DISSERTATIONES GEOGRAPHICAE UNIVERSITATIS TARTUENSIS
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DEPOSITION AND TRANSFORMATION OF AIR POLLUTANTS IN CONIFEROUS FORESTS

A study based on Estonian monitoring data

KATRIN PAJUSTE

TARTU UNIVERSITY
PRESS

Institute of Geography, Faculty of Biology and Geography, University of Tartu, Estonia

This dissertation is accepted for the commencement of the degree of *Doctor of Philosophiae* in geography (landscape ecology and environmental protection) at the University of Tartu on May 31, 2004 by the Doctoral Committee of the Faculty of Biology and Geography of the University of Tartu

Opponent: PhD Michael Starr
The Finnish Forest Research Institute, Vantaa Research Centre, Finland

Commencement: Hall of Scientific Council in the University Main Building, Ülikooli 18, Tartu, on September 24, 2004, at 14.15

The publication of this dissertation is granted by the Institute of Geography, University of Tartu

Tartu Ülikooli Kirjastus
www.tyk.ut.ee
Tellimuse nr. 391

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following articles, which are referred to by their Roman numerals:

I Treier K., Pajuste K., Frey J. 2004. Recent trends in chemical composition of bulk precipitation at Estonian monitoring stations 1994–2001. Atmospheric Environment (accepted).

II Pajuste K., Frey J., Asi E. Interactions of atmospheric deposition with coniferous canopies in Estonia (manuscript submitted to Environmental Monitoring and Assessment).

III Pajuste K., Frey J. 2003. Nitrogen mineralisation in podzol soils under boreal Scots pine and Norway spruce stands. Plant and Soil 257, 237–247.

IV Frey J., Frey T., Pajuste, K. 2004. Input-output analysis of macroelements in ICP-IM catchment area, Estonia. Landscape and Urban Planning 67, 217–223.

The author's contribution

I The paper was planned and the results was assessed jointly by K. Pajuste, K. Treier and J. Frey. K. Pajuste was responsible for trend estimates and discussion of results.

II The paper was planned by K. Pajuste and J. Frey. K. Pajuste wrote the first draft of the paper.

III The experiment was planned and carried out jointly by K. Pajuste and J. Frey. K. Pajuste performed the data analyses and prepared the first draft of paper.

IV The paper was initiated by J. Frey and T. Frey. K. Pajuste was responsible for mineralisation and assisted in the revision of manuscript.

K. Pajuste was jointly responsible for co-ordinating and data processing of the environmental monitoring programmes of precipitation chemistry and integrated monitoring (data included in papers I and II) during 1999–2002 in Estonian Environmental Research Centre.

ABBREVIATIONS

BD	bulk deposition
BP	bulk precipitation
CL	canopy leaching
CLTRAP	UN/ECE Convention on Long-range Transboundary Air Pollution
DD	dry deposition
EERC	Estonian Environmental Research Centre
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe, co-ordinated by UN/ECE
ENEMN	Estonian National Environmental Monitoring Network
ICP Forest level II	International Co-operative Programme "Assessment and Monitoring of Air Pollution Effects on Forests" intensive forest monitoring (level II)
ICP IM	UN/ECE International Co-operative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems
LF	litterfall (nutrient flux in litterfall)
NTF	net throughfall (throughfall - bulk deposition)
RW	run-off water flux and chemistry
SF	stemflow water flux and chemistry
SW	soil water flux and chemistry
TF	throughfall deposition
TPP	thermal power plants
W	weathering

1. INTRODUCTION

1.1. Background

Nutrient flows in forests. Forest ecosystems consist of organisms (plants, animals, fungi and micro-organisms) and their habitats (the air and soil). The functioning of a forest ecosystem is characterised by continuous flow of energy and nutrients between organisms themselves and their environment (Helmisaari, 2000).

A simple way of describing the nutrient status of a forest and defining forest vitality is to calculate nutrient budgets (Cerny et al., 1994). It is calculated by determining the input of nutrients into and the output of nutrients out of a stand (Fig. 1).

Atmospheric deposition is an important additional source of nutrients to an ecosystem. Forest canopies, which have a large surface area, are especially effective in intercepting both atmospheric dry and wet deposition (Bredemeier, 1988). Numerous processes like foliar leaching, canopy uptake and wash-off of gases, aerosols and particles modify the chemical composition of incoming wet deposition in canopy before it reaches forest floor (Parker, 1983). When the rainwater passes through the canopies and falls to the ground it is called throughfall. The fraction of precipitation that is collected by canopy and reaches the ground by running down by trunk is called stemflow. Bulk deposition is the operational term for a mixture of wet and dry deposition as measured by continuously exposed collectors (Ross and Lindberg 1994). Second major pathway of nutrients to the forest floor is litterfall. But nutrients are only slowly released from organic matter via mineralisation while throughfall nutrients are nearly all dissolved and readily available for uptake.

In short term retranslocation is an important process to prevent losses of important macro-nutrients (Helmisaari, 1990). Nitrogen is the most important plant nutrient in boreal forests, and its availability is one of the factors limiting growth under low nitrogen deposition conditions (Gozs, 1981). As the pool of mineral N in forest soil is small compared to the total N fluxes (Rosswall, 1976), the rate of N mineralisation is regarded as a key process affecting N availability for vegetation.

Monitoring the impact of air pollution on ecosystems. Numerous national and international programmes have been established for monitoring nutrient cycling in forest ecosystems. One of them — the International Biological Programme (IBP), was initiated in Estonia in 1970s (Frey et al., 1977; Frey, 1979; Frey et al., 1980). The first long-term national intensive ecosystem monitoring programme under LTRAP Convention in Estonia was initiated by the Nordic Council of Ministers in 1994 (TemaNord, 1996). Selection of a site for the programme followed the criteria presented in Integrated Monitoring Manual

(ICP IM Manual, 1998). Taking earlier investigations into account, an intensive monitoring site at Saarejärve forested catchment in eastern Estonia and a biomonitoring site in the westernmost Vilsandi island were established. Besides the integrated monitoring programme, Estonia contributes to international co-operation by taking part in monitoring of air pollution effects on forests (Saare et al., 2001). International monitoring network of air pollution effects is complemented by EMEP and local stations of precipitation monitoring. Although participation in international co-operation started much earlier, the CLRTAP and its first protocols were signed by Estonia as late as in 2000, and the protocol of financing EMEP only in 2001.

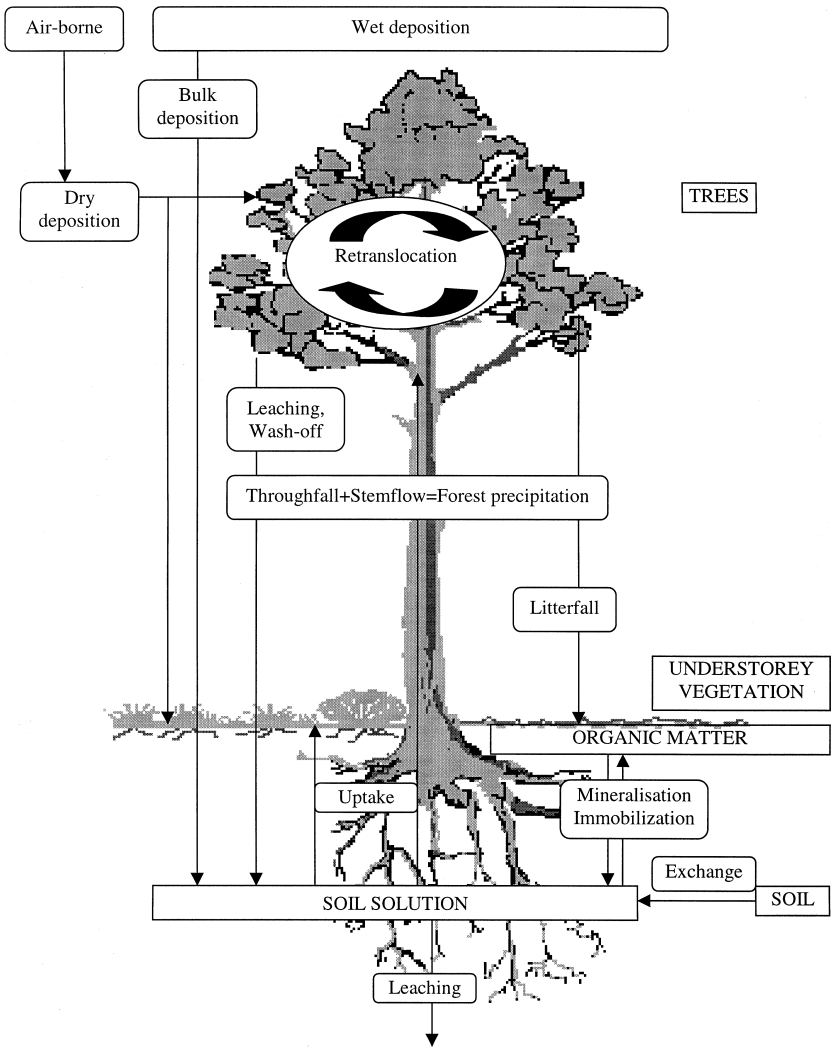

Fig. 1. Nutrient pools and flows in a forest ecosystem (modified from Helmisaari, 2000).

1.2. Climate

Estonia has a transitional climate from maritime along the coastal region to continental in the interior. The average temperature of the coldest months, January and February, is –3.5° to –7 °C, while that of the warmest month, July, is 16 to 18°C.

Rainfall is distributed unevenly throughout the year. Precipitation is highest in the end of summer, and relatively low in spring. Mean annual precipitation varies from 500 mm on the coast to almost 700 mm in the uplands. Permanent snow cover becomes established in the north-east at the beginning of December. Apart from the coast and the western islands, snow cover lasts for approximately 110 days. In mild winters, however, much of Estonia does not have permanent snow cover at all.

The length of the vegetation period in Estonia is 180–195 days; the length of the frost-free period is 110–190 days (Paal, 1997).

Because of the influence of the warm Gulf Stream, the prevailing winds in Estonia blow from the south-west and west. The average wind speed is low (3–4 m/s) in the southern and central part of mainland, while it is 6–7 m/s in the islands and coastal regions.

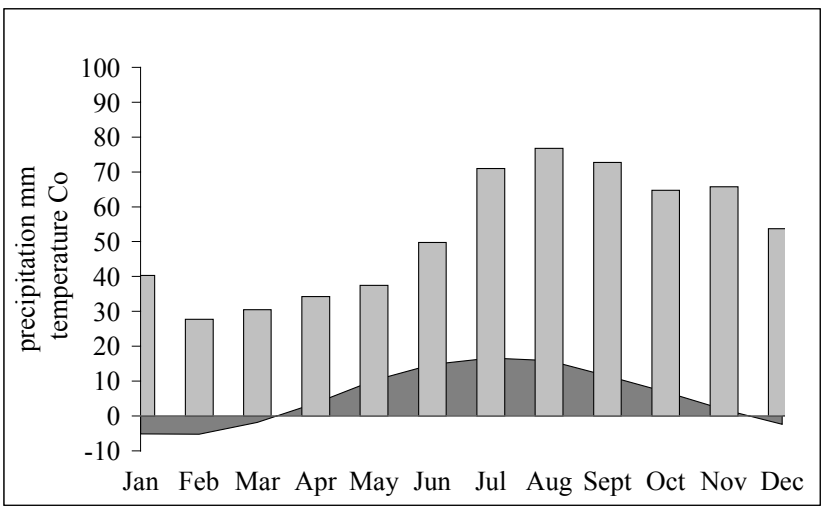

Fig. 2. Climatic diagram. The line shows long-term (1961–1990) average monthly values for temperature, the bars denote monthly precipitation values as a mean of 4 stations (Tallinn, Pärnu, Võru, Vilsandi). Source: Estonian Meteorological and Hydrological Institute.

1.3. Emissions of air pollutants

Sulphur oxides (such as SO_2) are generally formed when sulphur containing fuel is burnt but also in other industrial processes. The main branch of industry in Estonia is energy production. Approximately 89% of energy in Estonia is produced by combustion of fossil fuels. The remaining 11% comes from biomass.

Predominant sources of Estonian SO_2 emissions (Fig. 3a) are oil-shale based large thermal power plants and chemical industries. Estonian oil shale is characterised by a high ash content (45–50%), moderate sulphur content (1.4–1.8%) and low net caloric value. Oil shale mining and combustion, accounting for about 81% of the total harmful emissions of Estonia, has put a severe load on the environment. In 1999, 92% of electricity was generated from combustion of oil shale (Estonia's third national communication, 2001).

According to officially reported emission data (UNECE, 2003), local SO_2 emissions have declined by ~67% from their peak in the 1980s to 2000 (Fig. 3a). A rapid decrease took place in the early 1990's (53% in 1990–1995). This was caused by the reshaping of local economy, resulting in a gradual decline in the oil shale amounts used annually by the thermal power plants. In 2001 Estonia had the highest total national emission of SO_2 (92 kilotons) among the countries of the Nordic-Baltic region (EMEP Status Report 1/2003).

