

# EMEP ASSESSMENT REPORT – LITHUANIA

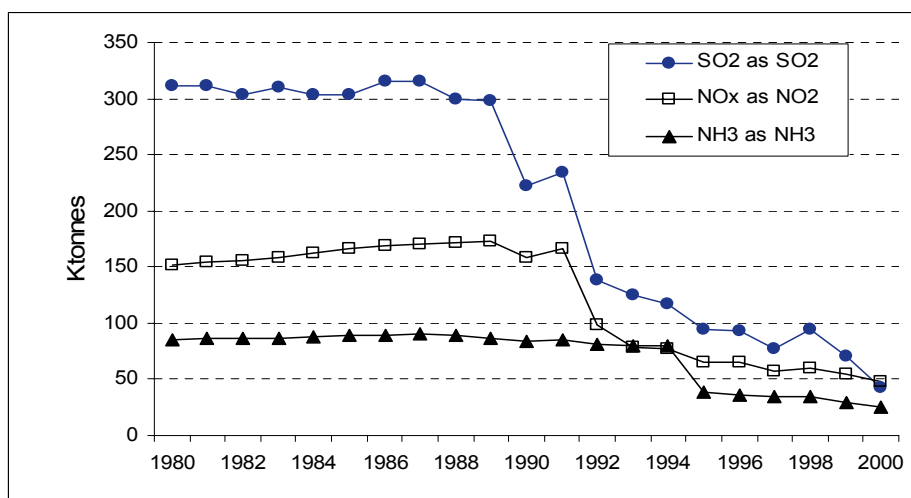
*Dalia Sopauskiene and Dalia Jasineviciene  
Institute of Physics  
Savanoriu pr.231, LT-2053 Vilnius, Lithuania*

## 1. Emissions

SO<sub>2</sub> emission after its sharp reduction in 1992 was steadily declining during the second half of the 1990s (Fig. 1). From 1980 to 2000 the total SO<sub>2</sub> emission decreased by 86 % (Table 1).

The largest reduction of NO<sub>x</sub> emission also occurred in 1992, but it remained almost at the same level during 1993-2000. The total NO<sub>x</sub> emission decreased by 69 % over 1980-2000 (Table 1).

The emission of NH<sub>3</sub>, which is predominantly of agricultural origin, had an evident fall from 80 to 40 ktonnes in 1995 and it remained stable till the end of the 1990s. From 1980 to 2000 the emission of NH<sub>3</sub> decreased by 70 %.



*Figure 1. Officially reported annual emissions of SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> in Lithuania*

*Table 1. The Lithuanian emissions in 1980 and 2000 and targets according to UNECE-CLRTAP protocols.*

Pollutants	Emission, ktonnes per year		Reduction %	Target, 2010 ktonnes
	1980	2000		
SO <sub>2</sub>	311	43.1	86	145
NO <sub>x</sub>	152	47.5	69	110
NH <sub>3</sub>	85	25.2	70	84

## 2. General information

In order to assess the background air pollution level a continuous monitoring of regional air pollution as well as the chemical composition of atmospheric precipitation at the background station in Preila in Lithuania has been carried out by the Institute of Physics since 1981. The station Preila (55°22' N and 21°02' E, 5 m a.s.l.) is located in western Lithuania on a coast of the Baltic Sea, on the Curonian Spit. It is a narrow sandy strip that separates the Baltic Sea and the Curonian Bay (Fig. 2).



The width of the spit varies from 0.4 to 4 km and its width is 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 surface of the spit, except the sandy dunes, is covered with forests, mainly conifers, dwarf pine trees of artificial plantation and shrubs. Marine climate is specific to this terrain.

