Environ Monit Assess (2009) 159:111–124
DOI 10.1007/s10661-008-0616-8

Vertical gradients of mineral elements in *Pinus sylvestris* crown in alkalised soil

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Received: 5 May 2008 / Accepted: 10 October 2008 / Published online: 8 November 2008

Abstract Alkalisation of soil has been assumed to be the principal cause of changes in vertical gradients of nutrients in *Pinus sylvestris* crown. The long-term influence of alkaline dust pollution (pH_{H_2O} 12.3–12.6) emitted from a cement plant on the element composition of soil and needles of Scots pine in different canopy layers was studied. In the polluted area, the pH of soils was >7, and high amounts of Ca, K and Mg were measured in the upper layers of soil (0–30 cm), while the mobility and solubility of some contaminants have decreased, nutrition processes have become complicated, and imbalance of mineral composition of trees was revealed. Reduced N and increased K, Ca and Mg concentrations in needles were observed in the heavily polluted area. Vertical gradients of elements and their ratios in canopies varied depending on the alkalisation level of soil. Needles on the upper-crown shoots had higher concentrations of N, C, Ca and Mg and lower concentrations of P and K compared to the lower layer of the crown. In the unpolluted area, higher concentrations of N, P, K and Ca were found in lower-crown needles and of C and Mg in needles at the top of the canopy. The P/N ratio below 0.125 indicated P deficiency in pines. The ratios N/Ca, N/Mg and N/K had significantly decreased, while the ratios Ca/Mg, K/Mg and K/Ca had a tendency to increase in heavily polluted sample plots. Magnitude of changes of element ratios indicates on the disbalances of availability and translocation of nutrients in the crown of trees.

Keywords Alkalisation · Cement dust · *Pinus sylvestris* · Vertical gradient · Nutrient · Partitioning · Crown

Introduction

Emissions of all air pollutants fell substantially during the period 1990–2004 in the European Environment Agency (EEA) member countries, where particulate matter emissions were reduced by 45% resulting in improved environmental quality over the region. However, this is not the case in industrial areas where pollution loads with alkaline solid particles have been critical over a long time. Although there are numerous comprehensive reviews of changes in forest ecosystems under stress induced by acidic types of air pollutants (Davis and Stokes 1986; Kaupenjohann 1989; Kim et al. 2004), research into the impact of alkaline

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types of air pollution on forests has never drawn so much attention.

Largest areas of airborne alkalisation are related to the production of cement and building materials, open-cast mining, metallurgical engineering and chemical industry. Yet problems of forest damages caused by alkaline dusts or fly ashes are not completely understood and interpreted. Many authors have found deviations in plant metabolism and physiology (Lal and Ambasht 1982; Klõšeiko 2003) and in growth and bioproduction (Jäger 1980; Ots 2002) caused by alkaline dust deposition. In conifers, an increase in the lignin content in needles but a decrease in the level of soluble sugars in stems and roots were found (Mandre et al. 1999; Mandre 2002). Degradation of chlorophylls was estimated by Kangur (1988). and a decrease in glucose and fructose in conifer needles was indicated by Klõšeiko (2003).

It is known that balanced metabolism, in which an optimum supply of nutrients is of prime importance, is indispensable to preserve functional and structural integrity of a plant organism. Pollutant stress may affect the whole-plant nutrient budget in case of both acidic and alkaline air pollutants. Although the sensitivity of plants to alkaline particulates is very different and its impacts described in the literature are contradictory, it is unanimously stated that deposition of alkaline dust or ashes on the underlying surface results in alkalisation of soil and input of excess nutrients into the ecosystem (Farmer 1993; Kaasik and Sõukand 2000; Świercz 2006), which complicates mineral nutrition processes of plants (Lal and Ambasht 1982; Marschner 2002). In any case, the response of tree species to alkaline dust depends on several species-specific peculiarities, pollution load and its chemical characteristics, climatic conditions etc. (Farmer 1993; Mandre et al. 1999; Pärn 2002). Many acidophilous plant species that are very sensitive to soil alkalisation have disappeared from forest ground vegetation communities or have been replaced by species common in calcium-rich soils (Kannukene 1995; Nilson 1995).

In Estonia, the area surrounding the cement plant in Kunda, Lääne-Viru County is an exceptional region suffering alkalisation. Over 40 years, thousands of tonnes of alkaline dust were emitted annually into the atmosphere there, causing alkalisation of the landscape. Cement dust contains large amounts of mineral elements, which have entered the environment and may provoke important deviations in the functioning of forest ecosystems due to nutrient recycling peculiarities.

The overall aim of the present study was to clarify the status of the forest soil and *Pinus sylvestris* in the area affected by cement dust 12 years after the dust emission stopped. Analysis of the chemical composition of soil and chemical characteristics of assimilative organs of trees will serve as a foundation for understanding the durability of alkaline soil reaction and for forecasting the time needed for the neutralisation of soil pH. No doubt, studies of mineral nutrition and mineral elements accumulation in plants can help to solve these problems.

Although nutrient uptake and translocation mechanisms in conifers have not been explored extensively, the limited evidence suggests that partitioning of nutrients among various tree compartments is of importance in the formation of crown architecture and in the acclimation of trees to environmental stresses (Rook 1991; Schaedle 1991). As tree crowns are characterised by gradients of light, temperature and water supply between the crown top and bottom (Pearcy and Sims 1994; Niinemets et al. 2007), foliar photosynthetic capacity (Grassi and Bagnaresi 2001; Han et al. 2003; Marcelis and Heuvelink 2007), carbohydrate concentration (Mandre et al. 1998) and anatomical characteristics (Richardson et al. 2001), our emphasis was on detailed comparison of the allocation of mineral elements dominating in cement dust in Scots pine crown and their concentration in soil at different distances from the emission source. Nutrient partitioning in trees can be influenced by a variety of internal and external factors, and the question whether a particular organ is adequately supplied with assimilates and can therefore fully realise its growth potential may not have a simple answer. Despite intense research in this area, there is still little information about nutrient partitioning in conifer canopies in natural forest conditions. However, assessing the nutritional state of trees and nutrient partitioning in them in alkaline growth conditions might be a way for understanding stress tolerance and survival of trees in damaged areas (Shalhevet 1993; Nilsen and Orcutt 1996). Integrated evaluation of the system soil–tree can show the state of an individual tree or a forest site. The findings will help to understand the dynamics in the forest ecosystem, prognosticate possible trends and forestall the development of contingencies in the alkalised territory of the cement industry.

Materials and methods

Study area

Investigations were carried out on a territory affected for over 40 years by a cement plant in the town of Kunda (59°30′ N, 26°32′ E), north-east Estonia. Considering the direction of prevailing winds (SW, S) and the spreading of pollutants, the sample plots were located on a transect parallel to the north Estonian coastline in an area rich in Scots pine stands. The sample plots were situated at distances of 2.5 and 5 km E and 3 km W from the emission centre.

The selected sample plots had been influenced by the highest loads of cement dust before 1996 when the plant was renovated and effective filters were installed. For comparison, a control sample plot was selected in similar climatic and edaphic conditions on a relatively unpolluted area in Lahemaa National Park (59°31′ N, 26°00′ E) at a distance of about 38 km W from the cement plant, opposite to prevailing winds. This area is considered to be relatively free of pollution on the basis of analyses of precipitation, bioindications by mosses and lichens as well as studies on biochemical indicators of air pollution (Kannukene 1995; Nilson 1995; Mandre and Tuulmets 1997; Roots et al. 1997).