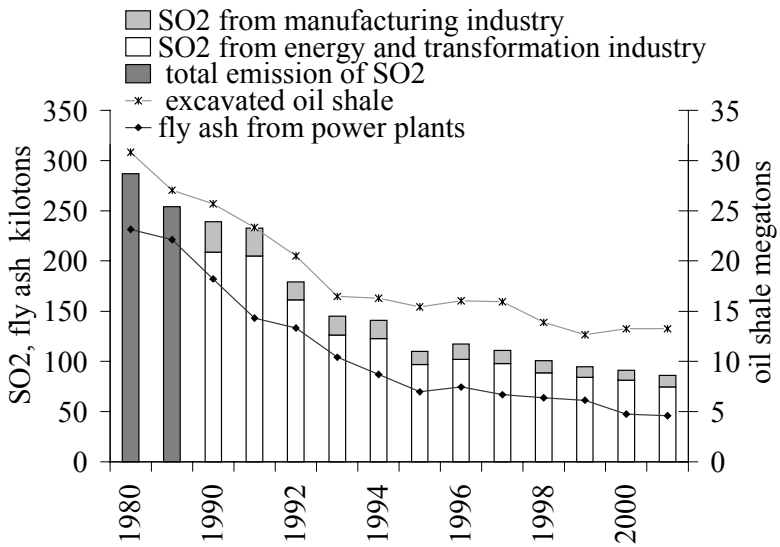

Fig. 3a. Annually excavated oil shale (Mt) and emissions of SO2 and fly ash (kt) from power plants (Statistical Yearbook of Estonia, 2003).

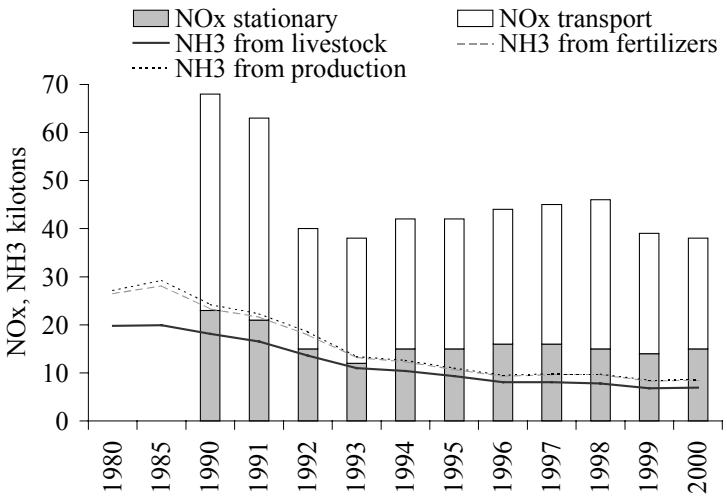

Fig. 3b. Emissions of NOx and NH3 (kilotons) in Estonia.

Nitrogen oxides (NOx) are formed when fuel is burnt at high temperatures. The main source of nitrogen oxides is exhaust from motor vehicles, but also stationary sources such as electric utilities and industrial boilers. A significant proportion of environmental problems in Estonia arises from transport. Less than 10% of SO_2 emissions, but nearly 65% of oxidised nitrogen, is emitted from different vehicles. Generally there has been no significant trend in national total NOx emissions after 1992 despite increasing traffic load. A rapid decrease took place between 1990 and 1992 (UNECE, 2003).

The main source of ammonia emission in Estonia is agriculture: manure management and fertiliser consumption. The emission of ammonia was reduced by 63% in 1990s due to a decrease in livestock numbers (especially dairy cows and cattle as the most significant sources of NH_3 emission) and reduced use of mineral fertilisers.

The main polluters emitting particles in Estonia are the same as those for SO_2 — energetic companies, heat production and oil shale chemistry in Ida-Virumaa. Other anthropogenic sources are small boiler houses, companies producing construction materials and wood processing enterprises (Kohv et al., 2003). There are also natural sources such as erosion of soil particles from areas of uncovered soil and unpaved roads, sea salt and pollen (Kimmel, 2002).

In spite of a 70%reduction in emissions in 1990–2000 (UNECE, 2003), Narva power plants are still the largest polluters by particles in Estonia. In 2001 their emissions were about 45 thousand tons. After installation of new efficient electrostatic precipitators, the projected emission rate for 2004 should decrease by ~90% (Liblik, Rätsep, 2002). Kunda Nordic Cement factory was often mentioned as a severe polluter in 1990s, but after investing into new filters in

1997, their emissions decreased by 99% and in 2001 their contribution to the total emission of particles was only 0.5% (300 t) (Kohv et al., 2003). Lövblad et al. (2000) found that estimation of base cation emissions from anthropogenic sources is subject to large uncertainties. Also, it is generally difficult to estimate natural base cation emissions. In Finland the biggest contributors to alkaline aerosols were combustion of wood and dust emissions raised by traffic (Anttila, 1990).

The official emission figures of air pollutants from Estonia involve some uncertainties discussed by Kimmel (2002). He found that, beside the anthropogenic sources, natural emissions are significant contributors to total emissions of particulates. The total emissions may be underestimated also for nitrogen oxides.

1.4. Air quality monitoring

In Estonia systematic measurements of air quality in background stations begun in western Estonia (Sõrve and Vilsandi stations) in the 80s, and soon after that in the Lahemaa National Park (Roots et al., 1992). At the beginning (1985–1991), Estonian stations were operated by the Hydrometeorological Institute using the measuring equipment and methods of the former USSR. The overall quality of these data is unknown (Kimmel, 2002).

Since 1994, collection of data on the state of the environment has been budgetary. The Estonian Environmental Research Centre (EERC) has been operating air quality monitoring stations since the same year. EERC was accredited internationally for precipitation analysis in 1998 and for air quality measurements in 2000.

An analysis of air monitoring results in urban and rural areas of Estonia (Kimmel et al., 2002; Pajuste et al., in press) shows a decrease in air pollution levels as a result of economic changes and reduction in emission. The estimation concerning the origin of the pollutants in Estonian background stations was made in the framework of EMEP assessment report (Pajuste et al., in press). From figure 4a it is seen that the direction of air masses with higher SO_2 concentrations refer to the location of measurement stations. At the western border of Estonia (Vilsandi station) higher concentrations are measured from southern and south-western air mass transport directions (Fig. 4a). At Lahemaa station, high concentrations are observable from sectors between NE and SE (Fig. 4b) where big power plants are located. Air masses with low concentration arrive from the north in both stations. The most frequent transport sectors at Estonian stations were the western ones with average concentration of SO_2-S 0.2 $\mu g/m^3$ (Vilsandi) and 0.4 $\mu g/m^3$ (Lahemaa).

Concentration roses of NO_2 median values are almost rounded in the background stations. The concentration roses with the highest 10% of NO_2 concentrations are with a shape similar to SO_2 roses.

At present, Estonian territory is quite well covered by wet deposition measurements (Chapter 2.1). Dry deposition measurements of gases and particles (except for throughfall) are lacking in the Estonian air quality measuring network.

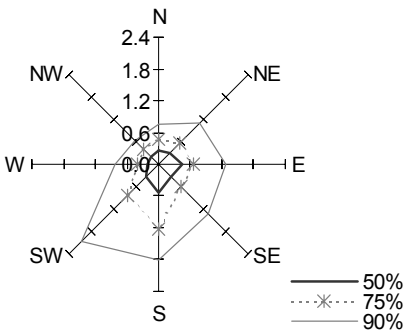

Fig. 4a. SO_2 concentrations (µg S/m^3) in air masses of different origin at Vilsandi station 1994–2001. the median, 75-percentile and 90-percentile.

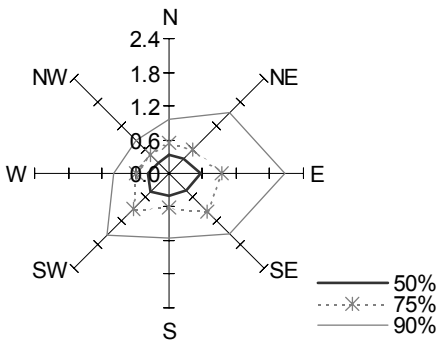

Fig. 4b. SO_2 concentrations (µg S/m^3) in air masses of different origin at Lahemaa station 1994–2001.

1.5. Objectives of this study

The overall aim of this thesis is to give an overview of the deposition levels of air pollutants on the Estonian territory after the regaining of independence in 1991. As such data are collected as part of different national environmental monitoring programmes, no study or programme has covered all of these data. During 1990s remarkable changes in air pollution levels still continued across Europe as a result of a cut in emissions. One of the aims of this study is to compare the changes in Estonia with those reported in the neighbouring countries.

As there is no monitoring of dry deposition in ENEMN, I have used throughfall measurements to quantify dry deposition of SO_4^{2-}, Cl^- and base cations into coniferous forests.

In order to compare deposition of air pollutants with internal cycling of macroelements, I have used litterfall data and a mineralisation experiment at a spruce and pine stand of Saarejärve catchment area. To estimate anthropogenic and natural causes of changes in the stands, nutrient mass balances are calculated.

The specific objectives were:

- to assess the changes and trends of anion and base cation concentrations in the available data of bulk precipitation during the period of 1994–2001;
- to estimate the importance of dry deposition and canopy leaching on formation of throughfall flux;
- to compare throughfall and litterfall as fluxes of internal cycling and atmospheric deposition of nutrients;
- to measure nitrogen mineralisation rate in acid forest soil and to compare the results with other N input fluxes at Saarejärve spruce and pine stands;
- to describe plot and catchment scale input-output budgets of nutrients at Saarejärve;
- to calculate proton budgets in order to identify the acidifying effect of anthropogenic pollution;
- to study data from different monitoring programmes together in order to find out shortages in data collection and methods, which could serve as a basis for optimising the monitoring network and methods in the future.

2. MATERIAL AND METHODS

2.1. Data of monitoring programmes

Data from Estonian National Environmental Monitoring Network (ENEMN) databases for local precipitation network, EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe, co-ordinated by UN/ECE), International Co-operative Programme on Integrated Monitoring (ICP IM) and ICP Forest Level II were used in papers I–IV (Table 1).

Table 1. Summary of ENEMN data and programmes used in the thesis.

Paper	Monitoring programme	No. of stations	Period	Sampling media (sampling/analysis frequency)
I	Local precipitation chemistry network:			
	Northern Estonia	8	1994–2001	BP (daily/monthly)
	Southern Estonia	7	1999–2001	
I	EMEP	2	1994–2001	BP (daily/weekly)
I	ICP Integrated Monitoring	2	1994–2001	BP (biweekly/monthly)
II		2	1995–2002	BP+TF (biweekly/monthly)
III		1	1996–1998	TF+LF+Soil (monthly)
IV		1	1995–2000	BP+TF +LF (monthly/yearly) +SW (monthly) +RW (monthly)
II	ICP Forests	5	1997–2002	BP + TF (monthly)
Total		23 stations		

The Estonian network of precipitation monitoring was started in 1994. The first stations were situated mainly in seaside areas, starting from Vilsandi, Estonia's westernmost island, continuing along Estonia's northern coast up to the industrial area in the North East. As background stations, westerly located Vilsandi, Lahemaa (on northern coast) and Saarejärve catchment area (in eastern Estonia) are part of the international monitoring network. Data collected in these stations is forwarded, within the framework of the Convention on Long-Range Transboundary Air Pollution (CLTRAP), to the databases of EMEP and ICP IM. In 1996 new monitoring sites in North- and South-Estonian coniferous forests were established for ICP Forests Level II network. In 1999 the number of monitoring stations in local precipitation network was increased in the southern region of Estonia. As a result, for the first time in history it is possible to estimate the level of air pollution on most of Estonia's territory on the basis

of a uniform methodology (I). The location of sites belonging to ENEMN is illustrated on Fig. 5.

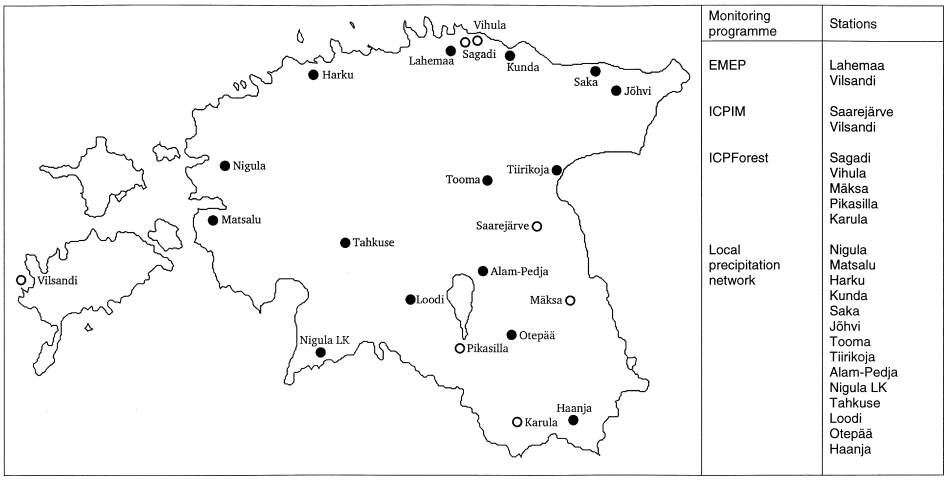

Fig. 5. Location of monitoring stations in 2001 and list of stations in different monitoring programmes (dot for BD sampling, circle for TF and BD sampling sites).

EMEP and local precipitation chemistry network are operated by Estonian Environmental Research Centre (EERC) and Laboratory of Environmental Studies in Tartu. EERC with Institute of Geography at University of Tartu as an expert institute are responsible for ICP IM programme in Estonia. Centre of Forest Protection and Silviculture is responsible for implementing ICP Forest programme. Each institution involved in the respective monitoring subprogramme have followed the methods described in the manuals (ICP IM Manual, 1998; ICP Forests Manual, 1999).

