Changes in precipitation chemistry in Lithuania for 1981–2004

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This paper considers the spatial and temporal variability in concentrations of the potentially acidifying ions in precipitation in Lithuania during the 1981–2004 period. Chemical analysis of precipitation included measurements of pH, conductivity, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), sodium (Na^+), potassium (K^+), and calcium (Ca^{2+}). Temporal trends in the potentially acidifying ion concentrations in precipitation and wet deposition were evaluated using the non-parametric Mann–Kendall test and Sen's slope estimator. A statistically significant decline was observed in non-sea salt sulfate ($nssSO_4^{2-}$) and hydrogen (H^+) ions concentrations (82% and 79%, respectively) and wet depositions (88% and 74%, respectively). Temporal trends both in concentration and wet deposition of nitrate and ammonium were not as pronounced as trends in sulfate concentration. Analysis of air mass backward trajectories was applied to reveal the influence of air mass originating in different regions on wet deposition of acidifying species in Lithuania. Sector analysis clearly showed that wet deposition of sulfur and nitrogen in Lithuania is to a large extent anthropogenic and the main source regions of acidifying species contributing to wet deposition in Lithuania are in South and Central Europe.

1. Introduction

In the early 1960s, it was pointed out that acidity in precipitation in large regions of northern Europe and eastern North America was directly related to increased anthropogenic sulfur and nitrogen emissions.[1–4] As a result of the abatement strategies for SO_2 and NO_2 anthropogenic emissions in Europe and control measures that were undertaken in most countries in Europe from the beginning of the 1980s, anthropogenic emissions of sulfur and nitrogen species have changed over the recent 20 years. Despite the fact that the SO_2 emission reduction was not uniform (40–90%) throughout Europe, total European SO_2 emission have decreased by nearly 67% since 1980, and by about 60% from 1990 to 2001. NO_2 emissions remained fairly constant throughout the 1980s and steadily decreased from the beginning of the 1990s. Although there were great differences in NO_2 emission reduction across the whole Europe, but in general, the overall reduction in Europe amounted to 24% from 1980 to 2001.[5] The largest changes in SO_2 and to a lesser extent in NO_2 emissions should be reflected in pollutant concentrations both in air and precipitation. Therefore, in recent years, there has been a considerable interest in assessing the effectiveness of the abatement strategies and in relating the decreases in anthropogenic emissions to reduced amounts of acidic deposition.[6–8]

In Lithuania, the prevailing wind is westerly and, therefore, Lithuania is highly exposed to transboundary air pollution from Central Europe.[9] In this paper we present the spatial and temporal patterns of concentrations in precipitation and wet deposition of acidifying species in Lithuania over 24 years.

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Specific objectives of this study are (1) to establish regional "background" concentrations of major ions in precipitation and wet deposition, (2) to examine the seasonal variations of concentrations and wet deposition of major ions, (3) to evaluate the trends in concentration of acidifying species in precipitation at selected two rural Lithuanian stations during the period from 1981 to 2004, and (4) to estimate the influence of air mass origin on the precipitation chemistry and wet deposition.