Climatically, the areas investigated belong to the mixed-forest subregion of the Atlantic-continental region, where the influence of the Baltic Sea is strongly felt. In this area, the dominant tree species are pine, spruce, birch and aspen, and their total volume are, respectively, 37.5%, 17.9%, 25.4% and 6.6% (Yearbook Forest 2007 2008). The soils are Gleyic Podzols (Lkg) on sand.

In the selection of sample plots, we proceeded from the principle of analogy of geographical and silvicultural characteristics. The selected 75- to 80(85)-year-old pine stands with sparse understorey (0.05 ha) were similar as to their crop density (0.7–0.8), quality class (II) and site type (*Myrtillus-Oxalis*). This made comparison of the results possible as the effect of numerous external (climatic, phytocoenotic, etc.) and internal (metabolism, age, etc.) factors affecting the physiological state of trees in addition to pollution could be eliminated.

Soil analysis

The nutrient status of the soil was determined in the Laboratory of Plant Biochemistry of the Estonian University of Life Sciences. Soil samples were collected with a steel bore cylinder from depths of 0–30 cm, taking into account that approximately 80% of the feeder roots of *P. sylvestris* are located in the layer of 10–30 cm (Lõhmus and Lasn 1990). Samples were collected in five replications from all sample plots in 2004–2007. Standard methods of ISO Standards (ISO/10390 1994; ISO/11260 1995; ISO/11261 1995) were used for K, Ca, Mg, N, P and pH determination. For showing temporal dynamics of the soil pH in the sample plots, previously published results were used in addition to recently obtained data (Mandre et al. 1986, 1999; Mandre 2002). Organic matter (OM) in the soil was determined after incineration at 360°C (Schulte 1995).

Plant material and chemical analysis

The investigation was performed on a 70- to 80(85)-year-old mixed stand of *Myrtillus-Oxalis* site type in the vicinity of a cement plant and in a control area. In September 2005, three dominant trees of *P. sylvestris* with a similar habitus of the crown were selected in each sample plot for analysis so that they would represent evenly the diameter classes (25–27 cm at breast height) of the stand in the sample plots and the average trees within each sample plot. Altogether, 12 model trees were felled, and the crown of each tree was divided into three equal horizontal layers (Fig. 1). Samples were collected from each tree and, taking into consideration individual variation of trees, samples of current year needles were taken from

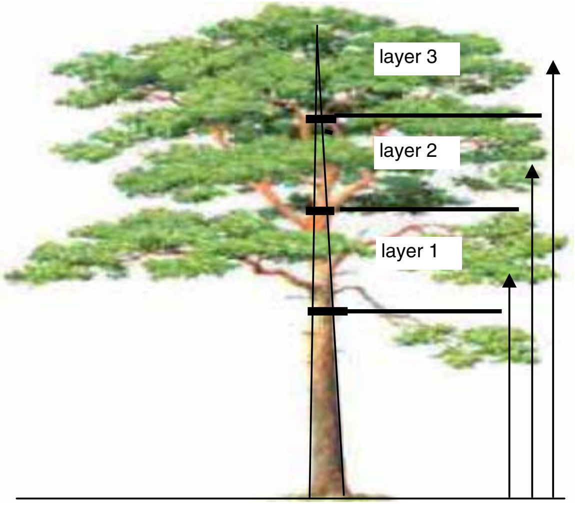


Fig. 1 Sampling of the material for analyses of Scots pine needles

all sides of the crown to get an average sample for analysis.

Carefully cleaned needles were oven-dried at 70°C to stop metabolic activity (Landis 1985) and ground. After grinding, 1–2 g of dried plant material was analysed for macronutrients (N, P, K, Ca and Mg). Concentrations of metals (Ca, K and Mg) were determined using an atom-adsorption analyser AAA-1N (Karl Zeiss, Jena). Nitrogen was measured by the method of Kjeldahl, and P was extracted with vanadium molybdate yellow complex. Analyses of nutrients were carried out in the Laboratory of Plant Biochemistry of the Estonian University of Life Sciences.

Statistical tests

Averages and standard deviations of results were calculated. All statistical effects were considered significant at $p < 0.05$. Linear regression analysis and determination coefficient (R^2) were used to estimate the statistical significance of the dependence between mineral elements in trees and between mineral elements and the pH of soil from different sample plots. Analysis of variance was used to test for the general differences between mean mineral element concentrations in soil and parameters of trees from different sample plots (t test). Statistical calculations were performed with Systat 10 (SPSS, USA) and Excel (Microsoft, USA).

Results and discussion

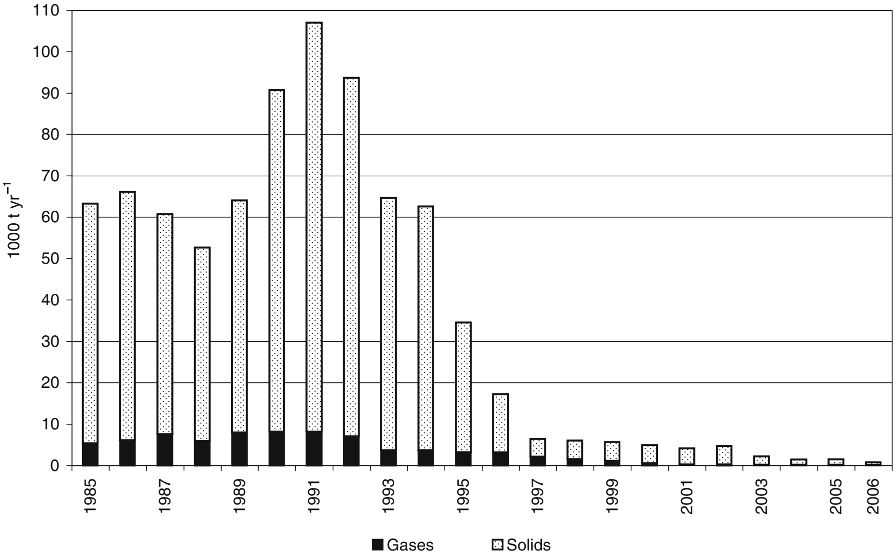
Peculiarities of the growth conditions

The production of cement in Kunda started in 1871. After the last reconstruction in 1960, cement production has rapidly increased and fluctuated between 0.5 and 1.2 million tons per year. Of the total air pollutants emitted from the plant, dust constituted 85–91% and was the main damaging factor for the ecosystems surrounding the emission source. It contained many components, among which the following were predominant: 40–50% CaO; 12–17% SiO_2; 6–9% K_2O; 4–8%SO_3; 3–5% Al_2O_3; 2–4% MgO; but also, Fe, Mn, Zn, Cu, B, etc. occurred. The water solution of dust from electric filters had pH values from 12.3 to 12.7 (Mandre 1995, 2000).