The most intensive monitoring programme has been carried out at Saarejärve forested catchment area (332 ha) (IV). Bulk precipitation in open area, throughfall, stemflow and litterfall were collected from two permanent plots: Scots pine (116-year old) and Norway spruce (85-year old) stand. The pine forest (*Rhodococcum* understorey) is located at an elevation where groundwater lies deep. The spruce stand (*Vaccinium* understorey) is situated lower than the pine stand, near the bottom of a slope where moisture conditions are more favourable. At both stands the parent material is fluvioglacial sand, on which moderately eluviated Haplic Podzols have developed. Soil water samples of the stands were collected from depths of 10 cm under organic horizon and of 40 cm under eluvial horizon. During 1996–1998 N mineralisation was studied in mor humus layer of the forest plots (III).

2.2. Sampling and chemical analyses

2.2.1. Water samples

Precipitation samples in EMEP and local precipitation chemistry network (I) were collected by bulk collectors (20 cm in diameter) placed in an open area at a height of about 120 cm. Samples were collected on a 24-h basis and after sampling collectors were rinsed with distilled water. The water volumes were measured in the field by graduated cylinder. Collected samples were stored in refrigerators and mixed in proportion to the total sample volume for weekly and monthly samples before analysis, as described in the EMEP manual (EMEP, 1996).

In the ICP IM and ICP Forests network, sampling frequencies for precipitation and throughfall measurements were once in a fortnight in summer and once a month in winter. There were 5 to 10 plastic collectors for precipitation with variable sampling area in different sites (Table 1, II). Chemical analysis was performed for pooled monthly samples.

Soil water samples at Saarejärve pine and spruce stands were collected monthly from depths of 10 cm under organic horizon and of 40 cm under eluvial horizon. In both cases six plate lysimeters of 0.1 m^2 (Voll and Roots, 1999) were used for collecting infiltration water.

Runoff water flow was measured daily, water samples were collected and analysed monthly from one subcatchment trench near the permanent sample plots.

Water samples were analysed in the laboratories of EERC in Tallinn and Environmental Studies in Tartu. Both laboratories have continuous quality control programmes and participate regularly in international intercalibration tests.

Major anions (Cl^-, NO_3^-, SO_4^{2-}) in precipitation and runoff water were analysed by ion chromatography. Base cations were determined using atomic absorption spectroscopy or ion chromatography depending on laboratory; pH was measured potentiometrically, and electrical conductivity conductometrically.

2.2.2. Soil and litter samples

At Saarejärve nitrogen mineralisation was studied (III) by incubating samples of mor humus in buried polyethylene bags in situ (Adams et al., 1989; Eno, 1960). Metal soil auger (5.3 cm in diameter) was used for sampling the entire depth of mor humus layer in the pine and spruce stands. Samples were collected from July 1996 till April 1998. The period of incubation was approximately 1 calendar month, except for wintertime when incubation lasted till thawing of

ground (December to April). Each time 2x24 intact soil cores per site were taken. Half of the cores were put undisturbed into individual polyethylene bags and reburied in their original holes. The remaining 24 soil cores were prepared for laboratory analysis. After a month the incubated soil samples were collected, together with new initial samples, and analysed chemically at Tartu Environmental Research Laboratory. The characteristics analysed were the following: pH_{H2O}, NH_4-N, NO_3-N, total N and soil organic matter on a dry soil mass basis. pH of the samples was measured electrometrically at 25ºC after extraction with distilled water (1:4). Concentration of ammonium was measured spectrophotometrically using indophenol in 0.1 M KCl extract (1:20), and nitrate concentration was measured using ion-chromatography. Total nitrogen was measured using the Kjeldahl method. Moisture content of fresh material was measured gravimetrically, after drying sub-samples at 70ºC to constant weight.

Litterfall traps at Saarejärve were funnel-shaped (collecting area 0.5 m^2), equipped with collecting bags made of mesh to prevent water logging and improve aeration. Litter samples were collected monthly but during winter the sampling frequency was dependent on snow cover in littertraps. Air-dry samples were fractionated to needles and the rest, and weighted for bulked samples. The chemical parameters determined were those listed in the IM Manual (ICP IM Manual, 1998).

2.3. Calculations and data handling

2.3.1. Bulk deposition and throughfall

In ENEMN all measuring of wet deposition is done using open, so called bulk, collectors for precipitation and throughfall sampling. This may involve some uncertainties because of water loss and also due to dry deposition into samplers as discussed in paper II. The contribution of dry deposition to bulk collectors in open area may vary between regions and components. In calculations made in Sweden (Lövblad et al., 2000), the mean difference between wet and bulk deposition has been estimated to be approximately 10% in rural sites.

Bulk deposition measurements were assumed to represent the wet deposition because of the absence of true wet deposition measurements in ENEMN. Comparisons with rainfall amounts from official weather stations were made to check consistency of measured rainfall amounts in the local precipitation network.

Monthly deposition values were calculated by multiplying the concentration from collected samples by the corresponding amount of precipitation (in mm). Before the calculation, the concentration values that were below detection limits were replaced by half the value of detection limit (ICP IM Manual, 1998). All the annual mean concentration values are volume-weighted averages. The pH

values were converted to H^+ before calculation of the mean pH value. The monthly values of May–October were used to calculate deposition of growing period, while the dormant period covered results from November till April (II).

Results of average annual depositions (iso-lines) were plotted on a contour map with Surfer software (Version 7.0) using the kriging method of interpolation.

In paper II total deposition of atmospheric pollutants to forest landscapes was estimated. Tree canopies serve as a natural surface and filter for atmospheric pollutants that enter an ecosystem. To estimate the contribution of dry deposition to throughfall flux, leaching and uptake of elements should be taken into account as precipitation passes through the canopy. Thereby, total deposition of elements may be bigger or smaller depending on prevailing processes. From studies comparing throughfall with deposition measurements, it is generally concluded that canopy exchange of sodium, chloride and sulphur is negligible.

Estimation of total atmospheric input of base cations was based on the canopy budget model developed by Ulrich (1983). In the model Na^+ is assumed not to be influenced by canopy exchange. Net throughfall flux (NTF) was calculated by subtracting bulk deposition (BD) from throughfall (TF) flux. NTF is equal to dry deposition (DD) if leaching or uptake does not take place, which is the case for Na^+. Other base cations captured by canopy are assumed to be deposited as particles, and, the size of these particles in atmosphere is assumed to be the same as that of Na-containing particles. Dry deposition of these cations can be calculated according to Eq. 1, and canopy leaching by Eq. 2.

$$DD_x=((TF_{Na}- BD_{Na})/BD_{Na})*BD_x \qquad x=Mg^{2+}, Ca^{2+}, K^+ \qquad [1]$$

$$CL = TF_x - BD_x - DD_x \qquad [2]$$

Dry-deposited H+ was estimated according to Mulder et al. (1987) as:

$$DD_{(H+)}=TF_{(SO42-)} -BD_{(SO42-)} + TF_{(NO3-)} -BD_{(NO3-)} + BD_{(NH4+)} -TF_{(NH4+)} \qquad [3]$$

where DD, TF, BD and CL denote dry deposition, throughfall, bulk deposition and canopy leaching flux of elements, respectively.

For calculating total deposition, bulk and dry deposition of elements were summed.

It should be taken into account that NTF values could be significantly affected by deposition of an ion that is left to the canopy from the previous event, as well as resulting from water retention after the given event (Houle et al., 1999). Thereby, it was preferred to calculate the mean values for dormant season for a continuos 6-month period, rather than following the boundaries of a calendar year.

Sea salt contribution to SO_4, Mg, K and Ca deposition was estimated from the assumption that all sodium is of sea-salt origin. However, this assumption is only partly correct because there was an excess of Na if Cl was used for checking for sea salt contribution.

2.3.2. Mineralisation

Nitrogen net mineralisation was calculated as the difference between mineral N (NH_4-N and NO_3-N) content of the incubated cores and that of the fresh samples taken at the beginning of the incubation period (Eq. 4–6).

$$\Delta NH_4^+ - N = NH_4^+ - N_{a(t+1)} - NH_4^+ - N_{i(t)} \quad [4]$$

$$\Delta NO_3^- - N = NO_3^- - N_{a(t+1)} - NO_3^- - N_{i(t)} \quad [5]$$

$$N_m = \Delta NH_4^+ - N + \Delta NO_3^- - N \quad [6]$$

$NH_4^+ - N_{i(t)}$ and $NO_3^- - N_{i(t)}$ — ammonium and nitrate nitrogen content of mor humus at the beginning of incubation experiment
$NH_4^+ - N_{a(t+1)}$ and $NO_3^- - N_{a(t+1)}$ — ammonium and nitrate nitrogen content of incubated samples
$\Delta NH_4^+ - N$=net ammonification
$\Delta NO_3^- - N$= net nitrification
N_m = net mineralisation of nitrogen

Uptake by trees and vegetation was calculated as the difference between mineral N content of the incubated cores at the end of the incubation period and that of the surrounding unincubated mor humus. Similar calculations have been used by Nadelhoffer et al. (1984), Raison et al. (1987) and Adams et al. (1989).

$$\Delta NH_4^+ - N_u = NH_4^+ - N_{a(t+1)} - NH_4^+ - N_{i(t+1)} \quad [7]$$

$$\Delta NO_3^- - N_u = NO_3^- - N_{a(t+1)} - NO_3^- - N_{i(t+1)} \quad [8]$$

$$N_u = NH_4^+ - N_u + NO_3^- - N_u \quad [9]$$

$\Delta NH_4^+ - N_u$ and $\Delta NO_3^- - N_u$ — ammonium and nitrate nitrogen assimilated during incubation period
$NH_4^+ - N_{i(t+1)}$ and $NO_3^- - N_{i(t+1)}$ — ammonium and nitrate nitrogen content of surrounding mor humus at the end of incubation experiment
N_u=net assimilation of mineral nitrogen

To calculate annual net assimilation of mineral nitrogen, net mineralisation (N_m), deposition (N_{dep}) and soil water nitrogen flux (N_l) were used:

$$N_u = N_m + N_{dep} - N_l \quad [10]$$

2.3.3. Nutrient budgets

Annual input into stands was calculated using 6-year average amounts of macroelements in throughfall, stemflow and litter. Stand consumption was calculated as the difference between substance input by forest precipitation and litter, and output through leaching into soil water. The plot-scale annual output was calculated using soil water samples from depths of 10 cm under mor humus and of 40 cm under eluvial horizon, averaged over 6 years in order to reduce yearly variability.

To calculate yearly input on sub-catchment level, the forest precipitation amounts were weighted by the area of these forests (pine and spruce) in the sub-catchment. For the rest of the catchment area, data on bulk deposition were used. Catchment output was calculated from RW concentrations, catchment runoff and area of the catchment.

The output flux of organic anions was calculated as the sum of cations (H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+) minus the sum of anions (SO_4^{2-}, NO_3^-, HCO_3^-, Cl^-).

Weathering (W) of base cations was estimated using the following formula:

$$W=O–I+\Delta B \qquad [11]$$

where O is output by runoff, I stands for input to the forest floor and ΔB denotes base cation accumulation in tree biomass.

For calculation of proton budgets, main proton sources and sinks (Nilsson, 1985; van Breemen et al., 1985) were converted to a common unit (keq ha^{-1}) and were then summed separately.

2.4. Statistical analysis

The basic data in paper I for trend analysis were the annual volume-weighted concentrations of precipitation components. The nonparametric Mann-Kendall test was used to estimate significance level ($p<0.05$) of the trends in annual values. The slope of a linear trend was estimated with the nonparametric Sen's method, and the median of the annual change was calculated (Salmi et al., 2002). The Spearman's nonparametric correlation analysis was used to assess covariance of monthly mean concentrations of precipitation components between stations. The statistical significance is given by the p-value. A significance level of $p<0.05$ has been chosen to represent a statistically significant difference between data sets.

In paper II weighted yearly and seasonal precipitation values were used. Beacause of non-normal distribution, non-parametric statistics were used: Sign test for testing differences between mean annual BD and TF fluxes, Mann-Whitney U-test for testing differences between 6-month-averaged growing and

dormant period, Spearman's rank correlation for differences between BD and TF deposition values, and Mann-Kendall test for detecting significance of annual trends ($p<0.05$).

Occurrence of net mineralisation, in paper III, was assessed as a statistically significant difference between the initial and final concentration of mineral nitrogen in mor humus. In order to establish seasonal differences, and those between the two different stands, methods of correlation- and regression analysis, and multiple comparison of means (Tukey's test) were used. In accordraama1dance with statistical requirements, regression was based on log-transformed data.

3. RESULTS

3.1. Trends in bulk deposition of air pollutants (I, II)

Volume-weighted mean concentrations of H^+, Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, NO_3^- and Cl^- in bulk precipitation are presented in Table 2 (I). As data of the 8-year study period show decreasing trends, mean values were calculated separately for two periods: 1994–1997 and 1998–2001.

Acidic anions. At all stations the prevailing anion in bulk precipitation was SO_4^{2-} (Fig. 6), which formed more than 50% of anionic composition on an equivalent basis (Vilsandi was an exception with only 39%). Anionic proportion of Cl^- and NO_3^- varied between 21%–39% and 16%–25%, respectively, on an equivalent basis. Sea salt correction (ratio between sodium and sulphate in seawater) shows that anthropogenic sulphur in precipitation constitutes the major fraction (95%) of sulphate in most stations. In two westward stations (Vilsandi and Nigula), the marine fraction of sulphate reached 10% on average.

Partly different data sets were used in papers I and II for bulk deposition calculations. On Fig. 7. stations (with data series at least from 1997) have been roughly grouped according to location. Over the last three years (2000–2002) the highest annual mean concentration (1.5 mg S l^{-1}) was measured in the north-eastern stations. Elevated concentration of sulphur was also observable in the eastern stations and in the vicinity of Tallinn (Harku station). The mean annual deposition of SO_4-S ranged from 2.5 kg ha^{-1} at Lahemaa to 13.4 kg ha^{-1} at Jõhvi for the same period. Updated mean sulphur deposition loads for the period of 2000–2002 with data from all the 23 stations included are presented on Figure 8.