2. Materials and methods

2.1. Sampling and analytical methods

Two stations representing western and eastern parts of Lithuania were chosen for precipitation sampling. Fig. 1 shows the location of the stations. The main criterion for selecting the monitoring sites was a sufficient distance from the substantial local anthropogenic air pollution sources and, thereby, both stations were set in the National Park zones and can be regarded as regionally representative. The background air quality station Preila is situated on the shore of the Baltic Sea, on the narrow sandy strip (Curonian Spit) which separates the Baltic Sea and the Curonian Lagoon. The width of the spit varies from 0.4 to 4 km and its length is 98 km. Its width is approximately 2 km at the station site. The dunes, up to 50 m height, as well as natural forests in low-lying lands predominate in the region. The marine climate is specific to this terrain. The background air quality station Rugsteliskes is an inland station and it is situated in the eastern forested part of the country, about 350 km to the east of Preila. Conifers, which are mainly Scots pine trees with a mixture of Norway spruce, dominate the site. The continental climate at the site is
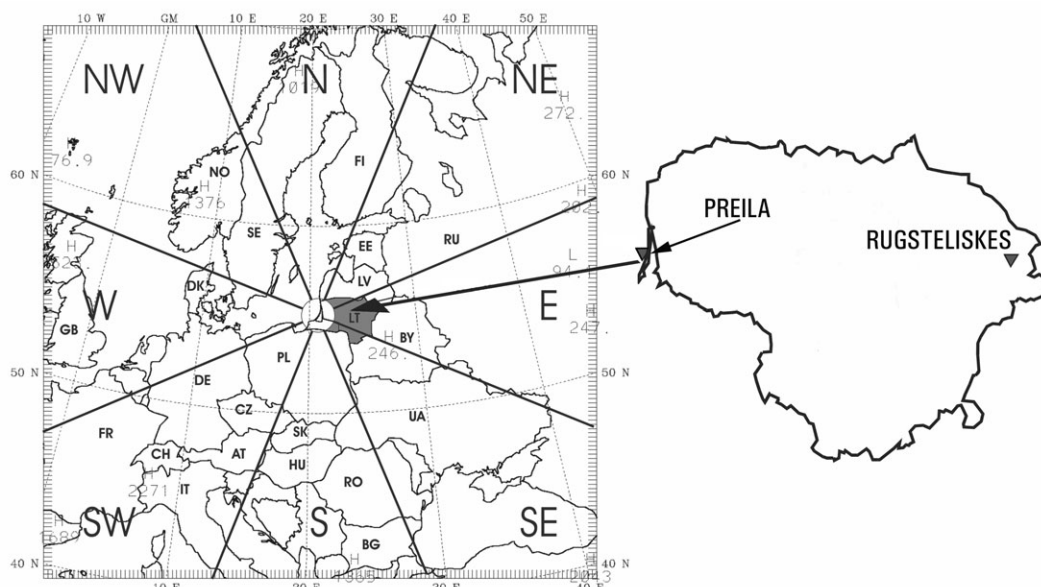
Fig. 1 Location of the background air quality stations (Preila and Rugsteliskes) in Lithuania and air mass transport sectors used to categorize backward trajectory origins: north (N), northeast (NE), east (E), southeast (SE), south (S), southwest (SW), west (W) and northwest (NW).

characterized as moderately cold and with abundant precipitation.

Weekly precipitation samples were collected using a bulk-collector during the winter (December–February) and an automatic wet-only sampler during the rest of the year. An automatic wet-only sampler for daily precipitation sampling has been used continuously year-round at the station Preila since 1996. Precipitation samples were stored in a refrigerator at 4 °C prior to chemical analysis in order to minimize the changes in chemical composition of the precipitation water. A pH meter (model PerpHecT LogR 320) with a glass combination electrode was used for pH measurement. The pH meter was calibrated before every measurement using commercially available standard pH buffer solutions (4.01 and 7.01). Conductivity was measured using a conductivity meter (Radelkis OK-102/1). The concentrations of SO_4^{2-}, NO_3^-, Cl^- and NH_4^+ ions were determined colorimetrically using a continuous flow system (CONTIFLO) until 1996. An ion chromatography method (Dionex 2010i, with conductivity detector) has been used for the determination of anions since 1996. The Na^+, K^+ and Ca^{2+} concentrations were determined by the atomic emission method. The indophenol-spectrophotometry method was used for the determination of the NH_4^+ concentration.

The quality control was routinely performed by using the Standard Reference Materials produced by Dionex Corporation, USA. In addition, the quality of the analytical data was checked by comparing the equivalent ratio of the cation sum to the anion sum and by comparing the ratio of the measured conductivity to the calculated one. Data quality was ensured according to the EMEP CCC (Co-operative Programme for Monitoring and Evaluation of the Long-Range transmission of Air Pollutants in Europe, Chemical Coordinating Centre) "Manual for Sampling, Chemical Analysis and Quality Assessment".[10] Non-sea salt sulfate ($nssSO_4^{2-}$) concentrations

were estimated as the difference between total and marine concentration of sulfate assuming Na^+ to be a tracer for sea salt.