The dust emission from the cement plant was extremely high in 1990–1992 being 80–100 kt per year (Keskkond'90 1991; Estonian Environment 1991 1991; Estonian Environment 1995 1996) (Fig. 2). In 1991 and 1992, anomalies in natural forest stands were registered at a distance of 1.0–2.5 km from the plant under the influence of yearly emissions of 2.3–2.7 kg m^{-2} and at a distance of 3–5 km from the plant where the dust deposition was rather modest: 300–1,000 g m^{-2} per year (Mandre et al. 1995). The pH of rain was between 7.5–7.7 in areas 0.5–5 km from the emission centre (Tuulmets 1995). The alkaline character of industrial pollution is still obvious despite the decrease in pollution loads. Still, the alkalinity of snow melt has considerably decreased in Kunda: the recent pH in 1999 was 8–10 versus 10–12 during 1884/1985 (Tuulmets 1995; Kaasik and Sõukand 2000). In the control area, the average ambient particles deposition was 7–60 g m^{-2} per year, and the pH of rain registered for 1991 and 1992 was 6.8 and of snow melt 7.0 (Mandre et al. 1995; Tuulmets 1995).

The emission of cement dust from the plant decreased notably after 1996 thanks to the installation of effective electric filters. At present, it is lower than the permitted quantity (543 t per year;

Fig. 2 Emissions of dust and gaseous pollutants into the atmosphere from the cement plant in Kunda, north-east Estonia, 1985–2006



Environmental Review 2007). However, the influences of the high level of dust pollution for over 40 years and its consequences can be established today.

The impact of cement dust upon soil was more evident in areas to about 5 km from the plant than farther away. Analyses of soil chemical composition and comparison of results from unpolluted and polluted areas indicated serious differences caused by dust deposition (Table 1). Although the dust emission from the plant has practically stopped, the concentrations of Ca, Mg and K are

Table 1 Chemical composition of soil upper layer (0–30 cm in depth) in *Myrtillus-Oxalis* site type of Scots pine stand located at different distances from the cement plant

Study area	Year	N		P		K		Ca		Mg		OM	
		%	±SD	mg kg^{-1}	±SD	mg kg^{-1}	±SD	mg kg^{-1}	±SD	mg kg^{-1}	±SD	%	±SD
38 km W	2004	0.78	0.02	82.8	2.4	254	8.6	650	66.1	101.6	8.3	21.4	1.2
	2005	0.83	0.06	71.5	7.1	239	12.3	380	38.2	100.2	8.6	31.9	1.0
	2006	0.92	0.02	67.7	6.9	294	11.2	450	54.1	153.5	5.8	34.8	1.1
	2007	0.93	0.01	73.2	4.6	262	12.3	672	43.2	141.2	8.9	34.1	1.2
	Average	0.87		73.8		262		538		124.1		30.5	
3 km W	2004	0.47	0.02	94.2	4.8	486	32.1	7559	102.1	341.7	16.4	27.9	0.7
	2005	0.52	0.03	67.5	7.8	600	44.1	6993	114.2	321.9	23.4	20.4	0.6
	2006	0.33	0.04	95.3	4.2	459	26.6	6999	163.2	396	18.5	21.1	0.2
	2007	0.50	0.02	70.0	0.2	524	43.1	8600	78.9	390.4	20.1	21.2	0.5
	Average	0.46		81.8		517		7538		362.5		22.7	
2.5 km E	2004	0.30	0.01	153.1	5.9	891	17.3	6382	93.6	344.8	23.8	15.1	0.7
	2005	0.40	0.01	209.0	13.1	1540	38.2	6045	211.3	384.5	27.3	21.1	1.9
	2006	0.41	0.04	183.6	10.4	1522	33.1	6234	42.1	213	15.8	15.3	1.5
	2007	0.63	0.06	78.6	7.9	1873	21.6	6821	52.1	370.5	18.3	16.2	1.6
	Average	0.44		156.1		1457		6371		328.2		16.9	
5.0 km E	2004	0.70	0.01	27.4	3.1	506	41.1	8439	75.9	682.5	56.1	29.0	1.7
	2005	0.49	0.04	31.2	2.5	588	28.7	7985	265.8	554.1	8.3	24.7	1.9
	2006	0.53	0.02	20.9	1.1	565	32.6	5235	112.8	448.8	36.6	18.7	0.4
	2007	0.73	0.02	30.1	0.9	492	22.6	5977	42.9	347.1	23.2	19.9	0.6
	Average	0.61		27.4		538		6909		508.1		23.1	

±SD, $n = 5$

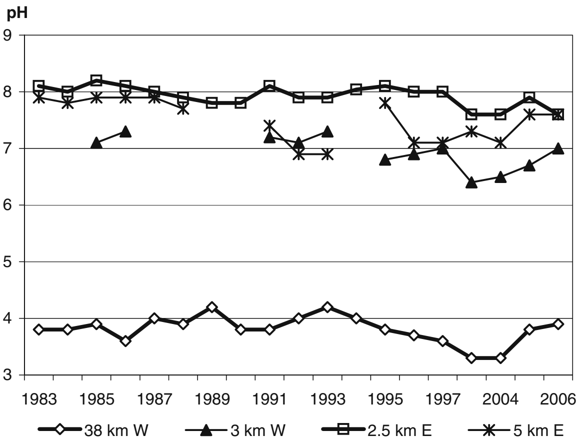


Fig. 3 Dynamics of the pH in the upper (0–30 cm depth) horizons of soil ($n = 5$) from sample plots at different distances from the cement plant

continuously high in soil. The concentration of Ca in soil upper layers exceeded that in unpolluted soils 11–14, of K 2–5 and of Mg 2–4 times. Moreover, significant differences were observed in the concentrations of Ca, K and Mg between sample plots ($p < 0.05$). The pH value of soils in the polluted areas was >7 for many years and was still high during the present study, being about twice as high as in the unpolluted sample plot (Fig. 3). Significance of differences between the soil pH of sample plots was established at the level $p < 0.005$.

At high pH values of soil, N concentrations decreased sharply, and thus, its deficiency may be a serious growth-limiting factor for trees. Nitrogen recycling in alkaline soils is of general interest. Earlier disbalances were found in the community of soil microorganisms toward increasing populations of denitrifiers (Mandre et al. 1986). Therefore, loss of N through denitrification may be a possible explanation for N deficiency in alkaline soil and in pines. The pH affects the denitrification rate and the form of N released (Simek et al. 2002). The earlier knowledge was summarised by Knowles (1981), who concluded that the optimum pH for nitrification is 7.0–8.0. However, the results of Simek et al. (2002) suggest a broader range: 6.3–8.3. A very rapid increase of denitrification was found in the pH range of 7.5 to 8.2 (Müller et al. 1980; Paul and Clark 1996). Some authors, on the contrary, argue that liming has no influence on N losses due to denitrification (Hellmann 1993; Papke-Rothkamp 1994). On the other hand, an increased C/N ratio might occur due to mineralisation, followed by nitrogen losses through leaching at the sites with a high pH of soil (Olsson 1986; Formánek and Vranová 2002). There may be several reasons for low N concentrations in soils affected by cement dust. In recent years also, the N concentration in upper layers of soil has had an increasing tendency in the territory surrounding the cement plant.