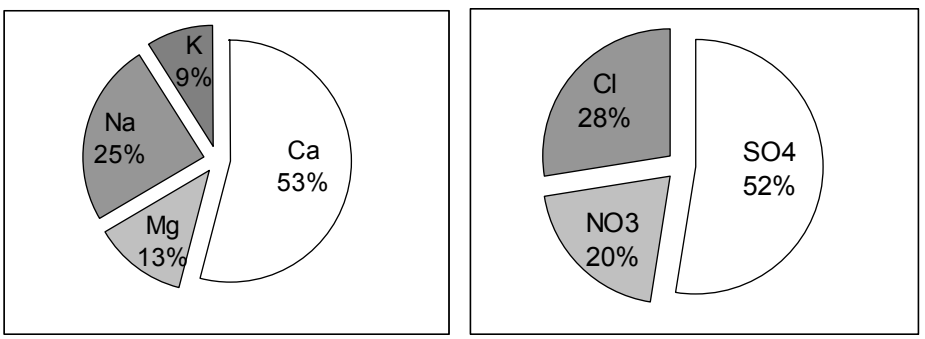

Fig. 6. Share of cations and anions in bulk precipitation in equivalents.

The negative linear trend for sulphate concentrations (Table 1, I) was statistically significant at all stations for the period 1994–2001. The slope estimates i.e. change per year for SO_4^{2-} varied from –5.7 mg l^{-1} at Kunda to –0.24 mg l^{-1} at Vilsandi. At most stations (except for Harku), the decline of chloride was significant as well, the slope estimates varied from –1.3 mg l^{-1} at Kunda to –0.089 mg l^{-1} at Tooma. The correlation of monthly concentrations of both anions was significant, the highest correlations were found between NE stations (r=0.69–0.78).

Throughout the study period NO_3^- was the most stable anion — its annual mean concentration shows a statistically significant decreasing trend at Lahemaa station only. The mean annual nitrate concentration varied between 0.3–0.6 mg N l^{-1} and the NO_3-N load was, on average, 1.6–4.0 kg ha^{-1} at different stations (Table 3, I).

Cations. Deposition of base cations neutralises the acidic deposition at majority of the stations. Figure 7 shows that precipitation was acidic at the remote island of Vilsandi (corresponding pH 4.7) and in rural areas at Lahemaa and Tooma (corresponding pH 4.8). The annual mean pH of precipitation did not change in most cases during the monitoring period. The only statistically significant decreasing trend was estimated at Kunda, where annual mean pH of precipitation dropped from 7.5 to 6.7. Average pH values for the period 2000–2002 are presented in Figure 8.

The share of cations in equivalents decreases in the order Ca^{2+}>Na^+>Mg^{2+}> K^+ in bulk deposition (Fig. 6). An exception was Vilsandi where, due to its location, the share of Na^+ was larger (40%) than that of Ca^{2+} (32%). The non-marine fraction of base cations was calculated using Na as a tracer element. The average sea salt fractions of deposited Ca^{2+}, K and Mg varied between 1%–4% (7% at Vilsandi), 3%–14% and 19%–77%, respectively, at different stations.

The mean annual concentration of Ca^{2+} has decreased 1.4–4.7 times during the study period, but the trend was statistically significant only at 3 out of 10 stations. The mean annual Mg^{2+} and K^+ concentrations have decreased 4.3 and 1.7 times, respectively. Kunda was not taken into account as the concentration levels there were higher than the national average (Table 2, I).

The decreasing trends of annual mean concentrations of summed base cations (the change per year varied from –0.44 meq l^{-1} at Kunda to –0.017 meq l^{-1} at Lahemaa) were statistically significant at 7 stations out of 10 (Table 1, I). The deposition of summed base cations in bulk precipitation decreased about 2 times at NE stations (at Kunda 3.9 times) and about 1.5 times at all others stations during the study period. The average annual bulk deposition of base cations varied between the level of 0.4 keq ha^{-1} in the west, and the highest levels that fluctuated around 1–1.6 keq ha^{-1} at E and NE stations (Table 3, I). The updated and sea-salt-corrected base cation loads are shown in Figure 8 where values from all the 23 stations are recalculated for the period 2000–2002.

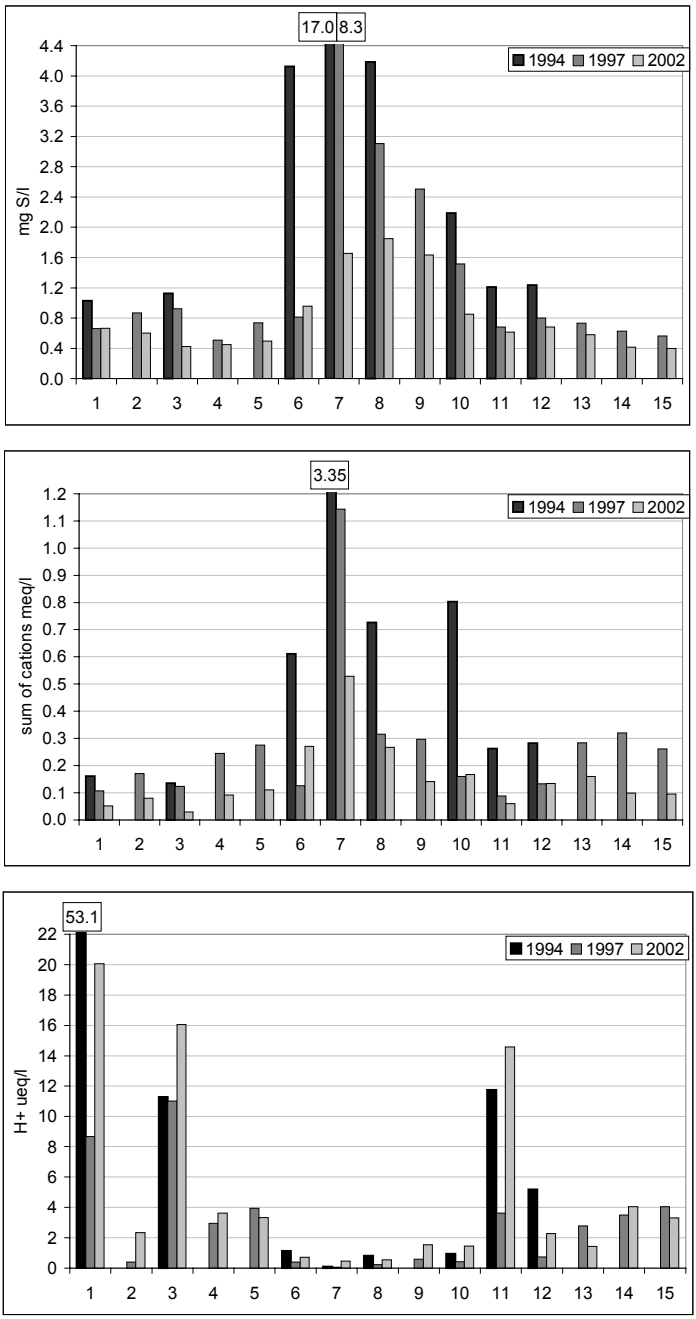

Fig. 7. Regional distribution of annual mean concentrations of sulphate, sum of cations and hydrogen in bulk precipitation. Location and numbering of stations is the following: west 1 – Vilsandi, 2 – Nigula; north 3 – Lahemaa, 4 – Sagadi, 5 – Vihula, 6 – Harku; northeast 7 – Kunda, 8 – Jõhvi, 9 – Saka; east 10 – Tiirikoja, 11 – Tooma, 12 – Saarejärve, 13 – Mäksa; south 14 – Pikasilla, 15 – Karula.

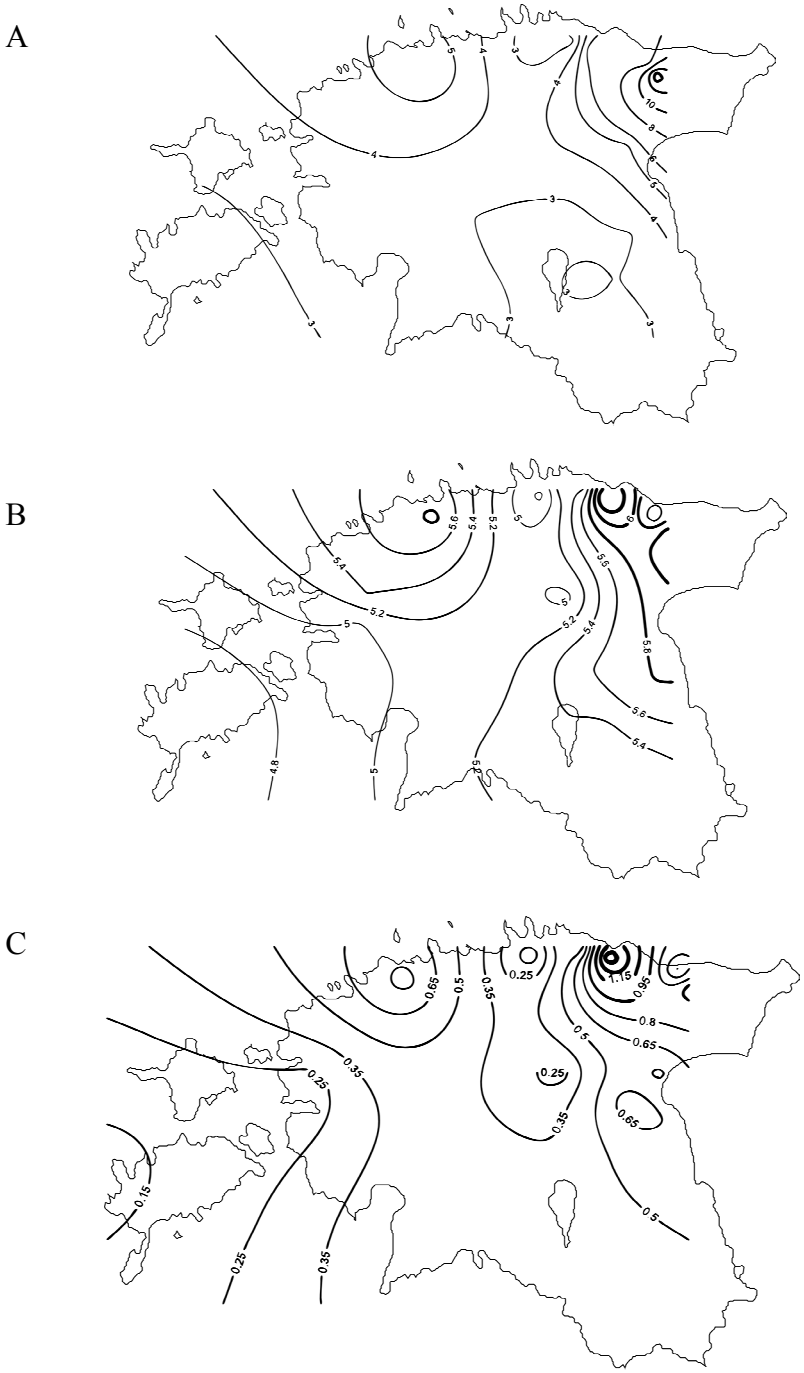

Fig. 8. Contour maps showing isolines for: A) deposition of sulphur (kg ha^{-1}), B) pH of precipitation, and C) deposition of summed cations (keq ha^{-1}) for period 2000-2002.

Correlations of summed cations at most stations were higher with the NE stations than with any other stations. Correlation between summed cations and sulphate was stronger at the NE stations (r=0.75–0.85) and weaker at the E stations (r=0.47–0.49). Figure 6 (I) presents the ratio between annual average sulphate concentrations and summed cations at the monitoring stations during the study period. The average ratio of sulphate and summed cations varied between 1.5–3.0, except for near Kunda cement factory where the ratio was around 5.

Average annual bulk deposition of ammonium (1–4.6 kg N ha^{-1}) was about the same range as for nitrate. Only a weak decreasing tendency could be observed in annual mean concentrations of ammonium in background stations (Pajuste et al., in press).

3.2. Interaction of atmospheric deposition with coniferous canopies

Sulphate and chloride. Concentrations and deposition loads of sulphate and chloride were significantly higher under canopies compared to bulk precipitation (Figure 9.). Average deposition of SO_4^{2-} under canopies was significantly higher for dormant period (1.65±0.64 mg S m^{-2} day^{-1}) than for growing period (1.24±0.44 mg S m^{-2}), while bulk deposition of S was significantly higher during growing season (1.07±0.38 mg S m^{-2}). Assuming that SO_4^{2-} behaves conservatively in coniferous canopies (at least during winter), the enrichment of TF was due to dry deposition of sulphur. Estimated share of dry deposition from total deposition was 1.5–4 times higher for dormant period compared to growing period.

TF enrichment with sulphur can be used as a measure characterising filtering efficiency of forest canopy. The filtering of sulphur was more efficient in Saarejärve and Mäksa spruce stands (TF/BD=2.2 and 2.0, respectively) than in the pine stands (TF/BD varied from 1.4 to 1.8). The higher ratio indicates a larger sampling area for dry deposition in spruce stand compared to pine stand.

