





DISSERTATIONES GEOGRAPHICAE UNIVERSITATIS TARTUENSIS

34

**TRENDS OF AIR POLLUTANTS  
IN PRECIPITATION  
AT ESTONIAN MONITORING STATIONS**

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## LIST OF ORIGINAL PUBLICATIONS

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

- I Treier, K., Kabral, N., Frey, J., 2008. Trends of air pollutants in precipitation at Estonian monitoring stations 1994–2005. *Oil Shale* V 25–3, 2008 (manuscript accepted).
- II Treier, K., Pajuste, K., Frey, J., 2004. Recent trends in chemical composition of bulk precipitation at Estonian monitoring stations 1994–2001. *Atmospheric Environment* 38, 2004, pp. 7009–7019.
- III Frey, J., Pajuste, K., Treier, K., Mander, Ü., Frey, T., Kask, P., 2006. Decreased deposition of sulphate and the responses in soilwater at Estonian integrated monitoring sites 1995–2004. *Geo-Environment & Landscape Evolution II* (Eds: J.F. Martin-Duque, C.A. Brebbia, D.E. Emmanoulodis and U. Mander) Vol. 89, WIT Press, Southampton, Boston 2006, pp. 69–78.

The author's contribution

- I The paper was planned by J. Frey, N. Kabral and K. Treier. K. Treier wrote the draft of the paper.
- II The paper was planned and the results were assessed jointly by K. Pajuste, J. Frey and K. Treier. K. Treier was responsible for the data analyses and the discussion of the results.
- III The paper was initiated by J. Frey and T. Frey. The experiments were planned and carried out jointly by J. Frey, K. Pajuste, K. Treier, Ü. Mander, T. Frey and P. Kask. K. Treier performed the data analyses and assisted in the revision of the manuscript.

## ABBREVIATIONS

BD	bulk deposition
BP	bulk precipitation
CAFÉ	Clean Air for Europe directive
CLTRAP UN/ECE	Convention on Long-range Transboundary Air Pollution
CFB	circulating fluidized-bed (technology)
DD	dry deposition
EERC	Estonian Environmental Research Centre
EMEP	Cooperative Programme for Monitoring and Evaluation of the Long-range Transboundary Air Pollutants in Europe, coordinated by UN/ECE
ENEMN	Estonian National Environmental Monitoring Network
EU	European Union
GHG	greenhouse gases
ICP Forest Level II	International Cooperative 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
LPN	Local Precipitation Network
NEC	National Emission Ceilings Directive
NMVOC	non-methane volatile organic compounds
NTF	net throughfall (throughfall- bulk deposition)
PM	particulate matter
Q	value of decline (per month, per year etc.)
SF	stemflow water flux and chemistry
SP	solid particle
TF	throughfall deposition
TPP	Thermal power plants
UNFCCC	United Nations Framework Convention on Climate Change
W	weathering
VWC	volume-weighted concentrations

# 1. INTRODUCTION

## 1.1. Air pollution issues in Europe

The driving forces behind air pollution are directly associated with human activities. The major classic air pollutants emitted into the atmosphere in Europe are sulphur dioxide ( $\text{SO}_2$ ), nitrogen oxides ( $\text{NO}_x$ ), ammonia ( $\text{NH}_3$ ), non-methane volatile organic compounds (NMVOC), particulate matter (PM) and carbon dioxide ( $\text{CO}_2$ ). Sulphur and nitrogen compounds emitted into the air are potentially acidifying and can cause harm when deposited in sensitive terrestrial or aquatic ecosystems. Nitrogen compounds are also potentially eutrophying, i.e. can cause an oversupply of nutrients in soils and water bodies. In Europe anthropogenic emissions are much greater than are natural (Berglen et al., 2007). The impact from the intercontinental transport of pollutants is small compared to the impact from local emissions. There is a certain long-range transportation into Europe from upwind areas, mainly from North-America; considering the fact that sulphur has a lifetime of a few days, some sulphur emitted overseas will reach Europe, and an estimated 10% of sulphur deposited in Europe originates from sources outside Europe (Tarrason et al., 2005).

During the last few decades, considerable changes in anthropogenic emission have taken place within Europe (Smith et al., 2001). The control of acidifying pollutant emissions in Europe since the early 1980s has been successful: sulphur dioxide emissions have been reduced by 70%, oxides of nitrogen by around 30% and ammonia by 25%. Today sulphur dioxide emissions are back at the levels characteristic of the beginning of the 20<sup>th</sup> century (Grennfelt, 2005). For the first time, total sulphur oxide emissions were lower than the level established by the 2010 by UN Gothenburg Protocol (1999). Sulphur deposition has declined mainly by the same order of magnitude as sulphur emissions (Löfblad et al., 2004). The 2006 NEC Directive status report concluded that all Member States except Greece and Cyprus report a decrease in  $\text{SO}_2$  emissions; an over 75% reduction was reported by Latvia (96%) (Table 1), by Germany (90%), by Denmark (88%), by Hungary (84%) and by Italy (72%) during the period 1990–2005.

The reduction is mostly due to new technologies, the switching of fuel (from coal to gas) and economic recession, mainly in Eastern Europe. Through the organisational framework of the United Nations (Convention on Long-range Transboundary Air Pollution, CLRTAP, 1979), European air pollution has been controlled by technical and political international agreements and legislation. More recently, the European Union has become an active part of the process (Strategy of Acidification, Air Quality Framework Directive and its daughter directives, the National Emissions Ceiling Directives and other directives: Clean Air for Europe (CAFÉ)). The EU has also added control requirements through EU-wide legislation within the energy and transportation sector.



A close accordance between sulphate decline and the decline in base cations (especially  $\text{Ca}^{2+}$ ) in deposition have been monitored in many parts of Europe. Base cations in deposition have decreased markedly between 1970 and 1990 (Lövblad, 1987). An inventory was also made for calcium emissions from industry sources in Europe (Lee and Pacyna, 1999). In some areas, mainly those influenced by emissions from Eastern Europe, there has been a decline in base cations in deposition from 1990 (Lövblad et al., 2000).

The main sources of calcium are cement, iron and steel plants and coal combustion in Europe. The anthropogenic contribution to base cation deposition is largest for  $\text{Ca}^{2+}$  and  $\text{K}^+$  but is usually below 15%, except over Scandinavia and Russia, where anthropogenic emissions can contribute up to 20–25% (van Loon et al., 2005). Hedin et al. (1994) show a dramatic decline in concentrations of non sea-salt Ca, Mg and K in precipitation over North America and Europe. Similar findings were reported by Lee et al. (1999) for the period 1974–1993 and by Tørseth et al. (1999) for the period 1986–1996.

During the period 1995–2005, the decline in  $\text{SO}_2$  emissions was quite similar (30–45 %) in Estonia, and also in Finland, Sweden and Norway (Table 1). Latvian  $\text{SO}_2$  emissions decreased more than 90% during the same period. The decrease in solid particle emissions in Estonia has been remarkable (70%) compared to neighbouring countries, where the average decrease was around 10% during the study period 1995–2005. Despite the great decline in  $\text{SO}_2$  and total solid particle (SP) emissions according to formal calculation dividing the  $\text{SO}_2$  emission value by country area, the sulphur load was sixteen-fold higher and the solid particle (base cations) load was about four-fold higher in Estonia than in neighbouring countries in 2005. This is a characteristic picture for countries in which both the energy sector and the chemical industry are based on oil shale (Aunela et al., 1995).

As sulphur emissions have fallen, ammonia emitted from agricultural activity and nitrogen oxides from combustion processes and transport have become the predominant acidifying and eutrophying agents affecting ecosystems. A reduction in the sulphate aerosol content in the European atmosphere may have a warming effect, and air pollution policy decisions may impact climate (Berglen et al., 2007). The concern about anthropogenic emission was previously mostly connected with the acid rain problem: the focus is now on climate effects due to sulphate aerosols (Lelieveld et al., 2002), as sulphate is a result of the oxidation of  $\text{SO}_2$ .

**Table 1.** Sulphur dioxide (SO<sub>2</sub>) emissions (Gg yr<sup>-1</sup>) and total solid particle (SP) emissions (Gg yr<sup>-1</sup>) in Estonia and neighbouring countries (EMEP data) and the reduction in SO<sub>2</sub> and solid particle (%) from 1990–2005 and the study period of this paper, i.e.1995–2005.

	1980		1990		1995		2000		2005		1990–2005		1995–2005	
	SO <sub>2</sub>		SO <sub>2</sub>	SP	SO <sub>2</sub>	SP	SO <sub>2</sub>	SP	SO <sub>2</sub>	SP	SO <sub>2</sub>	SP	SO <sub>2</sub>	SP
Country	Gg yr <sup>-1</sup>	Gg yr <sup>-1</sup>	Gg yr <sup>-1</sup>	Gg yr <sup>-1</sup>	Gg yr <sup>-1</sup>	Gg yr <sup>-1</sup>	Gg yr <sup>-1</sup>	Gg yr <sup>-1</sup>	Gg yr <sup>-1</sup>	Gg yr <sup>-1</sup>	%	%	%	%
Estonia	345	273	280		117	134	96	77	77	40	-72	-86	-34	-70
Finland	584	260	333*		120		85	80	69	77	-73	-77	-42	
Sweden	491	109	83		71	78	46	69	40	72	-63	-13	-44	-7
Norway	136	52	89		34	82	27	80	24	74	-54	-17	-29	-11
Latvia		100			48		10	18	4	21	-96		-93	

\* data from 1987, Anttila, 1990.

Some environmental consequences are evident in the globalization process; energy consumption, industrial activities, transport demand and agriculture husbandry are the driving forces that are most directly linked to air emissions, and the future levels and trends in Europe will depend on socioeconomic factors, technology and political decisions.

## **1.2. Air pollution prevention and control through legal measures**

### **International agreements**

Under various international agreements, Estonia has undertaken obligations to reduce emissions of sulphur dioxide, for example according to the Agreement between the Government of the Republic of Finland and the Government of the Republic of Estonia on Cooperation on Air Pollution, 1993 (1994), Estonia promised to reduce SO<sub>2</sub> emissions 50% by 1997, based on the 1980 level, and by 80% by 2005 in comparison with the 1980 level. Thereafter both parties agreed to 55,000 tons in 2005 (Eesti keskkonnastrateegia, 1997).

In 2000 Estonia joined the Convention on Long-Range Air Pollution (13 Nov 1979, Geneva) and accompanying protocols. By act of parliament (accepted 4 June 2003), Estonia joined the to the Convention on Long-Range Transboundary Air Pollution (reduction of SO<sub>2</sub> emissions (Oslo 1994, 14 June) and undertook the following obligations: to reduce SO<sub>2</sub> emissions 35% by 2005, based on the 1980 level, and by 40% by 2010 in comparison with the 1980 level.

All states that have joined the Geneva Convention must carry out direct measurements of pollutants within the framework of international monitoring programmes. Although Estonia ratified the Geneva Convention as late as 2000 and the EMEP financing protocol in 2001, environmental monitoring was reorganized from the beginning of the 90s. From 1985–1991, Estonian stations were operated by the Hydrometeorological Institute (using measuring equipment and methods of the former USSR). Since 1994 the collection of environment data has been funded from the national budget. In addition, Estonia followed the Geneva Convention while it was part of the Soviet Union (Lahemaa station, which has the longest available data series, and Sõrve station operated till 1991) (EMEP Assessment Report, 2001).

Since accession to the European Union, Estonia is required to perform EU Directives related to air. Here are described these directives, focusing on the reduction of SO<sub>2</sub> emission and the emission of solid particles, firstly Framework Directive 96/62/EC; Management of the Quality of Ambient Air (with the objective of maintaining and improving air quality within the Community's basic principles). Limit values for sulphur dioxide and particle matter in ambient air are specified in the first Daughter Directive 1999/30/EC. For Estonia, Directive 96/61/EC, Integrated Pollution Prevention and Control (the

obligation to use the best Available Technology), involved upgrading to new circulating fluidized-bed (CFD) technology. National Emission Ceilings 2001/81/EC related to the establishment of national emission ceilings for acidification (by 2010, areas with critical loads of acid deposition will be reduced by at least 50% compared with 1990). By 2010, the annual total emission of sulphur dioxide (SO<sub>2</sub>) must not exceed 100,000 tons in Estonia. The Large Combustion Plants Directive (2001/80/EC) related to the limitation of emissions of certain pollutants into the air from large combustion plants. 2001/80/EC will be fully implemented by January 1<sup>st</sup> 2016. In addition, by 2012 the annual emission of sulphur dioxide from oil shale power plants will not exceed 25,000 tons. Estonia agreed to present to the European Commission an action plan of investments for the reduction of emissions of certain pollutants in large combustion plants (the Narva Power Plants and Kohtla-Järve Thermal Company) according to the Directive for 2010–2015 by January 2008. Four new circulating fluidized-bed (CFD) boilers already began operations in 2005.

### **Estonian development plans and strategies**

The Estonia Environmental Strategy (1997) has set the goal of reducing SO<sub>2</sub> emissions by 80% by 2005 in comparison with the 1980 level, and reducing emissions of solid particles by 25% compared with the 1995 level, and here cut-off values are 55,000 tons (target not achieved) and 28,300 tons respectively. In fact, the reduction of the latter indicator, emissions of solid particles, was significantly higher, namely 84%.

There is a relief of requirements concerning the level of sulphur dioxide emissions by 2010, as specified in the new version of the Estonia Environmental Strategy (26 October 2005) – fell 35% by 2005 compared with the 1980 level, and 40% by 2010, thereby guaranteeing that the total amount of sulphur dioxide emitted by stationary and mobile sources in Estonia will not exceed 100,000 tons per year by 2010.

These targets leave room for growth in the production of oil shale electric energy until 2010, because by 2012 the annual emission of sulphur dioxide from oil shale power plants must not exceed 25,000 tons, repeating the tasks established in directives 2001/81/EC and 2001/80/EC.

There are several national strategies and development plans that are directly and indirectly related to the sectors of energy and nature protection: the Estonia Environmental Strategy by 2010, the Estonia Environmental Strategy by 2030, the Long-term Public Fuel and Energy Sector Development Plan until 2015. The draft version of the National Development Plan for the Use of Oil Shale 2008–2015, its implementation plan, the strategic assessment reports on environmental impact and the amendments to the Earth's Crust Act have been submitted for approval by the Estonian Parliament, which will have the final word on both the development plan and the amendments to the act. This will be

the key document for the long-term rational development of mining and utilization of oil shale and also the solution of social problems in NE Estonia.

As oil shale is fossil resource, its annual excavation must be limited to 20 million tons (Raukas, 2008). As the permits that have been issued allow larger amounts of oil shale to be mined, the ministry reached an agreement with mining companies for the reduction of these amounts.

Currently the energy sector is controlled more by the Kyoto Protocol, an agreement made under the United Nations Framework Convention on Climate Change (UNFCCC). Countries that ratify this protocol commit to reducing their emissions of carbon dioxide and five other greenhouse gases (GHG), or engaging in emissions trading if they maintain or increase emissions of these gases. Estonia ratified this protocol on 3<sup>rd</sup> September 2002. The EU member states each have individual obligations, and national limitations range from an 8% average reduction during 2008–2012 compared to the 1990 level.

On the one hand, in the energy sector, the introduction of the emission trading system for CO<sub>2</sub> has created an expectation for further innovations in this direction, with more sectors becoming included in the future. For example, in 2008 the Estonian Energy Company bought an 110,000 ton CO<sub>2</sub> quota for the Estonian internal electricity production for 35 million EEK (Postimees 05.02. 2008).

### **1.3. Emission of air pollutants in Estonia**

The reduction of emissions of air pollutants in Estonia has largely followed European trends. Nevertheless, energy production from a specific fossil fuel – oil shale combustion - has left its mark on the character of emissions, measures of emission reduction and the deposition of pollutants. About 95% of total electricity production in Estonia comes from oil shale, and 92% of electrical energy is generated by two of the world's largest oil shale fired power plants (the Narva Power Plants) (EE Annual report 2004/2005). In 2005, 14.8 million tons of oil shale was combusted for the production of electricity (Figure 2) and thermal energy (statistical database of Statistics Estonia, 2005), of which 11–12 million tons was used at the Narva Power Plants (Liive, 2007).

Estonian oil shale is quite unique, as its reserves are the largest commercially exploited deposits in the world (Dyni, 2002), and it is the most important mineral resource in Estonia. At the current rate of consumption, there should be sufficient reserves (8.66 GT) for at least 60 more years (Agabus et al., 2007). Estonian energy production is currently, and will continue to be based on oil shale, most likely until 2015 (Agabus et al., 2007).

The chemical composition of oil shale has the strongest influence on air pollution. About 82% of total air pollution originates from the Northeast Estonian oil shale industry (in addition to power production, this is also caused

by the oil shale chemistry industry and oil production) (Environmental Review, 2005).

Estonian oil shale as a fuel is characterised by a high ash proportion (45–50 %), by moderate sulphur (S) content (1.4–1.8%), and by low heating value (net heating value of moist fuel 8.5–9 MJ kg<sup>-1</sup>). One of the peculiarities is chlorine (0.75%) combined with organic matter (Ots, 2005). As oil shale is rich in mineral matter (the basic mineral components of the carbonate part are calcite and dolomite), the ash formed by the combustion is the most important particle emission source. Under the former technology of combusting pulverized oil shale (in use up to 2005), the amounts of ash from power plants were enormous.

Due to rather high chimneys (150 and 300 meters), the exhaust gases are distributed over a large area, even under still air conditions (Paat, 2002). The atmospheric emissions of four oil shale fired plants have become a cause of concern in Estonia as well as in neighbours Russia and Finland (Kulmala et al., 1998; Sofiev et al., 2003).

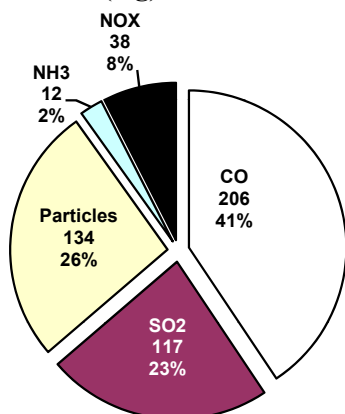
Oil shale power plants have comparatively high emissions of sulphur dioxide in spite of the capacity of SO<sub>2</sub> to bind with ash when the gas passes through the boilers. With pulverized oil shale combustion, approximately 15–20% of the total sulphur in the fuel goes into the stack as SO<sub>2</sub> (Kallaste et al., 1999). With old combustion technologies, the power plants utilised about 26 Mt of oil shale per annum in the 1980s, producing about 250,000 t SO<sub>2</sub> and 200,000 t of fly ash, according to expert estimates (Liblik et al., 2001). The high molar ratio of Ca/S (usually 8–10) enables buffering of the influence of the acidic compounds of oil shale (S and Cl) (Ots, 2005).

Economic changes resulting from decreasing industrial production and the collapse of the export market for electricity have substantially reduced oil-shale based energy production. Official data confirm that total SO<sub>2</sub> emissions in Estonia have fallen from 273 thousand tons to 77 thousand tons (about 72%), and the emission of solid particles decreased from 280 thousand tons to 40 thousand tons (86%) during the period 1990–2005 (Table 1, Figure 1). The EMEP data of emissions of air pollutants in Estonia confirm three-fold reduction in solid particles emission in 2005 compared to 1995 (Figure 1), solid particles proportion has declined from 26% to 13% of total of emission.

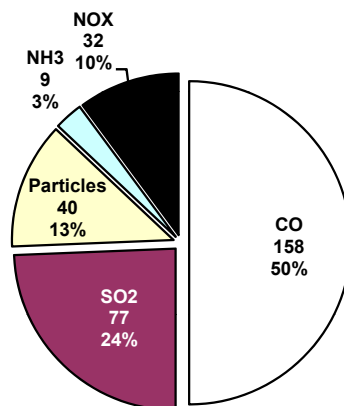
In spite of the reduced emissions, up to the present the most polluted region is Northern Estonia, where larger cities and heavier polluters like power plants, oil shale mines, chemical industries and the Kunda cement factory are situated. In 1992 the Nordic Kunda Cement Ltd plant in Estonia emitted 80 kilotons of particles in clinker milling and firing, which is approximately 40% of the oil shale fuelled power plant emissions (Jalkanen et al., 2000). The main constituents of clinker are CaO (62.8%), SiO<sub>2</sub> (20.3%) and Al<sub>2</sub>O<sub>3</sub> (5.3%); these components also dominate in fly ash mass (Nordic Kunda Cement Ltd 1992–1999). The use of new purification equipment in the cement factory at Kunda was the most important positive change in the air pollution situation (causing a

reduction in dust emission of about 80% in 1999 compared to 1997 (Paper I, Fig. 3, Treier et al., 2008) in the entire North-East region.

