

TRENDS IN PRECIPITATION OF AIR POLLUTANTS AT ESTONIAN MONITORING STATIONS 1994–2005

K. TREIER*, N. KABRAL, J. FREY

Department of Geography
University of Tartu
46 Vanemuise St., 51014 Tartu, Estonia

This study concentrates mainly on the 12-year time trends of annual average ion concentrations in bulk precipitation from 10 Estonian monitoring stations. Trends revealed 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 requirements Estonia has undertaken serious obligations to reduce emissions of air pollutants. Total SO₂ emissions from power plants in Estonia have fallen from about 60%, and emission of solid particles decreased twenty times during the period of 1990–2005. The highest decline of Ca concentrations occurred during the first three-year monitoring period of 1994–1996, and a high decline of SO₄-S in 1997–1999 and 2003–2005.

Introduction

The control over 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 20th century. The reduction has resulted from international agreements (the Convention on Long-range Transboundary Air Pollution and its protocols) and corresponding changes in local legislation, from economic restructuring in the 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 local emissions of air pollutants have largely followed the European reduction trends. However, energy production from a specific

* Corresponding author: e-mail kai@archimedes.ee

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

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

Oil shale is the most important mineral resource in Estonia, and at the current amount of consumption the reserves should be sufficient (8.66 GT) for at least 60 years [5]. Estonian energy production is currently, and will continue to be, based mostly 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 of 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 of 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 SO₂ emission 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 (20 times) 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 SO₂ 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_x 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.

As emission of air pollutants has been calculated, 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 measured 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

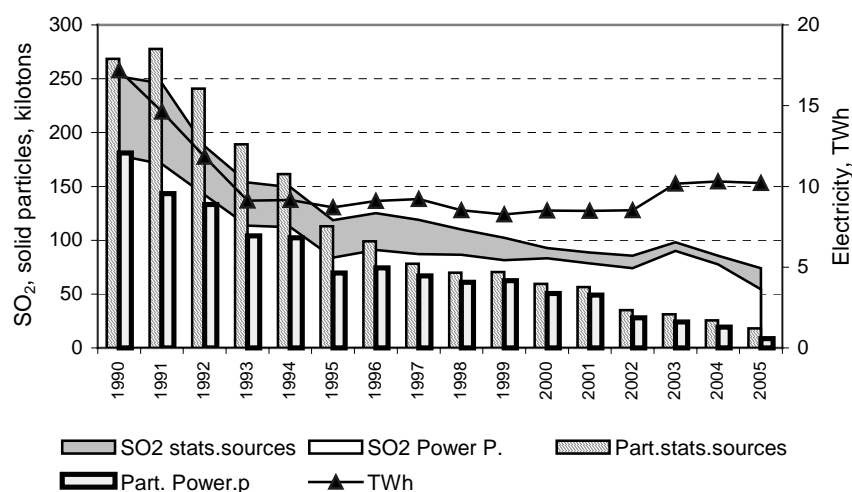


Fig. 1. Annual emissions of SO₂ and solid particles (kilotons) from power plants and stationary sources as well as with electricity production (TWh) during 1990–2005 [3].

(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 dates from 1994 (Fig. 2).

The aim of the present paper is to analyze the changes and trends in anion and cation concentrations basing on the available data of bulk precipitation related to the decreased emissions of SO₂ 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 from 6.3 °C in Western coast to 4.4 °C in Eastern Estonia. The warmest month is July, monthly rainfall is greatest in August, and February is the coldest and driest month. 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 24 h basis. The 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]. Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , NO_3^- and Cl^- concentrations in water samples were determined using ion chromatography (EN-ISO 14911 and EN-ISO 10304). 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 measurement of wet deposition is done using open, so called bulk collectors for precipitation. Possible uncertainties due to 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 Cl^-/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 parameters ($n = 12$) 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 weighted mean ion concentrations in bulk precipitation at 10 monitoring stations in Estonia during a twelve-year period (1994–2005). Annual average ion concentrations

