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Are Indicators for Critical Load Exceedance Related to Forest Condition?

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Abstract The aim of this study was to evaluate the suitability of the (Ca+Mg+K)/Al and the Ca/Al ratios in soil solution as chemical criteria for forest condition in critical load calculations for forest ecosystems. The tree species Norway spruce, Sitka spruce and beech were studied in an area with high deposition of sea salt and nitrogen in the south-western part of Jutland, Denmark. Throughfall and soil water were collected monthly and analysed for pH, NO_3-N, NH_4-N, K, Ca, Mg, DOC and Al_{tot}. Organic Al was estimated using DOC concentrations. Increment and defoliation were determined annually, and foliar element concentrations were determined every other year. The throughfall deposition was highest in the Sitka spruce stand (maximum of 40 kg N $ha^{-1}yr^{-1}$) and lowest in the beech stand (maximum of 11 kg N $ha^{-1}yr^{-1}$). The Sitka spruce stand leached on average 12 kg N $ha^{-1}yr^{-1}$ during the period 1988–1997 and leaching increased throughout the period. Only small amounts of N were leached from the Norway spruce stand whereas almost no N was leached from the beech stand. For all tree species, both (Ca+Mg+K)/Al and Ca/Al ratios decreased in soil solution at 90 cm depth between 1989 and 1999, which was mainly caused by a decrease in concentrations of base cations. The toxic inorganic Al species were by far the most abundant Al species at 90 cm depth. At the end of the measurement period, the (Ca+Mg+K)/Al ratio was approximately 1 for all species while the Ca/Al ratio was approximately 0.2. The lack of a trend in the increment rates, a decrease in defoliation as well as sufficient levels of Mg and Ca in foliage suggested an unchanged or even slightly improved health condition, despite the decreasing and very low (Ca+Mg+K)/Al and Ca/Al ratios. The suitability of these soil solution element ratios is questioned as the chemical criteria for soil acidification under field conditions in areas with elevated deposition rates of sea salts, in particular Mg.

Keywords Acidification · Base cations · (Ca+Mg+K)/Al ratio · Ca/Al ratio · Critical load · Defoliation · Forest vitality and health · N deposition · N leaching · N saturation · Tree species · Foliar concentrations

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1 Introduction

Atmospheric deposition of nitrogen (N) and sulphur (S) to terrestrial ecosystems leads to eutrophication and acidification. A concept called the critical load (CL) has been derived to identify the risk of such effects. The CL was defined at the Skokloster 1988 Critical Load Workshop as “the maximum input of acidic deposition to an ecosystem which will not cause long term damage to ecosystem structure and function” (Nilsson and Grennfelt 1988). A CL is thus a threshold value where no effect is observed on the system. If e.g. N and S deposition do not cause exceedance of this threshold, air pollution is assumed to have no detrimental effect on the ecosystem. Up to the point of CL (i.e. zero exceedance) there is no long-term negative effect on the ecosystem. If the threshold is exceeded, the ecosystem is harmed by the deposition of acidic substances (Skeffington 1999).

At increased acid loads, pH in soil declines. Base cations on the ion exchange complex can be exchanged with acidic cations and possibly lost by leaching. The soil is gradually depleted in base cations, mainly divalent cations like calcium (Ca^{2+}) and magnesium (Mg^{2+}). At low pH and high acidification, aluminium (Al) dissolves and tends to form toxic species. A larger fraction of exchange sites will become occupied by Al at the expense of sites occupied by Ca^{2+} and Mg^{2+}. Elevated Al concentration in the soil solution may damage fine roots and mycorrhizae and thus reduce nutrient and water uptake (Foy 1988; Ulrich 1983; Boudot et al. 1994). Aluminium toxicity is indicated by damage in the form of swollen and stubby roots, scarce root hairs, discoloration of root tips and no formation of lateral roots (Boudot et al. 1994; Göransson and Eldhuset 1991, 1995). Aluminium might also cause reduced root growth (Godbold and Hüttermann 1988; Godbold and Kettner 1991; Godbold et al. 1988). It seems to be mainly the monomeric inorganic Al species (Al_{inorg}, including Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^{+}$ and $Al(OH)_4^{-}$) which prevent root growth and inhibit Ca^{2+} and Mg^{2+} uptake (Kinraide 1991; Boudot et al. 1994; Wauer et al. 2004). Aluminium bound in fluoride or organic complexes are supposed to be non-toxic and less harmful (Arp and Strucel 1989; Asp and Berggren 1990; Boudot et al. 1994; Gjessing 1989; Bi et al. 2001).

Increased N deposition may cause eutrophication of the soil as well as elevated nitrate leaching losses from the ecosystem, a condition often referred to as N saturation (Aber et al. 1998, 1989; Gundersen 1991). The overall result may be nutrient deficiencies and severe forest growth reduction. Increased nitrate leaching is associated with soil acidification causing gradually decreasing concentrations of base cations in soil solutions followed by increased Al levels.

The CL is being calculated for European forest ecosystems, and is now widely used throughout Europe when policies are developed to mitigate emissions of air pollution. Hence, CLs have become a part of the work programme of the United Nations Economic Commission for Europe (UN-ECE), Convention on Long-Range Transboundary Air Pollution (CLRTAP).

The soil solution molar ratio between the base cations (Ca+Mg+K) and Al has been suggested as a chemical criterion for forest condition in CL calculations for forest ecosystems (Sverdrup and Warfwinge 1993). The simpler molar ratio between Ca and Al has also been suggested (Cronan and Grigal 1995; Ulrich 1981). In the literature, it is assumed that both ratios have the same critical value of 1, above which the trees (the biological indicators) will remain undamaged. Ulrich (1983) first suggested the threshold value of 1. This value is based on a large amount of experiments, mostly laboratory studies (Ulrich and Matzner 1983; Roelofs et al. 1985; Sverdrup and Warfwinge 1993; Sverdrup and de Vries 1994; Cronan and Grigal 1995). The species of Al used in both ratios has however not been consistent between studies. Today, the (Ca+Mg+K)/Al ratio is the most widely used criterion for estimating CL. Exceedance of the CL for forest soils is expected to show up as a deteriorated health condition for the biological indicator (e.g. decreased increment, high defoliation, yellowing of needles).

The connection between soil acidity (as indicated by the threshold value 1 for the (Ca+Mg+K)/Al or Ca/Al ratios) on the one hand and tree vitality and stand condition on the other hand has proven difficult to observe in the field for mature forest ecosystems (Derome et al. 2001; de Wit et al. 2001a, b). Although it is generally accepted, and has been shown in experiments on seedlings, that Al is toxic to plants, it is obviously difficult to set a limit for Al concentrations in soil solution in natural mature forest. The current use of the (Ca+Mg+K)/Al and Ca/Al ratios as predictive tools for estimating forest damage has been criticised, questioned and discussed by several authors (Högberg and Jensén 1994; Løkke et al. 1996; Göransson and Eldhuset 2001; Derome et al. 2001; de Wit et al. 2001a, b).

This study aims to evaluate the suitability of the threshold value for exceedance of CL in sea salt influenced forest stands and to explore the connection between the biological damage response and (Ca+Mg+K)/Al and Ca/Al ratios as indicators of CL in some Danish forest stands. The stands were part of a long-term experiment on nutrient-poor soil in the south-western part of Denmark where the deposition of N and base cations is high, and where Al concentrations in seepage water are high. We hypothesize (1) that these forest stands experience soil acidification as indicated by the (Ca+Mg+K)/Al and Ca/Al ratios as well as by nitrate leaching and (2) if so, an effect on forest condition and foliar nutrient concentrations can be detected.