Linear regression analyses were used to examine the statistical relationships between the pH and Ca, K, P and N concentrations in sample plots. Strong relationships were found for the sample plot 2.5 km E, while at a greater distance, on sample plots influenced by a modest dust load, relationships between the pH and elements varied. The concentration of organic matter in soil depended on the pH in all sample plots with alkaline soil (Table 2), being 27–46% lower than control (Table 1).

Responses of needles to an alkaline environment

Studies of source–sink relationships have been largely empirical in nature, but these have allowed predicting the responses of trees to altered growth conditions. Comparison of the content of mineral elements in Scots pine growing at different

Table 2 Determination coefficients (R^2) between the pH and chemical characteristics of soil in sample plots at different distances from the cement plant

Sample plot	Ca	K	Mg	P	N	OM
2.5 km E	0.650	0.828	0.402	0.542	0.812	0.634
5.0 km E	0.734	0.299	0.155	0.089	0.400	0.898
3.0 km W	0.129	0.585	0.570	0.349	0.201	0.704
38.0 km W	0.637	0.292	0.549	0.871	0.487	0.318

distances from the cement plant indicated that the influence of high levels of cement dust pollution in the past and the relatively high pH of the growth substrate on concentrations of mineral elements in trees is still detectable.

It is known that alkalisation of soil complicates mineral nutrition processes and inhibits the availability of several nutrients, causing serious deviations in the mineral composition of plants (Marschner 2002). The concentration of N in the Scots pine needles from the heavily polluted area (2.5 km E) was on average 12% lower, while those of K, Ca, P and Mg were higher as compared with the control trees. In the heavily polluted area, the average concentration of Ca in needles was 25%, K 24%, Mg 11% and P 10% higher than in the unpolluted area ($p < 0.005$). Needle C concentrations in the heavily polluted territory did not differ from the control (Table 3).

According to the literature, the proportion of N in *P. sylvestris* needles sufficient for its optimal growth and biomass formation is 2.4–3.0% (Ingestad 1962), 1.8–3.2% (Wehrmann 1963) or 2.0–2.5% (Porgasaar 1973). Considering this, there was N deficit in Scots pine in all sample plots studied. Later, Ingestad (1987) suggested that plant nutrient requirements can be defined by complete nutrient proportions in the plant. According to this scheme, great disbalances occurred in the mineral element compositions in needles in the alkaline growth conditions (Table 4). In the calculation, each nutrient in Scots pine needles was expressed as a ratio to N, where N was equalised to 100. Diagnosis of nutrient imbalance by comparing deviation from the optimum status indicated P deficiency as its proportion was lower, while higher proportions of Ca and Mg suggested N deficiency.

Table 3 Percentage of mineral elements in needles of *P. sylvestris* in sample plots at different distances from the emission centre (±SD, $n = 18$)

Parameter	Layer of crown	Distance and direction from the cement plant							
		38 km W, control		3 km W		2.5 km E		5 km E	
		%	±SD	%	±SD	%	±SD	%	±SD
N	1	1.667	0.090	1.410	0.060	1.420	0.080	1.517	0.090
	2	1.670	0.060	1.430	0.020	1.420	0.080	1.600	0.110
	3	1.590	0.050	1.507	0.070	1.470	0.030	1.580	0.140
	Average	1.642	0.070	1.449	0.060	1.470	0.060	1.566	0.110
P	1	0.166	0.004	0.152	0.004	0.181	0.008	0.155	0.004
	2	0.161	0.001	0.143	0.011	0.18	0.003	0.138	0.001
	3	0.160	0.006	0.152	0.012	0.173	0.001	0.140	0.001
	Average	0.162	0.008	0.149	0.009	0.178	0.004	0.144	0.002
C	1	49.513	3.210	49.527	4.010	49.460	3.910	50.233	4.330
	2	49.813	5.250	50.007	4.560	49.950	3.210	50.883	4.210
	3	50.023	4.970	49.883	4.110	50.340	4.320	50.073	3.160
	Average	49.783	4.320	49.806	4.220	49.917	3.670	50.396	4.720
K	1	0.620	0.012	0.580	0.011	0.719	0.043	0.592	0.056
	2	0.565	0.020	0.490	0.023	0.793	0.067	0.418	0.011
	3	0.503	0.041	0.399	0.031	0.587	0.056	0.386	0.011
	Average	0.563	0.035	0.490	0.040	0.700	0.061	0.465	0.026
Ca	1	0.362	0.021	0.245	0.011	0.402	0.021	0.247	0.022
	2	0.377	0.028	0.298	0.009	0.441	0.033	0.268	0.022
	3	0.304	0.031	0.324	0.017	0.458	0.036	0.293	0.028
	Average	0.348	0.028	0.289	0.018	0.434	0.025	0.269	0.024
Mg	1	0.112	0.001	0.119	0.011	0.133	0.012	0.137	0.009
	2	0.118	0.001	0.129	0.011	0.145	0.012	0.162	0.004
	3	0.162	0.001	0.164	0.015	0.156	0.014	0.181	0.012
	Average	0.131	0.002	0.137	0.012	0.145	0.013	0.160	0.012

1 lower layer, 2 middle layer, 3 upper layer

Table 4 Proportions of mineral nutrients ($N = 100$) in Scots pine needles in alkaline soils in comparison with proportions by weight considered optimum for maximum growth according to Ingestad (1987)

Sample plot	N	P	K	Ca	Mg
5.0 km E	100	9	30	17	8
2.5 km E	100	9	47	29	10
3.0 km W	100	10	34	20	10
38 km W	100	10	34	21	8
Optimum[a]	100	14	45	6	6

[a] According to Ingestad (1987)

In alkaline soils of increasing pH, decreasing soil organic matter and increasing Ca concentration, the mobility of P is limited, and its deficiency due to calcium phosphates of low solubility develops (Marschner 2002). Deficiency of N in needles could be understood as N uptake limitation from N-poor soil. Also, the uptake of other nutrients, which are in excess, reflects the uptake capacity of the roots under N deficiency. Both the total amount of soil N and its availability to plants are closely related to the OM content in soil. The soil pH is of minor importance for the level and turnover of N in alkaline soils as suggested by Marschner (2002).

Partitioning of mineral elements between crown layers

The strength and direction of nutrient transport and partitioning in different crown compartments have been demonstrated to be regulated by source–sink relationships. It was shown earlier that photosynthetic properties vary vertically in crowns for both broadleaved and coniferous trees (Kozlowski et al. 1991; Mandre et al. 1998; Grassi and Bagnaresi 2001). This allows us to assume also existence of variation in nutrient partitioning in different parts of the crown. Indeed, this study showed variation in the allocation of nutrients between upper and lower layers of the crown. Lower-crown needles had a higher N concentration in the unpolluted area under relatively optimal growth conditions (Table 3). Differences between the upper and lower crown layers may be associated with shade acclimation accompanied with chlorophyll (Chl) increase in lower layers (Posch et al. 2008) and leaf N and Chl reduction in the upper crown (Leal and Thomas 2003). Also, the Chl/N ratio was shown to be strongly correlated with the light distribution (Brooks et al. 1996). In addition, the vertical gradient of N in the crown in the control sample plot was associated with the P supply ($R^2 = 0.505$), which supported the standpoints of Ingestad and Ågren (1988), Marschner (2002) and Portsmuth (2007) on the relationship between N and P.