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

	mm		H^+ eq l^{-1}		$\text{SO}_4\text{-S}$ mg l^{-1}		Cl^- mg l^{-1}		$\text{NO}_3\text{-N}$ mg l^{-1}		Na^+ mg l^{-1}		Ca^{2+} mg l^{-1}		K^+ mg l^{-1}		Mg^{2+} mg l^{-1}		Sum of anions meq l^{-1}		Sum of cations 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
SAAREJÄRVE	+	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	0.00	**	-0.014	**	-0.004

mostly show statistically significant decreasing trends for $\text{SO}_4\text{-S}$ in 10 stations, for Cl and Na in 8, for Ca and K in 7, Mg in 6 and for $\text{NO}_3\text{-N}$ in 4 stations. In contrast to the others, H^+ increased (significantly in 6 stations) during the study period. Using the annual decline (Q) of summed anions plus cations (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) > Saare (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 Nigula and Tooma and for Ca in the case of Tiirikoja and 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 12-year study period, these stations were characterized by the highest annual decline of most ions (anions plus cations) in precipitation.

NE industrial region background stations. This group consists of Tiirikoja, Saare, Lahemaa and Tooma stations, where the variation of the annual decline of summed cations (from 0.005 to 0.014 meq l^{-1}) and summed anions (from 0.016 to 0.034 meq l^{-1}) 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 Lääne-Nigula station does not belong in this group due to its decline in $\text{SO}_4\text{-S}$ (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 $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$.

The greatest decline during the twelve-year period (1994–2005) was that of $\text{SO}_4\text{-S}$ in most stations except Kunda, where the leading decreasing ion was Ca. At the NE industrial region stations, the annual $\text{SO}_4\text{-S}$ change varied from 1.76 mg l^{-1} at Kunda to 0.46 mg l^{-1} at Saka, and at the NE industrial background stations from 0.37 mg l^{-1} at Tiirikoja to 0.21 mg l^{-1} at Lahemaa and at the natural background station of Vilsandi to 0.12 mg l^{-1} . Linear decreasing trends of summed anions and $\text{SO}_4\text{-S}$ followed the same pattern: decline per year varied from 1.167 mg l^{-1} at Kunda to 0.014 mg l^{-1} at Vilsandi (Table 1).