2 Materials and Methods

2.1 Site Description

The experimental site Lindet is situated in Lovrup Forest in the south-western part of Jutland, Denmark (55° 08′N, 8°53′E). At the Lindet site, biogeochemistry has been studied in stands of several tree species (planted 1964/1965; Holmsgaard and Bang 1977) as a part of the UN-ECE ICP Forests level II monitoring. This study deals with the stands of Norway spruce (*Picea abies* (L.) Karst.), Sitka spruce (*Picea sitchensis* (Bong.) Carr.) and beech (*Fagus sylvatica* L.). Each stand had an area of approximately 0.25 ha, and the three stands were situated right next to each other so that border and edge effects were negligible. Stand characteristics are given in Table 1. There was no understorey vegetation present in any of the stands. The Lindet site has been operated since 1988.

The site was formerly an oak thicket. The soil is a sandy Typic Arenosol, with a moderately low capacity to store plant available water. The soil was tilled down to 20 cm depth prior to planting. The three stands were situated on a gently sloping homogeneous till deposit from the Saale glaciation, overlaid by sand drifts. Soil data is presented in Table 2. Soil particle size distributions were very similar among the three stands. The clay content ranged from 1.6 to 7.3%, while the sand content ranged from 86.5 to 97.8%. The cation exchange capacity was low (CEC_e=0.5–1.1 cmol+ kg^{-1} at 50–75 cm depth and 2.6–5.2 cmol+ kg^{-1} in the upper 6 cm). In general, the base saturation (BS_e) was below 21% in the mineral soil horizon A_2 or below, while in the upper A_1 horizon (0–6 cm) BS_e was between 26–61%. In the organic horizon, BS_e was as high as 69–88%, lowest for Sitka spruce and highest for beech. The amount of exchangeable Ca^{2+} and K^+ was highest under Norway spruce and beech and lowest under Sitka spruce. These differences were not related to differences in biomass production since planting, but to differences in particle size distribution, although differences were small on this otherwise homogeneous site. The pH in the soil profiles under all tree species varied from 3.7 in the upper 5 cm to 4.8 at the bottom of the C horizon. The C/N ratio varied between 19 and 28. More information on soil characteristics can be found in Petersen (1993). Fine roots were found down to a depth of 60 cm.

The forest is surrounded by intensive agriculture and a large pig farm is located just 1 km southeast of the stands, which exposes this area to high N deposition. For further details about the Lindet site and the experiment see Hansen (2003).

Table 1 Stand characteristics for Norway spruce, Sitka spruce and beech at Lindet in the year 1998 after thinning (age: 36 years)

	Stems ha^{-1}	Height (m)	Diameter (cm)	Standing volume (m^3 ha^{-1})	Basal area (m^2 ha^{-1})
Norway spruce	892	15.3	18.8	395	27.9
Sitka spruce	842	16.9	20.6	368	28.0
Beech	1,005	12.8	14.9	229	15.5

Table 2 Soil characteristics for Norway spruce, Sitka spruce and beech at Lindet, all measured 1991 except C/N ratio which was measured 1996

	Horizon	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	pH (H_2O)	C/N (ratio)	CEC_e ($cmol_+ kg^{-1}$)	BS_e (%)
Norway spruce	O	3.0–0	–	–	–	4.0	26.3	19.7	80
	A_1	0–5	4.8	6.0	89.2	3.7	22.9	2.6	29
	A_2	5–12	5.8	4.5	89.7	3.9	28.3	2.4	13
	B_1	12–25	6.2	5.6	88.2	4.3	–	1.5	10
	B_2	25–50	6.1	5.2	88.7	4.4	–	1.2	12
	B_3	50–60	5.0	4.8	90.2	4.4	–	1.1	13
	C	60–75	2.8	1.5	95.7	4.7	–	0.5	16
	2C	75–125	1.6	0.6	97.8	4.7	–	0.3	13
Sitka spruce	O	2.9–0	–	–	–	3.8	21.1	9.8	69
	A_1	0–6	5.4	6.9	87.7	3.8	23.8	2.9	26
	A_2	6–14	5.0	6.5	88.5	3.9	–	2.2	14
	B_1	14–30	7.3	5.0	87.7	4.5	–	1.6	12
	B_2	30–45	7.2	6.1	86.7	4.4	–	1.2	18
	B_3	45–60	5.0	5.8	89.1	4.5	–	0.9	21
	C	60–72	3.2	5.2	91.6	4.6	–	0.6	17
	2C	72–125	6.3	3.9	89.8	4.8	–	0.8	17
Beech	O	2.9–0	–	–	–	4.3	24.0	31.4	88
	A_1	0–6	5.1	7.7	87.2	4.0	19.2	5.2	61
	A_2	6–11	5.9	6.7	87.4	4.0	25.7	2.4	14
	B_1	11–30	6.9	6.6	86.5	4.4	–	1.7	9
	B_2	30–49	6.9	6.6	86.5	4.4	–	1.1	16
	B_3	49–58	4.0	4.5	91.5	4.5	–	0.8	14
	C	58–88	3.6	5.2	91.2	4.6	–	0.6	14
	2C	88–125	4.7	3.9	91.4	4.8	–	1.1	11

2.2 Field Sampling

Throughfall was sampled by 12 funnels connected to polyethylene flasks in the Norway spruce and beech stands. The samples were collected every fortnight. In the Sitka spruce stand, 10 throughfall funnels were installed and sampled once a month. The number of funnels varied due to different sampling designs over the years. The throughfall samplers were placed at equivalent distances along a 20 m long transect through the forest. All funnels were placed 1 m above the ground in order to avoid soil splashing, and inside each funnel a filter (mesh size 45 μm) was installed in order to diminish the amount of particles in the samples. The water was led by black polyethylene tubing to bottles installed in soil pits to protect the samples from heat and light and prevent N transformations. Throughfall was sampled during 1989–1997 in the Norway spruce stand, 1990–1997 in the Sitka spruce stand, and 1992–1997 in the beech stand.

Soil water was sampled in all stands using 10 suction cup lysimeters installed in and below the root zone at 40 and 90 cm depths, respectively. The suction cup lysimeters installed in 1988 were of the ceramic type (P80). A new set of lysimeters made of teflon (PTFE, Prenart Super Quartz) were operated from 1994/1995 and the two sets ran parallel up to 1997. No difference was observed between the two sets of samplers. After 1997, soil water was only sampled with teflon lysimeters. Monthly samples were collected during the years 1989–1999. The lysimeters were also installed along the above described transect through the forest. A constant tension of 0.6 bar was applied to the lysimeters. As for throughfall, all sample bottles were kept in soil pits.

During the winter of 1997/1998, stem disks were removed at breast height (1.3 m) from 15 felled trees for each tree species and used to estimate the annual ring width. Of these 15 sample trees, five were small trees, five were medium-sized trees and five were large trees. A microscope-attached digital readout system magnified specimen images of annual ring boundaries down to 0.01 mm. Two radial lines were registered and averaged.

Foliage was sampled for element analysis in 1993, 1995, 1997 and 1999. In 1993, only the coniferous tree species were sampled. All sampling was performed from the same 10 trees every sampling year by climbing the trees. Current year needles from the 5th whorl were sampled from the coniferous tree species in October–November. Foliage samples from beech were taken in July from the upper 3rd part of the canopy. All leaves and needles were kept and transported in brown paper bags.