In the needles of pines growing in alkalised soils, statistically proved variation in N within crown layers was not found, but there were tendencies toward increasing in N in the upper layer of the crown. What is the factor increasing the translocation of N to upper layers in alkalised soils? Apart from only slight differences of N concentrations between crown layers, it was found that N scaled positively with Mg ($R^2 = 0.508$) and C ($R^2 = 0.501$) in needles in the polluted areas. Results suggest that factors other than light acclimation may play a role in determining the vertical gradients in needle N in crowns in stress conditions.

The trends in the needle P concentration in different layers of Scots pine crown in the alkaline growth substrate were similar to those of control trees: no essential differences between P concentrations of needles in different crown layers were established. Although the vertical gradients of P were rather equal, concentrations tended to be higher in the sample plot 2.5 km E and lower in the modestly polluted sample plots (3 km W, 5 km E; Table 3). Regression analysis revealed relationships between P and Ca ($R^2 = 0.521$) and K ($R^2 = 0.677$) for needles in different canopy layers in the polluted area.

The regulation of C allocation at the whole-plant level is still poorly understood, and no unequivocal theory is available at present (Marcelis and Heuvelink 2007). Results showed that alkalisation of the environment did not affect C distribution in the crown of Scots pine. There were no differences between different sample plots nor between different crown layers (Table 3, Fig. 4). However, some earlier studies in 1991 and 1992, when dust pollution was extremely high (Fig. 2) and needles were incrusted with cement, revealed a somewhat lower concentration of soluble sugars and starch in the polluted needles than in the unpolluted needles (Mandre and Klõšeiko 1997; Klõšeiko 2003).

Comparison of trends of Ca, Mg and K allocation showed that, in the polluted areas, Ca was more abundant in needles of the upper crown layer, while needles in unpolluted area had the highest concentration of Ca in the lowermost layer. Both Mg and K were accumulated predominantly in the needles of the lower part of the crown (Table 3, Fig. 4).

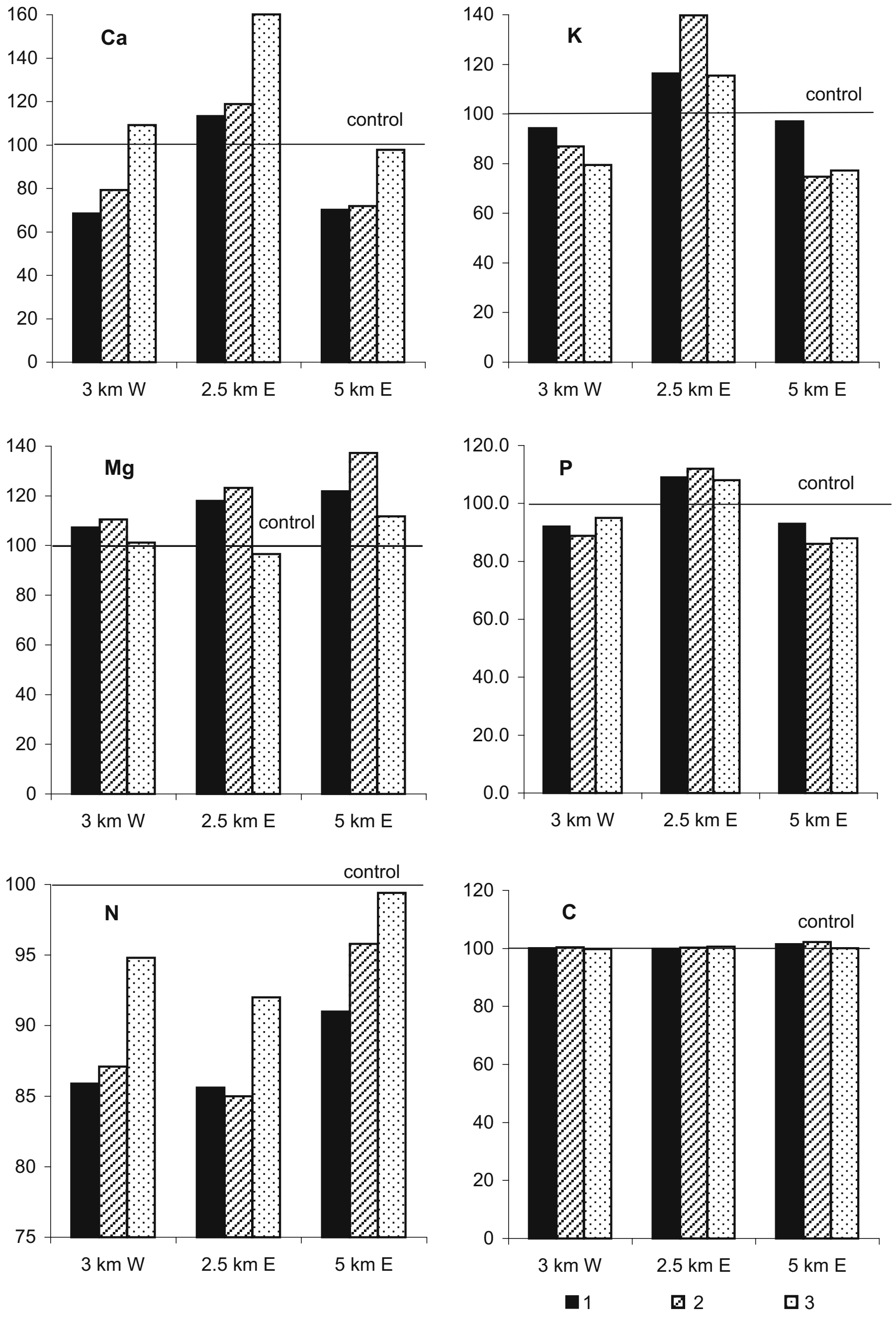


Fig. 4 Influence of alkaline growth substrate on the partitioning of mineral elements of the needles of Scots pine at different distances from the cement plant. Differences from the unpolluted area (control = 100%) were calculated for the lower (1), middle (2) and upper (3) layers of the crown

Influence of alkalisation of soil on the balance of mineral elements in needles

Many authors stress that the interaction of different mineral elements in plant tissues and their balance are of crucial importance in the growth and survival of trees under stress conditions rather than the concentration of single elements (Ingestad and Ågren 1988; Shuman 1994; Marschner 2002; Portsmuth et al. 2005). So, Marschner (2002) indicated that when the K supply is abundant, its effect on the nutrient composition of trees and its possible interference with the uptake and physiological availability of Mg and Ca deserve attention. On the other hand, Mg availability and translocation in plant tissues greatly depend on the Ca and K amounts in the organism. However, at higher pH levels in soil, the ratios of Mg/Ca and Mg/K rather than Mg alone are related to the influx, which substantiates the complementary ion effect (Shuman 1994). Also, K is important in N nutrition (Ali et al. 1987), and application of Ca was found to decrease N uptake on calcareous soils (Hons and Aljoe 1985). The N/P ratio in particular has been suggested as a tool for detecting nutrient limitation and determining fertiliser requirements in forestry (Güsewell et al. 2003; Tessier and Raynal 2003). Optimum nutrient

Table 5 Ratios of mineral elements in different crown layers of Scots pines growing at different distances from the cement plant in 2006