2.2. Air mass backward trajectory sector analysis

Air mass backward trajectory analysis was applied to identify the potential importance of different source regions to the acidic deposition in Lithuania. The air mass backward trajectories at 925 hPa for Preila were available from EMEP/MSC-W[11] (Meteorological Synthesizing Centre-West) and NOAA HYSPLIT-4 model.[12] The daily backward trajectories were calculated by tracking an air parcel every 2 h for 96 h and, therefore, each trajectory was defined by a total of 49 position points (including the arrival point). The area around the arrival point, *i.e.*, Preila, was divided into 8 equal airflow sectors (Fig. 1). Sector N (north) covers the area from $-22.5°$ to $22.5°$ and the sectors NE (northeast), E (east), SE (southeast), S (south), SW (southwest), W (west) and NW (northwest) were defined clockwise using the angles at $45°$ intervals. The criterion for the description of air mass to a certain sector was the availability of at least 50% of all 96 h back trajectory points within the sector. Otherwise, the sector was named as "undefined" (*i.e.*, mixed). Taking into consideration the geographical location of the most important anthropogenic emitters in Europe, air mass trajectories arriving in Preila were reallocated to five entry sectors (NE, E, SE, S–SW–W and NW–N) of different sizes in order to reduce the number of trajectories getting into undefined sector which amounted to up to 27% for Preila yearly.[9] Thus, the south-southwesterly sector (S–SW–W) includes the major emitters of SO_2 and NO_2 in West and Central Europe, while the northerly sector (NW–N) includes sources of SO_2 and NO_2 in Scandinavia and the Baltic Sea. The northeast (NE) and east (E) sectors represent pollutant sources in Estonia, Latvia, Lithuania, Belarus and Russia and the southeast (SE) sector represents the Ukraine.

Table 1 VWM concentrations of major ions in precipitation and wet deposition for each site for 2000–2004

| Ion	Concentration/μeq l^{-1}		Wet deposition/mg m^{-2} yr^{-1}	
	Preila	Rugsteliskes	Preila	Rugsteliskes
nssSO$_4^{2-}$–S	35.6	24.1	268	244
NO$_3^-$–N	36.9	24.0	244	213
Cl$^-$	94.6	13.5	1586	303
NH$_4^+$–N	34.2	20.3	226	180
Na$^+$	89.4	13.8	970	200
K$^+$	5.8	3.3	106	82
nssCa^{2+}	32.1	23.4	303	296
H$^+$	15.9	9.8	7.5	6.2

3 Results and discussion

3.1. Chemical characteristics of precipitation

To represent a regional background level of precipitation chemistry across Lithuania, concentrations in precipitation and wet deposition of major ions measured in Preila (western part of Lithuania) were compared with those measured in Rugsteliskes (eastern part of Lithuania). Table 1 lists the volume-weighted mean (VWM) concentrations of the major ions in precipitation and wet deposition at those rural sites for the period of 2000–2004. The results revealed the gradient of concentrations of all major ions in precipitation from the western to eastern part of Lithuania. Assessing the sodium ions first, it is seen that its concentration varies from 94.6 μeq l^{-1} in Preila to 13.5 μeq l^{-1} in Rugsteliskes. As can be expected, a similar pattern is observed for chloride. This indicates that chemical composition of precipitation at the coastal site is generally affected by sea salt particles generated from the Baltic Sea. Concentration of nssSO$_4^{2-}$ ranged from 35.6 μeq l^{-1} in Preila to 24.1 μeq l^{-1} in Rugsteliskes. The same pattern of spatial variability in the concentrations was also found for NO$_3^-$ and other major ions. It should be noted that the NO$_3^-$/nssSO$_4^{2-}$ ratio in equivalent concentration in rainwater for this period (2000–2004) is about 1.0, *i.e.* 2.5 times higher than that observed for the 1980s. This suggests that quantitative composition of the anions in precipitation in Lithuania is gradually changing and the contribution of both ions (NO$_3^-$ and nssSO$_4^{2-}$) to rainwater acidity is comparable. The data of the cumulative frequency distribution (Fig. 2) indicate that the monthly volume-weighted mean pH values of rainwater during the last five years (2000–2004) ranged between 4.25 and 6.75. However, the pH values distinctly shifted towards the lower ones in the western part of Lithuania.