Defoliation was assessed visually on 24 sample trees for each tree species. The assessments were performed each year in July or August according to the ICP Forests manual (UN-ECE 1998).

2.3 Chemical Analysis

In the laboratory, soil water, throughfall and bulk precipitation samples were stored at +4°C and analysed within 1 month from sampling. However, conductivity and pH were measured within 48 hours after the samples were received at the laboratory. Chemical analyses on water samples were performed using ion chromatography (NO_3–N), Flow Injection Analysis (NH_4–N), ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy for cations, Perkin Elmer Optima 3000XL (Al_{tot}, K, Ca and Mg)), and total combustion using a Shimadzu TOC-V (total organic carbon (TOC)).

Samples of foliage were dried at 55°C for 2 days and subsequently ground into powder. Carbon and nitrogen were analysed directly in the powder by the Dumas method on a LECO (CN 2000). Before cation analyses, the ground samples were digested in concentrated HNO_3 under pressure (200 PSI) in teflon bombs in a microwave oven (CEM MDS-2000). Thereafter, the element contents of the samples were analysed using ICP.

2.4 Hydrological Modelling

Soil water fluxes for the three tree species were derived from a simple water balance equation:

$$P = ET + D + \Delta S + R$$

where P is precipitation, ET is the actual evapotranspiration, D is percolation from the root zone, ΔS is the change in soil water content and R is the runoff. All components are expressed in mm water per day. At Lindet, R is assumed to be minimal. The actual evapotranspiration was calculated from daily potential evapotranspiration using the Makkink method (Makkink 1957) and corrected for loss of transpiration and for evaporation from trees, understorey vegetation and soil. The daily throughfall data was estimated based on daily precipitation measured outside the forest and the interception by the canopy. These data corresponded well with the throughfall data at Lindet.

Input data was supplied from meteorological towers situated in open areas just outside the forest (1 km distance). These included daily precipitation (mm), solar radiation ($W\ m^{-2}$), air temperature (°C) and relative air humidity (%). Initial model parameters like tree species, depth of the rooting zone, field capacity and wilting point of the soil were defined using measured values from the stands.

The model simulated the changes in soil water content in the root zone and was thereafter calibrated using measurements of soil water content (TDR, Time Domain Reflectrometry). Daily percolation from the soil reservoir was calculated as the amount of water exceeding the field capacity of the soil. Finally, the daily values were summed up to a monthly water balance in order to calculate the monthly soil water fluxes. Annual nitrate leaching fluxes were subsequently calculated by multiplying monthly measured nitrate concentrations in solution below the root zone with the corresponding soil water fluxes for a full year.

2.5 Calculations and Statistics

Only the total concentration of Al (Al_{tot}) was measured; however, the organic Al complexes (Al_{org}) were estimated using equations from studies by Nilsson and Bergkvist (1983) and Oulehle and Hruska (2005). Nilsson and Bergkvist (1983) found a linear correlation between the concentration of organic Al species and the concentration of dissolved organic carbon (DOC) in a mixed coniferous forest at Lake Gårdsjön Experimental Area in Sweden. For the soil (0–55 cm) the equation was $Al_{org}=1.12$ DOC [$mg\ l^{-1}$]+6.19 ($R^2=0.59$). The second equation was reported by Oulehle and Hruska (2005) for beech and Norway spruce stands in the Czech Republic. They found a strong relationship between $\mathrm{Al}_{\mathrm{org}}$ and DOC concentrations for all horizons and in both beech and Norway spruce stands ($\mathrm{Al}_{\mathrm{org}}$=10.907 logDOC [mol l^{-1}]+45.198; R^2=0.73) (Oulehle, personal communication). DOC concentrations at 90 cm depth were used in our estimation of $\mathrm{Al}_{\mathrm{org}}$ concentrations for the Lindet stands.

The tree species experiment is not replicated within the site, which precluded conventional testing of tree species effects. In order to discuss developments in indicator values over time, we focused on analyses of trends in these indicator values within each tree species. The trends in studied parameters over the monitoring period were explored by simple linear regression. All statistical tests of regressions were carried out using the procedure GLM in SAS (SAS Institute Inc. 2000). The accepted level of significance was $P<0.05$.

The number of months used for calculation of annual mean (Ca+K+Mg)/Al and Ca/Al ratios and SEM values varied somewhat according to the availability of water for collection in the suction cup lysimeters during the actual months. The number of monthly values for calculation of annual mean ratios was never lower than 7 and usually above 10.

3 Results and Discussion

3.1 Throughfall Deposition

Sea salt is a natural source of deposition in Danish forests since the sea surrounds Denmark. Sea salt spray therefore contributes a dominant portion of sodium (Na) and chloride (Cl^-) as well as important amounts of Mg, K, Ca and sulphate (SO_4^{2-}) of which

Table 3 Throughfall amount (mm) and fluxes in throughfall (kg ha^{-1} yr^{-1}, except for H^+ in g ha^{-1} yr^{-1}) of the main ions in the three tree species at Lindet during the period 1989–1997 in Norway spruce, 1990–1997 in Sitka spruce and 1992–1997 in beech

Tree species	Year	mm	Cl^-	SO_4^-–S	NO_3^-–N	NH_4^+–N	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+
Norway spruce	1989	325	158	30	9	19	82	25	13	13	98
	1990	586	220	35	10	21	109	28	13	17	65
	1991	442	100	20	7	14	52	16	8	8	78
	1992	489	95	17	8	13	50	17	6	7	74
	1993	625	123	22	8	16	63	20	7	9	69
	1994	619	141	23	9	14	74	18	8	11	148
	1995	438	120	17	7	14	67	13	7	9	48
	1996	345	101	21	9	17	67	18	7	8	22
	1997	404	125	17	8	17	68	14	7	9	8
Average	1992–1997	487	118	20	8	15	65	17	7	9	62
Sitka spruce	1990	636	225	33	11	21	122	26	12	16	107
	1991	480	163	30	12	22	92	20	11	11	115
	1992	501	141	27	11	22	79	21	9	9	98
	1993	646	173	30	10	18	93	31	10	12	70
	1994	558	251	38	13	24	132	22	13	16	112
	1995	415	190	25	15	21	100	20	9	11	50
	1996	339	163	34	14	26	78	23	11	12	35
	1997	456	206	27	14	27	99	23	12	13	26
Average	1992–1997	486	187	30	13	23	97	23	11	12	65
Beech	1992	539	53	10	5	6	27	15	4	4	98
	1993	634	68	13	6	6	33	17	4	4	63
	1994	691	65	12	4	6	33	13	5	4	93
	1995	597	56	8	5	5	27	14	4	4	88
	1996	426	50	8	4	5	21	12	4	4	158
	1997	536	46	7	4	6	28	13	10	5	39
Average	1992–1997	571	56	10	5	6	28	14	5	4	90

the latter four are essential plant nutrients. The throughfall fluxes of Na and Cl$^-$ were high at Lindet due to the closeness to the North Sea (15 km) and the prevailing westerly winds (Table 3). On average, the throughfall flux of Cl$^-$ to Sitka spruce was 187 kg ha^{-1} yr^{-1} and the Na flux was 97 kg ha^{-1} yr^{-1}. A smaller leaf area and roughness length as well as a smaller height (Table 1) of the other tree species caused the throughfall fluxes to be smaller.