*Figure 2. Location of station Preila*

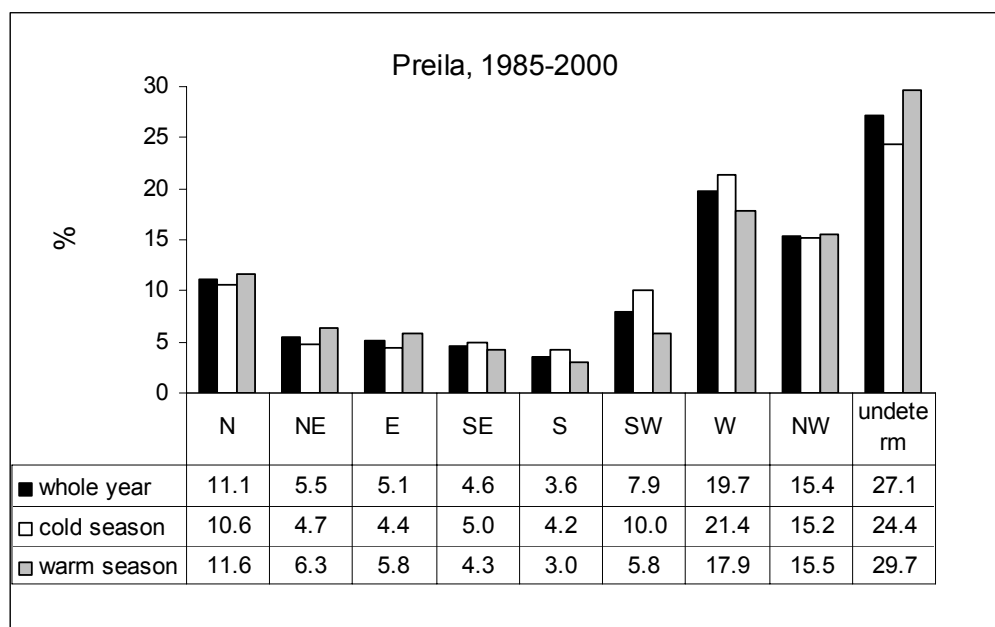
This monitoring site was selected according to strict sitting criteria designed to avoid undue influence from point sources, area sources and local activities. There are no great sources of anthropogenic pollution of the atmosphere close to the monitoring site. One of the nearest industrial cities, Klaipeda, is at a distance of about 40 km to the north and the other, Kaliningrad (Russia), is 90 km to the south from the site.

The methods of sampling and analysis of pollutants in air and precipitation have been changed over the course of monitoring in order to improve the data quality. The measurement programme and methods of sampling are summarized in Table 2. At the beginning, chemical components in the extracts from the filters as well from the diffusion tubes and in the precipitation samples were analysed using the spectrophotometric methods. Since 1996, the ion chromatography method has been used for anions. More detailed information concerning sampling and analytical methods is presented in (Sopauskiene et al., 2001). Air and precipitation data have been checked against EMEP database.

Nine sectors based on 96 h backwards trajectories for the Preila site provided by the EMEP/MSC-W (EMEP, 2003) were used to evaluate the effect of the sources of air pollutants located anywhere in Europe on the background air quality in Lithuania. Data presented in Fig. 3 show that western and northwestern sectors are prevailing for the monitoring site, whereas the south-southeasterly air flows exhibit the lowest percentage of recurrence. The obtained data are comparable to those reported for Preila for the period 1980-1999 (Sopauskiene and Budvytyte, 1994; Sopauskiene et al., 2001). Therefore, the air flows over the major source regions in the European continent, i.e. west to northwest, can be considered as a peculiar feature of the transport of air pollutants for the Lithuanian territory.

*Table 2. Measurement programme and techniques for sampling of gases, aerosols and precipitation in Preila.*

Medium	Components	Sampling time and frequency	Sampling techniques
<b>Gases</b>	SO <sub>2</sub>	24 hours, daily	Diffusion tube coated with NaHCO <sub>3</sub> , Since 1994 – KOH impregnated Whatman 40 Absorbing solution KI, Since 1999 – NaI – impregnated glass sinters
	NO <sub>2</sub>	24 hours, daily	
<b>Gases+aerosols</b>	HNO <sub>3</sub> +NO <sub>3</sub>	24 hours, daily	Since 1996 – KOH impregnated Whatman 40 Since 1996 – Oxalic acid impregnated Whatman 40
	NH <sub>3</sub> +NH <sub>4</sub>	24 hours, daily	
<b>Aerosols</b>	SO <sub>4</sub> , NO <sub>3</sub> , NH <sub>4</sub>	24 hours, daily	Petrianov filter AFA-XP-20, Since 1996 – Whatman 40
<b>Precipitation</b>	pH, conductivity, SO <sub>4</sub> , NO <sub>3</sub> , Cl, NH <sub>4</sub> , Na, K, Ca	Since 1981 – weekly, Since 1996 – weekly, Since 1999 – daily	bulk  wet only  wet only



*Figure 3. Percentage of annual recurrence of air mass sectors in Preila during 1985-2000.*

The nonparametric Mann-Kendall method (Salmi et.al., 2002) was used to test the trends using the annual means of pollutants.