The data also show that about 70% and 40% of rainwater samples have pH value below 5.0 in Preila and Rugsteliskes, respectively.

The difference in concentrations of major ions between the sampling sites in the region (Lithuania) is assumed to be related, in part, to a certain dilution effect taking place during the precipitation scavenging. Long-term precipitation monitoring data show that due to orographic effects the eastern part of Lithuania receives constantly more precipitation than the western part of Lithuania. Thus, a higher precipitation amount at the eastern site in Rugsteliskes directly suggests that the precipitation amount is an important controlling factor in
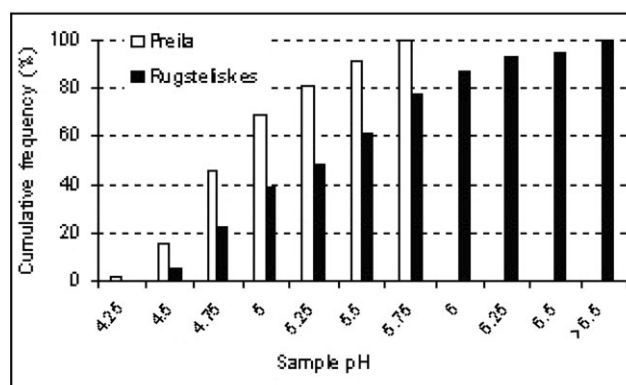
Fig. 2 Cumulative frequency distribution of the pH values in precipitation samples in Preila and Rugsteliskes for 2000–2004.

the formation of ion concentrations in rainwater. On the other hand, the differences between the concentrations of major ions in precipitation at these sites may be associated with the lower pollutant concentrations (such as SO$_2$ and NO$_2$) in the air in Rugsteliskes. Our previous research showed that atmospheric concentrations of acid-related species were lower by a factor of 1.5–2.0 in the easternmost part of Lithuania than those in the western and southern parts of Lithuania.[13] Wet deposition of acid-related species at each site varied spatially in concert with the precipitation amount and concentrations of potentially acidifying compounds, and generally, the load of pollutants decreased from the west to the east in Lithuania. The results revealed that the concentrations of most of the potentially acidifying components (nssSO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) measured in Lithuania are comparable to those measured in the neighboring countries (Latvia, southern Sweden, Poland, Germany and Denmark) over this period of time.[14]

3.2. Seasonal variations

Precipitation chemistry data for the 1994–2004 period were arranged into four seasons based on annual meteorological trends in the region: winter (December–February), spring (March–May), summer (June–August) and autumn (September–November). From Fig. 3 it is seen that concentrations of all major ions at both sites are subjected to seasonal influences, in particular due to variations in meteorological conditions and pollutant emissions, and show distinct seasonal patterns. In general, the seasonal average mean precipitation in Lithuania is at its maximum in autumn, while the nssSO$_4^{2-}$ and NH$_4^+$ concentrations in rainwater are highest in spring and summer. Thus, a large amount of precipitation could dilute the ion concentrations. Concentrations of NO$_3^-$ are typically high in winter. Wintertime data indicate the high equivalent ratio of NO$_3^-$ to nssSO$_4^{2-}$, 1.3 and 0.9, in Preila and Rugsteliskes, respectively. This means that sulfate and nitrate make approximately equal contributions to precipitation acidity. The most acidic precipitation was found during winter months along with higher NO$_3^-$ and lower NH$_4^+$ concentrations. During this time of the year, the pH value below 5.0 amounted to 93% and 70% when compared to the summer data of 50% and 18% in Preila and Rugsteliskes, respectively (Fig. 4). No
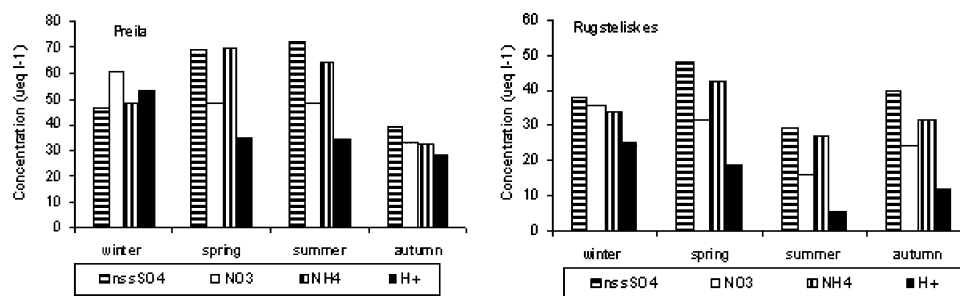
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Fig. 3 Seasonal variation in VWM concentration of major ions in precipitation in Preila and Rugsteliskes for 1994–2004.