The throughfall fluxes of nutrients like K, Ca and Mg were also highest for Sitka spruce compared to the other tree species (Table 3). However, the difference between tree species for K was less pronounced than for Na. This is probably because K is mainly supplied to the forest floor by canopy processes such as canopy leaching or exchange, as opposed to Na, which is mainly supplied from outside the stand by dry deposition. For Sitka spruce the throughfall fluxes of K, Ca and Mg were 23, 11 and 12 kg ha^{-1} yr^{-1}, respectively, averaged over the measurement period from 1992–1997.

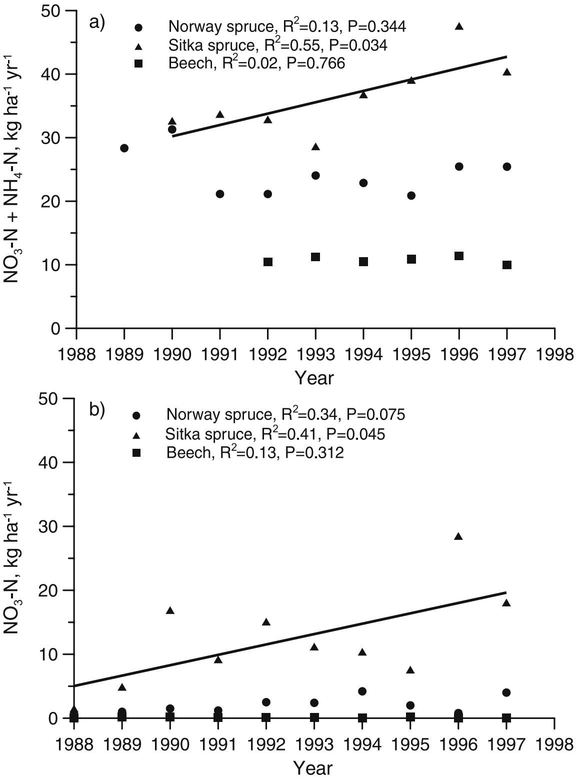

Fig. 1 **a** The annual throughfall deposition of total inorganic N (NO$_3$–N+NH$_4^+$–N) (kg N ha^{-1} yr^{-1}) and **b** estimated annual leaching of nitrate (NO$_3$–N) (kg N ha^{-1} yr^{-1}) in Norway spruce, Sitka spruce and beech stands, at Lindet during the period 1989–1997. The leaching of ammonium was negligible. Linear regression R^2 and P values are shown for each tree species

The throughfall deposition of N was highest in the Sitka spruce stand followed by Norway spruce and beech (Fig. 1a). For the Sitka spruce stand, the throughfall deposition of total inorganic N (NO$_3$–N+NH$_4^+$–N) increased significantly from the start of the measurements. The throughfall deposition under Sitka spruce was three to four times higher than under beech. The average throughfall N deposition under Sitka spruce was 35 kg ha^{-1} yr^{-1}. The lowest throughfall N deposition under Sitka spruce was observed in 1993 (28 kg ha^{-1} yr^{-1}). The total throughfall N deposition increased from 32 kg ha^{-1} yr^{-1} in 1990 to 40 kg ha^{-1} yr^{-1} in 1997 (Fig. 1a).

For the Norway spruce and beech stands, the total throughfall N deposition showed no apparent trend from 1991 to 1997 (Fig. 1a). The average throughfall N deposition under Norway spruce was 25 kg ha^{-1} yr^{-1}, varying from a minimum of 21 to a maximum of 31 kg ha^{-1} yr^{-1}. Under beech the average throughfall N deposition was 10–11 kg ha^{-1} yr^{-1}. Large differences in the throughfall deposition under different tree species have also been observed in other studies and attributed to differences in surface roughness and the ability of the trees to filter gases and particles from the atmosphere (Draaijers 1993; Nordén 1994; Robertson et al. 2000).

3.2 Nitrate Leaching

An average leaching of 12 kg N ha^{-1} yr^{-1} from the Sitka spruce stand (Fig. 1b) was estimated for the sampling period. This is one third to one half of the input of N to the forest ecosystem. Since the forest cannot retain all N, the deposition of N is thought to influence the ecosystem negatively by acidification.

In the very beginning of the sampling period in 1988, almost no leaching of nitrate was apparent from any of the three stands. However, leaching of nitrate increased significantly under Sitka spruce during the sampling period (Fig. 1b). The demand for N varies through a rotation. The N demand of young forests is believed to be greatest during canopy build-up and thereafter decreases considerably when canopy closure is reached (Miller and Miller 1988; Richter et al. 2000). Hence, in the first approximately 20 years, in which all the N-rich parts of the tree are established, the demand for N is high and often higher than the supply by atmospheric N deposition. During this period most stands can retain all N and no leaching of N is observed. After canopy closure the demand for N decreases and N deposition will often exceed the demand of the trees. This increases the risk of nitrate leaching (Gundersen et al 2003). When the measurements at Lindet started, the stands were 19 years old and the canopies were beginning to close. The demand for N decreased thereafter and the Sitka spruce stand could no longer retain the large N deposition (Fig. 1b). At the same time the filtering capacity of the forest increased as the trees grew taller, which increased the deposition and contributed to increased leaching with age. Increased nitrate leaching with age has earlier been observed for a Sitka spruce stand in Wales (Emmett et al. 1993) and in a chronosequence study of forests planted on former arable land in Denmark (Hansen et al. 2007).

The CL for N eutrophication has been calculated for forests in Denmark (Bak et al. 1999). The calculation is based on (1) the mean N assimilation that is removed over a rotation in managed forest, (2) a low long term soil N sink (0.5–1 kg/ha/yr) and (3) a low acceptable (and unavoidable) leaching. CL for N was determined as 8–15 kg N ha^{-1} yr^{-1} for spruce forest and 17–28 kg N ha^{-1} yr^{-1} for beech forest. This means that the CL for N deposition at Lindet is greatly exceeded for the coniferous tree species whereas it is not exceeded for the beech stand. One of the criteria for exceedance of the CL for N is increased nitrate leaching (Skeffington 1999). Nitrogen saturation and nitrate leaching will therefore be expected in the coniferous stands at Lindet. Only the Sitka spruce stand had so far become N saturated, as indicated by leaching of nitrate. The Norway spruce stand still immobilised N and did not leach significant amounts of nitrate (Fig. 1b), although throughfall deposition was 20–30 kg N ha^{-1} yr^{-1} and therefore well above the calculated CL for N. The fact that nitrate leaching has not been observed (yet) from the Norway spruce stand is not necessarily an indication that the estimated CL for N is adequate. Possibly, nitrate leaching will occur eventually when deposition of N continues to be high. For beech, the CL for N was higher (17–28 kg N ha^{-1} yr^{-1}) than for the coniferous tree species and the N deposition in beech never reached these amounts. It is unknown whether beech will tolerate these high N deposition levels without eventually reaching N saturation and experiencing nitrate leaching. According to Kristensen et al. (2004) a majority of deciduous forests in Europe have reached N saturation at well below these levels of N deposition.