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

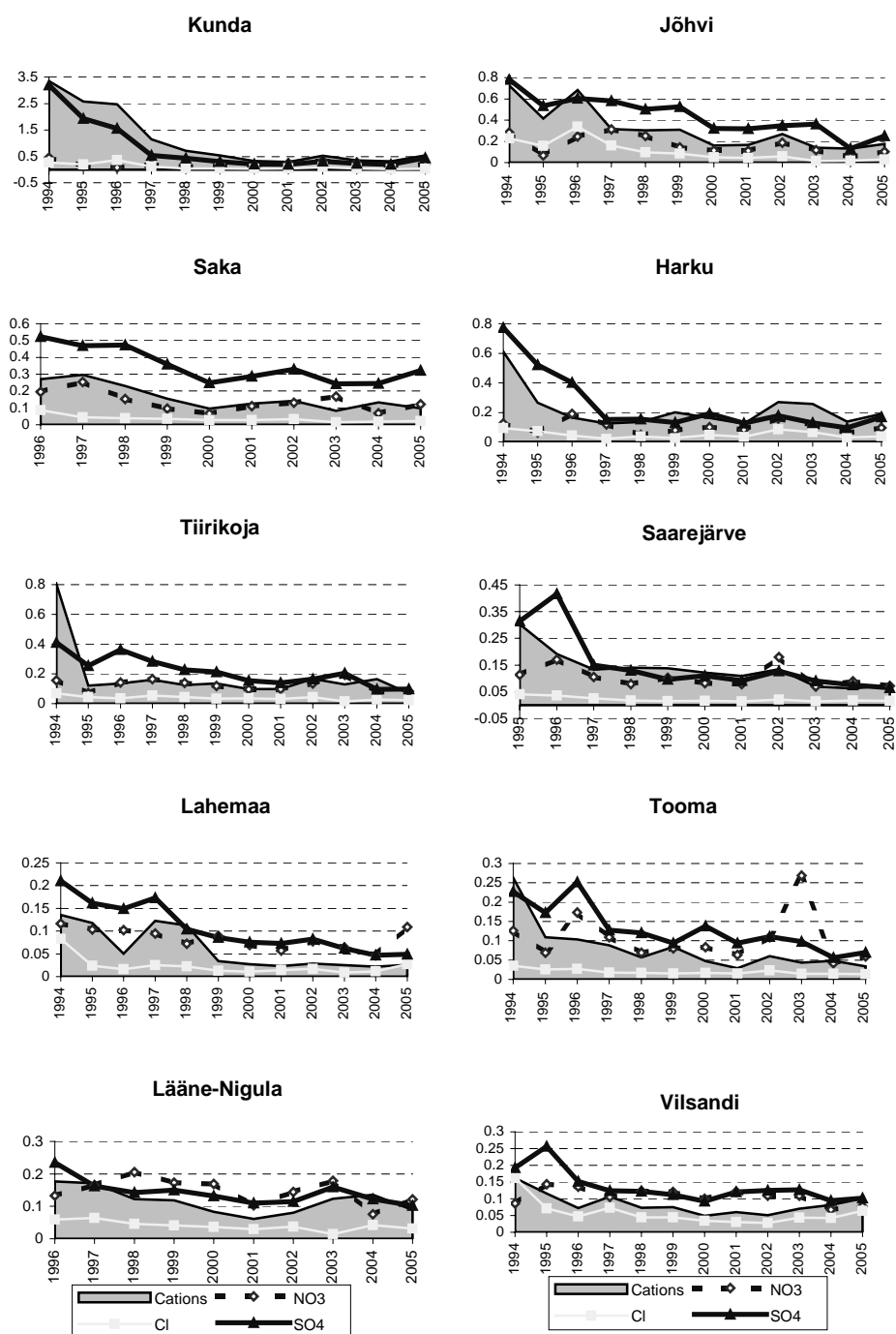


Fig. 2. Annual volume-weighted mean concentrations of SO_4^{2-} , Cl^- , NO_3^- and summed cations (meq l^{-1}) in bulk precipitation at Estonian monitoring stations during 1994–2005 (Data of Estonian Environment Monitoring Program).

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^{-1} at Jõhvi to 0.04 mg l^{-1} at Tooma.

The pH level varied from 7.68 at Kunda to 4.7 at Vilsandi during the first 3-year period, 1994–1996. The last station could be classified as weakly acidic ($4.6 > \text{pH} < 5.1$) [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 3-year period, 2003–2005. The most acidic annual 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].

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 mg l^{-1} per month) (Tab. 2). Such a sharp anionic decline was in close accordance with the fall in Ca^{2+} , Mg^{2+} and K^+ in precipitation at Kunda. All of these trends of purification in Kunda precipitation are responses to a 4-fold reduction in dust emissions from Kunda cement factory (Fig. 3) during the period. The second large drop in $\text{SO}_4\text{-S}$ concentrations (0.32 mg l^{-1} per month) characterised Harku precipitations, largely accompanied by 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.

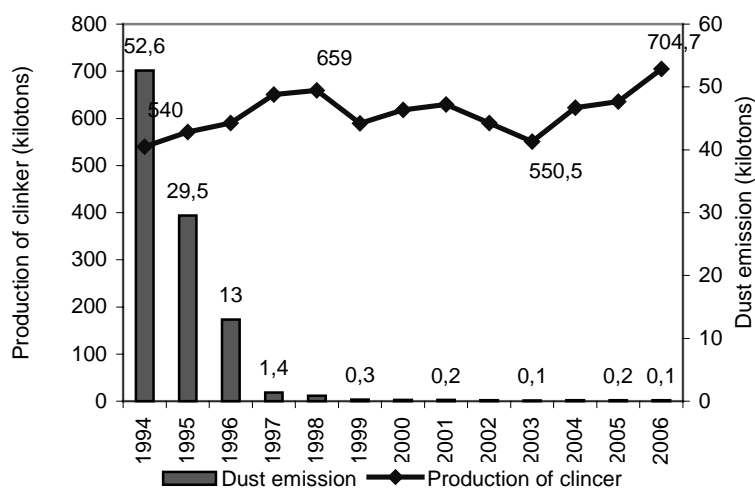


Fig. 3. Dust emission and production of clinker (kilotons) at Kunda Nordic cement factory in 1994–2006. [19].