clear seasonal variation could be detected for calcium concentrations. The results revealed a seasonal variability in wet deposition of major ions. The maximum wet deposition of acidifying ions was found in the western part of Lithuania in autumn and in the eastern part in winter and it was actually attributed to the largest amount of precipitation during those seasons.

3.3. Long-term trends

To test whether the decline in SO_2 and NO_2 emissions in Europe from 1991 has the anticipated effect on the acidic deposition at background sites in Lithuania, precipitation chemistry data were averaged for two periods: 1981–1990 and 1995–2004. In addition, such averaging of pollutant concentrations reduces the effect of intra- and inter-year variability of data that could be caused by meteorological variability, *e.g.*, precipitation amount, temperature. Table 2 presents VWM concentrations of major ions in precipitation and wet deposition in Preila and Rugsteliskes for those two periods. Data show that during the most recent 10 years the concentrations of $nssSO_4^{2-}$, NO_3^-, NH_4^+ and acidity have decreased by the factor of 1.5–3.5 as compared to the previous 1981–1990 period. However, a rather stable level in the annual VWM concentrations of species mentioned above has been observed at both sites during 1997–2004.

The temporal trends in the ion concentrations in precipitation and wet deposition for the 1981–2004 period were evaluated using the non-parametric Mann–Kendall test and the Sen's slope estimator.[15] The trend estimates that are statistically significant at the 95% confidence level are summarized in Table 3. The strongest statistically significant decreasing trend with a slope of 4.36 µeq l^{-1} yr^{-1} was obtained for non-sea salt sulfate concentration in precipitation. Such a decreasing rate

of concentration of $nssSO_4^{2-}$ yielded an overall reduction of 82% during 1981–2004. A total decline of 88% was calculated for wet deposition of sulfur. In fact, $nssSO_4^{2-}$ concentrations in precipitation were linearly related to the SO_2 regional concentrations measured in air in Lithuania. The data show an excellent coincidence of the reduction of $nssSO_4^{2-}$ concentration in precipitation with the value of 84% observed for the SO_2 concentration decrease in air in Lithuania.[9] The obtained data suggest that the marked reduction in the SO_2 emission in Europe has resulted in a sharp decrease in atmospheric load of sulfur across Lithuania. Nitrogen-containing components (NO_3^- and NH_4^+) also show a decrease in concentrations in precipitation but the trends are less significant than that of $nssSO_4^{2-}$. The rates of concentration decrease were 0.73 and 1.56 µeq l^{-1} yr^{-1} for NO_3^- and NH_4^+, respectively. Over the whole period, concentrations of nitrates decreased by 33% and those of ammonium by 47%. There was no significant time trend for the non-sea salt calcium concentration in precipitation. Substantial reduction (about 80%) is evident for H^+ concentration and deposition but with less significance than the $nssSO_4^{2-}$ decline.