**Emissions (Gg) in Estonia 1995**



**Emissions (Gg) in Estonia 2005**

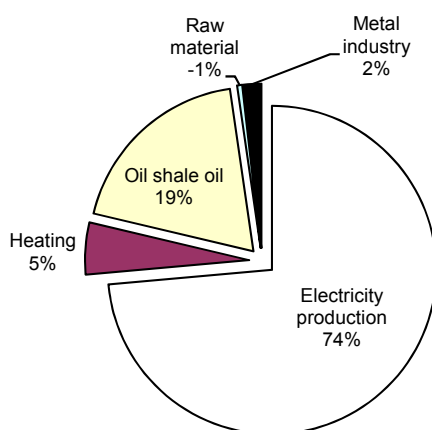


**Figure 1.** Emissions of air pollutants (Gg) in 1995 and 2005 (EMEP data).

Cations originate from natural sources such as sea salt (Mg and Na) and soil dust (Ca, Mg, K and Na), as well as from oil-shale fly ash (Ca, Mg, K, Na). Estonia, which has soils that have developed in high carbonate content parent materials, has an advantage over the acidifying world and especially over Scandinavia – acid parent materials develop thin soils and lead to low base cation deposition (Ruoho-Airola et al., 2003; Lövblad et al., 2004). Furthermore, the alkaline character of Estonian air pollution, predominantly originating from mineral-rich (about 45–50%) oil-shale-based large power plants and the chemical industry, cause several unique environmental problems (Karofeld et al., 1996; Mandre, 1997; Kont et al., 2007), especially in comparison with Nordic countries.

Estonia is unusual in that it produces electricity directly from oil shale; more than 80% of oil shale is used as solid fuel in power plants (Figure 2). In every other country, oil shale is converted into shale oil and then used. The remaining 20% of Estonian oil shale is currently processed for the production of oil, gas and cement (Veiderma, 2003). The Kiviter and Galoter retorting processes are used, and in 2004 ca 330 kilotons of shale oil were produced, of which 50% was exported. Producers of shale oil aim to increase production to 1.5 Mt by 2015. The main tasks in improving retorting can be found in Veiderma & Siirde, 2007.

The restoration of independent statehood led to rapid economic change and a 44% increase in the number of automobiles (1994 – 337,800 and 2006 – 554,000 automobiles (Statistical database of Statistics Estonia, 2006).



**Figure 2.** Exploitation of oil shale in Estonia 2005 (total amount 14.8 million tons) (Eesti Päevaleht, 01.11.2006).

In Southern and SE natural background areas, the comparatively large Ca load indicates the impact of road-dust from gravel roads (about 62%), and/or from the ca 25-year-old pavement of roads in the SE and S Estonian natural background area (Maaleht, 10.05.2005).

By the year 2005, the first two of six energy blocks were renovated and updated to new circulating fluidized-bed (CFB) technology, and this has set the goal to produce 6.6 TWh of electricity and achieve consistency in SO<sub>2</sub> emission standard (38,000 tons) as established in the Estonian Environmental Strategy. In accordance with the data of Statistics Estonia, in 2005 27% of gross production of electricity was produced using new technology. The share of SO<sub>2</sub> emissions from power plants compared to total emissions from stationary sources fell 74% (the maximum proportion during the study period was 92% in 2003), but still remained a dominant source of SO<sub>2</sub> emissions in Estonia. At the same time, the proportion of emissions of solid particles from power plants fell below 50% of the total emission of solid particles (Paper I, Fig. 1, Treier et al., 2008).

According to the EMEP database, polluted air was mostly transported to Estonia from Western and Central Europe and neighbouring countries. The majority of transboundary fluxes originate from international shipping, and the importation of pollution from Poland, Germany, Russia, Finland, and Latvia has decreased.

## 1.4. Climatic conditions

Estonia is located in the north-western part of the East European Plain between latitude 57°30' N and 59°50' N in the transition zone between Atlantic maritime



and Eurasian continental climates. The Estonian climate is influenced by the Atlantic Ocean, the North-Atlantic Stream and the Icelandic minimum. The latter constitutes a region of cyclonic activity where the average atmospheric pressure is lower than in adjoining regions. The Baltic Sea is the most important of the spatial division of factors influencing Estonian climate (solar radiation, temperature, cloudiness, precipitation, wind etc.). Based on the influence of the Baltic Sea, a maritime and continental climate region can be distinguished. The borderline between these two regions is marked by the zone where the change in the main climatic factors is comparatively sudden.

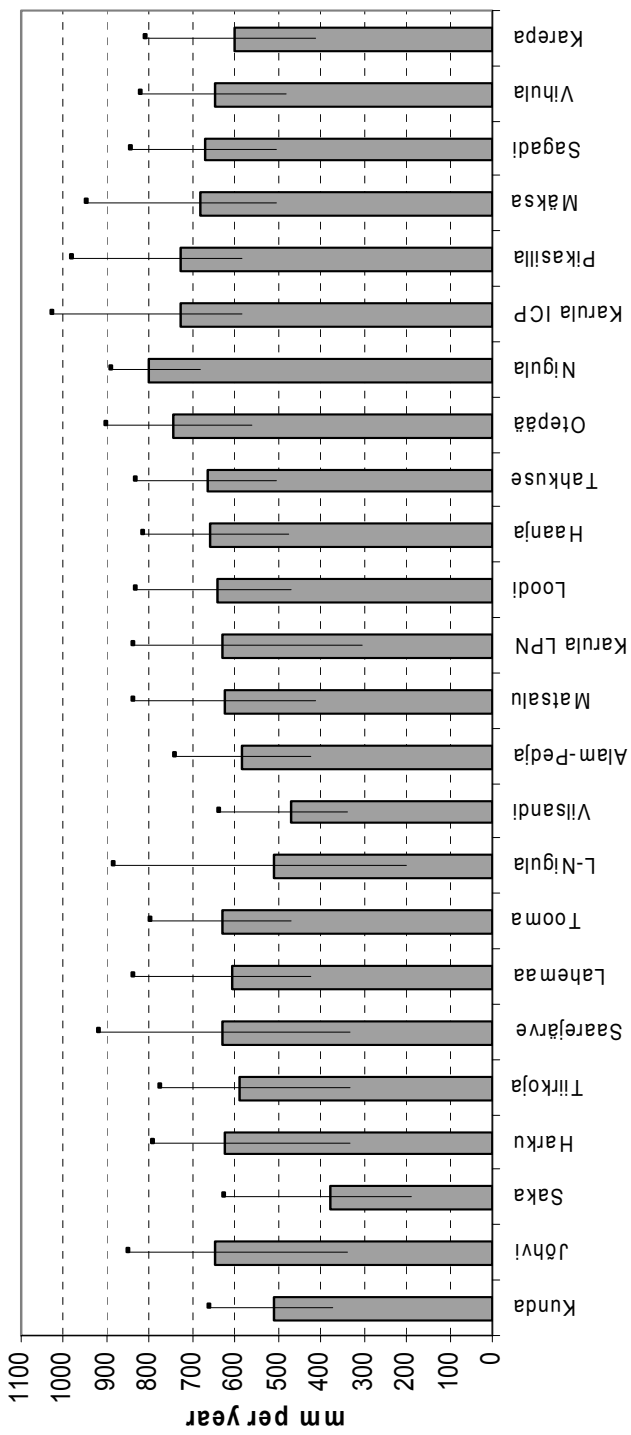
Estonian weather is highly variable during both cold and warm half-years. The rapid alternation in the weather is caused by the cyclones originating from the intermediate and higher latitudes of the Atlantic Ocean, producing abrupt fluctuations in atmospheric pressure.

Generous precipitation is brought to the region by the cyclones that during the cold period fall as snow or slush. Thunderstorms can occur during the warm period, accompanied by hail, occasionally also destructive whirlwinds i.e. tornados (average 1–3 a year) and heavy showers. Because of its maritime climate, Estonia's weather is cloudy for more than half of the year, and the mean annual precipitation ranges from 550 to 750 mm in the South-Eastern part of the country. Lower precipitation is measured in coastal regions (Vilsandi 472 mm, Kunda 510, Lääne-Nigula 512 mm), and the highest in the Western part of continental Estonia and the highlands of South-East Estonia (Otepää 744 mm, Haanja 660 mm, Jõhvi 645 mm, Tooma and Saarejärve 630 mm, Harku, Matsalu, Lahemaa under 625 mm, Tiirikoja, Alam-Pedja 590–580 mm). See Figure 3.

Most precipitation occurs in the South-West sector. The seasonal division of precipitation shows a clear distinction between the climates of the coastal and inland areas. The inland has the greatest precipitation in summer (July, August), whereas Western Estonia has more in autumn (September, October, November), which is a clear indication of a maritime climate. Differences in snow cover confirm this statement – the average duration of snow cover is 90 days on the islands (1966–1998) compared to 120–130 days in North-Eastern and South-Eastern Estonia (Jaagus, 1999).

The annual average temperature is 6°C on the Western coast and 4.2°C in Eastern Estonia during the coldest month (February: –3.5°C and –7.5°C, the warmest month July: 16–17°C. It is quite common for the temperatures in East and West Estonia to differ by more than 10 degrees.

The evaluation of long-term trends in precipitation is much more complicated than in the case of temperature. Precipitation has a local character, especially during the warm season, and the trends can be less trustworthy due to inaccuracies in the measuring of precipitation. It is, however, legitimate to claim that during the period 1951–2000, the amount of precipitation in Estonia has increased (Jaagus, 2003).



**Figure 3.** Annual mean precipitation data (mm) at 23 monitoring stations.

Mann-Kendall trend analysis carried out for the current thesis shows that the amount of precipitation has reliably decreased in only 3 stations (Lääne-Nigula, Jõhvi and Harku) since the second half of the 1990s. In the case of Jõhvi, this fact is also confirmed by the comparison of EMHI annual average precipitation data, which was 657mm in 1961–1990 and 645 mm from 1994–2006, resulting in a 12 mm difference.

## **1.5. Objectives of this study**

The main aim of this thesis is to give an overview of the deposition levels of air pollutants on Estonian territory in the context of EU requirements on emission reduction on the one hand and the introduction of new technologies in oil-shale power production in Estonia during the years 1995–2005 on the other hand. The overall aim can be broken down into the following objectives:

- To analyze changes and trends in anion and cation concentrations in the data available on bulk precipitation in relation to decreased emissions of SO<sub>2</sub> and solid particles during the last 12 years.
- To assess the present deposition patterns of SO<sub>4</sub>-S and base cations on Estonian territory.
- To estimate the efficiency of measures utilised for emission reduction at the Narva Power Plants as reflected by changes in deposition levels in bulk precipitation.
- To specify the proportion of Estonian territory that is or has been affected by air pollutants originating from the North-Eastern oil shale industrial region in retrospect.
- To understand whether acidification of the environment could potentially be influenced by a reduction in the deposition of air pollutants.
- To assess possible impacts of reduced SO<sub>4</sub>-S and cation deposition on soilwater chemistry of podzolized soils in coniferous stands at Saarejärve and Vilsandi ICP IM areas.

## **2. MATERIAL AND METHODS**

### **2.1. Data of monitoring programmes**

The Estonian Environmental Research Centre (EERC) has been operating air quality monitoring stations since 1994. The EERC was accredited internationally for precipitation analysis in 1998 and for air quality measurements in 2000. Although the systematic measurement of air quality already began in the 1980s (at Sõrve and Vilsandi stations and later at Lahemaa) the deposition data measured before 1994 are unfortunately not available. The Estonian Hydrometeorological Institute was responsible for monitoring data from 1985–1994, the measuring equipment and methods of the former USSR were used. Data concerning air pollution were confidential in the Soviet Union, and the overall quality of these data are unknown (Kimmel et al., 2002). After regaining independence in 1991, environmental monitoring underwent reorganization, new methods and equipment were introduced, and since 1994 there is a comparable database for precipitation compounds.

The first stations were mainly situated in seaside areas, starting from Vilsandi, Estonia's westernmost island, and continuing along Estonia's northern coast up to the industrial area in the North East. As background stations, Vilsandi, Lahemaa and Saarejärve are part of the international monitoring network, and the data collected there are forwarded, within the framework of the Convention on Long-Range Transboundary Air Pollution (CLTRAP), to the databases of EMEP (Cooperative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe) and the International Cooperative Programme on Integrated Monitoring. In the framework of ICP IM, an intensive monitoring site at Lake Saarejärve forested catchment area in eastern Estonia and a biomonitoring site in the westernmost part of Vilsandi Island were established. The IM monitoring sites represent areas of boreal coniferous forest receiving background loads of air pollution and deposition (Paper III, Frey et al., 2006). In 1996 six new monitoring sites in northern and southern Estonian coniferous forests were established for the ICP Forest Level II network. The EERC in cooperation with the Department of Geography of the University of Tartu are responsible for the ICP IM programme in Estonia. The Centre for Forest Protection and Silviculture is responsible for the implementation of the ICP Forest programme. All responsible institutions are obligated to follow monitoring subprogramme manuals in which the respective methods are described (ICP IM Manual, 1998; ICP Forests Manual, 1999).

In addition to the above-mentioned international programmes, since 1999 new local meteorological stations in Southern Estonia have been added to the local precipitation network (15 local meteorological stations). As a result, since 1994 there exists a comparative database for precipitation compounds, and it is possible to estimate the level of air pollution on most of Estonia's territory on

the basis of a uniform methodology and assess the changes and trends of anion and base cation concentrations in bulk precipitation during the period 1994–2006. This study concentrates mainly on the longest time series of the chemical composition of the precipitation from 10 monitoring stations, dating from 1994 (1995/1996). Data from the ICP Forest and Southern Estonian LPN have been used solely to illustrate the overall picture of the changes that have taken place in Estonia over more than last decade (Table 2).

As the emission of air pollution has been calculated, therefore all states that have joined the Geneva Convention must carry out direct measurements of pollutants within the framework of international monitoring programmes.

## 2.2. Sampling and chemical analyses

Precipitation was collected using bulk collectors (20 cm in diameter) placed in an open area at a height of 120 cm. Samples were collected on a 24h basis. Collected samples were stored in refrigerators and mixed in proportion to the total sample volume for monthly samples before analysis, as described in the EMEP manual (EMEP, 1996).

In Paper III at the International Co-operative Programme on Integrated Monitoring (ICP IM), the bulk deposition from monitoring areas (Saarejärve and Vilsandi stations) was collected using two NILU-type collectors (EMEP, 1996). Throughfall deposition was collected with polyethylene funnel-type bulk collectors (20 cm in diameter, at a height of about 150 cm) at a snow-free time and using buckets during winter. Spiral silicone collectors fitted to three trees per plot were used for the collection of stemflow. Water volumes were measured on the field with graduated cylinders. Sampling frequencies were once a fortnight in summer and once a month in winter.

Soil water was sampled with zero-tension plate lysimeters measuring area 0.1 m<sup>2</sup> (Voll & Roots, 1999). At Saarejärve pine and spruce stands, the lysimeters were inserted to depths of 5 to 10 cm under the organic horizon and about 40 cm under the eluvial horizon, with six replications per depth. At Vilsandi the lysimeters were installed under the humus horizon (to a depth of 5 to 10 cm) and the illuvial horizon (BC<sub>(g)</sub>) to a depth of about 35 cm). At both sites, percolation water was collected at approximately one-month intervals during the snow-free period along with deposition samples.

Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> concentrations in precipitation and Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in soilwater were determined using ion chromatography (EN–ISO 14911 and EN–ISO 10304). NH<sub>4</sub><sup>+</sup> was analysed using spectrophotometry. Acidity (pH) was measured potentiometrically, and the electric conductivity of samples was also measured conductometrically.

All samples were analysed at internationally accredited laboratories of the Estonian Environmental Research Centre in Tallinn and the Environmental

Studies Laboratory in Tartu. Both laboratories regularly participate in international inter-calibration tests and have continuous quality control programmes.

### **2.3. Calculations and data handling**

Every measurement of wet depositions is done using open, so called bulk, collectors for precipitation. Possible uncertainties because of water loss and also due to dry deposition into samplers are not taken into consideration. The contribution of dry depositions to bulk collectors (steadily open) in the open area may reach approximately 10% of total depositions in rural areas (Lövgren et al., 2000). Bulk deposition measurements were assumed to represent wet depositions because of the absence of true wet deposition measures in ENEMN. Comparisons with rainfall amounts from official weather stations were made to check the consistency of measured rainfall amounts in the local precipitation network.

Bulk concentrations reported in the tables are precipitation-weighted averages, which have not been corrected for sea salts. Although some stations are situated by the sea, the influence of sea salt is not considered relevant here, as the assumption is that the proportion of sea salt contribution has not changed over the short assessment period. In addition, the mean  $\text{Cl}^-/\text{Na}^+$  ratio in bulk precipitation was higher than could be predicted from seawater ( $\text{Cl}^-/\text{Na}^+=1.166$ ), indicating chloride depositions from additional sources (in our case, oil shale burning) (Pajuste et al., 2006).

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 the detection limit (ICP IM Manual, 1998). All of the annual mean concentration values are volume-weighted averages. The monthly values from October–April were used to calculate cold seasonal trends (winter = heating period) and values from May–September were used to calculate warm seasonal trends (non-heating period = summer). The pH values were converted to  $\text{H}^+$  before calculation of the mean pH value. Thematic deposition maps and mean pH for the period 2000–2006 were produced with MapInfo Professional 6.0 and using Surfer Version 7.

### **2.4. Statistical analysis**

The nonparametric Mann-Kendall test was used for the detection of trends in the time series of precipitation-weighted annual and monthly mean concentrations. The statistical method was used for the testing of the presence of a monotonic increasing or decreasing trend, and the nonparametric Sen's method was used for the estimation of the slope of the linear trend.

**Table 2.** List of Estonian National Monitoring Network (ENEMN) stations in different monitoring programmes.

Monitoring station	Coordiants		Monitoring programme	Period	Sampling media
	north latitude	east longitude			
Kunda	59° 29' 40"	26° 35' 30"	LPN	1994–2006	BP (daily/monthly)
Jõhvi	59° 18' 58"	27° 22' 43"	LPN	1994–2006	BP (daily/monthly)
Saka	59° 25' 39"	27° 14' 11"	LPN	1996–2006	BP (daily/monthly)
Harku	59° 23' 52"	24° 36' 09"	LPN	1994–2006	BP (daily/monthly)
Tiirikoja	58° 52' 09"	26° 57' 04"	LPN	1994–2006	BP (daily/monthly)
Saarejärve	58° 42' 05"	26° 45' 17"	ICP IM	1995–2006	BP (daily/weekly)
Lahemaa	59° 29' 40"	25° 55' 50"	EMEP	1994–2006	BP (daily/weekly)
Tooma	58° 52' 18"	26° 16' 11"	LPN	1994–2006	BP (daily/monthly)
Lääne-Nigula	58° 56' 58"	23° 48' 42"	LPN	1996–2006	BP (daily/monthly)
Vilsandi	58° 22' 34"	21° 50' 42"	EMEP/ ICP IM	1994–2006	BP (daily/weekly)
Karula'	57° 42' 47"	26° 30' 17"	LPN	1999–2006	BP (daily/monthly)
Karula	57° 42' 02"	26° 31' 03"	ICP Forest	1997/2006	BP+TF (monthly)
Sagadi	59° 33' 42"	26° 02' 46"	ICP Forest	1997–2006	BP+TF (monthly)
Vihula	59° 34' 42"	26° 07' 57"	ICP Forest	1997–2006	BP+TF (monthly)
Karepa	59° 31' 44"	26° 24' 48"	ICP Forest	1997–2006	BP+TF (monthly)
Pikasilla	58° 03' 29"	26° 06' 53"	ICP Forest	1997–2006	BP+TF (monthly)
Mäksa	58° 21' 38"	26° 58' 31"	ICP Forest	1997–2006	BP+TF (monthly)
Matsalu	58° 43' 02"	23° 49' 21"	LPN	1999–2006	BP (daily/monthly)
Tahkuse	58° 31' 25"	24° 55' 32"	LPN	1999–2006	BP (daily/monthly)
Haanja	57° 42' 37"	27° 04' 08"	LPN	1999–2006	BP (daily/monthly)
Otepää	58° 00' 36"	26° 24' 46"	LPN	1999–2006	BP (daily/monthly)
Nigula	58° 00' 58"	24° 43' 13"	LPN	1999–2006	BP (daily/monthly)
Alam-Pedja	58° 25' 17"	26° 14' 07"	LPN	1999–2006	BP (daily/monthly)
Loodi	58° 16' 33"	25° 35' 10"	LPN	1999–2006	BP (daily/monthly)

\*LPN – Local Precipitation network

The Mann-Kendall test requires at least four values, and calculation of the confidence intervals for the Sen's slope estimate requires at least ten values in a time series (Salmi et al., 2002).

A statistical significance threshold of  $p < 0.05$  (95% confidence means that the detected trend is significantly different from a zero trend) was applied to the trend analysis. We analysed twelve-year time trends using the annual means of chemical parameter ( $n=12$ ) and three-year time trends using the monthly means of chemical parameters ( $n=34-36$ ).

The Spearman's nonparametric correlation analysis was used to assess the covariance of monthly mean concentrations of precipitation components between stations. 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.