There was no statistically significant downward trend in sulphur at most background stations (except for Lahemaa, probably affected more by Kunda) and Saka – most affected by the Narva power plants. Consequently, the decline in SO₂ 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 Ca²⁺ 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 cation (especially Ca²⁺ and Mg²⁺, both of which are characteristic of the mineral part of oil shale,) was accompanied by a decline in anions, especially Cl⁻, and probably also HCO₃⁻ (not measured), but not SO₄²⁻. 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 SO₄-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 Sens 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 SO₂ emissions from both Narva power plants and the Kunda cement industry. Official emission data (Fig. 1) show a minimal reduction of SO₂ 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 Ca²⁺ was only statistically significant in precipitation at Kunda, Saka and Lahemaa. It should be mentioned that Ca²⁺ 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⁻ at Jõhvi, Saka, Lääne-Nigula, Saarejärve and Lahemaa. The decrease in Cl⁻ was in close correlation with decreasing

Table 2. Significant trends (“–“decreasing and “+” increasing) by three-year periods (1994–1996; 1997–1999; 2000–2002 and 2003–2005) in monthly mean concentrations of pollutants in precipitation, by Mann-Kendall nonparametric test, Q = decline per month (mg l^{-1}) and mean annual volume-weighted concentrations (VWC, 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 ₄ ²⁻	-1.10	34.8		10.2		8.4		9.1		5.4		6.0		-0.05		2.7		3.4		3.8		3.2
Cl ⁻		9.6		8.3		-0.74		2.5		1.8		1.3		-0.04		1.3		1.0		2.1		3.5
Na ⁺		4.3		5.3		-0.92		1.2		0.9		1.0		-0.01		0.4		0.5		1.5		1.0
Ca ²⁺	-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		1.4		1.6		-0.03	0.7
K ⁺	-0.29	13.4		1.7	-0.58	1.5		0.5		0.8		0.6		-0.01		0.2		0.3		0.7		0.5
Mg ²⁺	-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		0.7		0.2		0.4
1997–1999																						
SO ₄ ²⁻	-0.19	6.7		8.6	-0.13	6.7		2.3	-0.06	3.8	-0.03	2.0		-0.03		1.9		1.8		2.4		1.9
Cl ⁻		2.3	-0.13	4.0	-0.03	1.3		1.0		1.6	-0.02	0.7		-0.01		0.7		0.6		1.8		1.8
Na ⁺		1.1	-0.07	2.1	-0.01	0.6		0.6	-0.02	0.9		0.6		-0.01		0.3		0.3		1.0		1.0
Ca ²⁺	-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 ⁺	-0.05	1.1		1.1	-0.01	0.4		0.1	-0.01	0.8		0.5		0.002		0.1		0.1		0.6		0.3
Mg ²⁺	-0.02	0.9		0.4	-0.01	0.4		0.2		0.1		0.3				0.1		0.2		0.2		0.2
2000–2002																						
SO ₄ ²⁻		3.8		5.2		4.4		2.6		2.4		1.7				1.2		1.8		1.9		1.8
Cl ⁻	0.08	2.0		1.8		1.0		1.9		1.3		0.6				0.5		0.6		1.2		1.1
Na ⁺	0.05	1.2		1.0		0.3		0.8		0.7		0.3				0.2		0.2		0.7		0.5
Ca ²⁺		5.4		2.3		1.4		2.4	0.04	1.2		1.4				0.2		0.5		0.5		0.3
K ⁺	0.02	0.7		0.5		0.7		0.3		0.6		0.4				0.1		0.1		0.4		0.3
Mg ²⁺		0.4		0.2		0.2		0.2	0.005	0.1		0.3				0		0.1		0.1		0.1
2003–2005																						
SO ₄ ²⁻		4.6		4.0		4.3		2.0	-0.03	2.2	-0.02	1.2		-0.01		0.8		1.2		2.1		1.7
Cl ⁻	0.12	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 ⁺		0.8		0.6		0.4		1.0	-0.01	0.6		0.3				0.2		0.2		1.0		1.1
Ca ²⁺		6.3		1.9		1.3		2.5	-0.02	1.4		0.6				0.2		0.5		-0.03		0.4
K ⁺		0.7		0.3		0.3		0.1	-0.01	0.5		0.4				0.1		0.1		0.5		0.2
Mg ²⁺	0.01	0.4		0.2		0.2		0.2	-0.004	0.2		0.2				0		0.1		-0.003		0.2