Ratio	Layer of crown	Distance and direction from the cement plant			
		38 km W	3 km W	2.5 km E	5 km E
P/N	1	0.10	0.108	0.127	0.102
	2	0.10	0.101	0.118	0.086
	3	0.10	0.101	0.118	0.089
	Average	0.10	0.103	0.121	0.092
N/C	1	0.034	0.028	0.029	0.030
	2	0.034	0.029	0.028	0.031
	3	0.032	0.030	0.029	0.032
	Average	0.033	0.029	0.029	0.031
N/K	1	2.689	2.431	1.975	2.562
	2	2.955	2.918	1.791	3.828
	3	3.161	3.777	2.504	4.093
	Average	2.935	3.042	2.090	3.494
N/Ca	1	4.605	5.755	3.532	6.142
	2	4.430	4.800	3.220	5.970
	3	5.230	4.651	3.210	5.392
	Average	4.755	5.069	3.321	5.835
N/Mg	1	8.930	11.849	10.677	11.073
	2	14.152	11.085	9.793	9.877
	3	9.815	9.189	9.423	8.729
	Average	10.966	10.708	9.964	9.893
Ca/Mg	1	3.232	2.059	3.023	1.803
	2	3.194	2.240	3.041	1.654
	3	1.877	1.976	2.942	1.619
	Average	2.768	2.092	3.002	1.692
K/Mg	1	5.536	4.873	5.406	4.321
	2	4.788	3.798	5.469	2.580
	3	3.104	2.433	3.763	2.133
	Average	4.476	3.701	4.879	3.011
K/Ca	1	1.712	2.367	1.789	2.300
	2	1.499	1.644	1.798	1.560
	3	1.655	1.231	1.282	1.317
	Average	1.622	1.747	1.623	1.726

ratios for maximum relative growth rate have been found for a range of species (Ericsson 1994; Knecht Billberger 2006). It was ascertained that the ratios N/P and N/Mg in the needles of Norway spruce are relatively stable all year round in optimal conditions (Mandre and Tuulmets 1995) and that deviation of the ratio N/P from the optimum may cause drastic changes in plant metabolism (Marschner 2002). A P/N ratio below 0.125 indicates P deficiency in pines and spruces (Ingestad 1979, 1981). In this study, it was found that, in the needles of Scots pine growing in alkalised environments, the ratios of most nutrients analysed differed significantly from control (Table 5). This is a sign of disbalanced mineral nutrition and partitioning of nutrients in the organism. The average of the ratio P/N was below 0.125 in needles from both control trees and from trees in alkalised soils. The ratios N/Ca, N/Mg and N/K had significantly dropped (30%, 9% and 29%, respectively) in comparison to control (100%), while the ratios Ca/Mg, K/Mg and K/Ca had a tendency to increase (7–9% in the sample plot 2.5 km E). The situation was different in trees growing at greater distances from the emission source, that is 3 km W and 5 km E (Table 5): the ratio N/K was, respectively, by 19% and 29% higher than control; N/Ca by 7% and 23% higher and N/Mg had no difference from the control. Variations in the imbalance of nutrients in needles at different distances from the emission centre may depend on the size and chemical character of particles carried to greater distances by winds. Also Kaasik et al. (2005) indicated for fly ash that relatively small differences in particle size and composition can cause notably different deposition fluxes. Unfortunately, we still do not have reliable data on the size distributions of cement dust particles. In any case, our results suggest that alkalisation and excess of Ca, K and Mg in soil play an important role in determining the vertical gradients in nutrients and their ratios in the crown. In polluted areas, the ratios N/P, N/Ca and N/Mg were higher in the lower crown layer, while in control trees, the vertical gradients showed the opposite trends. The ratios N/K, Ca/Mg and K/Ca in different layers of the crown have similar vertical gradients in both alkalised and unpolluted areas.

Conclusions

Alkalisation of soil caused by a long-term impact of cement dust complicates mineral nutrition and causes imbalances in the mineral composition of trees. Deficit of N and excess of Ca and Mg in needles and differences in nutrient allocation in the crown referred to the sensitivity of Scots pine to the increased pH and excess of components of cement dust in soil. The high level and large range of damages in mineral nutrition processes and nutrient partitioning in the crown and changes in vertical gradients of the nutrients and their ratios, established in the present study, indicated to great changes in the crown structure and biomass formation in the alkalised environment. It is difficult to interpret causal relationships between the mineral composition and changes in nutrients allocation between different crown layers under the described complex stress conditions. These relationships require further research. Still, it is possible to state that the impact of alkaline dust pollution has a residual long-term effect on the physiological state of Scots pine, and prognostication of how much time neutralisation of the environment and stabilisation of the forest ecosystem will take is a complicated task.

Acknowledgements This study was funded by the Estonian Ministry of Education and Research (project no. 0170021s08). The author thanks her colleagues Dr. Jaak Pikk, Dr. Henn Pärn and Dr. Katri Ots for help in the collection of soil and needle samples, Kersti Poom for technical assistance and Tiia Kaare for linguistic help.

References

Ali, A. A., Ikeda, M., & Yamada, Y. (1987). Effect of the supply of potassium, calcium and magnesium on the absorption, translocation and assimilation of ammonium- and nitrate-nitrogen in wheat plants. *Soil Science and Plant Nutrition, 33*, 585–594.

Brooks, J. R., Sprugel, D. G., & Hinckley, T. M. (1996). The effects of light acclimation during and after foliage expansion on photosynthesis of *Abies amabilis* foliage within the canopy. *Oecologia, 107*, 21–32. doi:10.1007/BF00582231.

Davis, R. B., & Stokes, P. M. (1986). Overview of historical and paleoecological studies of acidic air pollution and its effects. *Water, Air, and Soil Pollution, 30*, 311–318. doi:10.1007/BF00305202.

Environmental Review Kunda 2007, No.16 (2007). (16 pp.). Kunda Nordic Heidelberg Cement Group, Kunda, Helsinki.

Ericsson, T. (1994). Nutrient dynamics and requirements of forest crops. *New Zealand Journal of Forestry Science, 24*, 133–168.

Estonian Environment 1991 (1991). *Environmental report 4* (64 pp.). Environmental Data Centre, Helsinki.

Estonian Environment 1995 (1996). (96 pp.). Ministry of the Environment of Estonia, Environmental Information Centre, Tallinn.

Farmer, A. M. (1993). The effect of dust on vegetation—a review. *Environmental Pollution, 79*, 63–75. doi:10.1016/0269-7491(93)90179-R.

Formánek, P., & Vranová, V. (2002). A contribution to the effect of liming on forest soils: Review of literature. *Journal of Forest Science, 48*, 182–190.

Grassi, G., & Bagnaresi, U. (2001). Foliar morphological and physiological plasticity in *Picea abies* and *Abies alba* saplings along a natural light gradient. *Tree Physiology, 21*, 959–967.

Güsewell, S., Koerselman, W., & Verhoeven, J. T. A. (2003). Biomass N: P ratios as indicators of nutrient limitation for plant populations in wetlands. *Ecological Applications, 13*, 372–384. doi:10.1890/1051-0761(2003)013[0372:BNRAIO]2.0.CO;2.