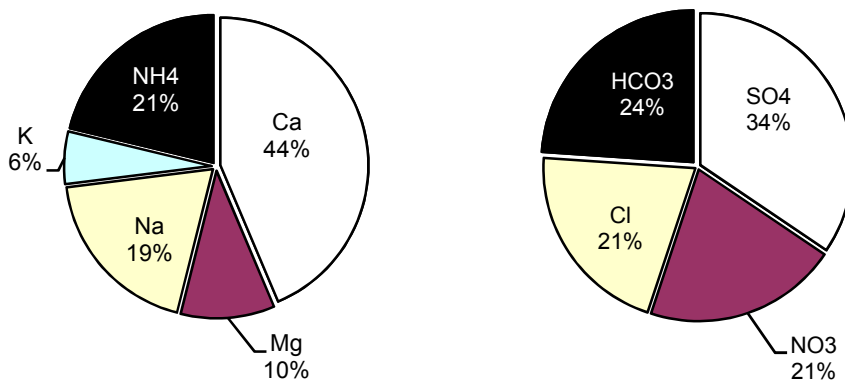
### 3. RESULTS

#### 3.1. Ion composition of bulk precipitation

##### Acidic anions

The share of anions in equivalents of total anionic charge varied; there were three different patterns, for example; in the industrial region and at background stations, the share of anions decrease in the order  $\text{SO}_4^{2-}$  (32–38%)  $\Rightarrow$   $\text{HCO}_3^-$  (27–33%)  $\Rightarrow$   $\text{Cl}^-$  (16–19%)  $\Rightarrow$   $\text{NO}_3^-$  (13–23%) in bulk deposition. In coastal located (EMEP stations and Matsalu) stations the anionic share decreases in the order  $\text{SO}_4^{2-}$  (33%) =  $\text{Cl}^-$  (31%)  $\Rightarrow$   $\text{NO}_3^-$  (28%)  $\Rightarrow$   $\text{HCO}_3^-$  (9%) and  $\text{SO}_4^{2-}$  (47%)  $\Rightarrow$   $\text{NO}_3^-$  (21%)  $\Rightarrow$   $\text{Cl}^-$  (16%) =  $\text{HCO}_3^-$  (16%) in South-Estonian LPN stations.

At the majority of stations, the prevailing anion in the bulk precipitations was  $\text{SO}_4^{2-}$ , which formed more than 32%–47% of anion composition in 1994–2006. Exceptionally, at Vilsandi and Matsalu the share of  $\text{Cl}^-$  was larger or equal (33–34%) than that of  $\text{SO}_4^{2-}$  (24–34%), due to its coastal location. In general, the anionic proportion of  $\text{Cl}^-$  and  $\text{NO}_3^-$  varied between 16–31% and 13–28% respectively on an equivalent basis during 1994–2006, and  $\text{HCO}_3^-$  varied between 9–33%. At Kunda, Harku and Saarejärve, the  $\text{HCO}_3^-$  proportion of anion composition was relatively high, i.e. 40–52%, and this exceeded the  $\text{SO}_4^{2-}$  proportion (22–25%).



**Figure 4.** Mean share of cations and anions in bulk precipitation on an in equivalent basis at ten stations, 1994–2006.



## Cations

The share of various cations in equivalents from summed cationic charge decrease in the order  $\text{Ca}^{2+}$  (59%-28%)  $\Rightarrow$   $\text{NH}_4^+$  (13–28%)  $\Rightarrow$   $\text{Na}^+$  (15–27%)  $\Rightarrow$   $\text{Mg}^{2+}$  (9–13%)  $\Rightarrow$   $\text{K}^+$  (4–8%) in bulk deposition at all stations. At NE industry stations the share of  $\text{Ca}^{2+}$  was greater than 59% (max. 75% at Kunda), at natural background stations (including South-Estonian LPN) 36–40% and at EMEP stations 28% during the period 1994–2006. An exception was Vilsandi, where due to its location, the proportions of  $\text{Na}^+$  (31%) and  $\text{NH}_4^+$  (30%) were greater than that of  $\text{Ca}^{2+}$  (23%). Higher proportions of  $\text{NH}_4^+$  are characteristic at Lääne-Nigula (34%), Saka 32% and Vilsandi (30%) compared with the mean of Fig 4.

## 3.2. Correlations between ions in precipitation

### Acidic anions in precipitation

Data for the 12-year study period (1994–2006) show linear decreasing trends in sulphate and chloride concentrations at nearly all of the stations (Paper I, Figure 2, Table 1, Treier et al., 2008).

The negative linear trend for sulphate was statistically significant at all stations ( $\text{SO}_4^{2-}$  slope estimates i.e. change per year varied from  $-1.76 \text{ mg l}^{-1}$  at Kunda to  $-0.12 \text{ mg l}^{-1}$  at Vilsandi). At most stations (except Harku and Lahemaa) the decline in chloride was also significant, and annual decline varied from  $-0.67 \text{ mg l}^{-1}$  at Kunda to  $-0.04 \text{ mg l}^{-1}$  at Tooma. Linear annual decreasing trends of summed anions ( $\text{SO}_4^{2-} + \text{Cl}^- + \text{NO}_3^-$ ) varied from  $0.167 \text{ meq l}^{-1}$  at Kunda to  $0.014 \text{ meq l}^{-1}$  at Vilsandi (Paper I, Table 1, Treier et al., 2008).  $\text{SO}_4^{2-}$  followed the same pattern: linear decline trends of annual concentrations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  were in good line with annual  $\text{SO}_2$  emissions and annually combusted oil shale amounts (Paper I, Fig. 1, Treier et al., 2008).

The greatest declined anion was  $\text{SO}_4\text{-S}$  in most stations except Kunda, where the leading decreasing ion was  $\text{Ca}^{2+}$ .

Monthly concentrations of both anions  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  were positively correlated (at  $p < 0.05$ ) with one another, and the highest correlations were found in NE stations ( $r = 0.69\text{--}0.78$ ). Although chloride is usually of marine origin, in our case both  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  anions are the mainly acidic components of flue gases of oil shale.

The decrease of sulfate and chloride concentration in bulk precipitation was more than three-fold on average (at Jõhvi  $\text{Cl}^-$  decreased even eleven-fold) compared to monitoring periods 1994–1996 and 2003–2005.

Radical changes at Kunda ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  decreased by seven-fold at the same time) are the result of the reduction in dust emissions from Kunda cement factory (1994–1999 average 32,000 tons, 2003–2005 136 tons) more than 200-fold. Official data confirm that total  $\text{SO}_2$  emission from stationary sources in

Estonia fell from 149 thousand tons to 74 thousand tons (about two-fold) during the period 1994–2005 (Paper I, Fig. 1, Treier et al., 2008).

Recent changes in 2006 confirm that the fall in  $\text{SO}_4\text{-S}$  concentrations has continued, e.g. at Kunda, Jõhvi, Saka, Tooma, Saarejärve, Harku, Kunda and Tiirikoja in comparison with the last period (2003–2005). In 2006 chloride concentration in bulk precipitation were variable; the decrease continued at Kunda, Lahemaa and Vilsandi but increasing at Saka, Lääne-Nigula, Harku and Jõhvi. The fact that monthly concentrations of both anions were positively correlated between stations suggests that the oil shale industry located in northeastern Estonia is an important pollution source, having an effect on the deposition content of a significant area of the country (Treier et al., 2004) up to latest technological measures implemented in the oil shale energy industry (2005–2006).

Throughout the study period mean concentration of  $\text{NO}_3\text{-N}$  varied from 0.3–0.6  $\text{mg l}^{-1}$  at different stations, and the annual load was higher, about 3  $\text{kg ha}^{-1}$  at NE industrial stations, and on average 2  $\text{kg ha}^{-1}$  at remaining stations. The annual mean concentration shows a statistically significant decreasing at Jõhvi, Lahemaa, Vilsandi and Saarejärve stations.

### Base cations

The decreasing trends of annual mean concentrations of summed base cations (the change per year varied from  $-0.203 \text{ meq l}^{-1}$  at Kunda to  $-0.006 \text{ meq l}^{-1}$  at Lahemaa) were statistically significant at six stations out of 10. At Vilsandi, Lääne-Nigula, Tiirikoja and Harku the decrease of summed base cations was not statistically significant.

Although annual mean concentrations of calcium declined on average three-fold (six-fold at Lahemaa and Kunda and 1.5 at Lääne-Nigula) during the study period the calculated loads remained quite high (10–20  $\text{kg ha}^{-1} \text{ year}^{-1}$ ) in the NE industrial region (Map 3). The decreasing trend of  $\text{Ca}^{2+}$  concentrations was statistically significant at seven out of 10 stations (the change per year varied from  $-3.1 \text{ mq l}^{-1}$  at Kunda to  $-0.06 \text{ mq l}^{-1}$  at Lääne-Nigula). Monthly mean concentrations of  $\text{Ca}^{2+}$  varied greatly, especially in summer. In 2006 the annual mean calcium concentrations have increased at Tooma, Lahemaa, Saarejärve, Jõhvis, Saka and Harku compared with the last period (2003–2005).

At most stations, the correlations of summed cations between stations were higher at the NE stations. The correlation between summed cations and sulphate was stronger at the NE stations ( $r=0.75\text{--}0.85$ ) and weaker at the E stations ( $r=0.47\text{--}0.49$ ).

Sodium is regarded as a sea salt element, but in our case it is emitted in fly ash along with magnesium and potassium. It is difficult to distinguish between Na of marine origin and fly ash Na. A significant correlation (at  $p<0.05$ ) was found between the monthly concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  (Paper II, Treier et al., 2004).

Annual mean concentrations of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  decreased at all stations, and the trends were statistically significant in 67% of cases (Paper I, Table 1, Treier et al., 2008). The annual mean concentration of  $\text{Na}^+$  decreased on average three-fold (at Jõhvi almost nine-fold) between 1994–1996 and 2003–2005). At Jõhvi  $\text{Na}^+$  originates from local industry, where emissions of  $\text{NaCO}_3$  and  $\text{NaOH}$  have been recorded (Kabral et al., 2008).

### 3.3. Seasonal trends

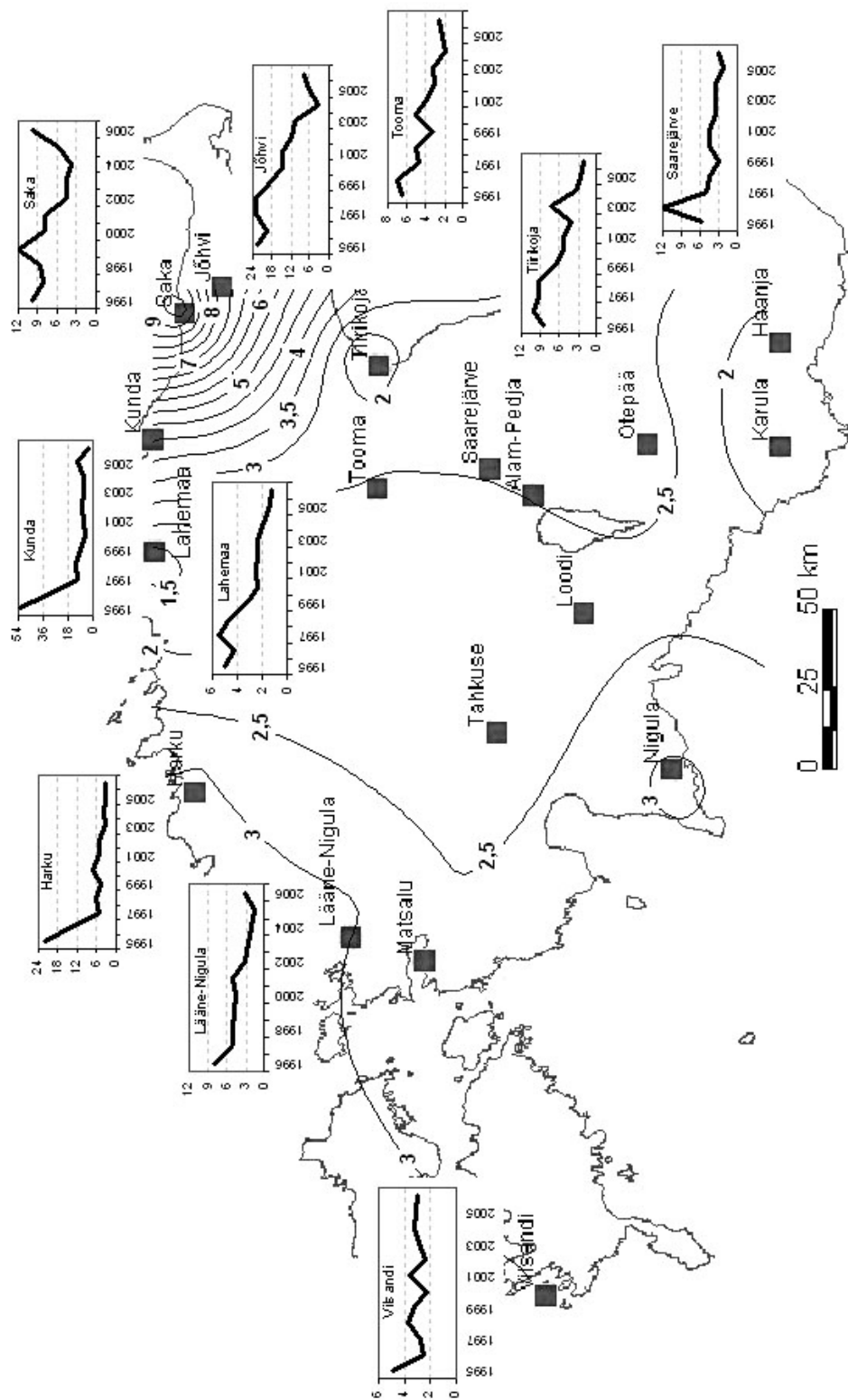
As a rule, the highest monthly mean concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in time series were measured from October to April (i.e. in the cold season (heating period) during the 12-year period.

There are statistically significant decreasing trends in both warm and cold seasons for  $\text{SO}_4\text{-S}$  at all 10 stations, for  $\text{Cl}^-$  at 9 stations and for  $\text{Ca}^{2+}$  at 7 out of 10 stations. There are no clear patterns in the seasonal trends for the rest of ion concentrations in bulk precipitations. The most intensive  $\text{SO}_4\text{-S}$  and  $\text{Cl}^-$  decline during the cold season is directly affected by the oil shale industry region and the most intensive production of electricity in power plants during the heating period. The more intensive downward trend of  $\text{Ca}^{2+}$  concentrations in the warm period indicates the dry season's effect on carbonate dust distribution; obviously the effect of the decline in particle emissions and the local impact of road dust from gravel roads appear more distinctly during the dustier (warm) season.

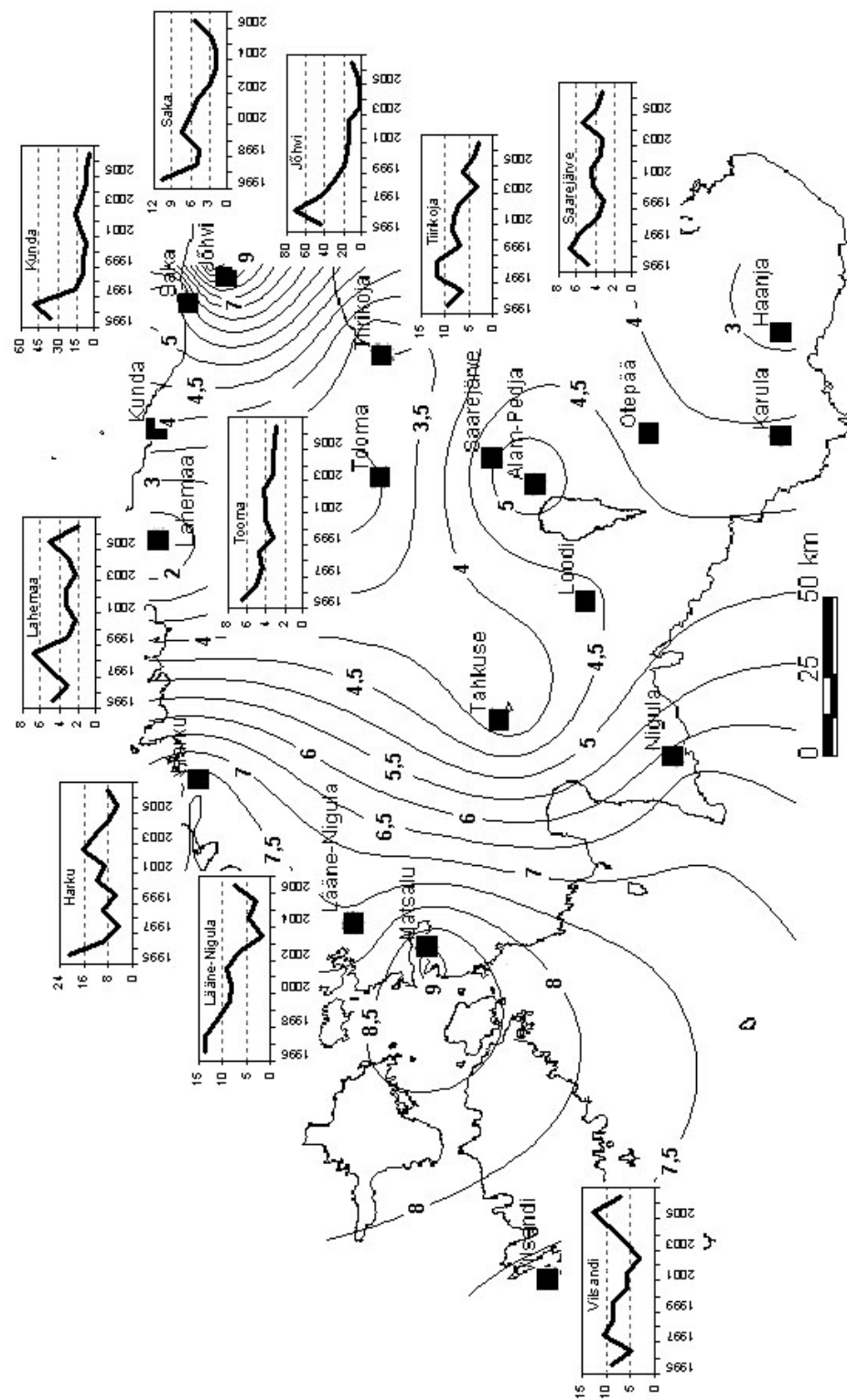
The greatest seasonal decline of ions was characteristic at Kunda station;  $\text{SO}_4\text{-S}$   $-0.13 \text{ mg l}^{-1}$  per month during the cold period and  $\text{Ca}^{2+}$   $-0.63 \text{ mg l}^{-1}$  per month during the warm season. Warm and cold season trends for  $\text{SO}_4\text{-S}$ ,  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  do not differ at the natural background stations (Vilsandi, L-Nigula and Lahemaa). At Harku station there were no statistically significant seasonal changes in monthly mean concentrations of  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$  and pH, except for decreasing trends of  $\text{SO}_4\text{-S}$  during cold and warm period (Table 3). The seasonal variation is partly due to meteorological factors; primarily differences in vertical mixing at different times of year (Norlund, 2000). Sulphate aerosols are formed at a faster rate during the light spring and summer months than during the dark autumn and winter months, and the seasonal variation in sulphate concentrations is rather small (lacking any clear trends) (Finnish Meteorological Institute, 1998).

**Table 3.** Significant seasonal trends of monthly mean concentrations in bulk precipitations at 10 monitoring stations by Mann-Kendall test, 1994–2005. Q=decline per month ( $\text{mg l}^{-1}$ ) for single ion. Significance level \*\*0.001; \*0.01; \*0.05. Cold season (October–April) and warm season (May–September).