Annual total deposition of SO_4^{2-} under canopies was 5.19 (±1.0) kg S ha^{-1} as an average for the period 1997–2002. The TF flux of S decreased significantly from 10.9 (±4.9) kg ha^{-1} in 1995 to 3.9 (±1.6) kg ha^{-1} in 2002, the respective values for BD flux of S were 6.1 (±1.7) kg ha^{-1} in 1995 and 2.7 (±0.3) kg ha^{-1} in 2002.

Chloride is also considered to behave conservatively in canopies, therefore difference in TF (average 7.7 kg ha^{-1}) and BD (average 5.5 kg ha^{-1}) fluxes is caused by the wash-off of dry deposition that has accumulated in canopies between rainfall events. The annual throughfall enrichment with Cl^- reached an exceptionally high value (27 kg ha^{-1}) in Vilsandi, indicating high interception of sea-borne particles. Due to marine influence, the results from this site are not used for calculations of mean values, and are treated separately.

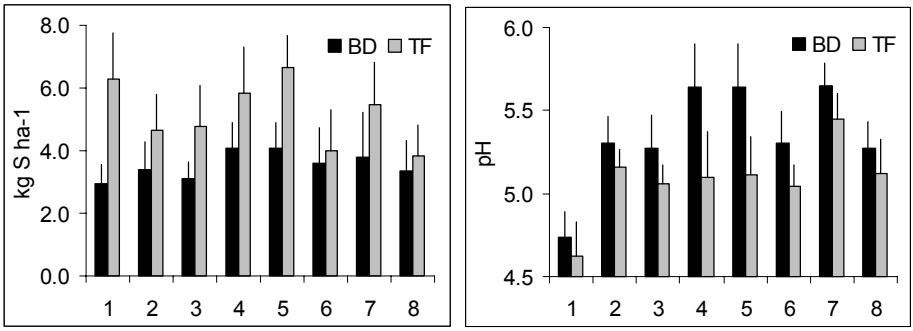

Fig. 9. Annual average SO_4-S deposition (kg ha^{-1}) and pH of precipitation (BD) and throughfall (TF) in various coniferous sites (1 – Vilsandi pine stand, 2 – Sagadi pine stand, 3 – Vihula pine stand 4 – Pikasilla pine stand, 5 – Mäksa spruce stand, 6 – Karula pine stand, 7 – Saarejärve spruce stand, 8 Saarejärve pine stand).

Assuming that sea salt is the dominant source of Cl as well as Na, their ratio should resemble the ion ratio in seawater (1.166). Weighted mean Cl:Na ratios on the equivalent basis in bulk precipitation and throughfall were higher than could be predicted from sea water. This could indicate Cl deposition from additional sources (oil shale burning in our case (Treier et al., in press)). The highest Cl:Na ratio was measured at Mäksa and the lowest at Saarejärve bulk precipitation. In both stands the Cl:Na ratio in TF was higher than that in BD. Thereby, it can be concluded that interception of Cl^- is higher than that of Na^+. There were no differences in enrichment factors between spruce and pine stands. Therefore, the higher enrichment by Cl^- indicates sea salt influence rather than canopy filtering efficiency.

Base cations. At most sites weighted mean concentrations and deposition of base cations under canopies were, on average, higher than that of open area. However, there were exceptions, which were assumed to have been caused by uncertainties in wet deposition estimates. Generally, TF enrichment with base cations increased in the order Mg<Na<Ca<K.

The significant increase of cation concentrations in TF may be attributable to two sources: leaching or exchange processes and washing off of dry deposition.

Assuming there is no leaching of Na^+ from canopy, the NTF flux corresponds to dry deposition amount of sodium. The average share of Na dry deposition varied from 3 to 32% of TF flux (except for Vilsandi where it was 77%). On the basis of the Na-ratio method (Eq. 1 and 2), the average dry deposition of base cations from TF flux was in the range of 2%–24%, 2%–30% and 1%–15% for Mg^{2+}, Ca^{2+} and K^+, respectively.

Average leaching of Mg^{2+}, Ca^{2+} and K^+ was estimated to be 8%–28%, 6%–31% and 40%–73% of TF flux, respectively (Figure 10). The share of dry

deposition and leaching as sources for Ca and Mg in TF flux were proportional. Leaching was the dominant process for TF enrichment by potassium. This suggestion was also supported by correlation analysis. Contrary to other constituents, the correlations of mean annual potassium fluxes of BD and TF were not statistically significant. Furthermore, K^+ was the only ion in TF that did not show any correlation with BD of other ions.

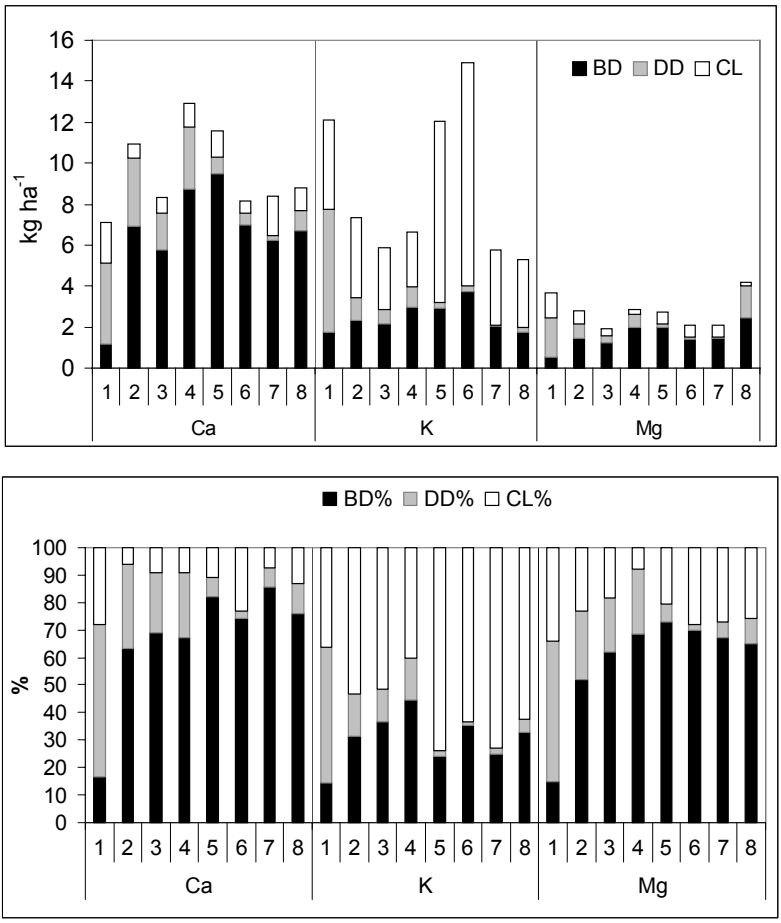

Fig. 10. Calculated annual average dry deposition (DD) and canopy leaching (CL) in kg $ha^{-1,}$ and their share (%) of throughfall deposition of base cations in coniferous stands: 1 – Vilsandi pine stand, 2 – Sagadi pine stand, 3 – Vihula pine stand, 4 – Pikasilla pine stand, 5 – Mäksa spruce stand, 6 – Karula pine stand, 7 – Saarejärve spruce stand, 8 – Saarejärve pine stand.

Leaching of base cations occurred in growing as well as during dormant period.

Comparison of wet deposition of base cations at Lahemaa and bulk deposition at Sagadi and Vihula supports the hypothesis that calculated dry deposition may be underestimated. Thus, average proportions of base cations leaching from the TF flux at Sagadi and Vihula should be 51%, 42% and 74% for Mg, Ca and K, respectively. Corresponding values of canopy leaching at Sagadi and Vihula pine stands are 1.1 kg ha^{-1}, 3.6 kg ha^{-1} and 4.7 kg ha^{-1} for Mg, Ca and K, respectively. Total base cation deposition can be calculated taking into account the proportion of canopy leaching from throughfall data. The total base cation deposition to these pine forests was 3 times higher than bulk deposition, and the corresponding values are 0.9 kg ha^{-1}, 4.8 kg ha^{-1} and 1.6 kg ha^{-1} for Mg, Ca and K, respectively, as an average for 2000–2002.

Hydrogen. Mean annual H^+ flux, calculated as an average of all stands, was significantly higher in TF (37.9±13.3 eq ha^{-1}) than in BD (27.0±11.3 eq ha^{-1}). The weighted annual mean pH values of bulk precipitation and TF are shown on Figure 9. Deposition of H^+ was significantly higher during dormant season in both fluxes (BD as well as TF) compared to growing season.

Dry deposition of H+ (calculated from Eq. 3) formed the main part of total deposition flux of hydrogen, BD of hydrogen constituted 6%–23%. DD flux of hydrogen, calculated from this equation, was on average 7 times higher than TF flux indicating consumption of H+ in canopies.

Nitrogen. Average annual bulk deposition of inorganic nitrogen was 5.2 kg ha^{-1}, of which 1.9 (±0.4) kg N ha^{-1} was deposited as nitrate and 3.4 (±2.3) kg N ha^{-1} as ammonium.

Throughfall flux of nitrate varied between 1.6–2.6 kg N ha^{-1} y^{-1} as an average for 1997–2002. Negative NTF indicates removal of NO_3-N by canopy during growing season, which on average was 24% of BD flux. During dormant period the TF flux of NO_3-N in pine stands was 30% higher than the BD flux. In spruce stands — Mäksa and Saarejärve, the retention of NO_3-N by canopies was 16% and 20% of BD flux, respectively, even during dormant period.

Average loads of ammonium under canopies varied between 0.9–3.2 kg N ha^{-1} on a whole-year basis, which was about 65% of BD. The average ammonium concentrations and loads under canopies were higher in growing season (0.89±0.46 mg N m^{-2} day^{-1}) compared to dormant season (0.32±0.12 mg N m^{-2}), but the differences between seasons in canopy retention of ammonium were not significant.

3.3. Nitrogen mineralisation and main N fluxes in spruce and pine stands

Seasonal fluctuation of ammonium concentration in mor humus. Ammonium was the dominant form of mineral nitrogen in mor humus of spruce and pine stands at Saarejärve catchment. Mean ammonium nitrogen concentration in mor humus varied between 6.8 and 55.8 μg N g^{-1} for the spruce and between 5.2 and 79.6 μg N g^{-1} for the pine stand. In both stands, the highest concentration of NH_4-N was measured in spring when mor humus was still unthawed. The concentration of ammonium nitrogen in mor humus during vegetation period was substantially lower, being the lowest in September and October. Thereafter, the ammonium concentration started to increase, probably as a result of decreasing plant uptake (Figure 2, III).

Rate of ammonification. Net ammonification was measurable all year round, including winter period (December–April) (Figure 3, III). The weighted mean ammonification rates were 0.54 and 0.59 μg N g^{-1} day^{-1} for the spruce and pine stands, respectively. Net ammonification under the pine and spruce stands was the greatest in August in both (1996 and 1997) summers when the calculated rate was higher in the pine (2.13±0.22 μg N g^{-1} day^{-1}) than in the spruce stand (1.39±0.19 μg N g^{-1} day^{-1}). In the spruce stand, the second peak of netmineralisation was in May, in the pine stand it occurred a month later — in June, 1997 (Figure 3, III).

Nitrification. NO_3-N content of mor humus varied between 0.2 and 5.8 μg N g^{-1}, which was considerably lower than that of NH_4-N for both sample plots. As a rule, the NO_3-N concentration of incubated samples did not differ significantly from the initial sample, or was lower than the original concentration indicating denitrification or immobilisation of nitrate. During the experimental period of the present study, net nitrification was significant at two of the thirteen incubation periods. These periods did not coincide on the two sample plots, and it is difficult to find any consistent pattern of NO_3 turnover.

Annual net mineralisation and N fluxes. Nitrogen uptake from soil and N release in litter decomposition are both important stages in biological cycling of nitrogen.

The annual mean net mineralisation was 29.24 kg N ha^{-1} in the spruce and 23.58 kg N ha^{-1} in the pine stand. The nitrogen released during mineralisation formed the main nitrogen flux for uptake by plants (Table 3, III).

Above-ground litterfall contained 36 and 34 kg N ha^{-1} yr^{-1} for the spruce and pine stands, respectively. Quantity of needles and that of the remaining fraction of litter were approximately the same, while N content of non-needle litter was higher (6.3–9.7 g kg^{-1} and 7.3–11.9 g kg^{-1} for the pine and spruce

stands, respectively) than that of needle litter (5.7–5.9 g kg^{-1} and 7.8–8.1 g kg^{-1} for the pine and spruce stands, respectively). Thereby, input of N by non-needle litter was the most important N supply — 23.3 kg N $ha^{-1}yr^{-1}$ and 24.2 kg N ha^{-1} yr^{-1} in the spruce and pine stands, respectively (Table 3, III).

N retranslocation was calculated as the difference between N in current year needles and litter needles. About 48% and 60% of N in current year needles of the spruce and pine stands, respectively, were retranslocated from senescing needles. In the pine stand the amount of annually retranslocating N (14.9 kg N $ha^{-1}yr^{-1}$) was greater than the amount of N supplied by the shed needles part of litter (9.8 kg N $ha^{-1}yr^{-1}$) (Table 3, III). The amount of N available for the annual production of above-ground biomass in a stand was calculated as the sum of N released by net mineralisation, retranslocation and deposition. As a result, the annual supply of N was estimated to be 42 kg ha^{-1} in the spruce and 43 kg ha^{-1} in the pine stand.