3.4. The influence of air mass origin on wet deposition

In order to examine the potential importance of different source regions to the acidic deposition in Lithuania, daily precipitation chemistry data were split up into six groups according to the air mass origin. Table 4 contains the VWM concentrations of acid-related ions in rainwater with respect to air mass origin. The VWM $nssSO_4^{2-}$ concentrations in rainwater measured in air masses arriving from the southeast and southwest (47.8 and 41.5 µeq l^{-1}, respectively) were about 2.5 times higher than those measured during air flows over Scandinavia and the Baltic Sea (NW–N). A similar pattern
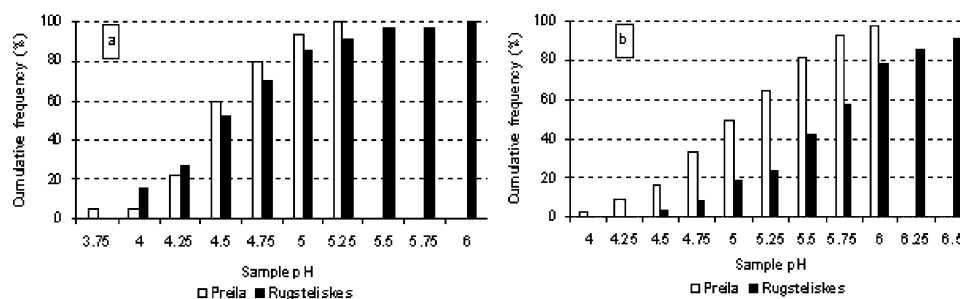

Fig. 4 Cumulative frequency distribution of the pH values in precipitation samples in Preila and Rugsteliskes for 1994–2004: (a) winter; (b) summer.

Table 2 Changes in VWM concentrations of ions in precipitation and annual wet deposition in Preila and Rugsteliskes during two periods: I (1981–1990) and II (1995–2004)

Site	Period	nssSO$_4^{2-}$–S	NO$_3^-$–N	NH$_4^+$–N	H$^+$	pH
VWM concentration/µeq l^{-1}						
Preila	I	116	49.3	72.2	53.3	4.27
	II	41.6	36.1	40.2	15.5	4.81
Rugsteliskes	I	126	38.6	82.8	23.5	4.60
	II	33.2	26.3	30.8	11.1	4.96
Wet deposition/mg m^{-2} yr^{-1}						
Preila	I	1299	513	751	39.6	
	II	315	240	240	7.4	
Rugsteliskes	I	1151	308	660	13.4	
	II	312	216	253	6.5	

is seen for NH$_4^+$. The highest NO$_3^-$ concentrations (54.2 µeq l^{-1}) were caused by the air mass transport over Estonia and Latvia as well as Central Europe (54.2 and 42.2 µeq l^{-1}, respectively). The most acidic rain was related to the north-eastern sector, followed by the south–southwestern sector, where the NO$_3^-$/nssSO$_4^{2-}$ ratio in equivalent concentration in rainwater was above 1.0. As can be seen from Table 4, there is a particularly notable difference in the precipitation amounts between sectors and this difference has a marked effect on the air mass contributions to wet deposition of acid-related species. Data indicate that the precipitation amount associated with the air flows in NE and E sectors was insignificant (8 mm yr^{-1}) for the site and, therefore, they did not make up more than 2% of the total annual deposition of non-sea salt sulfur and nitrogen. The maximum precipitation amount (253 mm yr^{-1}) was recorded when the air masses were

transported from the high emission region of SO$_2$ and NO$_x$ in Central and South Europe, in particular in Poland, Germany and the Czech Republic. Therefore, the annual wet deposition of both sulfur and nitrogen from the southwestern and western sectors was the highest and it accounted for about 68% of the annual wet deposition of pollutants. It seems quite obvious that most of the reduced annual wet deposition of sulfur and nitrogen in Lithuania during the 1981–2004 period is due to reduced emissions of those pollutants to the atmosphere in the western and southern European countries.