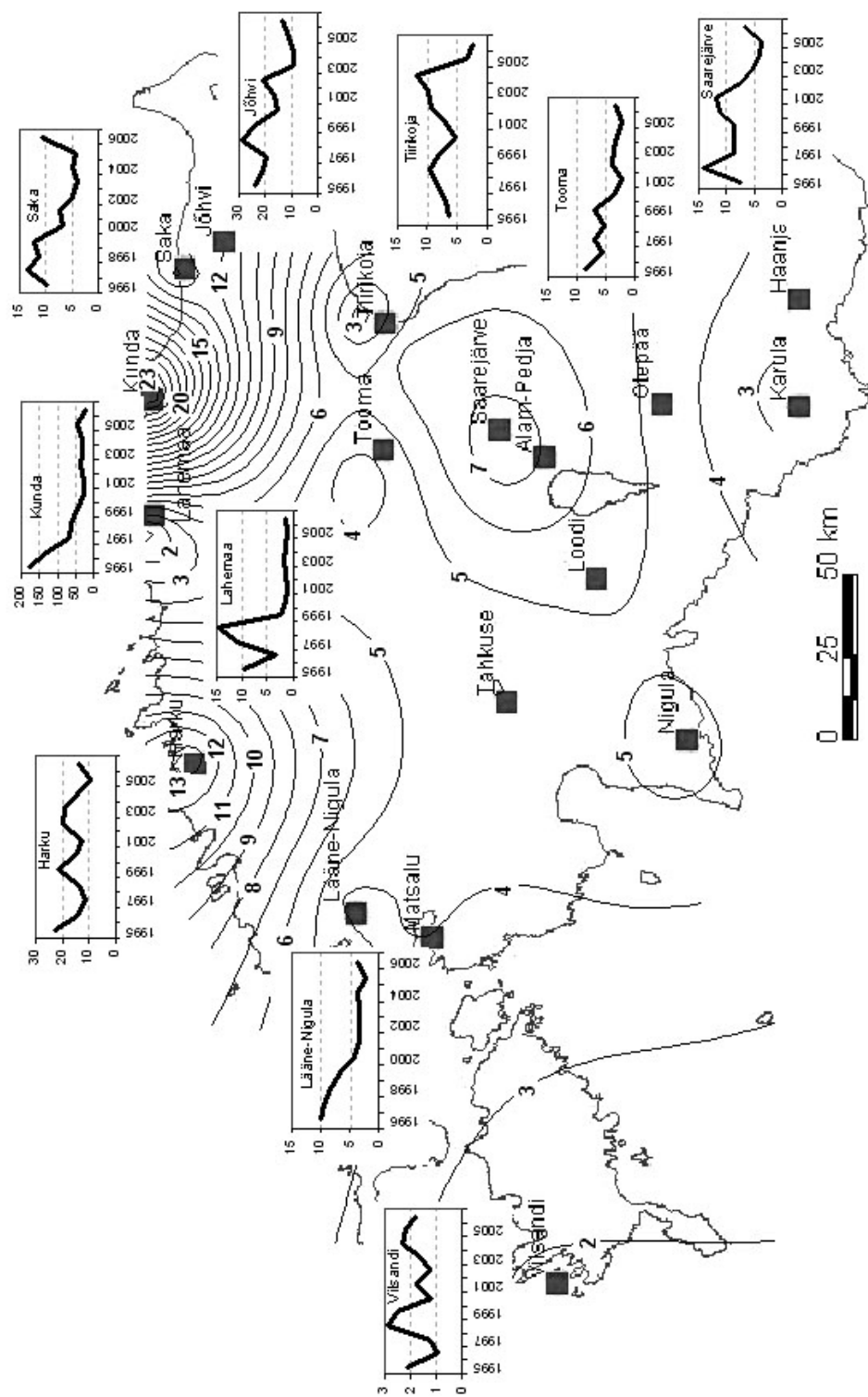
	Kunda		Jõhvi		Saka		Harku		Lahemaa		Tiirikoja		Tooma		Saarejärve		L-Nigula		Vilsandi	
	Sign	Q ( $\text{mg l}^{-1}$ )	Sign	Q ( $\text{mg l}^{-1}$ )	Sign	Q ( $\text{mg l}^{-1}$ )	Sign	Q ( $\text{mg l}^{-1}$ )	Sign	Q ( $\text{mg l}^{-1}$ )	Sign	Q ( $\text{mg l}^{-1}$ )	Sign	Q ( $\text{mg l}^{-1}$ )	Sign	Q ( $\text{mg l}^{-1}$ )	Sign	Q ( $\text{mg l}^{-1}$ )	Sign	Q ( $\text{mg l}^{-1}$ )
SO <sub>4</sub> S warm season	***	-0.06	***	-0.03	*	-0.02	***	-0.02	***	-0.01	***	-0.03	***	-0.01	***	-0.01	*	-0.01	*	-0.01
SO <sub>4</sub> S cold season	***	-0.13	***	-0.05	**	-0.02	***	-0.01	***	-0.01	***	-0.01	***	-0.01	***	-0.01	*	-0.01	***	-0.01
Cl <sup>-</sup> warm season	***	-0.07	***	-0.08	*	-0.01		-0.01	**	-0.01	***	-0.02	+	-0.004	**	-0.01	***	-0.02	+	-0.02
Cl <sup>-</sup> cold season	***	-0.09	***	-0.11	***	-0.02		0.0003	***	-0.01	***	-0.02	**	-0.01	**	-0.01	*	-0.02	*	-0.02
Ca <sup>2+</sup> warm season																				
Ca <sup>2+</sup> cold season	***	-0.53	***	-0.05	***	-0.04		0.0003	***	-0.01		-0.01	***	-0.01	***	-0.01	*	-0.01	*	-0.004



**Map 1.** Calculated annual bulk deposition of sulphur ( $\text{kg ha}^{-1}$ ) in the period 1994–2006 and in 2006.



**Map 2.** Calculated annual bulk deposition of chloride ( $\text{kg ha}^{-1}$ ) in the period 1994–2006 and in 2006.



**Map 3.** Calculated annual bulk deposition of calcium ( $\text{kg ha}^{-1}$ ) in the period 1994–2006 and in 2006.

### 3.4. pH variation

The fact that precipitation has become more acidified during the last 13 years is confirmed by the annual means of pH values at 23 stations. A trend towards acidification was recorded in 10 of 23 stations, whereas in 6 stations (in Jõhvi (max (-0.11), Kunda, Saka, Tiirikoja, Lahemaa and Tooma) the trend was statistically significant.

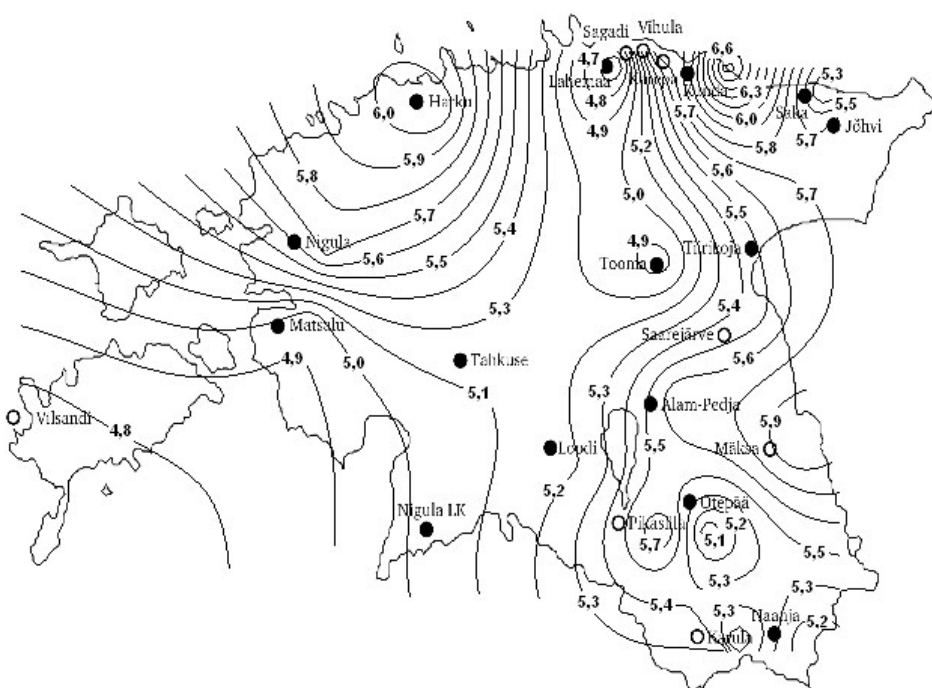
Whereas during the period 1995–1999, the annual mean pH was only classified as weakly acidic at Vilsandi station, 7 stations could be defined in the same group during the 2000–2006 (Lahemaa, Tooma, Vilsandi, Matsalu, L-Nigula, Otepää, Tahkuse). Whereas during the period 1994–1999, the annual mean pH varied from 4.3 (Vilsandi) to 7.7 (Kunda), during the last seven-years (2000–2006) the pH varied between 4.7 (Lahemaa) and 6.8 (Kunda).

The relative importance of acid rain ( $\text{pH} < 5.1$ ) has increased from 2000; the lowest annual mean pH levels were recorded at the majority of stations (except Vilsandi and ICP Forest stations) during the years 2000–2006, 11 of these stations had the lowest annual means pH during the period 2004–2006. The most acidic precipitation was found in both coastal EMEP stations, Vilsandi and Lahemaa, where all annual means of pH were lower than 5.1 during the years 1994–2006.

About 62% of monthly means of pH (from all 156 values) were lower than 5 in EMEP stations. The lowest annual mean pH (4.08) was recorded in Lahemaa in 2005. In Tooma station  $\text{pH} < 5.1$  has also been recorded in 9 years out of the 13-year study period. Weakly acidic precipitation ( $\text{pH} < 5.1$ , classified by Smidt, 1986) was measured for all study years in Matsalu and frequently (in 5 years out of 7) also in Tahkuse. Both W stations have been operating since 2000. Almost 40% of monthly means of pH (of all 97 values) were lower than 5 at Matsalu station.  $\text{pH} < 5$  is most often found during the heating period (from October to April), for example 100–70% of monthly mean precipitation from November to February had a pH lower than 5.1 at EMEP stations Lahemaa and Vilsandi and at coastal station Matsalu during the monitoring period. It is very unlikely for acid precipitation to fall during the summer (May or August).

Strongly acidic precipitation ( $\text{pH} < 4.1$  by Smidt, 1986) was rarely recorded: twice in Lahemaa and Saarejärve and once in Vilsandi, Tahkuse and Otepää. The lowest pH value ( $\text{pH} = 3.11$ ) was recorded at Lahemaa station in December 2005.





**Map 4.** Mean pH 2000–2006 at 23 monitoring stations.

A statistically significant decreasing trend was also estimated at Kunda, where the most basic precipitation was characteristic, and where the annual mean pH of precipitation dropped from 7.23 (strongly basic  $\text{pH} > 7.1$ ) (1995–1999) to 6.6 (2000–2006) (Map 4). The most intensive decrease at Kunda was during the years 1997–1999 (due to the use of new purification equipment at the Kunda cement factory).

A statistically significant decreasing trend was also estimated at NE industrial stations in Jõhvi and Saka. During the years 1995–1999 these stations ( $\text{pH} 6.4$ ) could be classified as weakly basic ( $\text{pH} = 6.1\text{--}6.5$ ), but the pH level decreased during the entire study period, reaching pH 5.7 at Jõhvi and pH 5.4 at Saka in the period 2000–2006.

### **3.5. Impact of air pollution on the environment of coniferous stands in IM areas (Vilsandi and Saarejärve)**

The results of trend analyses of a ten-year study (1996–2005) of deposition (throughfall+ stemflow) and soilwater in two pine stands and a spruce stand (ICP IM areas) are presented in Paper III (Frey et al., 2006). The IM monitoring

sites represent areas of boreal coniferous forests receiving background loads of air pollution and deposition. Although the two sites are not regionally representative, they provide an opportunity to monitor changes in air pollution and its impacts on the environment of coniferous stands on the western border of Estonia (Vilsandi), where higher concentrations of SO<sub>2</sub> are measured from southern and south-western air mass transport directions (Pajuste et al., 2003) and in eastern Estonia (Lake Saare area), which is more affected by local sources of air pollution from the region of the oil-shale industry in North-Eastern Estonia.

The detected decreasing trends of deposited sulphate and cations at the Saarejärve integrated monitoring area (in the east) are in close correspondence with the decline in SO<sub>2</sub> and fly ash emissions in Estonia. At Vilsandi pine stand, which is located in westernmost Estonia and is under marine influence, the decrease of sulphur deposition was comparable with that of the eastern Saarejärve pine stand. However, the total base cation load in the Vilsandi pine stand remained unchanged, resulting in a decrease in throughfall acidity. In the coniferous stands at Saarejärve, the deposition of base cations decreased more than that of acid anions, causing an increase in K leaching from canopies. A close accordance between sulphate decline in deposition and topsoil water was accompanied by base cation decline in soilwater under the organic horizon at both IM areas. In naturally podzolized soil at Saarejärve, the decline of SO<sub>4</sub><sup>2-</sup> and base cations resulted in increased levels of total soluble Al.

Statistically significant increasing time trends (estimated by Mann-Kendall nonparametric test) of total soluble Al in soilwater below the organics and eluvial horizon of the pine and spruce stands and of free Al<sup>3+</sup> in soil water from both horizon of the pine stand characterize the study period of 1996–2005. The same tendency towards a statistically significant decrease in pH and SO<sub>4</sub>-S with some increase of total soluble Al concentrations (not significant) is characteristic of soilwater below the organic horizon (about 10 cm), but not of the deeper layer in the Vilsandi pine stand.

Only additional H<sup>+</sup> can increase both total Al and soluble free Al<sup>3+</sup> concentration in soil water. The pH of solutions in the studied soil water was normally well below 5 at Saarejärve and, in fact, the pH of throughfall was commonly higher than that of the soil solution receiving it. The increase in total soluble Al in podzolised soil indicates an ongoing process of podzolisation due to dissociated organic acids derived from the mineralisation of conifer litter, and is probably attributable to the decreased deposition of cations and decreased retention of sulphate in soil horizons (Frey et al., 2006).

## 4. DISCUSSION

### 4.1 Comparison of ion content trends by three-year periods

#### 1994–1996

The decline in ion concentrations in bulk precipitation at most stations during the first three-year period of 1994–1996 was a response to the reduction in dust emissions from Kunda cement factory and flying ash emissions from the Narva Power Plants.

A sharp decrease in  $\text{SO}_4\text{-S}$  in bulk precipitation occurred at Kunda station ( $-13.25 \text{ mg l}^{-1}$  per year) (Table 4), which was in close correlation with the fall in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  in precipitation at Kunda. All of these trends of purification in Kunda precipitation are responses to a four-fold reduction in dust emissions from the town's cement factory during the period. The second large drop in  $\text{SO}_4\text{-S}$  concentrations ( $-3.80 \text{ mg l}^{-1}$  per year) characterised Harku precipitation, which was largely accompanied by a  $\text{Ca}^{2+}$  decline ( $-0.89 \text{ mg l}^{-1}$  per year); ion concentrations in Harku are probably impacted by industrial activity in Tallinn.

There was no statistically significant downward trend in sulphur at most background stations (except for Lahemaa, and this was probably affected more by Kunda) and Saka (the nearest and most heavily affected by the Narva Power Plants). The reduced emission of solid particles from power plants (from 102 to about 74 thousand tons, i.e. about 30%, (Paper I, Fig. 1, Treier et al., 2008) was distinctly reflected in the downward trends of cations at nearly all stations (Table 4). As a result, the highest statistically significant decreasing trend of  $\text{Ca}^{2+}$  in precipitation was characteristic of all stations (except for Lahemaa) during the first three years of the study. The reduced emissions of solid particles from power plants were most distinctly reflected in a decrease in various cation concentrations in Saka precipitation. The decline in cations (especially  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , both of which are characteristic of the mineral part of oil shale) was accompanied by a decline in anions, especially  $\text{Cl}^-$ , and probably also  $\text{HCO}_3^-$  (not measured), but not  $\text{SO}_4^{2-}$ .

#### 1997–1999

The use of new purification equipment in the cement factory at Kunda was the most important positive change in the air pollution situation (causing a reduction in dust emission of about 80% in 1999 compared to 1997 (Paper I, Fig. 3, Treier et al., 2008) in the entire Northeast region. There was a minimal reduction of  $\text{SO}_2$  emissions during the years 1997–1999 (14% from stationary sources and only 6% from the Narva Power Plants), especially compared to the first three-year period. Despite the sharp reduction in dust emissions from Kunda and to a certain extent from the Narva Power Plants, the most important decreasing trend in cation concentrations occurred during the first three-year

period. The decline in  $\text{Ca}^{2+}$  was only statistically significant in precipitation at Kunda ( $-6.82 \text{ mg l}^{-1}$  per year), Saka and Lahemaa.

The ca 1 TWh decrease in electricity production during the period 1997–1999 (Paper I, Fig. 1, Treier et al., 2008) may have been the main cause of the decline in chloride and  $\text{SO}_4\text{-S}$  concentrations in bulk precipitation at nearly all stations. The highest decline in  $\text{SO}_4\text{-S}$  concentration in the precipitation at nearly all stations (except for Jõhvi, Lääne-Nigula and Harku) occurred during the years 1997–1999 (Table 4). The downward trend in sulphur at various stations (as Q in the Table 4) followed this order: Kunda, Saka, Tiirikoja, Tooma, Saarejärve, Lahemaa and Vilsandi. This order of stations by decline per year also indicates the decrease of  $\text{SO}_2$  emissions from both Narva Power Plants and the Kunda cement industry.

A statistically significant decreasing trend of  $\text{Cl}^-$  in precipitation was found at Jõhvi, Saka, Lääne-Nigula, Saarejärve and Lahemaa. The decrease in  $\text{Cl}^-$  was in close correlation with decreasing trends in monovalent cations:  $\text{Na}^+$  and  $\text{K}^+$  at Saka, Lääne-Nigula and Lahemaa. It is generally agreed that sea salt is the dominant source of  $\text{Cl}^-$  and  $\text{Na}^+$  (Draaijers et al., 1997). In the case of Lahemaa and perhaps also Saka and Jõhvi, there could be a sea salt effect on precipitation, but in all cases an additional source of  $\text{Cl}^-$ , originating from oil shale burning, should be taken into consideration. Estonian oil shale contains chlorine (0.75%) in its organic part (Ots, 2005).

## 2000–2002

Official emissions data indicated a reduction in solid particles from power plants by about 20% and the lowest level of dust emissions, as well as cement production at Kunda cement factory (Paper I, Fig. 1 and 3, Treier et al., 2008). Gross production of electricity stabilised during the period 1993–2002, averaging 8.6 TWh per year. Due to the installation of new electrostatic precipitators and the renovation of old ones in both power plants (1997–2002) (Ots, 2005; Liblik et al., 2006), emissions of  $\text{SO}_2$  from power plants fell 1.4-fold during the period 2000–2002 (from 112.2 thousand tons to 78.4 thousand tons), and emissions of solid particles two-fold (from 102.2 thousand tons to 49.2 thousand tons).

No single downward trend in the monthly mean concentrations of major ions in precipitation at any station was revealed by trend analyses during 2000–2002 (Table 4). To the contrary, statistically significant upward trends in chloride and monovalent cations were found at Kunda, of  $\text{Ca}^{2+}$  and of  $\text{Mg}^{2+}$  at Tiirikoja and of  $\text{Cl}^-$  at Tooma (Table 4).

**Table 4.** Significant trends (“–“decreasing and “+” increasing) of annual mean concentrations in precipitation, by three-year periods (1994–1996; 1997–1999; 2000–2002; 2003–2005) and 1994–2005 by Mann-Kendall nonparametric test. Q= decline per year (mg l<sup>-1</sup>) for a single ion. Significance level \*\*\*0.001; \*\*0.01; \*0.05

		SO <sub>4</sub> -S mg l <sup>-1</sup>		Cl <sup>-</sup> mg l <sup>-1</sup>		NO <sub>3</sub> -N mg l <sup>-1</sup>		Ca <sup>2+</sup> mg l <sup>-1</sup>		Mg <sup>2+</sup> mg l <sup>-1</sup>		Na <sup>+</sup> mg l <sup>-1</sup>		K <sup>+</sup> mg l <sup>-1</sup>	
		Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q
Kunda	1994–1996	+	-13.25		-0.06		-0.27	+	-5.12	**	-1.44		0.20	+	-3.54
	1997–1999	+	-2.29		-0.10		-0.46	**	-6.82	*	-0.23		-0.06	**	-0.65
	2000–2002		0.32	*	1.01		0.34		0.53		0.01	**	0.58	*	0.22
	2003–2005	*	1.47		-0.19		-0.17		0.98	*	0.08		-0.14		0.03
	1994–2005	**	-1.76	*	-0.63		0.11	**	-3.01	***	-0.26	*	-0.26	*	-0.45
Jõhvi	1994–1996		-1.83		-0.59		-0.08	*	-1.30	**	-1.04		0.38		0.09
	1997–1999		-0.84	*	-1.54	**	-1.76		0.43		0.01	**	-0.82		-0.14
	2000–2002		-0.26		-0.05		0.04		0.60		0.03		0.06		0.05
	2003–2005		-0.30	+	0.20		-0.20		-0.18		-0.01		-0.15		-0.06
	1994–2005	**	-0.72	***	-0.67	*	-0.25	*	-0.18	**	-0.05	***	-0.33	***	-0.13
Saka	1994–1996		-5.49	+	-8.89		-0.65	*	-5.45	+	-0.71	+	-10.98	*	-6.95
	1997–1999	+	-1.57	+	-0.31	**	-1.28	**	-1.45	**	-0.14	*	-0.15	*	-0.13
	2000–2002		-0.64		-0.02		0.03		0.24		0.02		0.03		0.06
	2003–2005		0.92	+	0.14		-0.41		-0.03		0.01		0.03		0.03
	1994–2005	*	-0.46	**	-0.13		-0.15	*	-0.24	*	-0.03	*	-0.05	*	0.08
Harku	1994–1996	***	-3.80	**	-0.86		0.00	+	-0.98		-0.03		0.22		0.01
	1997–1999		-0.15		-0.03		-0.40		0.34		0.03		-0.12		0.01
	2000–2002		-0.18		-0.05		-0.39		0.49		0.03		0.10		0.00
	2003–2005		-0.07		0.32		0.19	+	-0.98		-0.03		0.22		0.01
	1994–2005	*	-0.48		-0.05		-0.02		-0.04		-0.01		0.00		-0.02
Tiirikoja	1994–1996		-0.66	**	-0.61	+	-0.44	+	-0.53	***	-0.62		0.00		0.00
	1997–1999	+	-0.68		-0.28		-0.52		0.10		0.01	*	-0.24	+	-0.15
	2000–2002		0.03		0.10		0.15	*	0.48	***	0.06		-0.04		-0.03
	2003–2005	+	-0.36		0.05	+	-0.53	*	-0.27	*	-0.05	+	-0.12	*	-0.17
	1994–2005	***	-0.37	**	-0.11		-0.07		-0.03		-0.01	*	-0.04	+	-0.04
Saare-järve	1994–1996		0.00	+	-0.45		-0.46	+	-1.01	**	-1.07	+	-0.40		0.00
	1997–1999	+	-0.33	**	-0.20		-0.27		0.00		-0.04		-0.03		0.01
	2000–2002		0.00		0.07		0.03		0.07		0.01		-0.01		0.04
	2003–2005	*	-0.29		-0.03		-0.20		-0.11		0.00		0.02		0.07
	1994–2005	***	-0.21	+	-0.05	*	-0.06	*	-0.17	*	0.03	**	-0.05		-0.01
Lahemaa	1994–1996	*	-0.65	***	-0.53		-0.19		-0.17	***	-0.11	**	-0.17	***	-0.14
	1997–1999	**	-0.40	*	-0.11		-0.23	*	-0.33		-0.01	*	-0.06	+	-0.02
	2000–2002		0.02		0.08		-0.05		-0.01		0.00		0.00		-0.01
	2003–2005	+	-0.14		0.05		-0.04		-0.02		0.00		0.01		-0.01
	1994–2005	***	-0.20		-0.05	*	-0.07	*	-0.09	**	-0.01	*	-0.02	***	-0.02
Tooma	1994–1996		-0.11		-0.15		0.00	*	-0.48	***	-0.31		-0.09		0.00
	1997–1999	*	-0.43		-0.03		-0.43		0.05		0.02		-0.05	+	-0.03
	2000–2002		-0.05	+	0.17		0.08		0.02		0.01		-0.01		-0.01
	2003–2005	+	-0.24		-0.06	*	-0.52		-0.06		-0.01		-0.03		-0.02
	1994–2005	**	-0.21	**	-0.04		-0.06	**	-0.10	***	-0.02	**	-0.03	**	-0.02
L-Nigula	1994–1996		-5.28		-0.46		-0.27	+	-2.58		-0.04		-0.72		-0.80
	1997–1999		-0.34	*	-0.51		-0.04		-0.24	*	-0.04	*	-0.22	**	-0.17
	2000–2002		-0.19		-0.09		-0.32		-0.01		0.00		-0.02		-0.03
	2003–2005	*	-0.68		0.34	*	-0.78	*	-0.34	*	-0.04		-0.17		-0.10
	1994–2005	*	-0.13	*	-0.15		0.08	+	-0.06		-0.01		-0.05	*	-0.03
Vilsandi	1994–1996		0.08	*	-1.48	+	0.61	**	-0.32	***	-0.22		-0.03	+	0.11
	1997–1999	+	-0.42		-0.45		-0.41		-0.06	+	-0.04	*	-0.26	+	-0.06
	2000–2002		0.02		-0.03		-0.17		-0.02		-0.01		-0.05		0.00
	2003–2005		-0.13		-0.01		-0.31		-0.05		0.00		0.12		0.01
	1994–2005	*	-0.12	*	-0.11	+	-0.06		-0.02		0.00		-0.02		-0.01

## 2003–2005

The studied period was an eventful one: after the renovation of old electric filters and the installation of new electric filters for power plants at Narva in 2002 (Ots, 2005), emissions of solid particles decreased by about 13% in 2003, despite a 19% increase in electricity production. At the same time, the increase in SO<sub>2</sub> emissions (15%) was in close correlation with the increase in electricity production (Paper I, Fig. 1, Treier et al., 2008). The start-up of two new fluidized bed (CFB) energy blocks (2004–2005) was the most important factor that caused a reduction in sulphur dioxide emissions of at least ca 13.7 thousand tons, as well as that of solid particles by 4.6 thousands tons compared to the year 2003 (Annual report of Estonian Energy 2004/2005).