3.4. Input-output of macro-elements in catchment

Plot-scale nutrient balance. Input (precipitation+litterfall) and output (soil percolation water) fluxes for the pine and spruce stand at Saarejärve catchment area are illustrated in Figure 11 (data in Tables 2 and 3, IV). The long-term (1995-2000) annual balances were positive for all nutrients: total deposition contained more nutrients than loss to leachate from mineral soil. Deposited N-compounds and ammonium released during mineralisation was efficiently removed by vegetation as can be seen from very low output values. As there was no net nitrification (III), only input from TF is indicated for nitrate. Atmospheric deposition (TF+SF) of base cations exceeded that of litterfall, even if canopy leaching is taken into account (II). An exception was potassium, which is characterised by intensive internal cycling (CL+LF fluxes). Chloride input was not available from LF flux, and Al and Mg were not measured from atmospheric deposition.

Buffering of soil acidity was observed as an increase in the pH and alkali concentration of soil water at the depth of 40 cm as compared to that of a 10-cm horizon. According to calculations, the most important process with respect to acidification of soil was accumulation of base cations into biomass (80% of proton production in the pine and 65% in the spruce stand). The most important neutralising process seems to be anion retention. In proton consumption sulphate retention has the decisive role (68% in the pine and 78% in the spruce stand) (Tables 4–5, IV).

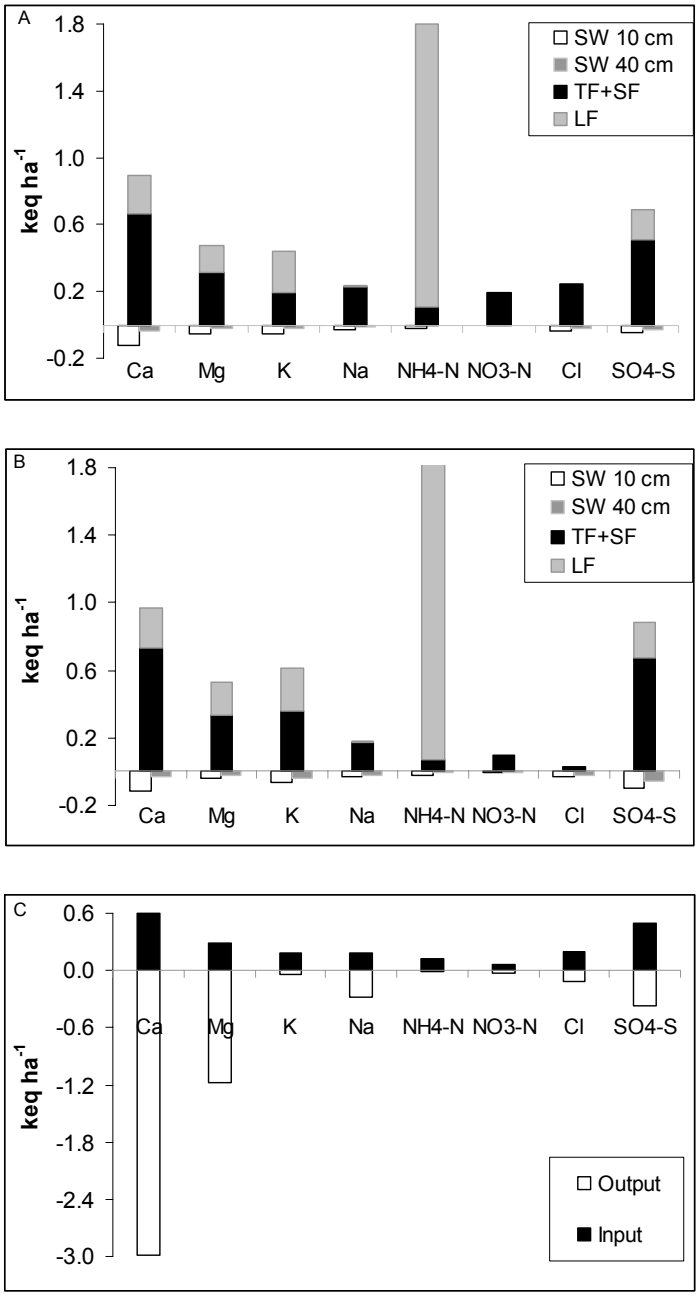

Fig. 11. Six year average (1995–2000) annual input-output budgets for: A) pine plot, B) spruce plot, and C) Saarejärve catchment area (keq ha^{-1}).

Catchment-scale budget. On the catchment scale, two distinct groups of ions were identified: those the annual deposition fluxes of which were less than the runoff fluxes (i.e. Na+, Ca^{2+}, Mg^{2+}, HCO_3^- and organic anions), and those with deposition fluxes greater than runoff (i.e., NH4+, NO_3^-, SO_4^{2-}, Cl^- and K^+). Base cation output in the drainage water was essentially higher than the deposition (Figure 11), reflecting high weathering capacity of the soil. A markedly higher calcium concentrations in the runoff water, as compared to that of soil water, is presumably the result of the weathering of carbonates from the soil parent material (fluvioglacial sand).

The proton budget (Table 6, IV) shows that base cation weathering+ exchange is the main process of proton consumption. The budget indicates high contribution from Ca+Mg weathering reactions and great importance of internal production of acidity due to the dissociation of carbonic acid that is characteristic to most natural systems.

At the subcatchment level, a distinct change in input-output balance of sulphate during 1995–2000 was apparent (Fig. 4, IV). The decrease in SO_4-S deposition since 1997 was not followed by a similar decrease of SO_4-S in runoff water. In autumn 1999, after a dry summer, the concentration of SO_4-S in runoff increased in spite of a low deposition level. In 1999 and 2000 runoff sulphate outputs exceeded inputs indicating a release from the catchment soils. Considering sulphate retention and leaching year by year, an evident trend of decrease in sulphate loads is noticeable in the last three years, so that the previous 6 kg per ha retention in soil and biomass has been replaced by desorbtion, mineralisation and leaching as the prevailing processes.

4. DISCUSSION

4.1. Atmospheric deposition levels and trends

Partly different data sets were used in papers I and II for wet (bulk) deposition calculations. Only data from two IM sites (Vilsandi and Saarejärve) were represented in both studies. However, as can be seen from deposition figures (Figure 8 and Treier et al., in press), this does not change the overall picture of the deposition pattern. The deposition loads of sulphur and base cations are significantly higher in NE region of Estonia.

The main anion in both BP and TF was sulphate as have been shown by earlier studies (Bredemeier, 1988; Rothe, 2002), except for maritime conditions (Blood et al., 1989).

Deposition of sulphate is a result of local emissions combined with long-range transported oxidised sulphur compounds. In the beginning of 1990s approximately one third of sulphur deposited on the area of Estonian was of domestic origin (Roots and Kört, 1996). The average deposition loads were 14 kg ha^{-1} and 12.6 kg ha^{-1} as estimated in 1988–1989 by Frey et al. (1991), and EMEP model calculations (Tuovinen et al., 1994) for 1988, respectively. Recent calculations based on the Unified EMEP model (Tarrason et al., 2003) refer to Poland (17%), Estonia's domestic share (12%) and international shipping on the Baltic sea (8%) as the three largest contributors to S deposition in Estonia. Contribution-weighted decline of SO_2 emissions from main emitter areas has been about 40% during 1994–2001. Reduction in the domestic SO_2 emissions has been the same. The effect of decreased emissions is not well expressed in background SO_2 concentrations, which is probably due to relatively short time series (Pajuste et al., in press), while it is reflected in deposition loads of SO_4^{-2}. The bulk deposition of anthropogenic sulphur has decreased by 50% compared to the 1994 level at background stations. Comparisons of S loads at the remote Vilsandi Island with those at N, NE and E stations support the suggestion that, at least till 1997, about one fourth of Estonia's territory (see Tallinn-Jõgeva-Tartu line on the map) was mostly influenced by locally originating oxidised sulphur (SO_4^{2-}) (Figure 3 and Table 3 in paper I). Average deposition load of SO_4–S in ENEMN for 2000–2002 ranged from 2.6 kg ha^{-1} at background stations to 13.4 kg ha^{-1} at NE (measured about 50km from TPPs). Most of it was anthropogenic, only 5% was of marine origin (except for the western stations). EMEP model-estimated average deposition of sulphur in Estonia was 5.3 kg ha^{-1} for 2000. The relatively high estimate of the mean deposition derived from the model could be the result of including NE area where the deposition is not regularly measured in the framework of ENEMN. Results obtained by Paalme et al. (1990) and Kaasik et al. (2000) showed 10–20 times higher deposition loads in the vicinity of TPPs compared to remote sites.

TF measurements indicated an additional (dry) deposition of sulphur into forests — the deposition was 1.5–2.2 times higher compared to bulk deposition of sulphate in open area. Mean total deposition of sulphur at Saarejärve spruce stand has been 4.1 kg ha^{-1} during 1997–2001, compared to 45 kg ha^{-1} in 1989 (Frey and Palo, 1993) at a nearby-located spruce stand. The enrichment factor was approximately 2.1 times in both cases.

During 1997–2002 the average deposition load of SO_4^{2-} in dormant period (1.65±0.64 mg S m^{-2} day^{-1}) was higher compared to TF flux in growing season (1.24±0.44 mg S m^{-2} day^{-1}). Using samples of permanent snow cover, Paalme et al. (1990) measured the total deposition of sulphate to be 5.5 mg S m^{-2} day^{-1} near Narva and Kohtla-Järve in 1986. Such high total sulphate deposition levels (5.6 mg S m^{-2} day^{-1}) were still measured in snow samples collected near the TPPs in winter of 1999 (Kaasik et al., 2000).

Another anion derived from oil shale burning is chloride, which can be transported as particles of $CaCl_2$ (Paalme et al., 1990). Statistically significant correlations were found between sulphate, chloride and sum of base cations. TF enrichment by chloride (1.5±0.3 times) indicated also significant dry deposition of chloride into forests.

Decrease of base cation mean concentrations in precipitation is in good accordance with emission data of solid particles from stationary sources, which have decreased 2.9 times (161 500 t in 1994 and 56 400 t in 2001). During the monitoring period there was a 1.9-fold decrease in fly ash emissions from the two biggest power plants (85 600 t in 1994 and 45 000 t in 2001). Moreover, in 1997 new particle emission controls were installed at the cement factory in Kunda. As a result, emission of solid particles decreased 8 times in 1997–2001.

As model calculations by Sofiev et al. (2003) have shown, about 30% of local annual alkaline emissions is deposited to Estonia and the Gulf of Finland area. In the deposition map of sea-salt corrected summed base cations (Figure 8), the high deposition area is clearly distinguishable. Taking into account the natural background level, the high-deposition area, affected by local sources (TPP), is about 200x200 km^2 (Sofiev et al., 2003). Thereby, the influence of Estonian emissions is reflected in Finnish monitoring stations (Kulmala et al., 1998; Ruoho-Airola et al., 2003; Ruoho-Airola et al., 2004). Time series of annual mean concentrations of SO_4-S, Ca^{2+} Mg^{2+} and K^+ at a Finnish south-eastern station (e.g. Virolahti) showed comparable significant decreasing trends in 1980–2000.

The relatively high deposition loads of base cations (up to 1.6 keq ha^{-1} at E and NE Estonia) neutralize the acidity of precipitations. Beside the NE area, elevated anthropogenic cation loads and alkaline precipitation were also measured in the vicinity of Tallinn. Between those two areas there is a region with lower pH values starting from Lahemaa and extending to W and SW of Estonia. Comparing two different regions – the North and South of Estonia with critical loads of acid deposition, it can be said that the acid deposition in NE Estonia is

fully buffered. In Southern Estonia the actual base cation deposition corresponds to the natural background level and the deposition of acidifying compounds may reach or exceed the critical loads in some more sensitive areas (Oja, 2000).

4.2. Base cation leaching and litterfall as parts of nutrient input fluxes

In throughfall deposition a part of base cation fluxes originate from canopy leaching or ion exchange. Thereby, such additions represent nutrient recycling rather than input to stand (Swank, 1984). In order to differentiate between these processes, Na-ratio method was used. This method assumes correct measurement of wet depositions. Low TF enrichment coefficients obtained for Na deposition may indicate that improvement of the sampling technique is needed as the basis for dry deposition calculations for other base cations. Comparison of results from daily sampling supported this suggestion but no attempt was made to correct bulk deposition for the probable contribution from dry deposition as parallel measurements are currently in progress. According to calculations based on daily sampling, the fraction of dry deposition to total deposition of base cations could reach and exceed 60%. Ferm and Hultberg (1999) have shown that the share of dry deposition from total atmospheric input of base cations in spruce stand in Sweden varied between 42% and 67% being the lowest for K and highest for Na and Mg. Highest proportion of leaching calculated from daily BD samples for base cations reached 42%, 74% and 51% for Ca, K and Mg, respectively, from TF flux in pine stands in northern Estonia (Vihula and Sagadi stations). The obtained results were slightly lower than those presented by Ferm and Hultberg (1999), especially for Ca, indicating that anthropogenic deposition is probably higher in our conditions. In Estonia the high base cation concentrations (especially Ca^{2+}) in bulk precipitation may also be related to (among other sources) dust emissions associated with traffic on unpaved roads and agricultural tillage practices (Kimmel, 2002). However, the calculated shares of internal cycling are in accordance with average foliar leaching 37%, 80% and 34% of TF flux for Ca^{2+}, K^{+} and Mg^{2+} respectively, from 15 European case studies (Rothe et al., 2002).