3.3 Soil Solution Base Cations, Al and the Ca/Al Ratio

Concentrations of Ca in the soil solution under Sitka spruce decreased over the sampling years at both 40 and 90 cm depth; however, the decrease was only significant ($P<0.001$; $R^2=0.79$) at 90 cm (Fig. 2a, b). The concentration decreased from 150 µmol l^{-1} in 1989 to 55 µmol l^{-1} in 1999. In contrast to these high Ca concentrations, the concentrations under Norway spruce and beech were much lower (approximately 40 µmol l^{-1}) and showed no trend through the measurement period. In studies of soil acidification in Sweden, Finland, Norway and the Czech Republic, concentrations of Ca in mineral soil solution were generally lower and ranged from 11 to 45 µmol l^{-1} at

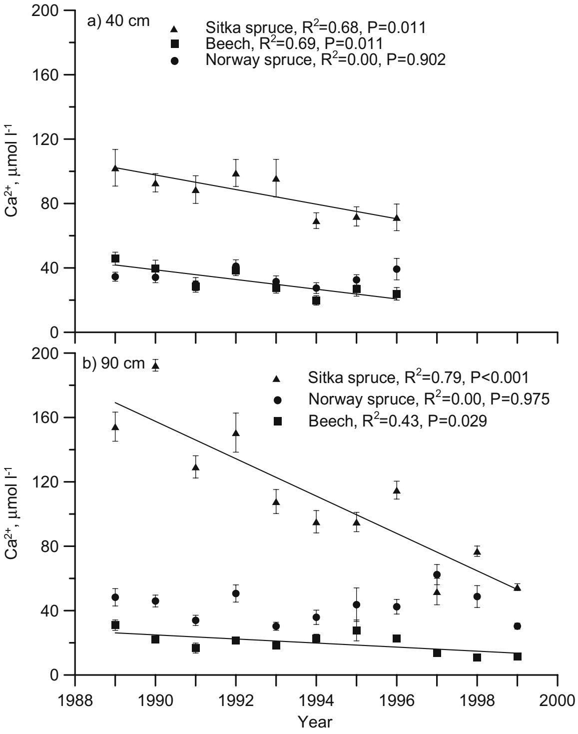

Fig. 2 The total Ca^{2+} concentration (µmol l^{-1})±the standard error of the mean (SEM) in soil solution for Norway spruce, Sitka spruce and beech stands at Lindet, measured at **a** 40 cm depth and **b** 90 cm depth during the years 1989–1999. Linear regression R^2 and P values are shown for each tree species

40–90 cm depth (Derome et al. 2001; Nilsson and Bergkvist 1983; Oulehle and Hruska 2005; Nygaard and de Wit 2004).

The average concentrations of Mg in the soil solution were 70, 177 and 244 µmol l^{-1} under beech, Norway spruce and Sitka spruce, respectively (data not shown). For K, the values were 49 µmol l^{-1} for beech and 70 µmol l^{-1} for both Norway and Sitka spruce. Compared to the Mg and K concentrations in the studies mentioned above (12–90 µmol l^{-1} for Mg and 5–49 µmol l^{-1} for K), the high input of sea salt to Lindet is evident. As for Ca, the concentrations of K and Mg decreased at 90 cm depth for both beech (K: $P<0.001$, $R^2=0.76$; Mg: $P=0.011$, $R^2=0.53$) and Sitka spruce (K: $P=0.014$, $R^2=0.51$; Mg: $P=0.046$, $R^2=0.37$) while the K and Mg concentrations in soil solution under Norway spruce did not change over time ($P>0.39$). At 40 cm depth, K concentrations decreased significantly during the measurement period for all three tree species, most strongly for beech ($P=0.009$, $R^2=0.70$) and less strongly for Sitka spruce ($P=0.015$, $R^2=0.66$) and Norway spruce ($P=0.030$, $R^2=0.57$). Magnesium concentrations at 40 cm decreased significantly only for beech ($P=0.034$, $R^2=0.56$), while there were no significant trends for Norway and Sitka spruce ($P>0.25$). This could be attributed to the higher sea salt deposition to the coniferous stands as discussed above. Magnesium concentrations in soil solutions under Norway and Sitka spruce were clearly higher than under beech throughout the measurement period.

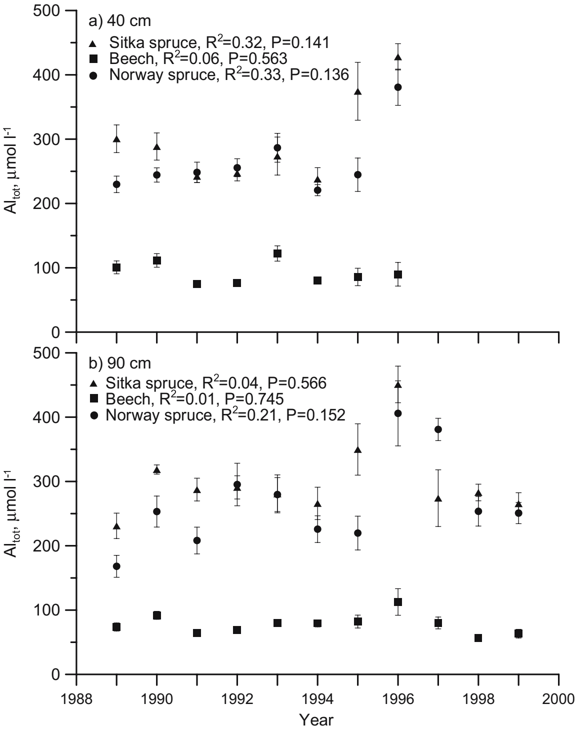

Fig. 3 The concentration of Al_{tot} (µmol l^{-1})±the standard error of the mean (SEM) in soil solution for Norway spruce, Sitka spruce and beech stands at Lindet, measured at **a** 40 cm depth and **b** 90 cm depth during the years 1989–1999. Linear regression R^2 and P values are shown for each tree species

The Al_{tot} concentrations in the soil solution were much higher for the Norway and Sitka spruce stands (200–400 µmol l^{-1}) compared to the beech stand (75–100 µmol l^{-1}) at both 40 and 90 cm depth (Fig. 3a,b). There was no apparent trend over time. In comparison, Oulehle and Hruska (2005) found concentrations of Al_{tot} in mineral soil solutions (90 cm depth) of 135 and 57 µmol l^{-1} under Norway spruce and beech, respectively, while Nilsson and Bergkvist (1983) observed a maximum of 116 µmol l^{-1} in Sweden. In Finland, the average concentration of Al_{tot} at 40 cm depth in six Norway spruce stands was below 57 µmol l^{-1}; however, a very high concentration (1,400 µmol l^{-1}) was observed in one stand (Derome et al. 2001). Pannatier et al. (2005) found concentrations of 33–48 µmol Al_{tot} l^{-1} at 50 cm depth in a Swiss chestnut stand. Even lower concentrations of Al_{tot} (2 µmol l^{-1}; 50 cm depth) were observed in a Norway spruce stand at Nordmoen (Nygaard and de Wit 2004). Al_{tot} concentrations in our stands seem rather high compared to these literature values. However, higher concentrations have also been observed, e.g. for three acidic oak–birch woodland soils in the Netherlands where the Al_{tot} concentrations ranged from 810–2,330 µmol l^{-1} at 40 cm depth and from 80–1,860 µmol l^{-1} at 90 cm depth (Mulder et al. 1987).