Han, Q., Kawasaki, T., Katahata, S., Mukai, Y., & Chiba, Y. (2003). Horizontal and vertical variations in photosynthetic capacity in a *Pinus densiflora* crown in relation to leaf nitrogen allocation and acclimation to irradiance. *Tree Physiology, 23*, 851–857.

Hellmann, B. (1993). N_2O-Emissionen aus unterschiedlich behandelten Fichtenstandorten im Höglwald. *Schriftenreihe des Fraunhofer-Institut für Atmosphärische Umweltforschung 19*, 278.

Hons, F. M., & Aljoe, K. D. (1985). Effects of applied calcium on growth and ammonium utilization by corn. *Communications in Soil Science and Plant Analysis, 16*, 349–360.

Ingestad, T. (1962). Macroelement nutrition of pine, spruce and birch seedlings in nutrient solutions. *Meddelanden från Statens Skogsforskningsinstitut, 51*, 1–150.

Ingestad, T. (1979). Mineral nutrient requirements of *Pinus sylvestris* and *Picea abies* seedlings. *Physiologia Plantarum, 45*, 373–380. doi:10.1111/j.1399-3054.1979.tb02599.x.

Ingestad, T. (1981). Nutrition and growth of birch and grey alder seedlings in low conductivity solutions and at varied relative rates of nutrient addition. *Physiologia Plantarum, 52*, 454–466. doi:10.1111/j.1399-3054.1981.tb02716.x.

Ingestad, T. (1987). New concepts on soil fertility and plant nutrition as illustrated by research on forest trees and stands. *Geoderma, 40*, 237–252. doi:10.1016/0016-7061(87)90035-8.

Ingestad, T., & Ågren, G. I. (1988). Nutrient uptake and allocation at steady-state nutrition. *Physiologia Plantarum, 72*, 450–459. doi:110.1111/j.1399-3054.1988.tb09150.x.

ISO/10390 (1994). Soil quality. Determination of pH.

ISO/11260 (1995). Soil quality. Determination of CEC and base saturation.

ISO/11261 (1995). Soil quality. Determination of total nitrogen. Modified Kjeldahl Method.

Jäger, H. J. (1980). Indikation von Luftverunreinigungen durch morphometrische Untersuchungen an höheren Pflanzen. In R. Schubert, & J. Schuh (Eds.), *Bioindikation 3. Wissenschaftliche Beiträge 26* (pp. 43–52). Halle, Wittenberg: Martin-Luther-Universität.

Kaasik, M., & Sõukand, Ü. (2000). Balance of alkaline and acidic pollution loads in the area affected by oil shale combustion. *Oil Shale, 17*, 113–128.

Kaasik, M., Alliksaar, T., Ivask, J., & Loosaar, J. (2005). Spherical fly ash particles from oil shale fired power plants in atmospheric precipitations. Possibilities of quantitative tracing. *Oil Shale, 22*, 547–561.

Kangur, A. (1988). Changes of chlorophyll content in pine needles in the industrial region of northern Estonia. In T. Frey (Ed.), *Problems of contemporary ecology* (pp. 53–57). Tartu: Tartu State University, (in Estonian).

Kannukene, L. (1995). Bryophytes in the forest ecosystem influenced by cement dust. In M. Mandre (Ed.), *Dust pollution and forest ecosystems. A study of conifers in an alkalized environment. Publication 3* (pp.141–148). Tallinn: Institute of Ecology.

Kaupenjohann, M. (1989). Effects of acid rain on soil chemistry and nutrient availability in the soil. In E.-D. Schulze, O. L. Lange, & R. Oren (Eds.), *Forest decline and air pollution: A study of spruce (Picea abies) on acid soils* (pp. 297–335). New York: Springer.

Keskkond'90 (1991). Eesti Keskkonnaministeerium, Tallinn. (97 pp.) (in Estonian).

Kim, S.-T., Maeda, Y., & Tsujino, Y. (2004). Assessment of the effect of air pollution on material damages in Northeast Asia. *Atmospheric Environment, 38*, 37–48.

Klõšeiko, J. (2003). *Carbohydrate metabolism of conifers in alkalised growth conditions. Doctoral thesis* (183 pp). Tartu: Estonian Agricultural University.

Knecht Billberger, M. F. (2006). *Plant growth—stoiciometry and competition. Theory development in ecosystem ecology. Doctoral thesis.* (20 pp.). Department of Ecology and Environmental Research, Swedish University of Agricultural Sciences. Uppsala.

Knowles, R. (1981). Denitrification. In E. A. Paul, & J. N. Ladd (Eds.), *Soil biochemistry* (Vol. 5, pp. 323–369). New York: Marcel Dekker.

Kozlowski, T., Kramer, P. J., & Pallardy, S. G. (1991). *The physiological ecology of woody plants* (657 pp). San Diego, New York: Academic.

Lal, B., & Ambasht, R. S. (1982). Impact of cement dust on the mineral and energy concentration of Psidium guayava. *Environmental Pollution, 29A*, 241–247.

Landis, T. D. (1985). Mineral nutrition as an index of seedling quality. In M. L. Duryea (Ed.), *Evaluating seedling quality: Principles, procedures and predictive abilities of major tests* (pp. 29–48). Corvallis: Forest Research Laboratory, Oregon State University.

Leal, D. B., & Thomas, S. C. (2003). Vertical gradients and tree-to-tree variation in shoot morphology and foliar nitrogen in an old-growth *Pinus strobus* stands. *Canadian Journal of Forest Research, 33*, 1304–1314.

Lõhmus, K., & Lasn, R. (1990). Spruce and pine root structures and chemical characteristics in moderate acid soils. In H. Persson (Ed.), *Above- and below-ground interactions in forest trees in acidified soils. Air Pollution Research Report 32* (pp. 74–78). Uppsala: Environmental Research Programme of the Commission of the European Communities.

Mandre, M. (1995). Dust emission and deposition. In M. Mandre (Ed.), *Dust pollution and forest ecosystems. A study of conifers in an alkalized environment. Publication 3* (pp. 18–22). Tallinn: Institute of Ecology.

Mandre, M. (2000). Stress induced changes in lignin and nutrient partitioning in *Picea abies* L. Karst. *Baltic Forestry, 6*, 30–36.

Mandre, M. (2002). Relationships between lignin and nutrients in *Picea abies* L. under alkaline air pollution. *Water, Air, & Soil Pollution, 133*, 361–377.

Mandre, M., & Klõšeiko, J. (1997). Changing carbohydrate partitioning in 6-year-old coniferous trees after prolonged exposure to cement dust. *Zeitschrift für Naturforschung, 52c*, 586–594.

Mandre, M., & Tuulmets, L. (1995). Changes in the pigment system. In M. Mandre (Ed.), *Dust pollution and forest ecosystems. A study of conifers in an alkalized environment. Publication 3* (pp. 66–77). Tallinn: Institute of Ecology.

Mandre, M., & Tuulmets, L. (1997). Biochemical diagnosis of forest decline. *Baltic Forestry, 3*, 19–25.

Mandre, M., Kangur, A., Laur, L., Pihlakas, E., & Ploompuu, T. (1986). *Physiological-Biochemical state of plants in Kunda in 1985. II. Scots Pine* (96 pp.). Report in Kunda Tsement, Tallinn, (in Estonian).