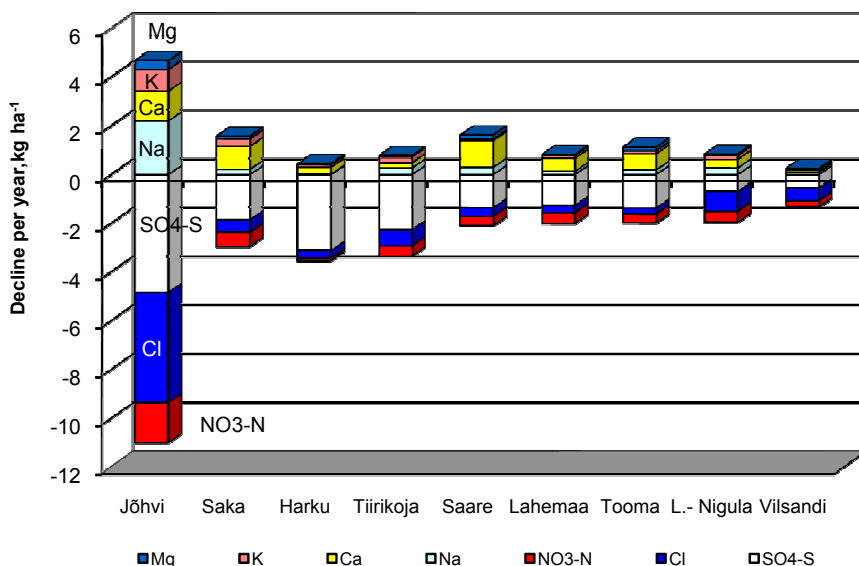
Trend analyses of annual ion concentrations in bulk precipitation indicated statistically significant downward trends of SO<sub>4</sub>-S at Lääne-Nigula, Tiirikoja, Tooma, Saarejärve and Lahemaa during the last study period. The decline in SO<sub>4</sub>-anions was accompanied by a significant decline in Ca<sup>2+</sup> and Mg<sup>2+</sup> at Tiirikoja and Lääne-Nigula (Table 4). Reductions in the concentrations of bivalent cations also occurred at other stations, but there the decrease was not statistically significant. Thus the deposition data shows an improvement, especially as concerns emissions from the Narva Power Plants.

The increasing concentrations of SO<sub>4</sub>-S and Ca<sup>2+</sup> in precipitations at Kunda characterised the last period of 2003–2005 (Table 4). The increasing concentrations of in depositions are closely correlated with the increase in dust emissions, and also with cement production at Kunda.

## 4.2. Decline in depositions during monitoring period

An annual decline in depositions (kg ha<sup>-1</sup>) over a twelve-year period was calculated on the basis of the decline in annual mean concentration and mean precipitation quantity (mm) for all 10 stations. The annual decline in depositions was exceptionally high at Kunda (Ca 15.3 kg ha<sup>-1</sup>, SO<sub>4</sub>-S 8.96 kg ha<sup>-1</sup>), and therefore this station was excluded from Figure 5.

In general, the annual average decline in acid anions (calculated on an equivalent basis) were higher (75%) than the annual average decline of base cations (25%) calculated for the entire study period. Theoretically, summed anions and cations should be equal. In this calculation we do not measure HCO<sub>3</sub><sup>-</sup>, but we can assume that the greater decline in summed anthropogenic anions is compensated by natural HCO<sub>3</sub><sup>-</sup> ions.



**Figure 5.** Calculated decline in annual deposition of main ions ( $\text{kg ha}^{-1}$ ) in bulk precipitation at nine stations (with the exception of Kunda) during the period 1995–2005.

From Figure 5 can we see that the decline of annual  $\text{SO}_4\text{-S}$  deposition has been most significant at all stations (average proportion 50%), and has varied between 84 and 32%. The average reduction in the annual deposition of Cl and  $\text{NO}_3\text{-N}$  has been 9% and 16% respectively. At Jõhvi, Vilsandi and Lääne-Nigula, however, the Cl annual declining proportion compared with the rest of anions was 17–19%.

The annual decline in cation deposition has been more intensive at stations directly affected by an industrial region and at NE industrial region background stations (all changes are statistically significant). The average annual decline in Ca deposition was 13%, and Na, Mg and K had respective proportions of 6%, 4% and 2%. At costal area stations and stations directly affected by an industrial region, Na and Cl held different positions in the declining trend (at Jõhvi Na  $2.2 \text{ kg ha}^{-1} = 13\%$  and  $4.5 \text{ kg ha}^{-1} = \text{Cl } 17\%$ , at Lääne-Nigula Na 9% and Cl 17 %).

EMEP station Vilsandi as a natural background station, was undoubtedly not characteristic of Estonian industrial emissions. The low depositions presented by the Vilsandi station are more characteristic of broader European declining trends, especially as regards  $\text{SO}_4\text{-S}$  and  $\text{NO}_3\text{-N}$ . EMEP station Lahemaa reflects Estonian pollution more distinctly.

### Deposition of anions

The annual mean deposition of sulphates ranged between 3–8 kg ha<sup>-1</sup> in Western Estonia, 7–14 kg ha<sup>-1</sup> in Eastern Estonia (Tiirikoja, Tooma and Saarejärve), 12 kg ha<sup>-1</sup> in NW Estonia and 20 kg ha<sup>-1</sup> in NE Estonia (Kunda 31 kg ha<sup>-1</sup>) in 1996. The annual mean load of SO<sub>4</sub>-S at the 10 stations differed more than ten-fold during the first three-year period (1995–1996), and the annual mean SO<sub>4</sub>-S deposition differed five-fold by 2006 (Map 1).

The dynamic of the SO<sub>4</sub>-S load is similar in most of the stations during the study period (the mean SO<sub>4</sub>-S load declined homogeneously at Saka, Jõhvi, Tiirikoja, Tooma, Lahemaa and Lääne-Nigula). This was caused by the enormous decrease (about 75%) in sulphur deposition (from about 53 kg ha<sup>-1</sup> to 13 kg ha<sup>-1</sup> per year) that occurred at Kunda station during 1995–1998 (Map 1) due to the reconstruction of the Kunda cement factory. At the same time, at the stations most directly affected by the power plants (at Saka and Jõhvi), S deposition remained comparatively stable (ca 21 kg ha<sup>-1</sup> in Jõhvi and ca 9 kg ha<sup>-1</sup> in Saka). The decrease in S deposition in Saka and Jõhvi stations began from 2000, and the lowest deposition was recorded in 2004 (about 3.6 kg ha<sup>-1</sup> in both stations).

Comparing all of the time series of S depositions measured at Estonian background areas (at N, E and W natural background stations: 2 ICP IM, 2 ICP EMEP and 2 meteorological station) at 5 ICP Forest stations and at 5 South-Estonian monitoring stations, we can emphasise the period 1995–1998, when background annual S deposition exceeded 5 kg ha<sup>-1</sup> (Map 1). The SO<sub>4</sub>-S deposition declined below 4 kg ha<sup>-1</sup> from 1999 and remained relatively stable, on average 3.1 kg ha<sup>-1</sup> (varied from 2.6 to 3.7 at 16 monitoring stations all over Estonia) at natural background area up to 2005.

During the last two years (2005–2006) the SO<sub>4</sub>-S deposition declined below 3 kg ha<sup>-1</sup> (averagely 2.4 kg ha<sup>-1</sup>) in the background area (Map 1). The last decline is in close correlation with the reconstruction of two production units of oil shale power plants using new fluidized bed combustion technology, which raises oil shale use efficiency and minimizes SO<sub>2</sub> emissions.

At the same time, at stations most directly affected by the power plants, i.e. Saka and Jõhvi, a new increase in S deposition occurred in the last two years: 9.9 (Saka) and 7.7 (Jõhvi) kg ha<sup>-1</sup> for 2006. The last increase of S deposition was caused more by local industrial activity (probably oil production from oil shale) than by emissions from power plants (Map 1). The annual mean sulphate depositions at Saka recovered the 1996 level in 2006, despite the decrease during 2000–2003.

There have been statistically significant decreasing trends in annual loads of SO<sub>4</sub>-S during the periods 1995–1999 in most of the 10 stations except at Vilsandi. These trends continued during 2000–2006 at Jõhvi, Harku, Tiirikoja, Lahemaa and Lääne-Nigula.



The longest time series from 1995 in 9 W, N, NE, and E stations pointed to the decline in NO<sub>3</sub>-N annual deposition since 1999, when the annual N load declined below 2 kg ha<sup>-1</sup>, but the decreasing trend was only statistically significant in Jõhvi, Saka and Lääne-Nigula. Official data concerning NO<sub>x</sub> emissions point to the increasing trend during the period 1995–2006.

The annual mean deposition of chloride ranged between 5 kg ha<sup>-1</sup> at Vilsandi, 6–8 kg ha<sup>-1</sup> in Eastern Estonia (Tiirikoja, Tooma and Saarejärve), and over 20 kg ha<sup>-1</sup> in NE-Estonia (Kunda 53 kg ha<sup>-1</sup>) in 1995. The annual mean chloride load at the 10 stations differed more than eleven-fold during the first 3-year period (1995–1996), whereas deposition differed eight-fold by 2006.

The distinct decline in Cl<sup>-</sup> deposition in Kunda (averagely 1.6 kg ha<sup>-1</sup> per year by Mann-Kendall test) and in Jõhvi (averagely 4.3 kg ha<sup>-1</sup> per year) during 1995–2006 (Map 2) indicates the link between Cl<sup>-</sup> deposition and oil shale use or/and reconstruction of the oil-shale industry. The downward trends of Cl<sup>-</sup> annual deposition: from 7–8 kg ha<sup>-1</sup> during 1995–1999 to 5–6 kg ha<sup>-1</sup> in 2000–2003 up to 3–4 kg ha<sup>-1</sup> for the last study period 2004–2006, was also characteristic of W, N and E stations (Map 2). The decline in the annual load of Cl<sup>-</sup> was statistically significant at Kunda, Saka, Jõhvi, Tooma, Tiirikoja and Lääne-Nigula (1995–1999) and Jõhvi, Tiirikoja (2000–2006).

In directly marine influenced EMEP stations at Vilsandi and at Lahemaa the annual load of Cl<sup>-</sup> varied between 4–7 and 2–7 kg ha<sup>-1</sup>, depending mostly on annual amounts of precipitation without any time trends. At marine type stations such as Vilsandi and Lahemaa, high peaks of mean chloride depositions occurred during the periods 1997–1999 and 2003–2005. The most stable annual mean deposition of chloride was found at inland stations Saarejärve and Tooma, where the highest and the lowest annual load of chloride varied two-fold during the study period.

The current annual deposition of Cl in Estonia varies from 3–4 kg ha<sup>-1</sup> at inland background areas, about 6–8 kg ha<sup>-1</sup> in the westernmost costal area and 5–10 kg ha<sup>-1</sup> in the NE industrial region.

### **Deposition of cations**

The annual mean deposition of calcium ranged from 3 kg ha<sup>-1</sup> at W station Vilsandi, 7–10 kg ha<sup>-1</sup> at E stations (Tiirikoja, Tooma ja Saarejärve) and over 20 kg ha<sup>-1</sup> in NE-Estonia (Kunda 178 kg ha<sup>-1</sup>) in 1996 (Map 3). The annual mean calcium annual load at the 10 stations differed more than nine-fold during the first three-year period (1994–1996). The reduction in solid particle emissions during the study period is mostly reflected in Ca deposition in W, E and N natural background area stations, where annual Ca load decreased below 5 kg ha<sup>-1</sup> after 2000, whereas during 1995–1999 the Ca deposition of W, E and N natural background area stations was 7–8 kg ha<sup>-1</sup>. The lowest Ca depositions were recorded in 2005, when mean annual Ca load was 2.5 kg ha<sup>-1</sup> in background area stations.

At NE industrial region stations (Jõhvi, Saka) and Harku station (influenced by industrial and building activity in Tallinn), the mean Ca deposition varied from 12 kg ha<sup>-1</sup> to 19 kg ha<sup>-1</sup> during 1995–1999. The downward trend in annual Ca load was not statistically significant in Harku, Tiirikoja and Vilsandi during the period 1995–1999. Ca deposition decreased almost four-fold at Kunda, i.e. from 178 kg ha<sup>-1</sup> to 47 kg ha<sup>-1</sup>, during 1995–1999. At Jõhvi, Saka and Harku, the mean Ca deposition varied from 8–15 kg ha<sup>-1</sup> during 2000–2006, and at Kunda the mean annual Ca deposition was 33 kg ha<sup>-1</sup>. Despite the changes during the 12-year period, the annual mean deposition of calcium at Saka and Saarejärve recovered the level of 1995(6) in 2006.

Although in the last year (2006), the mean Ca deposition was higher than in 2005 (in Harku, Saka, Jõhvi, Tooma, Saarejärve and Haanja), it can be concluded from 12-year monitoring that annual mean Ca load of 2–3 kg ha<sup>-1</sup> is characteristic of the Western, Northern and Eastern inland background area (Map 3).

At present, annual Ca deposition was only lower than 2 kg ha<sup>-1</sup> year<sup>-1</sup> at Vilsandi and Lahemaa. During the period 1995–1999 the annual Ca load varied between 2–14.8 kg ha<sup>-1</sup>, and Ca deposition remain below 2 kg ha<sup>-1</sup> year<sup>-1</sup> since 2000.

Relatively high annual loads of Ca (2–3 kg ha<sup>-1</sup>) at natural background areas compared with Ca background loads in Finland (Ruho-Airola et al., 2003) are caused by carbonate-rich soil dust from traffic on unpaved roads and also from increased building activity in recent years. Despite the dramatic decline of solid particle emissions from the NE Estonian oil-shale region, relatively high Ca depositions (10–20 kg ha<sup>-1</sup>) are characteristic at Kunda, Jõhvi, Saka stations as well as at Harku station (Map 3). At the same time, the changes in annual Ca loads in Southern and SE natural background areas did not reflect the reduction in industrial particle emissions, and the mean annual cation deposition in ICP Forest and local Southern Estonian precipitation network stations remained within the range of 5–6 kg ha<sup>-1</sup> compared to about 3 kg ha<sup>-1</sup> at W, N and E stations (Map 3). This indicates the impact of road dust from gravel roads in the SE and S Estonian natural background area.

## 5. CONCLUSIONS

- After the restoration of Estonia's national independence in 1991, emissions of airborne pollutants have decreased remarkably. Official data confirm that total SO<sub>2</sub> emissions from power plants in Estonia have fallen from 179 thousand tons to 55 thousand tons (about 60%), and the emission of solid particles decreased from 181 thousand tons to 8.7 thousand tons (twenty-fold) during the period 1990–2005.
- Twelve-year trends (1994–2005) of annual average ion concentrations in bulk precipitation from 10 monitoring stations mostly show a statistically significant decline for SO<sub>4</sub>-S at all 10 stations, for Cl<sup>-</sup> and Na<sup>+</sup> in 8, for Ca<sup>2+</sup> and K<sup>+</sup> in 7, Mg<sup>2+</sup> at 6 and for NO<sub>3</sub>-N at 4 stations. In contrast to the others, H<sup>+</sup> increased (significantly at 6 stations) during the study period.
- Three groups of stations can be differentiated according to the rate of ion content decline per year in bulk precipitation.

**Stations directly affected by industrial regions.** Kunda, Jõhvi and Saka stations are affected by the North-Eastern industrial region (predominantly by the Kunda cement industry and Narva Power Plants), and the Harku station, which is clearly influenced by industrial activity in Tallinn.

**NE industrial region background stations.** At Tiirikoja, Tooma, Lahemaa and Saarejärve stations, the variation of the annual decline of cations and anions were very similar, and the downward trends of ion concentrations were in close accordance with the trends at NE stations.

**Natural background stations,** Vilsandi and Lääne-Nigula, stations are more characteristic of European than Estonian trends in declining depositions, especially for SO<sub>4</sub>-S and NO<sub>3</sub>-N.

- The greatest decline in Ca<sup>2+</sup> in precipitation occurred during the first three-year monitoring period, i.e. 1994–1996. The Ca<sup>2+</sup> decline was a response to the reduction in dust emissions from Kunda cement factory and flying ash emissions from the Narva Power Plants during the same period.
- The greatest decline in SO<sub>4</sub>-S concentrations in bulk precipitation at all stations occurred from 1997–1999, and the decline reflected the reduction of emissions of SO<sub>2</sub> more from the former monitoring period (1994–1996) than the investigated period.
- The statistically significant downward trends of SO<sub>4</sub>-S in bulk precipitation for the last three-year period (2003–2005) at industrial background stations pointed to the emission reduction from the Narva Power Plants after the start-up of two new fluidized bed energy blocks (2004–2005).
- The decrease in sulphate sulphur and chloride concentrations in bulk precipitation was on average more than three-fold compared to the monitoring periods 1994–1996 and 2003–2005. Deposited loads of SO<sub>4</sub>-S declined below 5 kg ha<sup>-1</sup> from 1998 and remained relatively stable, on average

3 kg ha<sup>-1</sup> (this varied within the range of 2.6 to 3.7 at 16 monitoring stations throughout Estonia) in a natural background area up to 2005.

- Although annual mean concentrations of Ca decreased on average three-fold at most stations when comparing period 1994–1996 and 2003–2005, the deposited loads of Ca remained high in the NE industrial region (10–20 kg ha<sup>-1</sup>) and relatively high at E and S stations (2–3 kg ha<sup>-1</sup>), enabling neutralization of acidic deposition in most cases. The annual mean pH of bulk precipitation at both EMEP stations (Vilsandi and Lahemaa) were lowest in Estonia (pH<5.1), and at the same time Ca deposition was less than 2 kg ha<sup>-1</sup> at Vilsandi during all period and at Lahemaa from 1999.
- Changes in depositions in coniferous stands at the Saarejärve IM monitoring area resulted in increased trends of H<sup>+</sup> and total soluble Al in the percolation water of natural podzolic soils, which points to enhanced podzolization processes, probably attributable to the reduced deposition of base cations and decreased retention of sulphates in soil horizons.

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## 7. SUMMARY IN ESTONIAN

### Saasteainete trendid Eesti sademetes

Käesoleva töö peamine eesmärk on anda riikliku keskkonnaseire andmestiku põhjal ülevaade viimasel 12 aastal toimunud muutustest õhusaasteainete sadenemises Eesti territooriumil seoses rahvusvahelistest keskkonnalepetest johtuvate emissioonide vähendamise kohustuste täitmisega, põlevkivi-elektrijaamade puhastusseadmete renoveerimise ja muude tehnoloogiliste uuendustega. Eesmärk on

- analüüsida anioonide ja katioonide kontsentratsioonide ajalisi trende eri seirejaamade sademetes;
- hinnata sademetega maapinnale jõudvate peamiste saasteainete koormuste mustreid ja nende muutusi Eesti territooriumil;
- analüüsida deponeerunud saasteioonide sesoonset dünaamikat;
- hinnata, kas aluselise õhusaaste üldise fooni alanemine ohustab keskkonda hapestumisega;
- hinnata depositsiooninäitajate põhjal emissioonide vähendamise meetmete efektiivsust (põlevkivielektrijaamades ja Kunda tsemenditehases);
- hinnata retrospektiivis põlevkivi elektrijaamade õhusaaste mõjuala kogu Eesti territooriumil;
- hinnata, kas emissioonide ja depositsioonide vahel on usaldusväärseid seoseid;
- hinnata Eesti sademete seirejaamade sobivust depositsioonitrendide monitooringuks.