4.   Summary and conclusions

The regional difference in the concentration of major ions in precipitation was found in Lithuania and it was particularly apparent for those ions, whose source is predominantly the sea. Wet deposition of nssSO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ varied spatially in concert with the precipitation amount and the concentrations of ions, and showed a decrease (up to 20%) from the west to the east. During the most recent 10 years (1995–2004) the concentrations of nssSO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and acidity have decreased by the factor of 1.5–3.5 as compared to the previous period (1981–1990) despite the fact that volume-weighted annual concentrations of above mentioned species show a rather stable level in Preila and Rugsteliskes for the 1997–2004 period. The relative contribution of non-sea sulfates and nitrates to acidity of precipitation has recently changed, and currently, the increasing contribution of nitrates to the acidity of precipitation is anticipated. The trend analysis of wet atmospheric deposition at the background site in Lithuania during 1981–2004 has revealed a statistically

Table 3 The trend significance (***, $p = 0.001$; **, $p = 0.01$; *, $p = 0.01$; +, $p = 0.1$ and blank cell $p > 0.1$), Sen's slope estimate (est.) with its 95% confidence interval (min., max.) and total reduction of ion concentrations in precipitation and wet deposition in Preila for 1981–2004

	Precipitation					Wet deposition				
		Sen's slope/µeq l^{-1} yr^{-1}					Sen's slope/mg m^{-2} yr^{-1}			
Ion	Trend	Est.	Min.	Max.	Reduction per period (%)	Trend	Est.	Min.	Max.	Reduction per period (%)
nssSO$_4^{2-}$–S	***	−4.36	−5.58	−2.76	82	***	−62.6	−78.8	−48.6	88
NO$_3^-$–N	*	−0.73	−1.28	−0.17	33	**	−16.3	−22.8	−10.1	50
NH$_4^+$–N	+	−1.56	−3.23	0.03	47	*	−31.1	−41.6	−18.9	67
nssCa^{2+}		−0.26	−1.09	0.58	17	**	−13.1	−19.6	−5.1	31
H$^+$	*	−1.92	−3.43	−0.74	79	**	−1.6	−2.5	−1.0	74

Table 4 Annual VWM concentration of ions and annual wet deposition for five air mass sectors in Preila for 2001–2004

Ion	NE	E	SE	S–SW–W	NW–N	Undefined
Volume–weighted mean concentration/µeq l^{-1}						
nssSO$_4^{2-}$–S	31.1	39.6	47.8	41.5	17.5	32.4
NO$_3^-$–N	54.2	37.2	24.0	42.2	26.8	31.3
NH$_4^+$–N	33.6	42.6	45.2	37.3	17.5	24.1
Cl$^-$	81.4	9.6	20.0	79.1	204	93.8
H$^+$	23.2	13.4	6.0	20.1	15.3	14.8
Wet deposition/mg m^{-2} yr^{-1}						
nssSO$_4^{2-}$–S	2.1	2.6	24.8	168	31.7	60.7
NO$_3^-$–N	3.3	2.1	10.9	149	42.5	51.3
NH$_4^+$–N	2.0	2.4	20.5	132	27.8	39.6
Cl$^-$	12.5	1.4	23.1	711	821	390
H$^+$	0.1	0.1	0.2	5.1	1.7	1.7
Precipitation/mm yr^{-1}	4	4	32	253	113	117

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significant sharp decrease in non-sea sulfate concentrations and wet deposition. The concentrations and wet deposition of NO_3^- and NH_4^+ also showed the downward trends, however, they were not well statistically defined. Data based on backward trajectory calculations clearly show that wet deposition of sulfur and nitrogen in Lithuania is to a large extent anthropogenic and a consequence of long-distance transport. The main contributors (up to 68%) to the annual wet deposition of acidifying components are pollutants from the emission sources in South and Central Europe. The low contribution ($<15\%$) of non-sea salt sulfur and nitrogen to the annual wet deposition with the precipitation associated with northerly and easterly air masses may be mostly related to the negligible quantity of precipitation. The observed data suggest that the regulations restricting emissions of SO_2 and NO_x in Europe have resulted in the evident decrease in the atmospheric load of sulfur as well as nitrogen in Lithuania.

Acknowledgements

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