trends in monovalent cations: Na^+ and K^+ at Saka, Lääne-Nigula and Lahemaa. It is generally agreed that sea salt is the dominant source of Cl^- and Na^+ [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^- , 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 chlorides, as well as in $\text{SO}_4\text{-S}$ concentrations in bulk precipitation at nearly all stations.

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 Ca^{2+} and of Mg^{2+} at Tiirikoja and of 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 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 (2.1 times). 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, Saare and Lahemaa during the last study period. The decline in SO_4 anions was accompanied by a significant decline in Ca^{2+} and 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, 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 thousands tons, as well as that of solid particles by 4.6 thousands 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 Mg^{2+} , 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_2 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_2 fell 59.6% during the above-mentioned period (from 274,800 to 111,000 tons per year). Thereafter, both parties agreed [21] on 55,000 tons. According to Fig. 1, there was non-compliance.

The Estonia Environmental Strategy (1997) [22] has set the goal of reducing SO_2 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 the 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 it fell by 35% by 2005 and will fall 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_2 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_2 emission standard (38,000 tons) as established in the Estonian Environmental Strategy [25]. In accordance with the data of Statistics Estonia in 2005, 27% of gross production of electricity was produced using new technology. The drop off in emissions of SO_2 and solid particles in 2005 compared with 2004 showed a logical outcome, 10% and 36% respectively. The share of SO_2 emission from power plants compared with total emission from stationary sources fell 74% (maximum share during the study period was 92% in 2003), but the plants still remained a dominant source of SO_2

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 a constant increase in 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

12-year time trends of annual average 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 Cl and Na in 8, for Ca and K in 7, Mg in 6 and for $\text{NO}_3\text{-N}$ in 4 stations. In contrast to the others, H^+ increased (significantly in 6 stations) during the study period.

The highest decline of Ca in precipitation occurred during the first three-year monitoring period of 1994–1996. The Ca 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 to 1999, and the decline reflected the reduction of emissions of 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).

Acknowledgements

The current research was supported by Estonian Ministry of Environment in the framework of the national environmental monitoring program.

REFERENCES

1. Grennfelt, P., Hov, O. Regional air pollution at a turning point // *Ambio*. 2005. Vol. 34, No. 1. P 2–10.
2. Annual report of Estonian Energy 2004/2005. Eesti Energia Ltd. 2005. P. 2. <http://www.energia.ee/index.php?id=141&L=0>.
3. Statistical database of Statistics Estonia. Statistical Office of Estonia. 2005. <http://pub.stat.ee/pxweb.2001/Database/Majandus/02Energeetika/02Energeetika.asp>.