Välisõhu kvaliteeti mõjutab oluliselt inimtegevusest põhjustatud saaste (näiteks vääveldioksiid, lämmastikoksiidid, süsinikmonoksiid, tahked osakesed, osoon, müra ja vibratsioon, ioniseeriv ja mitteioniseeriv kiirgus). Eestis saastab praegu enim õhku põlevkivil baseeruv energeetika (väävliühendid, tahked osakesed ning süsinikdioksiid). Peamised lämmastikoksiidide ja lenduvate orgaaniliste ühendite allikad on transpordivahendid ja vähemal määral põllumajandus.

2005. aastal emiteeris Eesti välisõhku 158 000 tonni CO<sub>2</sub> (mis moodustab 50% saasteainete koguemissioonist), 77 000 tonni SO<sub>2</sub> (24%) ja 40 000 tonni tahkeid osakesi (13%) (joonis 1). Võrreldes neid koguseid 1995. aasta kogusaastega, on märgatavalt alanenud tahkete osakeste osakaal koguemissioonist (26%, langenud 13%), mis koguliselt tähendab vähenemist enam kui kolm korda. Eestis kaevandati 2005. aastal 14,8 miljonit tonni põlevkivi (Eesti Statistikaameti andebaas, 2005), millest 11–12 miljonit tonni kasutasid Ida-Virumaal paiknevad Narva elektrijaamad (Balti ja Eesti elektrijaam) (Liive, 2007). Ligi kaudu 82% saasteainetest pärineb põlevkivi baasil töötavast energiatööstusest (Keskkonnaülevaade, 2005). Põlevkivil baseeruvate soojuselektrijaamade

põhilised õhku paisatavad saasteained on süsinikdioksiid, vääveldioksiid ja tahked osakesed, vähesemal määral NO<sub>x</sub> ja Cl<sub>2</sub>. Elektrijaamad emiteerisid 2005. aastal 74% SO<sub>2</sub> ja 48% tahkete osakeste paiksetest allikatest pärinevast koguemissioonist (artikkel I, joonis 1, Treier *et al.*, 2008). Põlevkivielektri- jaamade osakaal selliste saasteainete nagu lämmastikoksiidide ja lenduvad orgaaniliste süsivesinike puhul on suhteliselt väike ning see väheneb transpordisektorist tuleva heitmehulga kiire kasvu tõttu.

Ametlikud andmed kinnitavad, et Eestis alanes SO<sub>2</sub> emissioon paiksetest allikatest kaks korda (149 000 tonnilt 74 000 tonnini) perioodil 1994–2005 (artikkel I, joonis 1, Treier *et al.*, 2008). Kui uurimisperioodi alguses (1994) energia tootmine põlevkivist aasta-aastalt vähenes, siis 2003. aastast alanud elektritootmise kasvust hoolimata (2003. aastast üle 10 TWh aastas) on saasteainete emissioonide alanemistrend jätkunud, mis tõestab uute tehnoloogiliste meetmete rakendumist.

Ida-Virumaa oli Eestimaal ainus koht, mis 1980. aastatel tunnistati ökoloogilise katastroofi lävel seisvaks regiooniks, põlevkivi kasutamine oli selle muutnud tööstusplatsdarmiks ning unikaalse looduse hoid jäi teisejärguliseks (Liblik, 2007).

Viimase 20 aasta jooksul on SO<sub>2</sub> emissioon alanenud Euroopas tervikuna ligikaudu 70% (Grennfelt, 2005). Vääveldioksiidi heitmete vähenemist aastatel 1980–2005 Põhjamaades, Lätis ja Eesti EMEP-i seirejaamade andmetel illustreerib tabel 1. EMEP-i andmete põhjal on vääveldioksiidi ja tahkete osakeste emissiooni vähenemine käesoleva uurimisperioodi vältel (1995–2005) Eesti naaberriikides sarnase kaaluga (30–45%), näiteks Eestis alanes SO<sub>2</sub> 116,9 Gg-lt 77,2 Gg-le aastas. Suurim suhteline SO<sub>2</sub> emissiooni alanemine (93%) on toimunud Lätis. Tahkete osakeste emissiooni alandamine on võrreldes naaberriikidega, kus alanemise määr oli samal ajal keskmiselt 10%, olnud märksa aktiivsem Eestis (70%; 133,7 Gg – 39,6 Gg aastas).

Hoolimata suurest langusest näitab emissiooni taseme formaalne arvutus vastava riigi pindala kohta veel 2005. aastal, et Eestis on väävlisaaste 16 korda ja tahkete osakeste saaste ligikaudu 4 korda suurem kui naaberriikides. Kõrge SO<sub>2</sub> ja tahkete osakeste emissioon on iseloomulik maadele, kus energeetikas kasutatakse tooraineks peamiselt põlevkivi (Aunela *et al.*, 1995).

Eesti Statistika andmebaasi põhjal toodeti 2005. aastal Eesti energia- toodangust 27% põlevkivi põletamise uue tehnoloogiaga (põlevkivi tolmpõletamine asendati keevkihis põletamisega), mille tulemusena peaks oluliselt alane- nud vääveldioksiidi eriheitmete tase võimaldama järgida väävliühendite, aga ka CO<sub>2</sub> kohta kehtestatud nõudeid.

Peale lokaalsete saasteallikate mõjutab saastatuse taset õhusaaste kaugkanne, mis oleneb Eestis peamiselt läänest ja lõunast liikuvatest õhumassidest (jälgi- tavad Lääne-Eesti sademetejaamades). Narva elektri- jaamade emissioonidest tingitud kõrge- nenud väävliühendite sadenemist on registreeritud naabruses

paiknevatel aladel nii Soomes kui ka Venemaal (Kulmala *et al.*, 1998; Sofiev *et al.*, 2003).

Eesti elektrienergeetika põhilised raskused Euroopa Liidu keskkonnanõuete täitmisel on senini olnud seotud väävliühendite heitmetega välisõhku ja põlevkivituha ladestamisega elektrijaamade tuhaväljadele. Alates 2008. aastast saab aga põlevkivielektri tootmisel limiteerivaks teguriks CO<sub>2</sub> heitmete lubatud kogus.

### **Keskkonnavalased õigusaktid ning rahvusvahelised lepingud**

Kuni aastani 2000 oli Eesti õhukaitse alal seotud vaid ühe konkreetse rahvusvahelise kohustustega vähendada hiljemalt 1997. aasta lõpuks vääveldioksiidi aastast emissiooni 1980. aastaga võrreldes vähemalt 50% . Selleks oli 1993. aastal sõlmitud Eesti ja Soome vaheline õhukaitse koostööleping. Kaks riiki leppisid kokku ka selles, et 1994. aasta lõpuks koostatakse uus tegevusplaan vähendada hiljemalt 2005. aastaks vääveldioksiidi heitmeid 1980. aasta tasemest lähtuvalt 80% võrra. Kokku lepiti ka 2005. aasta SO<sub>2</sub> heitmete piirkoguses, mis on 38 000 tonni.

2000. aastal ühines Eesti piiriülese õhusaaste kauglevi nn Genfi konventsiooniga (koostatud 13.11.1979) ning selle kolme protokolliga. Lisaks võttis Riigikogu 06.12.2000 vastu selle konventsiooni õhusaasteainete kauglevi seire ja hindamise Euroopa koostööprogrammi (EMEP) pikaajalise finantseerimise protokolliga ühinemise seaduse ning 04.06.2003 väävli heitkoguste edasise vähendamise protokolliga ühinemise seaduse (koostatud 14.06.1994 Oslos). Ühinemisel kohustus Eesti vähendada väävli heitkoguseid 2005. aastaks 35% võrra ja 2010. aastaks 40% võrra, võttes aluseks 1980. aasta taseme (Eesti elektrimajanduse arengukava, 2005).

Eesti keskkonnanstrateegias, mille Riigikogu kiitis heaks 1997. aastal, on õhukvaliteedi parandamiseks võetud ülesannete hulgas kohustus vähendada aastaks 2005 väävliühendite emissiooni 1980. aasta tasemega võrreldes 80% ning tahkete osakeste emissiooni 1995. aasta tasemega võrreldes 25%.

Eesti uuendatud keskkonnanstrateegias aastani 2010 on mõningaid varem rangemana kavandatud eesmärged „pehmendatud”. Näiteks väävliühendite heitkoguste vähendamine (1980. aasta tasemega võrreldes) 2005. aastaks 35% ja 2010. aastaks 40% ning aastast 2010 tuleb kindlustada, et Eesti paiksetest ja liikuvatest saasteallikatest välisõhku eralduv summaarne heitkogus ei ületaks aastas 100 000 tonni vääveldioksiidi ega 60 000 tonni lämmastikoksiidi.

Eesti allub pärast ühinemist Euroopa Liiduga direktiividele, mis reguleerivad välisõhu kvaliteeti (neist tähtsamad on välisõhu kvaliteedi raamdirektiiv 96/62/EÜ; direktiiv 1999/30/EÜ SO<sub>2</sub>, NO<sub>2</sub>, NO<sub>x</sub>, tahkete osakeste ja plii piirväärtuste kohta välisõhus; 2001/80/EÜ direktiiv suurtest põletusseadmetest

väljuvate saasteainete heitkoguste piiramise kohta; 2001/81/EÜ direktiiv teatavate õhusaasteainete heitmete siseriiklike piirkoguste kohta).

Direktiivi 2001/80/EÜ (suurtest põletusseadmetest väljuvate saasteainete kohta) rakendamiseks võimaldati põlevkivil töötavatele Eesti elektrijaamadele (AS Narva Elektrijaamad ja AS Kohtla-Järve Soojus) üleminekuperiood maksimaalse tähtajaga 31. detsember 2015. Eesti võttis kohustuse, et põlevkivil töötavates elektrijaamades saavutatakse SO<sub>2</sub> heitkoguste vähenemine ning aastaks 2012 ei tohi see ületada 25 000 tonni. Samuti võttis Eesti kohustuse esitada 1. jaanuariks 2008 Euroopa Komisjonile tegevuskava (sh investeringud) AS-i Narva Elektrijaamad (Eesti EJ ja Balti EJ) ning AS-i Kohtla-Järve Soojus kateldest eralduvate saasteainete heitkoguste järk-järgulise vähendamise ja direktiivi nõuete täitmise kohta aastatel 2010–2015.

Välisõhu kaitse valdkonna Euroopa Liidu seadused on kooskõlla viidud Eesti õigusaktidega, tulevikku suunatud piirangutega on arvestatud nii strateegiliste dokumentide eesmärkides kui ka õigusaktides.

Uus välisõhu kaitse seadus hakkas kehtima 30. septembril 2004. Seadus reguleerib tegevust, millega kaasneb välisõhu keemiline või füüsikaline mõjutamine, osoonikihi kahjustamine ja kliimamuutust põhjustavate tegurite ilmumine. Seaduses on käsitletud kõiki rahvusvaheliselt tunnustatud, välisõhu kaitsega seotud põhiprobleeme.

Vabariigi valitsuse määrusega nr. 299 on alates 1. jaanuarist 2010 Eestis kehtima hakkav paiksetest ja liikuvatest saasteallikatest vääveldioksiidi emissiooni summaarne piirkogus 100 000 tonni kalendriaastas ja alates 1. jaanuarist 2012 on põlevkivi kasutavatest suurtest põletusseadmetest välisõhku paisatava vääveldioksiidi emissiooni summaarne piirkogus 25 000 tonni kalendriaastas.

Praegu piiravad energeetikasektori arengut mitte niivõrd SO<sub>2</sub> normid, vaid eelkõige CO<sub>2</sub> normid, mis tulenevad ÜRO kliimamuutuste raamkonventsiooni (27.07.2004) Kyoto protokollist, mille Eesti ratifitseeris 3. septembril 2002. Vastavalt ratifitseeritud protokollile kohustub Eesti, nagu ka teised Euroopa Liidu riigid, vähendama ajavahemikus 2008–2012 kasvuhoonegaaside heitmeid 1990. aastaga võrreldes 8%.

Kuigi Eesti energeetikasektoris on toimunud märkimisväärsed uuendused ning tööstuses ja põllumajanduses on tehtud 1990. aastatest alates kvalitatiivseid ja kvantitatiivseid muudatusi, on põlevkivi baasil elektrienergiat tootev Eesti silmitsi olukorraga, kus Eesti Energia ostis Eesti-sisese elektrimüügi tagamiseks 2008. aasta jaanuaris 110 000 tonni CO<sub>2</sub> heitmekvoote maksumusega 35 miljoni krooni (06.02.2008 Postimees).

Käesoleva töö andmebaasiks on Eesti Riikliku Keskkonnaseire programmide raames kogutud avamaa sademete keemiliste analüüside andmed. Sademetekeemia seireprogrammi koordineerib Eesti Keskkonnauuringute Keskus alates 1994. aastast, mil alustati sademete keemiliste analüüsidega Harku, Kunda, Jõhvi, Tooma ja Tiirikoja ilmajaamades. 1996. aastal lisandusid seirejaamad

Sakas ja Lääne-Nigulas ning 1999. aastal Matsalus. Tartu Keskkonnauuringute poolt alustati sademeproovide kogumist ja analüüsi seitsmes Lõuna-Eesti jaamas 1999. aastal: Tahkusel, Karulas, Haanjas, Otepääl, Alam-Pedjal, Loodil ja Nigulas. Lisaks eelmainitud jaamadele on töös kasutatud Vilsandi, Lahemaa ja Saarejärve seirejaamade sademete andmeid alates 1994 aastast. Vilsandi töötab koos Saarejärvega rahvusvahelise kompleksseire (International Co-operative Programme on Integrated Monitoring) jaamana ning koos Lahemaaga ka EMEP-i (Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe) jaamana. Alates 1999. aastast on olemas rahvusvahelise metsaseire (International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests) programmi kuue jaama – Sagadi, Vihula, Mäksa, Pikasilla ja Karula – avamaa sademete andmed. Metsaseiret koordineerivad Eesti Metsakaitse- ja Metsauuenduskeskus, EMEP, kompleksseiret korraldavad Eesti Keskkonnauuringute Keskus ja IM Saare koostöös Tartu Ülikooli Ökoloogia ja Maateaduse Instituudi geograafia osakonnaga. EMEP-i programmis on Eesti osalenud alates 1981. aastast Vilsandi (Sõrve) ja Lahemaa taustajaamadega. Kahjuks on varasemad sademete keemilised analüüsid (analüüsiti Riias) läinud kaduma. Mõningad varasemad andmed aastatest 1981, 1985, 1987–1990 Sõrve, Vilsandi, Lahemaa, aga ka Tooma, Tiirikoja, Tallinna ja Jõhvi ilmajaamade sademete  $\text{SO}_4\text{-S}$ ,  $\text{NO}_3\text{-N}$  ja  $\text{NH}_4\text{-N}$  kohta on esitatud O. Rootsi artiklites (Roots, 1992; Roots *et al.*, 1992). O. Rootsi esitatud andmeid on analüüsitud Eesti Hüdrometeoroloogia laboris paralleelselt NSVL-s kontrollitud ja Riias analüüsitud andmetega. Aastatel 1991–1993 kogus ja analüüsis Harkus, Jõhvis, Toomal, Tiirikojal, Lahemaal ja Vilsandil iga kuu sademeid hüdrometeoroloogia teenistus, kuid kahjuks ei ole nendest andmetest midagi säilinud, mõnes artiklis on vaid vihjeid nende olemasolu kohta (näiteks Martin *et al.*, 1994).

Territoriaalse saasteainete leviku hindamiseks kasutati 23 jaama andmeid. Saasteainete kontsentratsioonide ajaliste trendide uurimiseks on kasutatud kümne, pikimate aegriididega (1994–2006) jaama sademete andmeid.

Sademete seireprogrammi täitmisel lähtutakse õhusaasteainete kauglevi koostööprogrammi käsiraamatu „EMEP Manual for Sampling and Chemical Analysis” (1996) proovide võtmise ja töötlemise, keemilise analüüsi meetodite, laboratoorse aparatuuri ning kvaliteedikontrolli nõuetest. Sademete analüüsi parameetrid on järgmised: sademete hulk, kaalium- ( $\text{K}^+$ ), naatrium- ( $\text{Na}^+$ ), kaltsium- ( $\text{Ca}^{2+}$ ), magneesium- ( $\text{Mg}^{2+}$ ), nitraat- ( $\text{NO}_3^-$ ), kloriid- ( $\text{Cl}^-$ ), sulfaat- ( $\text{SO}_4^{2-}$ ) ja ammooniumiooni ( $\text{NH}_4^+$ ) sisaldus, pH ning elektrijuhtivus. Ajaliste trendide analüüsimisel kasutasin mitteparameetrilist Mann-Kendalli testi (Salmi *et al.*, 2002), mis loeb aastase (kuu) erinevuse statistiliselt usaldusväärseks alates  $p < 0,05$ .

Seireperioodil 1994–2005 alanesid statistiliselt usaldusväärselt järgmiste ionide aasta keskmised kontsentratsioonid:  $\text{SO}_4\text{-S}$  kümnes,  $\text{Cl}^-$  ja  $\text{Na}^+$  kaheksas,  $\text{Ca}^{2+}$  ja  $\text{K}^+$  seitsmes,  $\text{Mg}^{2+}$  kuues ja  $\text{NO}_3\text{-N}$  neljas jaamas. Aastase

keskmiste anioonide ja katioonide summaarse kontsentratsiooni ( $\text{meq l}^{-1}$ ) alanemise trendi tugevuse järgi reastusid jaamad järgmiselt: Kunda > Jõhvi > Saka > Harku > Tiirikoja > Saarejärve > Lääne-Nigula > Lahemaa > Tooma > Vilsandi. Kontsentratsioonide alanemistrendi järgi jagunesid jaamad otsese tööstuspiirkonna mõjuga jaamadeks (Kunda, Jõhvi, Saka ja Harku), Kirde-Eesti tööstuspiirkonnast mõjutatud taustajaamadeks (Tiirikoja, Saarejärve, Lahemaa ja Tooma) ning looduslikeks taustajaamadeks (Lääne-Nigula ja Vilsandi).

Trendianalüüs näitas sulfaatse väävli usaldusväärset alanemist kõikides jaamades (aastane vähenemine varieerudes  $-1,76 \text{ mg l}^{-1}$  Kundas kuni  $-0,12 \text{ mg l}^{-1}$  Vilsandil). Kloriidi ja anioonide summa alanemistrendid sarnanesid sulfaatse väävli alanemistrendiga, mis omakorda järgis  $\text{SO}_2$  emissiooni ja põlevkivi-energia tootmise vähenemise trende. 12-aastase perioodi jooksul toimus suurim  $\text{SO}_4\text{-S}$  kontsentratsiooni alanemine enamikes jaamades, välja arvatud Kundas, kus domineeris kaltsiumiiooni alanemise trend. Kloriidi ja sulfaadi keskmised aastased kontsentratsioonid alanesid enam kui kolm korda perioodide 1994–1996 ja 2003–2005 võrdluses. Tööstuspiirkonna jaamades (näiteks Jõhvis) registreeriti 11-kordne  $\text{SO}_4\text{-S}$  sisalduse alanemine, Kundas 7-kordne alanemine.

$\text{Ca}^{2+}$  kontsentratsiooni alanemine oli statistiliselt usaldusväärne seitsmes vaatlusjaamas kümnest ja aastane keskmine alanemine varieerus  $-3,1 \text{ mg l}^{-1}$  Kundas kuni  $-0,06 \text{ mg l}^{-1}$  Lääne-Nigulas.

Aluselistel katioonidel ( $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^{+} + \text{Na}^{+}$ ) summaarne alanemine oli tugevasti seotud tahkete osakeste emissiooni alanemisega, mis vähenes ligikaudu 9 korda (161 500 tonnilt 1994. aastal 18 000 tonnile 2005. aastal).

Kunda tsemenditehase renoveerimise tulemusena aastatel 1996–1997 vähenes tolmuemissioon mitusada korda (32 000 tonnilt 1994–1999 136 tonnini 2003–2005) (Paper I, Fig. 3, Treier *et al.*, 2008).

Kuigi aasta keskmine kaltsiumikontsentratsioon alanes seireperioodil keskmiselt kolm korda (6 korda Lahemaal ja 1,5 korda Lääne-Nigulas), jäävad keskmised koormused ikkagi suhteliselt kõrgeks, näiteks Kirde-Eesti tööstuspiirkonnas ulatub kaltsiumi aastane koormus kuni  $20 \text{ kg ha}^{-1}$  (kaart 3). Sademetekeemia uuringud näitasid, et aastekoormused vähenesid Eestis seireperioodil 1994–2006 reeglina igal aastal. Vaadeldud perioodi tulemuseks on ka märkimisväärne saastatuse taseme langemine Kirde-Eestis (vt kaart 1–3), kuigi nii S koormused ( $5\text{--}9 \text{ kg ha}^{-1}$ ) kui ka Ca koormused ( $9\text{--}20 \text{ kg ha}^{-1}$ ) jäävad seal Eesti keskmistest (vastavalt  $2\text{--}3 \text{ kg ha}^{-1}$  ja  $3\text{--}5 \text{ kg ha}^{-1}$  aastas) kõrgemaks. Kui kloriidi keskmine depositatsioon Kirde-Eesti tööstuspiirkonnas oli perioodi alguses (1995)  $20 \text{ kg ha}^{-1}$  (Kundas  $53 \text{ kg ha}^{-1}$ ), siis perioodi lõpus on see Kirde-Eesti tööstuspiirkonnas  $5\text{--}10 \text{ kg ha}^{-1}$  ning varieerub looduslikes sisemaa jaamades  $3\text{--}4 \text{ kg ha}^{-1}$  ja Lääne-Eesti merelise mõjuga jaamades  $6\text{--}8 \text{ kg ha}^{-1}$ .