Mandre, M., Rauk, J., Poom, K., & Pöör, M. (1995). Estimation of economical losses of forests and quality of agricultural plants on the territories affected by air pollution from cement plant in Kunda. In F. Kommonen, A. Estlander, & P. Roto (Eds.), *Economic evaluation of major environmental impacts from the planned investments at Kunda Nordic Cement Plant in Estonia. Report IFC, App. 1.* Washington: Soil and Water Ltd., Tampere Regional Institute of Occupational Health, International Finance Corporation.

Mandre, M., Tullus, H., & Tamm, Ü. (1998). The partitioning of carbohydrates and biomass of leaves in *Populus tremula* L. canopy. *Trees—Structure and Function, 12*, 160–166.

Mandre, M., Klõšeiko, J., Ots, K., & Tuulmets, L. (1999). Changes in phytomass and nutrient partitioning in young conifers in extreme alkaline growth conditions. *Environmental Pollution, 105*, 209–220.

Marcelis, L. F. M., & Heuvelink, E. (2007). Concepts of modelling carbon allocation among plant organs. In J. Vos, L. F. M. Marcelis, P. H. B. de Visser, P. C. Struik, & J. B. Evers (Eds.), *Functional-structural plant modelling in crop production* (pp. 103–111). Dordrecht: Springer.

Marschner, H. (2002). *Mineral nutrition of higher plants* (889 pp). London: Academic.

Müller, M. M., Sundman, V., & Skujinš, J. (1980). Denitrification in low pH spodosols and peats determined with the acetylene inhibition method. *Applied and Environmental Microbiology, 40*, 235–239.

Niinemets, Ü., Lukjanova, A., Turnbull, M. H., & Sparrow, A. D. (2007). Plasticity in mesophyll volume fraction modulates light-acclimation in needle photosynthesis in two pines. *Tree Physiology, 27*, 1137–1151.

Nilsen, E. T., & Orcutt, D. M. (1996). *The physiology of plants under stress* (689 pp). New York: John Wiley and Sons.

Nilson, E. (1995). Species composition and structure of epiphytic lichen assemblages on Scots pine around the Kunda cement plant. In M. Mandre (Ed.), *Dust pollution and forest ecosystems. A study of conifers in an alkalized environment. Publication 3* (pp. 134–140). Tallinn: Institute of Ecology.

Olsson, M. T. (1986). Long-term impact of lime on the humus form in a beech stand on sandy till. *Studia Forestalia Suecica, 174*, 12.

Ots, K. (2002). *Impact of air pollution on the growth of conifers in the industrial region of northeast Estonia. Doctoral thesis* (222 pp.). Estonian Agricultural University, Tartu.

Papke-Rothkamp, H. (1994). Einfluß saurer Beregnung und kompensatorischer Kalkung auf die Emission gasförmiger Stickstoffverbindungen aus Böden eines Fichtenbestandes. *Schriftenreihe des Fraunhofer-Institut für Atmosphärische Umweltforschung, 25*, 175.

Pärn, H. (2002). Relationships between radial growth of Scots pine and climate in the northeastern industrial region of Estonia. *Metsanduslikud Uurimused/Forestry Studies, 36*, 47–61.

Paul, E. A., & Clark, F. E. (1996). *Soil microbiology and biochemistry* (340 pp.). San Diego: Academic.

Pearcy, R. W., & Sims, D. A. (1994). Photosynthetic acclimation to changing light environments: Scaling from the leaf to the whole plant. In M. M. Caldwell, & R. W. Pearcy (Eds.), *Exploitation of environmental heterogeneity by plants: Ecophysiological processes above and below ground* (pp. 145–174). San Diego: Academic.

Porgasaar, V. (1973). *Mineral nutrition of scots pine and its diagnostics. Doctoral thesis* (196+42 pp). Tartu: Tartu State University, (in Estonian with Russian summary).

Portsmuth, A. (2007). *Ecophysiological mechanisms of forest plant growth and biomass distribution. Dissertations on natural sciences 16* (189 pp). Tallinn: Tallinn University.

Portsmuth, A., Niinemets, Ü., Truus, L., & Pensa, M. (2005). Biomass allocation and growth rates in *Pinus sylvestris* are interactively modified by nitrogen and phosphorus availabilities and by tree size and age. *Canadian Journal of Forest Research, 35*, 2346–2359.

Posch, S., Warren, C. R., Kruse, J., Guttenberger, H., & Adams, M. A. (2008). Nitrogen allocation and the fate of absorbed light in 21-year-old *Pinus radiata. Tree Physiology, 28*, 375–384.

Richardson, A. D., Ashton, P. M. S., Berlyn, G. P., McGroddy, M. E., & Cameron, I. R. (2001). Within-crown foliar plasticity of western helmlock, *Tsuga heterophylla*, in relation to stand age. *Annals of Botany, 88*, 1007–1015.

Rook, D. A. (1991). Seedling development and physiology in relation to mineral nutrition. In R. van den Driessche (Ed.), *Mineral nutrition of conifer seedlings* (pp. 85–111). Boca Raton: CRC.

Roots, O., Frey, T., Kirjanen, I., Kört, M., & Kohv, N. (1997). Air pollution: Emissions and loads. In *Estonian Environmental Monitoring 1996* (pp. 10–12). Ministry of the Environment, Estonian Environment Information Centre, Tallinn.

Schaedle, M. (1991). Nutrient uptake. In R. van den Driessche (Ed.), *Mineral nutrition of conifer seedlings* (pp. 25–59). Boca Raton: CRC.

Schulte, E. E. (1995). Recommended soil organic matter tests. In T. J. Sims, & A. Wolf (Eds.), *Recommended soil testing procedures for the northeastern United States. Northeast Regional Bulletin 493* (pp. 47–56). Newark: Agricultural Experiment Station, University of Delaware.

Shalhevet, J. (1993). Plants under salt and water stress. In L. Fowden, T. Mansfield, & J. Stoddart (Eds.), *Plant adaptation to environmental stress* (pp. 133–155). London: Chapman and Hall.

Shuman, L. M. (1994). Mineral nutrition. In R. E. Wilkinson (Ed.), *Plant–environment interactions* (pp. 149–182). New York: Marcel Dekker.

Simek, M., Jsova, L., & Hopkins, D. W. (2002). What is the so-called optimum pH for denitrification in soil? *Soil Biology and Biochemistry, 34*, 1227–1234.

Świercz, A. (2006). Suitability of pine bark to evaluate pollution caused by cement-lime dust. *Journal of Forest Science, 52*, 93–98.

Tessier, J. T., & Raynal, D. J. (2003). Use of nitrogen to phosphorus ratio in plant tissue as an indicator of nutrient limitation and nitrogen saturation. *Journal of Applied Ecology, 40*, 523–534.

Tuulmets, L. (1995). Chemical composition of precipitation. In M. Mandre (Ed.), *Dust pollution and forest ecosystems. A study of conifers in an alkalized environment. Publication 3* (pp. 23–32). Tallinn: Institute of Ecology.

Wehrmann, J. (1963). Möglichkeiten und Grenzen der Blattanalyse in der Forstwirtschaft. *Landwirtschaftliche Forschung, 16*, 130–145.

Yearbook Forest 2007 (2008). Centre of Forest Protection and Silviculture, Estonian Ministry of Environment, Tartu (217 pp.).