4. *Liive, S.*, Oil shale energetics in Estonia // Oil Shale. 2007. Vol. 24, No. 1. P. 1–4.
5. *Agabus, H., Landsberg, M., Tammoja, H.* Reduction of CO₂ emission in Estonia during 2000–2030 // Oil Shale. 2007. Vol. 24, No. 2. P. 209–224.
6. Environment survey 2005. – Estonian Environment Information Centre. Tallinn, 2005 [in Estonian]. <http://www.envir.ee/orb.aw/class=file/action=preview/id=474775/Keskkonna%FClevaade+2005.pdf>.
7. *Ots, A.* Formation and emission of compounds affecting environment // Oil Shale. 2005. Vol. 22, No. 4. Special. P. 499–535.
8. *Ots, A.* Formation of air-polluting compounds while burning oil shale // Oil Shale. 1992. Vol. 9, No. 1. P. 63–75.
9. *Karofield, E.* The effects of alkaline fly ash precipitation on the Sphagnum mosses in Niinesaare bog, NE Estonia // Suoseura. 1996. Vol. 47, No. 4. P. 105–114.
10. *Liblik, V., Pensa, M., Rätsep, A.* Air pollution zones and harmful pollution levels of alkaline dust for plants // Water, Air & Soil Pollution. 2003. Vol. 3, No. 5–6. P. 199–209.
11. EMEP manual for sampling and chemical analysis // EMEP CCC-Report 1/95. Rev. 1 / 96. Chemical Coordinating Centre. Norwegian Institute for Air Research. Kjeller, 1996. P. 199.
12. *Lövblad, G., Persson, C., Roos, E.* Deposition of base cations in Sweden. – Report 5119. Swedish Environmental Protection Agency, Stockholm, 2000. P. 59.
13. *Treier, K., Pajuste, K., Frey, J.* Recent trends in chemical composition of bulk precipitation at Estonian monitoring stations 1994–2001 // Atmospheric Environment. 2004. Vol. 38, No. 40. P. 7009–7019.
14. *Pajuste, K., Frey, J., Asi, E.* Interactions of atmospheric deposition with coniferous canopies in Estonia // Environmental Monitoring and Assessment. 2006. Vol. 112, No. 1–3. P. 177–196.
15. *Salmi, T., Määttä, A., Anttila, P., Ruoho-Airola, T., Amell, T.* Detecting trends of annual values of atmospheric pollutants by Mann-Kendall test and Sen's slope estimates – the Excel template application MAKESENS. – Publication on Air Quality, Finnish Meteorological Institute, Helsinki, 2002. No. 31. P. 35.
16. *Smidt, St.* Bulk-Messungen in Waldebieten Österreichs/ FBVA-Berichte. 1986. Nr. 13. S. 1–28.
17. *Kabral, N., Truuts, T., Merilo, A., Iher, H., Kolk, R.* Chemistry of precipitations. Estonian Ministry of the Environment. Tallinn. 2007 In Press [in Estonian].
18. *Draaijers, G. P., van Leeuwen, E. P., De Jong, P. G. H., Erisman, J. W.* Base-cation deposition in Europe – Part II. Acid neutralization capacity and contribution to forest nutrition // Atmospheric Environment. 1997. Vol. 31, No. 24. P. 4159–4168.
19. Kunda Nordic cement factory (Aivar Reimus – Quality Manager, e-mail 25.05.2007)
20. *Liblik, V., Kaasik, M., Pensa, M., Rätsep, A., Rull, E., Tordik, A.* Reduction of sulphur dioxide emissions and transboundary effects of oil shale based energy production // Oil Shale. 2006. Vol. 23, No. 1. P. 29–38.
21. Development plan of Estonian power economy 2005–2015 // RTL (State Gazette). 2006. No. 7. P. 134. <https://www.riigiteataja.ee/ert/act.jsp?id=979263> [in Estonian].

22. Estonian environment strategy // RT I (State Gazette). 1997. No. 26. P. 390 [in Estonian].
23. Estonian environment strategy till 2010 // RT I (State Gazette). 2005. No. 58. P. 462. <https://www.riigiteataja.ee/ert/act.jsp?id=955023> [in Estonian].
24. Laur A., Soosaar, S., Tenno, K. Influence of environmental claims on Estonian power market and power production costs in 2005–2015. – Report of the contract No. 041027. TUT, Tallinn, 2004. P. 21 [in Estonian].
25. Tammoja, H. Needs for production and transmission of electric power and development scenarios in Estonian power system in 2005–2015. – Report of the contract No. 478L.TUT, Tallinn, 2004. <http://www.seit.ee/files/Elektritootmine.pdf> [in Estonian].

Presented by J.-M. Punning

Received September 28, 2007