Input-output calculations in their simplest form do not separate deposition quantitatively from leaching contribution. Still, input of base cations (Ca^{2+}, Mg^{2+}, K^{+}) through canopy leaching and ion exchange processes may be equal or even higher than atmospheric input as demonstrated by throughfall studies (Ferm and Hultberg, 1999; Houle et al., 1999). According to calculations based on data collected at Saarejärve spruce and pine stands, the atmospheric deposition was a more important source for Na and Ca (Na, Ca and Mg in spruce stand) than sum of internal cycling fluxes (litterfall+canopy leaching). At the

same time, main part of potassium flux originated from litterfall (9.6 kg ha^{-1} and 10.0 kg ha^{-1} for pine and spruce stands, respectively) and also canopy leaching (2.7 in pine and 8.9 kg ha^{-1} in spruce stand) compared to total atmospheric deposition (4.0 and 3.2 kg ha^{-1} in pine and spruce stand, respectively). The study conducted by Ukonmaanaho and Starr (2001) showed that in Finnish ICP IM coniferous sites litterfall was the major source for Ca, Mg, K and N, while TF was the dominant pathway for Na and S only. The discrepancy in major Ca and Mg sources may result from higher base cation deposition in Estonia.

Compared to atmospheric deposition, litterfall formed major part of nitrogen input. Annual average ammonium nitrogen flux decreased in order BD> TF>SW. Nitrate nitrogen was removed by canopy in growing season, but in dormant period the TF flux of nitrate in pine stands was higher compared to BD. Assuming canopy leaching of nitrate is negligible (Draaijers et al., 1996), the enrichment of TF by nitrate was due to dry deposition. Assuming further that dry deposition is in the same range during growing period, the annual dry deposition of 0.7 kg N ha^{-1} in pine canopies could be estimated. Studies in Finnish mixed boreal forests have estimated inorganic dry deposition of N to be about 1.23 kg ha^{-1} yr^{-1} (Piirainen et al., 1998).

4.3. Ion budget calculations for spruce and pine stands and Saarejärve catchment area

4.3.1. Sulphur budget

Sulphur is considered to behave conservatively on catchment level (Hultberg and Grennfelt, 1992). Prechtel et al. (2001) have shown a positive relationship between yearly mean atmospheric input loads and yearly mean output fluxes of sulphate in 20 European freshwater catchments. At Saarejärve atmospheric deposition accounted for ~75% of total sulphate input – 11 kg ha^{-1} and 14 kg ha^{-1}, in pine and spruce stand, respectively, on an average. During the study period the sulphur input has decreased. Sulphate output (in soil water) indicates retention of S in organic layer. Compared to the input flux, the output is very low (0.40–0.85 kg ha^{-1}). Release of sulphur at catchment level has exceeded input since 1999 showing removal of earlier accumulated sulphur. In Scandinavian catchments (Moldan et al., 2001), output fluxes of SO_4 have generally decreased since 1980s. The decline accelerated in the 1990s as a response to the decreased input. Decreasing SO_4 input generates desorption of sulphate from large pools in deeper soil layers which function as long-term memory of high deposition regime in the past. There can also be additional SO_4 sources in processes causing net release like excess mineralisation of organically-bound S, oxidation of reduced S compounds, and weathering of S-containing minerals.

As long as climate conditions are stable, net loss of S from catchment should not be influenced by S reduction/oxidation cycles or the weathering as the rate of this processes is assumed to be stable over time. The factors regulating excess mineralisation and the influence of decreased deposition are not yet clear (Prechtel et al., 2001).

4.3.2. Nitrogen budget

Nitrate is a minor acid anion compared to sulphate in input as well as output fluxes. As has been shown by mineralisation experiments at Saarejärve, nitrification may occur in acid mor humus of coniferous soils but the dominant process is ammonification. Nitrogen leaching of either of the N compounds was negligible compared to atmospheric deposition or release of ammonium during mineralisation indicating tight nitrogen cycling. The nitrogen released during mineralisation (29.2 kg N ha^{-1} in the spruce and 23.6 kg N ha^{-1} in the pine stand) formed the main nitrogen flux for plant uptake. Calculated annual net mineralisation was on the low end for conifer forests (Nadelhoffer et al., 1984; Persson and Wiren, 1995; Popovic, 1980; Williams, 1992). A part of stand's N demand is supplied directly from senescing needles and is made available through retranslocation (Helmisaari, 2000). At Saarejärve 48%–60% of N in current year's needles was retranslocated from senescing needles. In the pine stand the amount of annually retranslocating N was even greater than the amount of N that reached the forest floor as the shedding needles part of litter. The amount and character of litter input in forests is heavily dependent on the age of stands and their composition of species. The structural composition of litter changes with the ageing of a stand, the percentage of dying woody tissue increasing over time (Staaf and Berg, 1981).

Vogt (cited by Thomas and Prescott, 2000) used residence time of litter mass, C and N for characterising the rate of decomposition and mineralisation processes in steady state forest ecosystems. Utilising the ratio between total nitrogen reserve in forest floor of spruce and pine stands and corresponding annual N input by litter, the residence time of N was about 45 and 34 years for the spruce and pine stand, respectively. Despite the fact that annually available nitrogen seems to be the same in both stands, as estimated by mineralisation study, it may be assumed that on a long-term scale, N cycle is faster and, therefore, more efficient (the share of translocation) in pine stand. The claim that N cycle could be faster and more efficient in pine stand seems to be supported by the fact that the highest NH_4-N concentrations were measured in the pine stand, although the annual net mineralisation as well as N input by litterfall were higher in the spruce stand.

4.3.3. Proton budget

Both nitrogen and sulphur transformations are considered to be important sources of acidity (Nilsson, 1985; Rothe et al., 2002). According to van Breemen et al. (1984), proton loading associated with nitrogen transformations depends on whether ammonium input minus output (H^+ production) is greater or less than nitrate input minus output (H^+ consumption). At Saarejärve the output of nitrogen as well as sulphate in soil water was significantly lower than their TF deposition on stand level.

Theoretically, the sources and sinks of protons should be equal. In this calculation (paper IV), input from soil stores (weathering) remains unknown. It is assumed that annual litter formation and mineralisation of soil organic matter are more or less balanced in mature stands. Another uncertainty is the real nutrient uptake, the calculation of which presupposes taking into account the data of annual biomass production. In respect to acidification of soil, the most important process in both plots might be the accumulation of base cations into biomass. Thus, acidification was caused mainly by internal proton flux. The most important neutralising process seems to be anion retention, in our case, mainly in the soil. In proton consumption, sulphate retention has the decisive role.

On the catchment scale, the proton budget calculation shows high contribution from Ca+Mg weathering reactions, and great importance of internal production of acidity due to dissociation of carbonic acid. Such H^+ source-sink budget is characteristic to most natural systems (Starr et al., 1998).

5. CONCLUSIONS

During the period 1994–2002 the quantities of emitted SO_2 and fly ash have decreased about 40% and 65%, respectively, mostly due to a decline in annually combusted oil shale amounts i.e. due to a decrease in the production of electric energy in the power plants.

A significant decline in concentrations of both anions (SO_4^{2-} and Cl^-) and cations (Ca^{2+}, Mg^{+2}, Na^+ and K^+) in bulk precipitation was observed in most monitoring stations. Even though precipitation amounts have slightly increased during study period, the total deposition of the above-mentioned ions has decreased. The deposition loads show that regional air pollution levels in Estonia varied significantly. The highest deposition levels of anthropogenic sulphate measured in NE Estonia are more than 5 times higher compared to the background level, the difference in deposition of summed anthropogenic cations was up to 4 times. Mean annual concentrations of N compounds showed no overall trends.

The relatively high deposition of base cations (about 1 keq ha^{-1} in NE of Estonia compared to 0.20 keq ha^{-1} in SE of Finland) neutralises the acidic deposition in most of the stations. Mean annual pH of precipitation was acidic only at rural areas (e.g. Vilsandi, Lahemaa, Tooma stations). The acidity of precipitation did not change in most cases during the monitoring period. The only statistically significant decrease was found at Kunda, where annual mean pH of precipitation dropped from 7.5 to 6.7. This decrease is due to reduced local alkaline deposition, which has lead to the normalisation of pH.

The chemical composition of precipitation was significantly modified after passing through coniferous canopies. The deposition fluxes of SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and H^+ were significantly higher under coniferous canopies compared with bulk deposition. The enrichment of TF by SO_4^{2-} and Cl^- was higher in spruce stands than pine stands indicating that canopy filtering efficiency is species-related. Excess of Na in TF is assumed to be derived from dry deposition only. Using Na as a tracer ion for DD calculations, canopy leaching was found to be the main source of enrichment (40%–73%) of K flux. Annual calculated leaching reached 3.9 kg ha^{-1} and 10.9 kg ha^{-1} of potassium in pine and spruce stands respectively. For Mg and Ca the dominant process contributing to enrichment of TF varied between stands but CL remained under 30% of TF flux. If daily bulk samples are taken as the basis of DD and CL calculations, the dominant process for TF enrichment by Ca and Mg can be claimed to be canopy leaching. Corresponding amounts were up to 1.96 kg ha^{-1} and 0.65 kg ha^{-1} for Ca and Mg, respectively, in pine stands. According to calculations, leaching of base cations occurred in growing season as well as during dormant period.

Litterfall was the main source of potassium and nitrogen to the forest floor in the stand internal cycling of nutrients.

Ammonium was the dominant inorganic form of nitrogen produced by mineralisation in mor humus. Net ammonification occurred all year round, including the winter period when soil was partly frozen. The rate of nitrification was very low, and most of the annual net nitrification occurred during just one or two months. Taking into account retranslocation and atmospheric deposition, the mineral nitrogen stock available for uptake was 42 kg ha^{-1} and 43 kg ha^{-1} for spruce and pine stand, respectively.

Annual input-output balances of all nutrients were positive at the pine and spruce stands in Saarejärve, so that leaching into soil water (40-cm depth) was smaller than the corresponding deposition load.

A proton budget approach at Saarejärve pine and spruce stands shows that the main soil buffering process is retention of sulphate, which exceeds weathering of base cations (Ca+Mg). At the catchment scale, input-output analysis shows essential output of cations due to weathering from the soil.

A distinct change in input-output balance of sulphate was evident during the study period. The retention of sulphur was replaced by its release from the catchment area.

The input-output analysis of main macroelements suggests that the Saarejärve catchment area belongs to a natural background landscape where the only evident anthropogenic impact is sulphate pollution.

6. REFERENCES

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7. SUMMARY IN ESTONIAN

Õhusaasteainete sadenemine Eestis ja transformeerumine okaspuumetsades

Käesolev töö annab esmakordselt ülevaate iseseisvas Eestis erinevate seireprogrammide raames kogutud õhusaasteainete sadenemise andmetest. Seoses keskkonnaseire ümberkorraldustega peale Eesti riigi iseseisvumist tekkis 1990. alguses mõningane katkestus seiretegevuses. Pidevad, kontrollitud andmeread sademete peamiste saasteainete sisalduse kohta on kättesaadavad alates 1994. aastast. Peamiselt piki põhjarannikut paiknevates kohaliku tähtsusega seirejaamades on "Sademete keemia" programmi täitjaks olnud OÜ Eesti Keskkonnauuringute Keskus (EKUK). 1999. a. lisandusid seirevõrku Lõuna-Eesti jaamad, mille tööd korraldab OÜ Tartu Keskkonnauuringud. Lisaks on töös kasutatud ÜRO Piiriülese õhusaaste kauglevi (PÕK) konventsiooni raames tehtavate rahvusvaheliste koostööprogrammide — EMEPi (PÕK seire ja hindamise Euroopa koostööprogramm), kompleks- ja metsaseire — depositisooniandmeid. Metsaseiret (Õhusaaste mõju jälgimine ja hindamine metsades) koordineerib Eestis Metsakaitse- ja Metsauuenduskeskus, kompleksseiret (Õhusaaste kompleksseire ökosüsteemides) viivad läbi EKUK Vilsandil ja teadusühistu IM Saare koostöös Tartu Ülikooli Geograafia Instituudiga Saarejärvel. Kompleks- ja metsaseires kogutakse sademeid nii avamaal kui puistus. Eesti keskkonnaseire süsteemis on okaspuumetsade võrasademete keemiline analüüs ainus õhusaasteainete kuivsadenemise mõõtmise meetod.

Saasteainete territoriaalse leviku hindamiseks kasutati kokku 23 Eesti seirejaama mõõtmistulemuste interpoleerimist kriging meetodiga.

Töö peamisteks eesmärkideks oli:

1) sademetega maapinnale jõudvate peamiste saasteioonide keskmise taseme ja koormuste arvutamine ning trendianalüüs;
2) kuivdepositsiooni ja leostumise osatähtsuse selgitamine sademete keemilise koostise muutumisel okaspuuvõrades;
3) okaspuu võrades toimuvate leostumisprotsesside ja varise koostises taasringlusesse minevate toitainete osakaalu võrdlemine atmosfäärse depositsiooniga;
4) lämmastiku mineraliseerumise kui kooslusesisese lämmastikuvoo mõõtmine ja puistule kättesaadava mineraalse lämmastiku koguse hindamine
5) atmosfäärse depositsiooniga ja varise koostises lisanduvate toitainete sisse- ja väljakande hindamine Saarejärve valgala näitel;
6) antropogeense mõju hindamine Saarejärve valgala ainebilansile vesinikubilansi meetodil
7) erinevate seireprogrammide depositsioonitulemuste ühtse käsitlemise abil luua eeldused depositsiooni seirevõrgu optimeerimiseks ja metoodikate ühtlustamiseks eesmärgiga parandada andmete võrreldavust;

Suurimaks kohalikuks saasteallikaks Eestis on põlevkivielektrijaamaad. Seoses elektrienergia tootmise langusega on vaadeldaval ajavahemikul (1994–2002) vähenenud ka SO_2 ja lendtuha emissioonid (vastavalt 40% ja 65%). Kuna rahvusvaheliste kokkulepete tulemusena algas emissioonide oluline piiramine Euroopas 80-ndatel ja suuremad majanduslikud muutused Eestis leidsid aset 90-ndate alguses, on seda kajastavad trendid eristatavad eelkõige pikema andmereaga seirejaamades (Põhja- ja Kirde-Eestis).