Based on experiments with the response of tree seedlings to Al, Schaedle et al. (1989) divided forest trees into three classes according to their sensitivity to soluble Al. In their definition, sensitive species such as Norway spruce exhibit sensitivity for Al concentrations ≤150 µmol l^{-1}. These species recover only slowly once Al stress has ceased. Beech belongs to the intermediately sensitive species (concentrations of Al ranging from 150 to 800 µmol l^{-1}) that recover rapidly once Al stress has decreased. The last class contains the tolerant species (concentrations of Al ≥800 µmol l^{-1}) to which Sitka spruce belongs. At

Lindet we did not observe these high Al concentrations in soil solutions. On the other hand, it can be argued that you cannot look at Al concentrations in isolation since the effects of other nutrients are ignored. For example, Hecht-Buchholz et al. (1987) found that a number of species are more tolerant to Al in Ca- and Mg-rich solutions. Roots of Norway spruce did not show injury in cation-rich solutions (concentrations of Al: 1,700 μmol l^{-1}; Ca: 1,300 μmol l^{-1}; Mg: 300 μmol l^{-1}) but were strongly damaged when Ca and Mg concentrations were low (concentrations of Al: 1,700 μmol l^{-1}; Ca: 130 μmol l^{-1}; Mg: 30 μmol l^{-1}). The concentrations of Ca in the Ca-rich solutions were however much higher than those in our stands.

Only inorganic species of Al (Al_{inorg}), and then mainly polycationic Al (Al_{pc}, charge>2), are considered rhizotoxic (Kinraide 1991), and organic nontoxic complexes of Al are widespread in acid soils like at Lindet. In this study, we only measured total soluble Al (Al_{tot}), and the proportion of toxic Al_{inorg} to Al_{tot} is unknown. The Al_{org} has been found to follow the distribution of DOC (e.g. Bi et al. 2001) and was estimated using the relationships between Al_{org} and DOC found by Nilsson and Bergkvist (1983) and Oulehle and Hruska (2005). Estimated Al_{org} was found to correlate well for the two methods; however, the method of Nilsson and Bergkvist (1983) estimated a higher proportion of Al_{org} (in general 30% more) than the method of Oulehle and Hruska (2005). There is no way of telling which method is most appropriate for our soil, but Bi et al. (2001) modelled the distribution of Al species in acid soil solutions (pH 3–4 as at Lindet) and found Al_{org} to be less than 10%. Therefore, it appears reasonable to use the average of the two methods (Fig. 4). A maximum of 15% of Al_{tot} was estimated to be Al_{org} in the Norway and Sitka spruce stands; however, Al_{org} was on average 5–6% of Al_{tot} for both species. For beech, the proportion of Al_{org} to Al_{tot} was much higher, on average 18%. The concentrations of the toxic Al_{inorg} in the mineral soil were consistently 82–95% of Al_{tot}. Bi et al. (2001) similarly found that almost 90% of Al_{tot} was free Al^{3+}.

The Ca/Al_{tot} molar ratio decreased significantly over the years for Sitka spruce and beech at 90 cm depth, while the ratio did not decrease significantly with time at 40 cm depth (Fig. 5a,b). In 1996–1999, the ratio converged towards a value of 0.2. The $(Ca+Mg+K)/Al_{tot}$ ratio decreased significantly for all three species at 90 cm depth, and at 40 cm depth this ratio also decreased significantly for beech (Fig. 6a,b). In 1996–1999, this ratio converged towards a value of 1.0. The decline in ratios was mainly caused by decreasing concentrations of base cations over time. Since concentrations of DOC were only available for a 3-year period, it was impossible to calculate the ratios with the inorganic Al only for the whole period.

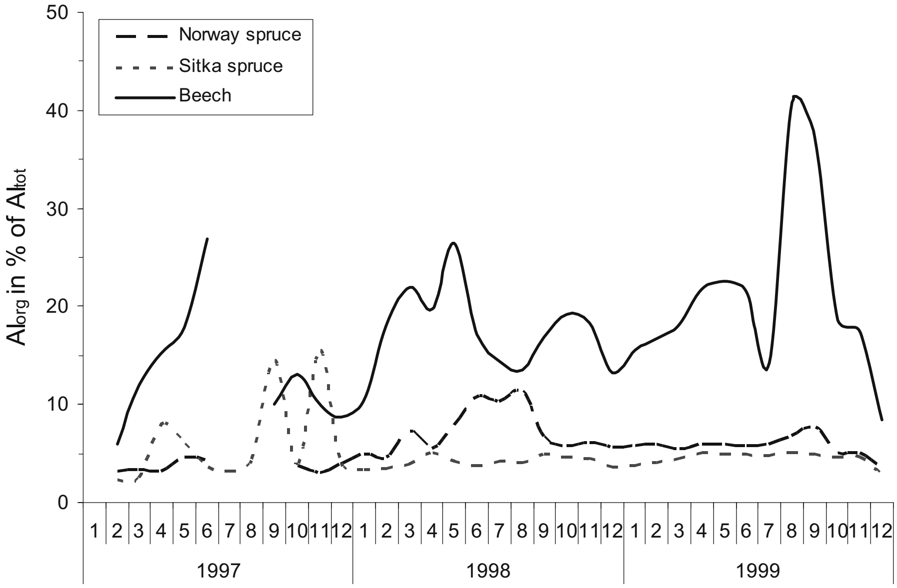

Fig. 4 Al_{org} in percent of Al_{tot} estimated for Norway spruce, Sitka spruce and beech stands at Lindet as an average of estimates obtained from two methods given by Nilsson and Bergkvist (1983) and Oulehle and Hruska (2005). DOC at 90 cm depth was used in the calculations

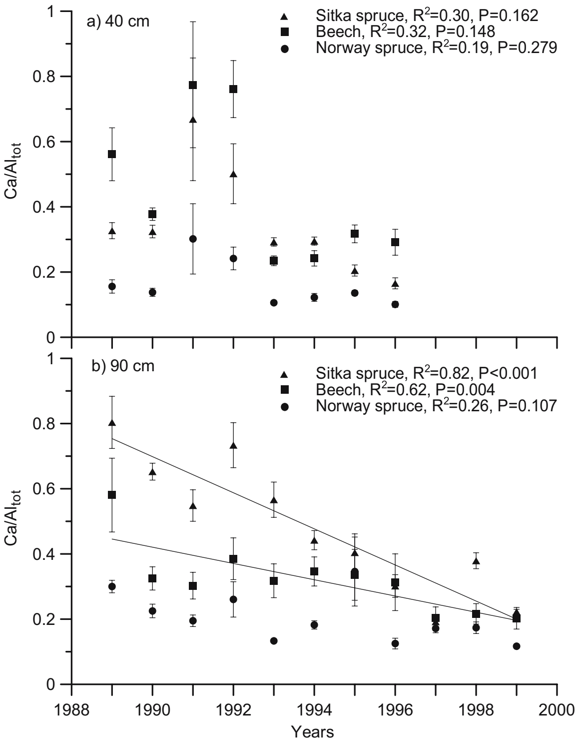

Fig. 5 The Ca/Al$_{tot}$ (molar) ratio±the standard error of the mean (SEM) in soil water from **a** 40 cm and **b** 90 cm depth for Norway spruce, Sitka spruce and beech stands at Lindet in the period 1989–1999. Linear regression R^2 and P values are shown for each tree species

Therefore, Al$_{tot}$ was used while recognizing that approximately 95% of Al$_{tot}$ is Al$_{inorg}$ in the Norway and Sitka spruce stands and 82% is Al$_{inorg}$ in the beech stand. However, in a similar acidic soil (pH 3–4.4) under 40–60 year-old Norway spruce, Baur and Feger (1992) found that the DOC concentration was highest below the litter layer and decreased sharply with depth. At 30 cm depth, Al$_{org}$ was approx. 50% of Al$_{tot}$. Accounting for such a change with depth, Al$_{inorg}$ would be reduced and the Ca/Al$_{inorg}$ ratio higher, e.g. for Norway spruce at Lindet in 1995 this would mean a Ca/Al$_{inorg}$ ratio of 0.28 at 40 cm depth instead of the Ca/Al$_{tot}$ ratio of 0.1 (Fig. 5a): this ratio is still far below 1.

