected, the strongest pH decrease was observed in the surface soil of Plot C (De Oude Maat), a soil that showed a less advanced state of soil acidification at the beginning of the research than the other plots at this site.

As pointed out by Mulder et al. (1989), neutralisation of acidity by dissolution of Al tends to decrease in strongly acidified surface soils, where the pool of active Al has been depleted by strong soil acidification in the past decades. This may explain the small or even decreasing trends in dissolved Al at shallow depth in Plots A and B, where surface soils are strongly acid. The increasing level of dissolved Al at greater depth at De Oude Maat indicates that the zone of predominant acid neutralisation shifts to greater depth, as the acid neutralising capacity near the soil surface is depleted. In most of the other sites, increasing Al concentrations are observed only just below the surface soil, pointing to a less advanced stage of soil acidification. In agreement with the observations discussed above, pH tends to decrease in surface soils, and to stay more or less constant at greater depth. The strongest pH decrease is observed in the surface soils of Plots C (De Oude Maat), and Y (Gerritsfles). As evidenced by the current relatively high surface soil pH values (3.8–4.5), these soils can still undergo some drop in pH before pH buffering becomes very strong as a result of acid neutralisation by soil aluminium compounds at a pH of about 3.5. No explanation can be given for the significant pH increase in the subsoil of Plot B.

Conclusion

The time series analysis of solute concentrations in soil solutions and atmospheric input water as presented here provides evidence for increasing soil acidification caused by the formation of nitric acid in forest soils that have been acidified strongly by atmospheric deposition in the past decades. However, in view of the relatively short monitoring periods (4–6 years) available and the possibility of longer cycles in soil–vegetation processes in such forested ecosystems (Bormann and Likens, 1979), these conclusions should be viewed with caution. Similar analyses with longer time series are needed to further test the results presented here.

Acknowledgment

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