Kirde-Eesti tööstuspiirkonnast ligikaudu 135 km kaugusel Soome lahe vastaskaldal asuva Virolahti EMEP-i seirejaama andmeil väheneb  $\text{SO}_2$  tase pidevalt, seda suuresti Narva elektrijaamadest tuleneva heite vähenemise tõttu (Liblik, 2007). Virolahti sulfaatse väävli ja kloriidi paari viimase aasta

keskmised koormused ( $2,5 \text{ kg ha}^{-1}$ ) ning Ca koormused ( $1,1 \text{ kg ha}^{-1}$ ) on võrdsed Eesti keskmiste koormustega või neist madalamad, kuid võrreldes teiste Soome vaatlusjaamadega siiski kordi kõrgemad. Virolahti jaama  $\text{SO}_4\text{-S}$ ,  $\text{Ca}^{2+}$  ja  $\text{Mg}^{2+}$  kontsentratsioonide alanemistrendid samal vaatlusperioodil (1994–2005) on statistiliselt usaldusväärsed ning sarnased Kirde-Eesti tööstuspiirkonna ja selle mõjuala jaamade (Tooma, Tiirikoja, Saarejärve) alanemistrendidega, kuigi kordi väiksemad.

13-aastase vaatlusperioodi jooksul on Eesti sademed muutunud happelisemaks, mille kinnituseks on 10 jaama pH alanemise trend, sealjuures 6 jaamas (Jõhvi, Kunda, Saka, Tiirikoja, Lahemaa ja Tooma) oli trend statistiliselt usaldusväärne. Kui 1990. aastate teisel poolel 1995–1999 olid vaid Vilsandi sademed nõrgalt happelise aasta keskmise pH tasemega ( $\text{pH} < 5.1$ ), siis aastatel 2000–2006 lisandus sellise pH tasemega jaamade hulka veel 6 jaama: Lahemaa, Tooma, Matsalu, Nigula, Otepää ja Tahkuse.

Sademed on happelisemad Lõuna- ja Lääne-Eestis, kuhu happeline õhusaaste kandub õhumassidega Kesk- ja Lääne-Euroopast (Kabral *et al.*, 2008). Näiteks EMEP jaamades Vilsandil ja Lahemaal jäi kogu seireperioodi (1994–2006) vältel sademete aasta keskmine  $\text{pH} < 5.1$ . Kuu sademete keskmine pH Vilsandi, Lahemaa ja Matsalus vaatlusjaamades jäi 70–100% ulatuses kütteperioodi kuudel (oktoobrist kuni aprillini) alla viie.

Eeldatavalt suurema tööstussaaste piirkondades (sulfaatide ja kaltsiumiga on enim saastunud Kirde-Eesti ja Harjumaa) on sademete happesus kohati keskmisest väiksem ( $\text{pH}$  kõrgem kui 6), seda põhjustab tsemenditolmu ja põlevkivituha, aga ka pinnase- ja teetolmu suur karbonaatide sisaldus. Uute efektiivsemate tolmufiltrite kasutuselevõtt kahandas oluliselt aluseliste tahkete osakeste heitkoguseid, mistõttu sademed muutusid mõnevõrra happelisemaks, kuid üldjuhul on sademete hapestumise protsess nii Skandinaavia kui ka praeguste Kesk-Euroopa andmetega võrreldes täiesti ohutu. Eesti on endiselt Põhja- ja Lääne-Eesti ning paljude muude Eesti piirkondade muldade lubjarohkuse, Lõuna-Eesti kruusateede ja muidugi Kirde-Eesti tööstustolmu tõttu tolmu riik, kus ükskõik kust pärit happesed sademed enamasti neutraliseeritakse. Vaid mereäärsetes jaamades Vilsandil, Lahemaal ja ka Matsalus, kus igasuguse aluselise tolmu osakaal on väike, võib jälgida sademete hapestumise edasisi trende.

Nii elektrienergia tootmise, põlevkivikeemia kui ka üleeuroopaliste arengusuundade kontekstis pakub sademeteseire Eestis jätkuvat huvi ka tulevikus.

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## **PUBLICATIONS**





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Trends of air pollutants in precipitation at Estonian monitoring stations 1994–2005.  
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# **Trends of air pollutants in precipitation at Estonian monitoring stations 1994–2005**

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## ***Abstract***

*This study concentrates mainly for the twelve-year time trends of annual average ion concentrations in bulk precipitation from 10 Estonian monitoring stations. Trends by the nonparametric Mann-Kendall test mostly show a statistically significant decline and according to the order of ion decline per year three groups of stations could be differentiated: stations directly affected by an industrial region, NE industrial region background stations and natural background stations. Under different international agreements, Estonia has undertaken serious obligations to reduce emissions of air pollutants. Total SO<sub>2</sub> emissions from power plants in Estonia have fallen from about 60%, and emission of solid particles decreased twenty-fold during the period 1990–2005. The highest decline of Ca concentrations occurred during the first three-year monitoring period of 1994–1996 and the high decline of SO<sub>4</sub>-S from 1997–1999 and 2003–2005.*

## **Introduction**

The control of acidifying pollutant emissions in Europe since the early 1980s has been successful: sulphur dioxide emissions have been reduced by 70%, oxides of nitrogen by around 30% and ammonia by 25%. Today sulphur dioxide emissions are back at the levels characteristic to the beginning of the 20<sup>th</sup> century. The reduction has resulted from international agreements (under the Convention on Long-range Transboundary Air Pollution and its protocols) and legislation followed up nationally, from economic restructuring in Eastern Europe after the fall of The Berlin Wall, from switching from coal to gas and from increased desulphurization of power plant emissions [1].

Estonian national emissions of air pollutants have largely followed the European reduction trends. However, energy production from a specific fossil

fuel – oil shale combustion – has left its mark on the character of emissions, measures of emission reduction and deposition of pollutants.

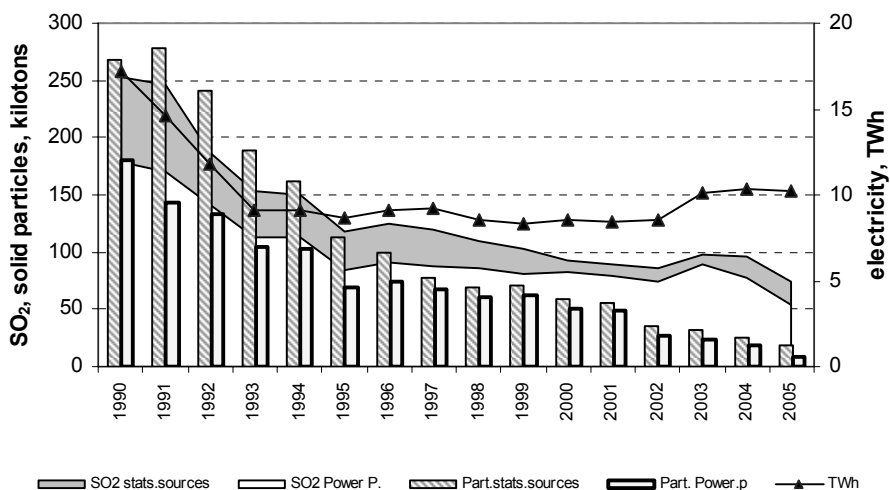
In Estonia about 95% of the total electricity production comes from oil shale, and 92% of electrical energy is generated by two of the world's largest oil shale fired power plants (the Narva Power Plants) [2]. In 2005, 14.8 million tons of oil shale was combusted for the production of electricity and thermal energy [3], of which 11–12 million tons was used in the Narva Power Plants [4].

Oil shale is the most important mineral resource in Estonia, and at the current amount of consumption there should be sufficient reserves (8.66 GT) for at least 60 more years [5]. Estonian energy production is currently, and will continue to be mostly based on oil shale, most likely until 2015 [5].

The chemical composition of oil shale has the strongest influence on air pollution. In Estonia about 82% of total air pollution originates from oil shale-based energy production [6]. The sulphur content in oil shale (1.4–1.8%) is the primary source of sulphur dioxide emission. The high content of carbonate minerals (45–50%) in oil shale accounts for particle emission (fly ash), while the high molar ratio of Ca/S (usually 8–10) enables buffering of the influence of the acidic compounds of oil shale (S and Cl) [7]. The average chlorine content in the organic part of oil shale is 0.75% [8]. So far Estonia is not familiar with the problem of the acidification of precipitation and its impact on the ecosystem, quite the contrary: the long-term cumulative load of alkaline fly ash has deteriorated the ecosystems of ombrotrophic raised bogs [9; 10].

After the restoration of Estonia's national independence in 1991, emissions of air pollution have decreased remarkably. Official data confirm that total SO<sub>2</sub> emission from Power Plants in Estonia has fallen from 179 thousand tons to 55 thousand tons (about 60%), and the emission of solid particles decreased from 181 thousand tons to 8.7 thousand tons (twenty-fold) during the period 1990 – 2005 (Fig. 1).

Under different international agreements Estonia has undertaken serious obligations to reduce emissions of air pollutants. The Estonian Environmental Strategy and agreements with Finland state that SO<sub>2</sub> emissions in 2005 should not exceed 20% of the 1990 level, the emission of solid particles must be reduced by 25% as compared to 1995, and NO<sub>x</sub> emissions should not exceed the 1987 level. Same targets have been set by the Protocols of the Convention on Long-Range Trans-boundary Air Pollution (CLTRAP), or the so-called Geneva Convention.



**Fig. 1.** Annual emissions of SO<sub>2</sub> and solid particles (fly ash) (kilotons) from power plants and stationary sources together with electricity production (TWh) during 1990–2005 [3].

As emission of air pollution has been calculated, therefore all states which have joined the Geneva Convention must carry out direct measurements of pollutants within the framework of international monitoring programmes. The deposition levels and precipitation concentrations are currently being carried out within the EMEP (Co-operative Programme for the Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe, co-ordinated by the UN/ECE) since 1994 at two stations; within the ICP IM (International Co-operative Programme on Integrated Monitoring) since 1994 at two stations and within the ICP Forest Level II at 6 stations since 1997. In addition to the above-mentioned international programmes, there are now monitoring programmes for air pollutant depositions at 15 local meteorological stations. The longest time series of chemical composition of precipitation of 10 monitoring stations date from 1994 (Fig. 2).

The aim of the present paper is to analyze the changes and trends of anion and cation concentrations in the available data of bulk precipitation in connection with the decreased emissions of SO<sub>2</sub> and solid particles during the last 12 years.

## Material and methods

The average annual precipitation in Estonia is 530–730 mm, and the average annual air temperature varies 6.3°C in Western coast to 4.4°C in Eastern Estonia. The warmest month is July, August has the greatest amount of monthly rainfall, and February is the coldest and driest. Total annual precipitation has slightly increased during the assessment period, which is mainly due to relatively warmer winters that are rich in precipitation.

### *Sampling*

Precipitation was collected using bulk collectors (20 cm in diameter), placed in an open area at a height of 120 cm. Samples were collected on a 24h basis. Collected samples were stored in refrigerators and mixed in proportion to the total sample volume for monthly samples before analysis, as described in the EMEP manual [11].  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  concentrations in water samples were determined using ion chromatography (EN-ISO 14911 and EN-ISO 10304).  $\text{NH}_4^+$  was analysed using spectrophotometry. The acidity (pH) and electric conductivity of samples were also measured. Samples were analysed at internationally accredited laboratories of the Estonian Environmental Research Centre in Tallinn and the Environmental Studies Laboratory in Tartu.

Every measuring of wet deposition is done using open, so called bulk, collectors for precipitation. Possible uncertainties because of water loss and also due to dry deposition into samplers are not taken into consideration. The contribution of dry deposition to bulk collectors (steadily open) in the open area may reach approximately 10% of total depositions in rural areas [12].

### *Data*

Bulk concentrations reported in the tables are precipitation-weighted averages, which are not corrected for sea salts. Although some stations are situated by the sea, the influence of sea salt is not considered relevant here, as the assumption is that the proportion of sea salt contribution has not changed over the short assessment period. In addition the mean  $\text{Cl}^-/\text{Na}^+$  ratio in bulk precipitation was higher than could be predicted from seawater ( $\text{Cl}^-/\text{Na}^+=1.166$ ) indicating chloride deposition from additional sources (oil shale burning in our case) [13; 14].

### *Statistics*

The nonparametric Mann-Kendall test was used for the detection of trends in the time series of precipitation-weighted annual and monthly mean concentrations. The statistical method used is for the testing of the presence of the monotonic increasing or decreasing trend and the nonparametric Sen's method was used for the estimation of the slope of the linear trend. The Mann-Kendall test requires at least 4 values, and calculation of the confidence intervals for the Sen's slope estimate requires at least 10 values in a time series [15]. A statistical



significance threshold of  $p < 0.05$  (95% confidence means that the detected trend is significantly different from a zero trend) was applied to the trend analysis. We analysed twelve-year time trends using the annual means of chemical parameter ( $n=12$ ) and three-year time trends using the monthly means of chemical parameters ( $n=34-36$ ).

## Results and discussion

### Twelve-year trends in precipitation chemistry at 10 monitoring stations

Table 1 presents the results of the trend analyses of annual mean ion concentrations in bulk precipitation at 10 monitoring stations in Estonia during a twelve-year period (1994- 2005). Annual average ion concentrations mostly show statistically significant decreasing trends for  $\text{SO}_4\text{-S}$  in 10 stations, for  $\text{Cl}^-$  and  $\text{Na}^+$  in 8, for  $\text{Ca}^{2+}$  and  $\text{K}^+$  in 7,  $\text{Mg}^{2+}$  in 6 and for  $\text{NO}_3\text{-N}$  in 4 stations. In contrast to the others,  $\text{H}^+$  increased (significantly in 6 stations) during the study period. Using the annual decline (Q) of summed anions plus cations ( $\text{meq l}^{-1}$ ) as an integrated parameter for indicating the reduction of ion concentration in precipitation, the following order of the stations emerged: Kunda(0.37) > Jõhvi (0.12) > Saka(0.07) > Harku(0.04) > Tiirikoja(0.04) > Saarejärve(0.03) > Lääne-Nigula(0.03) > Lahemaa(0.03) > Tooma(0.02) > Vilsandi (0.02).

Decreasing trends of  $\text{SO}_4\text{-S}$  and Ca at the 10 stations give a nearly similar order of stations (except that for  $\text{SO}_4\text{-S}$ , exchanged positions were revealed in the case of Lääne-Nigula and Tooma and for  $\text{Ca}^{2+}$  in the case of Tiirkoja and Lääne-Nigula (Fig. 2.). Three groups of stations could be differentiated according to the order of ion decline per year.

**Stations directly affected by an industrial region.** This group includes Kunda, Jõhvi and Saka stations, which were affected by the North-Eastern industrial region (predominantly by the Kunda cement industry and Narva Power Plants), and the Harku station, which is clearly influenced by industrial activity in Tallinn. During the twelve-year study period, these stations were characterized by the highest annual decline of most ions (anions plus cations) in precipitation.

**Table 1.** Trends (“–“decreasing and “+” increasing) of annual mean concentrations in precipitation, 1994–2005 by Mann-Kendall nonparametric test. Significance level \*\*\*0.001; \*\*0.01; \*0.05 and (Q), decline per year ( $\text{mg l}^{-1}$ ) for single ion and ( $\text{meq l}^{-1}$ ) for summed ions.

	mm		$\text{H}^+ \text{eq l}^{-1}$		$\text{SO}_4\text{--S mg l}^{-1}$		$\text{Cl}^- \text{mg l}^{-1}$		$\text{NO}_3\text{--N mg l}^{-1}$		$\text{Na}^+ \text{mg l}^{-1}$		$\text{Ca}^{2+} \text{mg l}^{-1}$		$\text{K}^+ \text{mg l}^{-1}$		$\text{Mg}^{2+} \text{mg l}^{-1}$		Sum of anions $\text{meq l}^{-1}$		Sum of cations $\text{meq l}^{-1}$	
	Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q	Sign	Q
KUNDA	+	15.64	**	0.0000	**	-1.76	*	-0.63		0.11	*	-0.26	**	-3.01	*	-0.45	***	-0.26	*	-0.167	**	-0.203
JÖHVI		-20.46	+	0.0002	**	-0.72	***	-0.67	*	-0.25	***	-0.33	*	-0.18	***	-0.13	**	-0.05	***	-0.089	**	-0.035
SAKA		-6.87	*	0.0005	*	-0.46	**	-0.13		-0.15	*	-0.05	*	-0.24	*	-0.08	*	-0.03	*	-0.048	*	-0.020
HARKU		-15.29		-105.5	*	-0.48		-0.05		-0.02		0.00		-0.04		-0.02		-0.01	+	-0.036		-0.004
TIIRIKOJA		2.64		0.0002	***	-0.37	**	-0.11		-0.07	*	-0.04		-0.03	+	-0.04		-0.01	**	-0.034		-0.005
SAARE-JÄRVE	+	33.79		0.0001	***	-0.21	+	-0.05	+	-0.06	**	-0.05	*	-0.17		-0.01	*	-0.03	**	-0.018	**	-0.014
LAHEMAA		16.84	*	0.0012	***	-0.20		-0.05	*	-0.07	*	-0.02	*	-0.09	***	-0.02	**	-0.01	**	-0.020	**	-0.006
TOOMA		-4.84	*	0.0009	**	-0.21	**	-0.04		-0.06	**	-0.03	**	-0.10	**	-0.02	***	-0.02	*	-0.016	**	-0.008
L-NIGULA	*	-42.18		0.0000	*	-0.13	*	-0.15		-0.08		-0.05	+	-0.06	*	-0.03		-0.01	**	-0.021		-0.008
VILSANDI	+	17.08	+	-0.0017	*	-0.12	*	-0.11	+	-0.06		-0.02		-0.02		-0.01		0.00	**	-0.014		-0.004

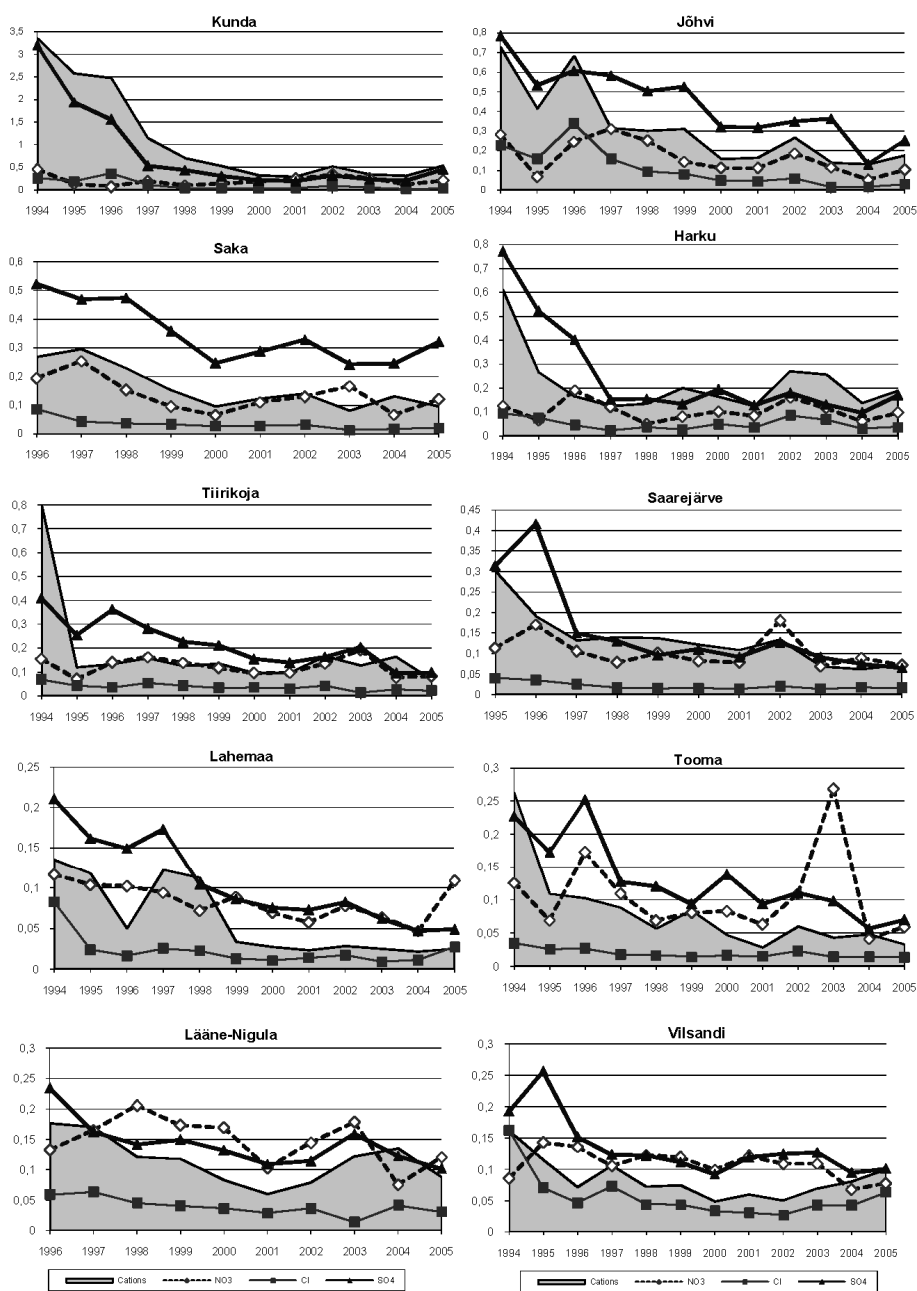
**NE industrial region background stations.** This group consists of Tiirikoja, Saarejärve, Lahemaa and Tooma, where the variation of the annual decline of summed cations (from 0.005 to 0.014 meq l<sup>-1</sup>) and summed anions (from 0.016 to 0.034 meq l<sup>-1</sup>) were very similar. The Lääne-Nigula station in W-Estonia had an annual decline of cations (0.008) and anions (0.021) that was quite similar to the above-mentioned stations, although the L-Nigula station does not belong in this group due to its decline in SO<sub>4</sub>-S (Table 1). Instead it belongs in the same group with Vilsandi, and the two can be defined as **natural background stations**, without doubt characterizing more European declining trends, especially for SO<sub>4</sub>-S and NO<sub>3</sub>-N.