The Ca/Al$_{tot}$ ratio was highest for Sitka spruce followed by beech and Norway spruce, whereas the (Ca+Mg+K)/Al$_{tot}$ ratio was highest for beech, lowest for Norway spruce, and intermediate for Sitka spruce. This difference in the two ratios between species was mainly caused by the high Ca concentrations in the soil solution under Sitka spruce. At the beginning of the measurement period, both ratios were up to 1.5–2.5 times higher under Sitka spruce than under Norway spruce, especially at 90 cm depth, but the difference between the species decreased over the years as the ratios converged from 1989 to 1999. Since there are no replications of tree species in the experiment, we are unable to attribute the differences to tree species alone. The natural variation in the soil properties between the different plots might play a role too. In 1999, the (Ca+Mg+K)/Al ratio at 90 cm depth was 0.9 for the coniferous species and 1.3 for beech (Fig. 6b). In the same year, the Ca/Al ratio was 0.1–0.2, lowest for Norway spruce (Fig. 5b). The ratios, therefore, showed very different values; one was approaching the threshold value of 1 rapidly while the other was far below the threshold value. This difference can be attributed to the vicinity of the North Sea and the large input of base cations (mainly Mg and K) with sea salt. Aherne et al. (2001) argue that the (Ca+Mg+K)/Al ratio is sensitive to atmospheric deposition of marine salts and use of this chemical

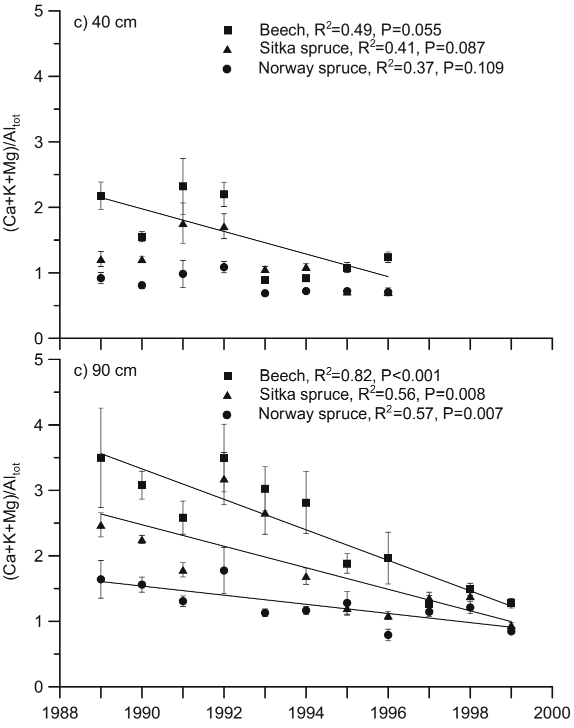

Fig. 6 The (Ca+Mg+K)/Al$_{tot}$ (molar) ratio±the standard error of the mean (SEM) in soil water from **a** 40 cm depth and **b** 90 cm depth for Norway spruce, Sitka spruce and beech stands at Lindet in the period 1989–1999. Linear regression R^2 and P values are shown for each tree species

criterion will provide a picture of high acid neutralising capacity (ANC) and consequently high CL, suggesting that marine depositions offer protection against acidification. Cronan and Grigal (1995) estimated that Ca/Al ratios below 1 would indicate a risk for damage to shoots and roots greater than 50%, and that at Ca/Al below 0.1 the risk would be 95%. According to this, all stands at Lindet had a high risk of damage. Such low Ca/Al$_{tot}$ ratios have been observed in other field studies as well (e.g. Derome et al. 2001) without any damage to forest condition. Several studies now question the use of the Ca/Al$_{tot}$ ratio and the critical value of 1 (Mulder et al. 1989; Högberg and Jensén 1994; Løkke et al. 1996), and point to the use of the Ca/Al$_{inorg}$ ratio, since there are large differences between Al$_{tot}$ and Al$_{inorg}$ in for example podzolic and more organic soils in Finland (Derome et al. 2001). However, the use of the (Ca+Mg+K)/Al$_{inorg}$ ratio may be more justified, since it will include the beneficial effect of important elements such as Mg, especially in areas with high marine deposition. Sverdrup and de Vries (1994) reviewed experimental data where the (Ca+Mg+K)/Al ratios ranged from 0.01 to 100. Evidently, the variation in (Ca+Mg+K)/Al ratios is large. It can be discussed whether these concentration ratios are good expressions for assessing Al toxicity. Boudot et al. (1994) argue against them and instead propose to calculate an Al toxicity index based on ionic activities of all base cations as well as all toxic Al species. This method requires the determination of Al species.

3.4 Tree Condition

There was a general tendency towards a decrease in annual increment for all tree species; however the decrease was not significant for any of them (Fig. 7). After 1993, there was no time trend for increment. From 1988 to 1993 there was a tendency to an increase in defoliation of Norway spruce and beech (Fig. 8), but later on (1993–1999) the defoliation of these two species decreased significantly. There was no clear trend in the defoliation of Sitka spruce throughout the shorter monitoring period from 1994 to 1999.

The foliar chemistry of the three species was measured two to four times (Table 4). The foliar Mg concentration in Norway spruce was higher in the two last years than in the first two. Such an increase was not apparent for Sitka spruce or beech. For Ca, there was no trend over the years in the foliar concentration of Norway spruce needles; however, the concentration of Ca in Sitka spruce needles decreased. Conversely, Al in needles of Sitka spruce and Norway spruce increased during 1995–1999, while the foliar Al concentration in beech showed no trend over the years.

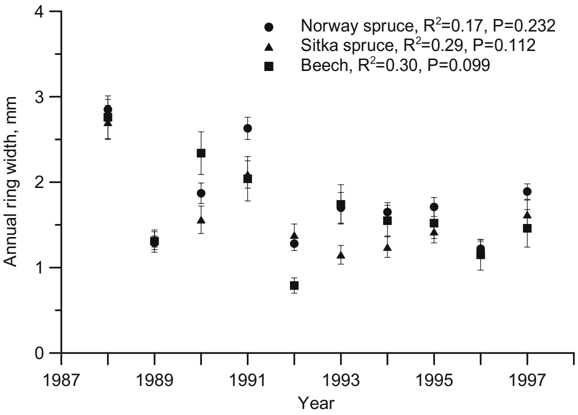

Fig. 7 The average annual increment (mm)±the standard error of the mean for Norway spruce, Sitka spruce and beech at Lindet during the period 1988–1997

Calcium and Mg concentrations in foliage from Norway spruce were both above the optimum values according to Brække (1994) who found these to be above 0.7 and 0.8 mg g^{-1} for Ca and Mg, respectively. In Sitka spruce and beech, optima for Ca were estimated to be above approximately 1.0 and 3.0 mg g^{-1}, which indicated that both species are well supplied with Ca. Optimal values for Mg are estimated to be above approximately 1.0 and 1.5 mg g^{-1} in Sitka spruce and beech, respectively (Van den Burg 1985, 1990). Another large European study by Stefan et al. (1997) suggested normal values for Mg to be 0.6–1.5 mg g^{-1} in spruce and 1.0–1.5 mg g^{-1} in beech, within which ranges the foliage at Lindet is found. It is therefore difficult to conclude whether Sitka spruce and beech trees at Lindet are well supplied with Mg or not.