Enamuses seirejaamades vähenes sademete koostisesse kuuluvate peamiste anioonide (SO_4^{2-}, Cl^-) ja katioonide (Ca^{2+}, Mg^{+2}, Na^+, K^+) sisaldus statistiliselt usaldusväärselt. Lämmastikühendite keskmised kontsentratsioonid kindlasuunalist tendentsi ei väljendanud. Vaatamata emissioonide vähenemisele on saasteainete kontsentratsioonid jätkuvalt kõrgemad Kirde-Eestis. Viimase kolme aasta (2000–2002) keskmised sulfaadi saastekoormuste erinevused Kirde-Eesti ja fooniliste seirejaamade vahel on ligi 5 kordsed (13.4 kg ha^{-1} ja 2.5 kg ha^{-1} vastavalt Jõhvis ja Lahemaal). Antropogeense päritoluga katioonide erinevuse näitena võib tuua summaarse depositsiooni Kundas 1.7 keq ha^{-1} ja Lahemaal 0.09 keq ha^{-1}. Üldiselt tasakaalustab aluseliste katioonide kõrge kontsentratsiooni Eestis sademete happesust. Vaid Vilsandil, Lahemaal ja Toomal olid sademed nõrgalt happelised (aasta keskmine pH 4.7–4.8).

Okaspuuvõrade all oli saasteioonide (SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, H^+) sadenemine üldiselt kõrgem kui avamaal. Kirjanduse andmetel on SO_4^{2-}, Cl^- ja Na^+ kontsentratsiooni suurenemine puude võrasid läbinud sadevees tingitud puu okstele ja lehtedele sademete vaheajal kogunenud kuivdepositsiooni lahustumisest. Väävli sadenemine võrade all oli kuusikutes keskmiselt 2.0–2.2 ja männikutes keskmiselt 1.4–1.8 korda kõrgem kui avamaal. Vegetatsiooni puhkeperioodil (novembrist aprillini) oli sulfaadi sadenemine oluliselt kõrgem (1.65±0.64 mg S m^{-2} päevas) kui kasvuperioodil maist oktoobrini (1.24± 0.44 mg S m^{-2} päevas), mis viitab väävli depositsiooni sesoonse dünaamika seosele inimtegevusega. Väävli (merelise komponendi suhtes korrigeeritud) aastaseks summaarseks sadenemiskoormuseks (kuiv+märgdepositsioon) okasmetsadele saadi 3.0 kg ha^{-1} männikutes ja 5.9 kg ha^{-1} kuusikutes 2000.–2002. a keskmisena.

Võrasademete rikastumine kloriidiga oli samuti kuusikutes suurem kui männikutes. Eeldades, et kloriid on merelise päritoluga, peaks Cl:Na suhe sademetes ja võravees olema kooskõlas vastava suhtega merevees (1.166). Mõõtmistulemustest selgub, et Cl:Na suhe oli võrasademetes kõrgem kui avamaa sademetes, mis tähendab kloriidi pärinemist lisaks ka antropogeensetest saasteallikatest.

Sarnastes uurimistöödes tihti kasutatav arvutusmeetod võimaldab teatud eeldustel (Na^+ käitub võras passiivselt; Ca^{2+}, Mg^{2+} ja K^+ kuivsadenemine on proportsionaalne naatriumiga) võra- ja avamaa sademete Na-depositsiooni vahe järgi hinnata füsioloogiliselt aktiivsete aluseliste katioonide kuivdepositsiooni ja leostumise osatähtsust võravee keemilise koostise kujunemises.

Võrasademetes suurenes K^+ sisaldus valdavalt leostumise (40%–73% võravee kaaliumi voost) tagajärjel, mis arvutuslikult ulatus 3.9 kg ha^{-1} männikutes ja 10.9 kg ha^{-1} kuusikutes. Ca^{2+} ja Mg^{2+} leostumise osakaal maapinnale jõudnud sadenemisvoogudes oli alla 30%, vastavalt kuni 0.65 kg ha^{-1} Mg^{2+} ja 1.96 kg $ha^{-1}Ca^{2+}$.

Kuna Vihula ja Sagadi männikud asuvad Lahemaa (Palmse) foonijaama läheduses, arvutati võrdluseks katioonide leostumise ja kuivdepositsiooni osakaalud kasutades Lahemaa päevaste sademete kuukeskmisi analüüsitulemusi. Arvutused näitavad, et kasutades sademeproovide kogumiseks kuivdepositsioonile avatud proovinõusid, võib katioonide märgsadenemine avamaal olla ülehinnatud. Selle tulemusena alahinnatakse Ca ja Mg võradest leostumise kui aineringe sisemise voo osatähtsust. Lahemaa sademete ja Sagadi ning Vihula männikute võravee põhjal võib Ca^{2+} ja Mg^{2+} leostumise osakaal ulatuda vastavalt 42 ja 51 protsendini maapinnale jõudvast depositsioonivoost.

Võrreldes atmosfäärse sadenemisega oli kaaliumi ja lämmastiku kooslusesisene voog (võradest leostumine+varis) suurema osatähtsusega. Ca ja Mg osas jääb küsimus kuni ühtse mõõtmismetoodika kasutusele võtmiseni lahtiseks. Leostumise ja kuivsadenemise osa maapinnani jõudva Ca voo kujunemisel Sagadi ja Vihula männikutes on peaaegu võrdne (mõlemad kokku moodustavad ligikaudu 80% võradepositsioonist). Kuid Ca^{2+} märg- ja kuivsadenemise summa (10.3 ja 11.7 kg ha^{-1}) ületab siiski kooslusesisest ringlust (5.97 ja 5.81 kg ha^{-1}) Saarejärve kuusikus ja männikus.

Lämmastiku kooslusesisese ringe olulisust võrreldes atmosfäärse sadenemisega näitab Saarejärve kuusiku ja männiku leedemulla orgaanilises kihis tehtud mineraliseerumiskatse. Kinnitust leidsid varasemad uurimistulemused ammooniumi kui peamise lämmastiku esinemisvormi kohta happelises metsakõdus ja nitrifikatsiooni üldiselt madal tase. Aastane lämmastiku netomineraliseerumine oli uuritud mustikakuusikus 29.2 kg N ha^{-1} a ja pohlamännikus 23.6 kg N ha^{-1}. Arvestades okastes enne varisemist aset leidvat retranslokatsiooni (N ümberjaotumist) (hinnanguliselt 48 ja 60% kuusikus ja männikus) ja õhust sadenemisel lisanduvat lämmastikku, saadi aastaseks mineraalse lämmastiku koguseks vastavalt 42 kg ha^{-1} ja 43 kg ha^{-1} kuusikus ja männikus.

Saarejärve valgala kuusikus ja männikus arvutatud pikaajalised keskmised ainetebilansid näitavad, et toitainete sisendvoog kõigi elementide suhtes (võrasademed+varis) ületab väljakande (mõõdetud 40 cm sügavusel mullavees). Vesinikubilanss näitab, et suurim kogus prootoneid vabaneb katioonide bioloogilises sidumises, peamine happesust vähendav protsess on antropogeense sulfaadi saastega seotud väävli peetumine mulla orgaanilises osas.

Valgala tasemel (pinnavee suhtes) koostatud vesinikubilanss näitab, et valdavaks prootonite tarbimisreaktsiooniks on glatsiofluviaalses liivas aset leidvad porsumisreaktsioonid, vähemal määral ka anioonide omastamine ja peetumine taim-muld süsteemis. Seoses sulfaadi depositsiooni alanemisega on toimunud valgala väävlibilansis oluline muutus: väävli väljakanne ületas alates 1999.

aastast sissekannet, iseloomustades kõrge väävlikoormuse tingimustes valgalal peetunud sulfaadi väljapesemist mullast.

Saasteainete sadenemise edaspidised muutused ja nende mõju koosluste aineringele olenevad nii majanduse kui keskkonnameetmete edasisest arengust. Soojuselektrijaamade rekonstrueerimine ja põlevkivi keevkihis põletamisele üleminek, samuti efektiivsemate puhastusseadmete kasutuselevõtt ja rangemate keskkonnanõuete kehtestamine peaks tagama pikaajaliselt kõrge väävli ja aluseliste katioonide saastekoormuse mõju all olnud ökosüsteemide järk-järgulise puhastumise. Ajapikku täieneb ka emissioonide andmebaas ja koos meteoroloogiliste taustaandmetega parandab see saasteainete päritolu ja liikumise selgitamise võimalusi.

ACKNOWLEDGEMENTS

My warmest thanks go to my supervisor Dr. Jane Frey for her encouragement, support and patience concerning my thesis. It has been much more than just work during these years together.

I am thankful to the referee of this thesis Dr. Olevi Kull for his valuable and constructive comments.

I am grateful to Estonian Environmental Research Centre for providing me with excellent working facilities. I appreciate the support of my colleagues and friends from the Air Quality Department, the Methodology Department and the Laboratory of Environmental Chemistry.

Since several organisations have been involved in the data collection and maintenance of the monitoring network, I would like to express my gratitude to Vilsandi National Park, Centre of Forest Protection and Silviculture, Estonian Environmental Information Centre and Estonian Meteorological and Hydrological Institute for friendly collaboration. Special thanks also go to Eva Nilson, Urve Ratas and Martin Voll from the Institute of Ecology, Tallinn Pedagogical University.

Many people from the Institute of Geography Tartu University have helped me during my doctoral studies and deserve to be thanked.

I also wish to express my gratitude to Krista Lõhmus and Ivika Ostonen for many useful research discussions at Lossi Street. The time we spent together doing fieldwork is unforgettable.

I would like to thank Linet Frey for excellent linguistic help with the original papers as well as with this thesis.

And last but not least, I am greatly indebted to my family: to my grandparents and parents for their love and support throughout my studies, which sometimes seemed to be endless, and my brother Martin who has also made his contribution to this thesis.

I can especially thank You, dear Antti, for the difficulty in finishing this work as we often found funnier things to do together. Still, I have reached this far thanks to your support.

The environmental monitoring data collection was financed by Estonian Ministry of Environment.

PUBLICATIONS

CURRICULUM VITAE

Katrin Pajuste

Date and place of birth: April 1, 1973, Tallinn, Estonia
Citizenship: Estonian
Address: Estonian Environmental Research Centre
Marja 4D Tallinn, Estonia
Phone: +372 611 2938
Fax: +372 611 2901
Email: katrin.pajuste@klab.ee

Education

1998 Tartu University, M. Sc. in plant ecology and ecophysiology
Dissertation "Seasonal dynamics of nitrogen mineralization in podzol of boreal Scots pine and Norwey spruce stands"
1996 Tartu University, B.Sc in botany and ecology
1991 Tallinn Secondary School No 3

Additional studies and courses

- Biology Teacher of Secondary School (one-year course in 1995/1996)
- NorFa (Nordic Academy of Advanced Study) financed course "Integrated approaches to drainage basin nutrient inputs, atmospheric deposition and effects on coastal eutrophication" 30.08.–05.09.2001 Tartu
- CIMO (Centre for International Mobility) scholarship for study at the Finnish Forest Research Institute during November 2001
- JICA (Japan International Cooperation Agency) group training course in "Air Quality Management Policy" at Ministry of the Environment and Japan Environmental Sanitation Centre from 23.01.–07.03.2003 Tokyo, Japan

Professional employment

- Head Deputy of Air Quality Department of Estonian Environmental Research Centre since 2000
- Specialist of ICP Integrated Monitoring project by EERC 1998
- Temporary senior research assistant at the projects of Estonian Science Foundation 1996–1998
- Participation in plant ecological field research group for mapping vegetation of small islands of Hiiumaa, 1993–1996

List of publications

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ELULUGU

Katrin Pajuste

Sünniaeg ja -koht:	1. aprill 1973, Tallinn
Kodakondsus:	eestlane
Aaddress:	Eesti Keskkonnauuringute Keskus Marja 4D Tallinn
Tel.	611 2938
Email	katrin.pajuste@klab.ee

Haridus

1991	Tallinna 3 Keskkool
1996	bakalaureus TÜ botaanika ja ökoloogia erialal
1998	magister taimeökoloogia ja ökofüsioloogia erialal (TÜ BÖI, 1998), teema: "Toorhuumuse lämmastiku mineraliseerumise sesoonne dünaamika mustikakuusikus ja pohlamännikus

Täiendõpe

- Gümnaasiumi bioloogiaõpetaja (1 aastane kursus) 1995/1996
- Põhjamaade Ministrite Nõukogu Teaduskoolituskeskuse (NorFa) rahvusvaheline kursus: "Valgala toitainete koormuse ja atmosfäärse depositsiooni integreeritud mõju rannikumere eutrofeerumisele" Tartus 30.08.–05.09.2001
- Soome Haridusministeeriumi Rahvusvahelise Mobiilsuse Keskuse (CIMO) stipendiaat Soome Metsauuringute Instituudis Vantaas, Soomes. November 2001
- Jaapani Rahvusvahelise Koostöö Agentuuri (JICA) kursus "Välisõhu kvaliteedi juhtimine" Tokyos, Jaapanis 23.01.–07.03.2003

Teenistuskäik

- TÜ geograafia instituudi vanemlaborant ETF grandiprojektis 1996–1998
- EKUK insener, kompleksseire programmi kontaktisik alates 01.10.1998
- EKUK Õhukvaliteedi osakonna juhataja asetäitja alates 2000.a.

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