The greatest decline during the twelve-year period (1994–2005) was that of SO<sub>4</sub>-S in most stations except Kunda, where the leading decreasing ion was Ca<sup>2+</sup>. At the NE industrial region stations, the annual SO<sub>4</sub>-S change varied from 1.76 mg l<sup>-1</sup> at Kunda to 0.46 mg l<sup>-1</sup> at Saka, and at the NE industrial background stations from 0.37 mg l<sup>-1</sup> at Tiirikoja to 0.21 mg l<sup>-1</sup> at Lahemaa and at the natural background station of Vilsandi to 0.12 mg l<sup>-1</sup>. Linear decreasing trends of summed anions and SO<sub>4</sub>-S followed the same pattern: decline per year varied from 1.167 mg l<sup>-1</sup> at Kunda to 0.014 mg l<sup>-1</sup> at Vilsandi (Table 1).

As a rule, the second largest decreasing cation in precipitation was Ca<sup>2+</sup> (except at Jõhvi where Ca<sup>2+</sup> held 5<sup>th</sup> position), and the second largest decreasing anion was Cl<sup>-</sup>. The linear decline in Ca<sup>2+</sup> and summed cations followed the same pattern (annual decline from 3.01 mg l<sup>-1</sup> at Kunda to 0.02 mg l<sup>-1</sup> at Vilsandi (Table 1). At Vilsandi, Tiirikoja, and Harku the decreasing trend of calcium was not statistically significant.

At most stations (except Harku and Lahemaa), the decline of chloride was statistically significant as well, while the slope estimates varied from 0.67 mg l<sup>-1</sup> at Jõhvi to 0.04 mg l<sup>-1</sup> at Tooma.

The pH level varied from 7.68 at Kunda to 4.7 at Vilsandi during the first three-year period, 1994–1996. The last station could be classified as weakly acidic (4.6 > pH < 5.1) [16]. The pH level decreased during the entire study period, reaching pH 5.1 at Tooma and pH 4.7 at Lahemaa in the last three-year period, 2003–2005. The most acidic annual mean precipitations were measured at Lahemaa (pH 4.90) and at Tooma (pH 4.92) in 2006, and the most basic at Kunda (pH 6.75) and Harku (pH 6.0) [17].



**Fig. 2.** Annual volume – weighted mean concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and summed cations (meq  $\text{l}^{-1}$ ) in bulk precipitation at Estonian monitoring stations during 1994–2005.

## Comparison of ion content trends by three-year periods from 1994–2005

### 1994–1996

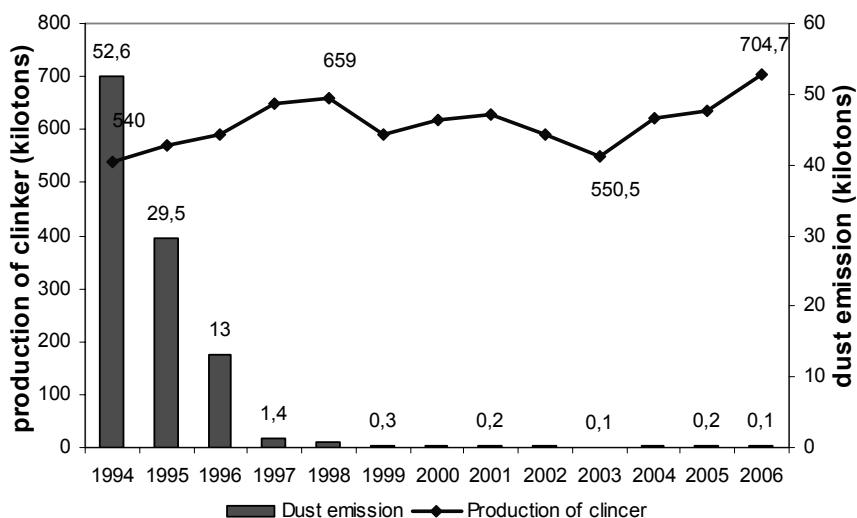
During the first three-year period, a sharp decrease in  $\text{SO}_4\text{-S}$  in bulk precipitation occurred at Kunda station ( $1.1 \text{ mg l}^{-1}$  per month) (Tab. 2). Such a sharp anionic decline was in close accordance with the fall in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  in precipitation at Kunda. All of these trends of purification in Kunda precipitation are responses to a reduction in dust emissions from a cement factory, the amount of which decreased four-fold (Fig. 4) during the period. The second large drop in  $\text{SO}_4\text{-S}$  concentrations ( $0.32 \text{ mg l}^{-1}$  per month) characterised Harku precipitations, largely accompanied by  $\text{Ca}^{2+}$  decline. It is difficult to draw a connection between the ion decline at Harku and the positive changes at Kunda station, as it is more likely that ion concentrations of Harku are impacted by industrial activity in Tallinn.

There was no statistically significant downward trend in sulphur at most background stations (except for Lahemaa, probably affected more by Kunda) and Saka – is most affected by the Narva Power Plant. Consequently, the decline in  $\text{SO}_2$  emissions from the Narva Power Plants (from 112 to about 91 thousand tons, i.e. about 20%, Fig. 1) did not produce a response in the deposition data. At the same time, the reduced emission of solid particles from power plants (from 102 to about 74 thousand tons, i.e. about 30%, Fig. 1) was distinctly reflected in the downward trends of cations at nearly all stations (Table 2). As a result, the highest statistically significant decreasing trend of  $\text{Ca}^{2+}$  in precipitation was characteristic of all stations (except for Lahemaa) during the first three years of the study. The reduced emissions of solid particles from power plants were most distinctly reflected in a decrease of various cation concentrations in Saka precipitation. The decline in cations (especially  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , both of which are characteristic of the mineral part of oil shale,) was accompanied by a decline in anions, especially  $\text{Cl}^-$ , and probably also  $\text{HCO}_3^-$  (not measured), but not  $\text{SO}_4^{2-}$ . Therefore the decline of ion concentration in bulk precipitation at most stations during the first three-year period of 1994–1996 was a response to the reduction in dust emissions from Kunda cement factory and flying ash emissions from the Narva Power Plants.

### 1997–1999

The highest decline in  $\text{SO}_4\text{-S}$  concentration in the precipitation at nearly all stations (except for Jõhvi, Lääne-Nigula and Harku) occurred during 1997–1999. The downward trend in sulphur at various stations as described by Sen's slope estimates (the Q in the table designates the mean monthly decrease in concentrations) followed this order: Kunda, Saka, Tiirikoja, Tooma, Saarejärve, Lahemaa and Vilsandi (Table 2). Such an order of stations by incline per month indicates the decrease of  $\text{SO}_2$  emissions from both Narva Power Plants and the

Kunda cement industry. Official emission data (Fig. 1) show a minimal reduction of SO<sub>2</sub> emissions during 1997–1999 (14% from stationary sources and only 6% from Narva Power Plants), especially compared to the first three-year period. The use of new purification equipment in the cement factory at Kunda was the most important positive change in the air pollution situation (causing a reduction in dust emission by about 80% in 1999 compared to 1997 (Fig. 3) in the entire North-East region. Despite the sharp reduction of dust emissions from Kunda and to a certain extent from the Narva Power Plants (about 8% during the period), the most important decreasing trend in cation concentrations occurred during the first three year period. The decline of Ca<sup>2+</sup> was only statistically significant in precipitation at Kunda, Saka and Lahemaa. It should be mentioned that Ca<sup>2+</sup> concentrations also decreased at all stations, but not significantly, which points to the high variability in monthly concentrations. Trend analyses indicated a significant decrease in Cl<sup>-</sup> at Jõhvi, Saka, Lääne-Nigula, Saarejärve and Lahemaa. The decrease in Cl<sup>-</sup> was in close correlation with decreasing trends in monovalent cations: Na<sup>+</sup> and K<sup>+</sup> at Saka, Lääne-Nigula and Lahemaa. It is generally agreed that sea salt is the dominant source of Cl<sup>-</sup> and Na<sup>+</sup> [18]. In the case of Lahemaa and perhaps also Saka and Jõhvi, there could be a sea salt effect on precipitation, but in all cases an additional source of Cl<sup>-</sup>, originating from oil shale burning, should be taken into consideration. Estonian oil shale contains chlorine (0.75%) in its organic part [6]. Thus the decrease in electricity production by about 1 TWh during 1997–1999 (Fig. 1) may have been the main cause of the decline in chloride, as well as in SO<sub>4</sub>-S concentrations in bulk precipitation at nearly all stations.



**Fig. 3.** Dust emission and production of clinker (kilotons) from Kunda Nordic cement factory 1994–2006 [19].

**Table 2.** Significant trends (“–“decreasing and “+” increasing) by three-year periods (1994–1996; 1997–1999; 2000–2002 and 2003–2005) of monthly mean concentrations in precipitation, by Mann-Kendall nonparametric test, Q= decline per month ( $\text{mg l}^{-1}$ ) and mean annual volume-weighted concentrations (VWC ( $\text{mg l}^{-1}$ )).

	KUNDA		JÖHVI		SAKA		HARKU		TIIRIKOJA		SAAREJÄRVE		LAHEMAA		TOOMA		L-NIGULA		VILSANDI	
	Q	VWC	Q	VWC	Q	VWC	Q	VWC	Q	VWC	Q	VWC	Q	VWC	Q	VWC	Q	VWC	Q	VWC
1994–1996																				
SO <sub>4</sub> -S	-1.10	34.8		10.2		8.4	-0.3	9.1		5.4		6.0	-0.05	2.7		3.4		3.8		3.2
Cl <sup>-</sup>		9.6		8.3	-0.74	3.1	-0.1	2.5	-0.05	1.8	-0.04	1.3	-0.04	1.3		1.0		2.1	-0.12	3.5
Na <sup>+</sup>		4.3		5.3	-0.92	1.5		1.2		0.9	-0.03	1.0	-0.01	0.4		0.5		1.5		1.0
Ca <sup>2+</sup>	-0.43	38.0	-0.11	3.9	-0.45	2.8	-0.1	3.4	-0.04	2.6	-0.08	2.5		1.2	-0.04	1.4	-0.22	1.6	-0.03	0.7
K <sup>+</sup>	-0.29	13.4		1.7	-0.58	1.5		0.5		0.8		0.6	-0.01	0.2		0.3		0.7	0.01	0.5
Mg <sup>2+</sup>	-0.12	4.1	-0.09	1.5	-0.06	0.3		1.4	-0.05	2.1	-0.09	0.6	-0.01	0.2	-0.03	0.7		0.2	-0.02	0.4
1997–1999																				
SO <sub>4</sub> -S	-0.19	6.7		8.6	-0.13	6.7		2.3	-0.06	3.8	-0.03	2.0	-0.03	1.9	-0.04	1.8		2.4	-0.03	1.9
Cl <sup>-</sup>		2.3	-0.13	4.0	-0.03	1.3		1.0		1.6	-0.02	0.7	-0.01	0.7		0.6	-0.04	1.8		1.8
Na <sup>+</sup>		1.1	-0.07	2.1	-0.01	0.6		0.6	-0.02	0.9		0.6	-0.01	0.3		0.3	-0.02	1.0	-0.02	1.0
Ca <sup>2+</sup>	-0.57	12.2		3.2	-0.12	2.8		2.2		1.3		1.5	-0.03	1.3		0.9		1.3		0.4
K <sup>+</sup>	-0.05	1.1		1.1	-0.01	0.4		0.1	-0.01	0.8		0.5	0.002	0.1	-0.003	0.1	-0.01	0.6	-0.01	0.3
Mg <sup>2+</sup>	-0.02	0.9		0.4	-0.01	0.4		0.2		0.1		0.3		0.1		0.2	-0.003	0.2	-0.003	0.2
2000–2002																				
SO <sub>4</sub> -S		3.8		5.2		4.4		2.6		2.4		1.7		1.2		1.8		1.9		1.8
Cl <sup>-</sup>	0.08	2.0		1.8		1.0		1.9		1.3		0.6		0.5	0.01	0.6		1.2		1.1
Na <sup>+</sup>	0.05	1.2		1.0		0.3		0.8		0.7		0.3		0.2		0.2		0.7		0.5
Ca <sup>2+</sup>		5.4		2.3		1.4		2.4	0.04	1.2		1.4		0.2		0.5		0.5		0.3
K <sup>+</sup>	0.02	0.7		0.5		0.7		0.3		0.6		0.4		0.1		0.1		0.4		0.3
Mg <sup>2+</sup>		0.4		0.2		0.2		0.2	0.005	0.1		0.3		0		0.1		0.1		0.1
2003–2005																				
SO <sub>4</sub> -S	0.12	4.6		4.0		4.3		2.0	-0.03	2.2	-0.02	1.2	-0.01	0.8	-0.021	1.2	-0.06	2.1		1.7
Cl <sup>-</sup>		1.4	-0.03	0.7	0.01	0.6		1.5		0.7		0.6		0.5		0.5		1.0		1.8
Na <sup>+</sup>		0.8		0.6		0.4		1.0	-0.01	0.6		0.3		0.2		0.2		1.0		1.1
Ca <sup>2+</sup>		6.3		1.9		1.3	-0.1	2.5	-0.02	1.4		0.6		0.2		0.5	-0.03	1.0		0.4
K <sup>+</sup>		0.7		0.3		0.3		0.1	-0.01	0.5		0.4		0.1		0.1		0.5		0.2
Mg <sup>2+</sup>	0.01	0.4		0.2		0.2		0.2	-0.004	0.2		0.2		0		0.1	-0.003	0.1		0.2

## 2000–2002

No single downward trend in the monthly mean concentrations of major ions in precipitation at any station was revealed by trend analyses during 2000–2002 (Table 2, Fig. 2). To the contrary, statistically significant upward trends of chloride and monovalent cations at Kunda, of  $\text{Ca}^{2+}$  and of  $\text{Mg}^{2+}$  at Tiirikoja and of  $\text{Cl}^-$  at Tooma were found. Official emission data indicated a reduction in solid particles from power plants by about 20% (Fig. 1) and the lowest level of dust emissions, as well as cement production at Kunda cement factory (Fig. 3). Gross production of electricity stabilised during the period 1993–2002, averaging 8.6 TWh per year. Emissions of  $\text{SO}_2$  from power plants reduced during the same period from 112.2 thousand tons to 78.4 thousand tons (1.4 times), and emissions of solid particles from 102.2 thousand tons to 49.2 thousand tons (two-fold). This is especially due to the installation of new and the renovation of old electrostatic precipitators in both power plants (1997–2002) [7, 20].

## 2003–2005

Trend analyses of monthly ion concentrations in bulk precipitation indicated statistically significant downward trends of  $\text{SO}_4\text{-S}$  at Kunda, Lääne-Nigula, Tiirikoja, Tooma, Saarejärve and Lahemaa during the last study period. The decline in  $\text{SO}_4$ -anions was accompanied by a significant decline in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at Tiirikoja and Lääne-Nigula (Table 2). The decrease in the concentrations of two-valent cations occurred at others stations too, but there the decrease was not statistically significant. Therefore, the deposition data indicate an improvement, especially in emissions from Narva Power Plants. The studied period was an eventful one: after the renovation of old and the installation of new electric filters for power plants at Narva in 2002 [7], emissions of solid particles decreased by about 13% in 2003, in spite of an increase in electricity production (about 19%). At the same time,  $\text{SO}_2$  emissions increased by about 15%, which is in close correlation with the increase in electricity production (Fig. 1). The start-up of two new fluidized bed (CFB) energy blocks (2004–2005) was the most important factor causing, at the very least, the reduction of sulphur dioxide emissions by about 13.7 thousand tons, as well as that of solid particles by 4.6 thousand tons compared to the year 2003 [2].

As we can see in table 2, the increasing concentrations of  $\text{SO}_4\text{-S}$  and of  $\text{Ca}^{2+}$  in precipitation at Kunda characterised the last period of 2003–2005. The increasing concentrations of ions in the deposition are closely correlated with the increase in dust emissions, as well as of cement production at Kunda (Fig. 3).



## Comments on results

Under different international agreements, Estonia has undertaken obligations to decrease emissions of sulphur dioxide, for example according to the Estonian–Finnish Air Protection Agreement (1993), Estonia promised to reduce emissions of the SO<sub>2</sub> 50% by 1997, based on the 1980 level and by 80% by 2005, in comparison with the 1980 level. According to the data of the Estonian Environment Information Centre, emissions of SO<sub>2</sub> fell 59.6% during the above-mentioned period (from 274,800 to 111,000 tons per year). Thereafter, both parties agreed [21] to 55,000 tons. According to Fig. 1, there was non-compliance.

The Estonia Environmental Strategy (1997) [22] has set the goal of reducing SO<sub>2</sub> emissions by 80% by 2005 in comparison with the level of 1980, and reducing emissions of solid particles by 25% compared with the level of 1995, and here cut-off values are 55,000 tons (was not achieved) and 28,300 tons respectively. In fact, the reduction of the latest indicator, emissions of solid particles, was significantly higher, namely 84% (Fig. 1).

There is a relief concerning the level of emission of sulphur dioxide in the new version of Estonia Environmental Strategy [23] – compared with the 1980 level fell 35% by 2005 and 40% by 2010, thereby guaranteeing that the total amount of sulphur dioxide emitted by stationary and mobile sources in Estonia will not exceed the level of 100,000 tons per year by 2010. These targets leave room for the growth of production of oil shale electric energy until 2010, because by 2012 the annual emission of sulphur dioxide from oil shale power plants cannot exceed 25,000 tons. The same targets for the reduction of SO<sub>2</sub> emission have been set as a direction at the ratification of the Convention on Long-Range Air Pollution & four Protocols (Geneva, 6.12.2000) and also accession to the European Union (EU directives) [24].

By the year 2005, the first two of 6 energy blocks were renovated and updated to new circulating fluidized-bed (CFB) technology, and this has set the goal to produce 6.6 TWh of electricity and to achieve the consistency of SO<sub>2</sub> emission standard (38,000 tons) as established in the Estonian Environmental Strategy [25]. In accordance with the data of Statistics Estonia in 2005 27% from gross production of electricity was produced using new technology. The drop off in emissions of SO<sub>2</sub> and solid particles in 2005 compared with 2004 showed a logical outcome, 10% and 36% respectively. The share of SO<sub>2</sub> emission from power plants compared with total emission from stationary sources fall 74 % (maximum share during the study period was 92% in 2003), but still remained a dominant source of SO<sub>2</sub> emissions in Estonia. At the same time, the share of emission of solid particles from power plants fell below 50% compared with the total emission of solid particles (Fig. 1). A previous brief analysis of emission data demonstrated that with current new technologies, it is not possible to totally eliminate emissions of air pollution, but on the condition of constant increase of production of electric energy there is an option of achieving

a decrease in emissions of air pollution through the decisions (directives) of local and international environmental politics.

## Conclusions

Twelve-year time trends of annual mean ion concentrations in bulk precipitation from 10 monitoring stations mostly show a statistically significant decline for  $\text{SO}_4\text{-S}$  in all 10 stations, for  $\text{Cl}^-$  and  $\text{Na}^+$  in 8, for  $\text{Ca}^{2+}$  and  $\text{K}^+$  in 7,  $\text{Mg}^{2+}$  in 6 and for  $\text{NO}_3\text{-N}$  in 4 stations. In contrast to the others,  $\text{H}^+$  increased (significantly in 6 stations) during the study period.

The highest decline of  $\text{Ca}^{2+}$  in precipitation occurred during the first three-year monitoring period of 1994–1996. The  $\text{Ca}^{2+}$  decline was a response to the reduction in dust emissions from Kunda cement factory and flying ash emissions from the Narva Power Plants during the same period.

The highest decline of  $\text{SO}_4\text{-S}$  concentrations in precipitation occurred from 1997–1999, and the decline reflected the reduction of emissions of  $\text{SO}_2$  more from the former monitoring period (1994–1996) than the studied one.

For the last three-year period (2003–2005), the statistically significant downward trends of  $\text{SO}_4\text{-S}$  in precipitation indicated an improvement, especially in emission from the Narva Plants after the start-up of two new fluidized bed energy blocks (2004–2005).

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