Cronan and Grigal (1995) suggested that the Ca/Al ratio in foliage could be used as an indicator of Al stress, where a ratio of less than 12.5 would indicate Al stress. Our data show Ca/Al ratios of 14–49 in current year needles, indicating that our stands are not currently subject to Al stress. However, foliar Ca/Al

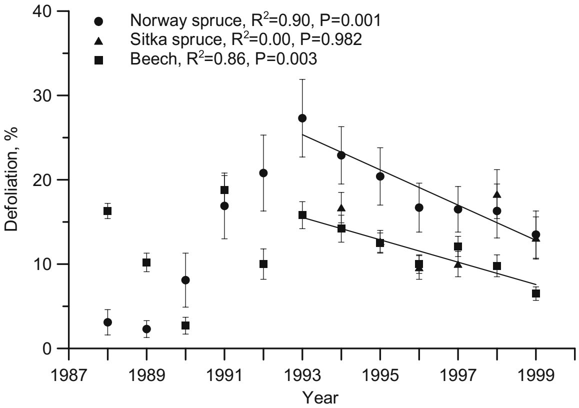

Fig. 8 The average defoliation (%)±the standard error of the mean (SEM) in Norway spruce, Sitka spruce and beech at Lindet during the years 1988–1999 estimated by visual assessment of 24 sample trees for each tree species. Linear regression R^2 and P values for the period 1993–1999 are shown for each tree species

ratios are decreasing and may soon approach the suggested threshold value of 12.5 in Norway spruce and Sitka spruce.

Although the Ca/Al$_{tot}$ and (Ca+Mg+K)/Al$_{tot}$ ratios in soil solution decreased (Figs. 5 and 6) and the concentrations of Al$_{tot}$ in the soil solution were high (Fig. 3a,b), a stable increment and even less defoliation during the later years suggest an improved health condition for all tree species. For Sitka spruce, however, the increasing and high N leaching is indicative of an N saturated ecosystem.

In this study, we found no apparent connection between the low and decreasing Ca/Al$_{tot}$ and (Ca+Mg+K)/Al$_{tot}$ ratios and the health condition of the stands. On one hand, it can be argued that the ratio ≥1 is set from a no-effect perspective (Sverdrup and Warfwinge 1993), and that the threshold value 1 for CL indicates more than adequate protection from soil acidification at Lindet. On the other hand, the Ca/Al ratio is far below 1, and there is no observed connection between the ratios and forest condition for mature forests. Other authors also failed in detecting a relationship between the Ca/Al ratio or the (Ca+Mg+K)/Al ratio and forest decline parameters (Derome et al. 2001; de Wit et al. 2001a, b; Strand 1997; Örlander et al. 1994). The threshold value of 1 and even the ratio itself have been criticised for being unsuitable for assessing the adverse effects of acidification (Högberg and Jensén 1994; Løkke et al. 1996).

It seems obvious that the ratios used in the calculations of CL ought to differ for different tree species since they have different root systems and filter different amounts of deposition. In particular, spruce is known to have a superficial rooting system, and at Lindet, the nutrient supplies (N, Ca, Mg and K) to the stands are intermediate. The low ratios deeper in the soil are primarily due to the high Al concentrations,

Table 4 Average foliar concentrations (mg g^{-1} for Ca and Mg and µg g^{-1} for Al$_{tot}$) in Norway spruce, Sitka spruce and beech at Lindet during the four measurement years 1993, 1995, 1997 and 1999

Concentrations	Year	Norway spruce	Sitka spruce	Beech
Ca	1993	3.85 (0.32)	4.11 (0.42)	–
	1995	3.27 (0.37)	3.04 (0.27)	4.25 (0.22)
	1997	3.70 (0.46)	2.70 (0.29)	4.55 (0.26)
	1999	3.46 (0.29)	2.81 (0.33)	4.64 (0.50)
Mg	1993	1.11 (0.09)	0.80 (0.08)	–
	1995	0.98 (0.05)	0.78 (0.03)	1.38 (0.08)
	1997	1.51 (0.08)	0.98 (0.06)	1.41 (0.09)
	1999	1.53 (0.09)	0.87 (0.06)	1.33 (0.15)
Al$_{tot}$	1993	–	–	–
	1995	128.30 (13.70)	47.30 (4.38)	–
	1997	147.30 (14.98)	123.50 (34.02)	27.80 (2.10)
	1999	168.44 (9.02)	128.19 (7.75)	65.61 (5.95)
Ca/Al$_{tot}$	1993	–	–	–
	1995	21.23 (5.33)	48.77 (7.75)	–
	1997	18.87 (3.38)	18.24 (2.39)	115.54 (10.19)
	1999	14.27 (1.49)	15.41 (2.15)	48.93 (3.83)

The standard error of the mean (SEM) is presented within brackets. For Norway and Sitka spruce current year needles (C0) are presented.

and not to deficiency of Ca, Mg and K. As shown earlier, the deposition of base cations was high since the forest was located close to the North Sea. These nutrients entered the soil in high annual amounts. This available nutrient supply to the top soil (0–20 cm) and the upper part of the root system is one possible explanation why tree species tolerate extremely high Al stress and low (Ca+Mg+K)/Al ratios in the deeper soil horizons and yet survive in good condition. Also, low molar (Ca+Mg+K)/Al ratios seem to be a natural phenomenon in podzolic soils (Derome et al. 2001; de Wit et al. 2001a, b; Strand 1997) and do not appear to pose a danger to the health condition of the studied forest stands. However, the Ca/Al ratio might still be a suitable criterion in CL in K and Mg poor areas such as Sollingen, Germany, where the ratio was first suggested by Ulrich (1981).

Another explanation might be that the trees avoid uptake of Al from the soil solution. Although soil solution Al concentrations were considerably increased, it was observed by de Wit et al. (2001b) that there was no change in Al concentration in the needles of Norway spruce. de Wit et al. (2001b) concluded that the trees might have effective mechanisms to keep Al from entering the roots or xylem vessels. In our experiment, however, we definitely saw signs of increased Al concentrations in the foliage of all tree species and a Ca/Al ratio that is approaching the proposed critical value of 12.5 suggested by Cronan and Grigal (1995).

4 Conclusions

The coniferous tree species in the acid soils at Lindet had a throughfall deposition above the calculated CL for N in Denmark. High N leaching from the Sitka spruce stand suggested that the system is N saturated. Although Norway spruce received N deposition above the CL for N, the stand was not yet N saturated, as there was only limited leaching of nitrate. However, N leaching might be expected to occur in the future. Beech stands had higher (Ca+Mg+K)/Al_{tot} ratios than Sitka and Norway spruce stands in 1989, but the ratios gradually converged towards 1 for all three species by 1999.

The very low and decreasing Ca/Al_{tot} and (Ca+Mg+K)/Al_{tot} ratios observed in this study contrasted with the indication of improved or unchanged health conditions. This questions the applicability of these ratios as chemical criteria for exceedance of acidic deposition. A response to the constantly low and decreasing (Ca+Mg+K)/Al_{tot} ratio would have been expected in the tree health status. However, the closeness to the sea and the large input of base cations to the topsoil might help the stands to endure the nutrient-poor conditions in the deeper soil layers. Low molar (Ca+Mg+K)/Al_{tot} ratios seem to be a natural phenomenon in some soils and do not appear to pose a danger to the health condition of the studied stands.

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