### 3. Time series concentrations and trends of atmospheric pollutants

#### *Sulphur dioxide and particulate sulphate.*

A large variation in the monthly mean concentrations of sulphur dioxide and particulate sulphate (Fig.4 and 5) shows that there were clear differences in factors governing the background pollution level in the region through the period from which the data were compiled. In general, concentrations of SO<sub>2</sub> have undergone a considerable change since 1989 with a significant decrease of concentrations measured during the cold seasons and an increase during summertime. After 1995, a strong decrease in SO<sub>2</sub> daily and annual mean values was observed.

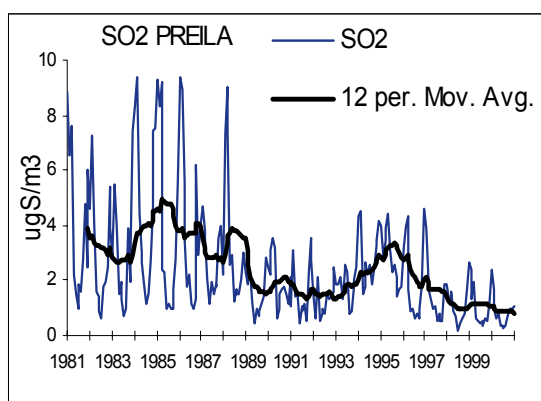


Figure 3. Monthly means of SO<sub>2</sub>

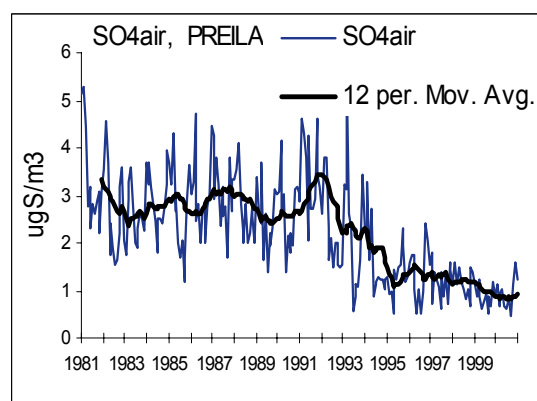


Figure 4. Monthly means of SO<sub>4</sub>

An obvious decrease in particulate sulphate concentration is seen from 1992 with the fluctuation of monthly mean concentrations generally from 0.5 to 1.5  $\mu\text{gSm}^{-3}$ . The annual means of SO<sub>2</sub> varied from 2.7 to 4.6  $\mu\text{gSm}^{-3}$  in the 1980s and decreased to values below 2.0  $\mu\text{gSm}^{-3}$  after 1990 (with the exception of 1995-1996). The annual mean of particulate sulphate concentration decreased from 3.3  $\mu\text{gSm}^{-3}$  in 1981 to below 1.0  $\mu\text{gSm}^{-3}$  in 1999-2000.

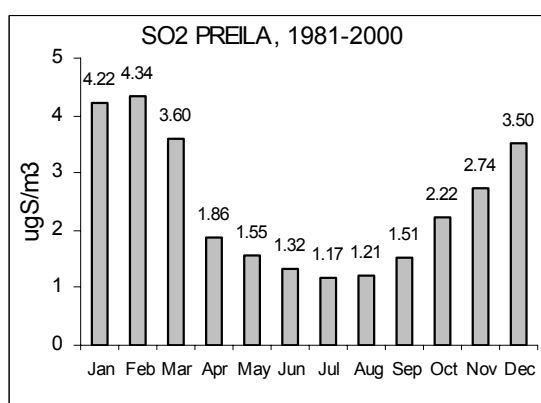


Figure 6. Annual cycle for SO<sub>2</sub>

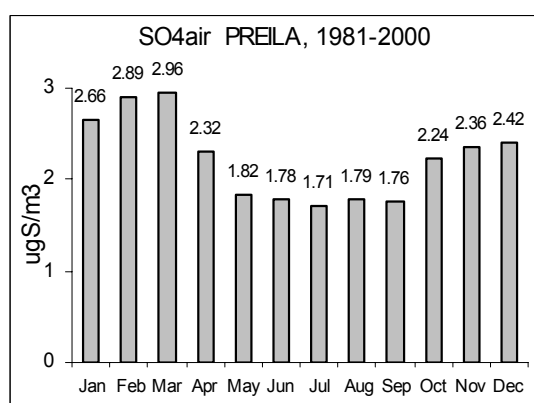


Figure 7. Annual cycle for SO<sub>4</sub>

Data of both sulphur components indicate very clear seasonality (Fig.6 and 7) with higher concentrations during the cold period (January – March and October – December)

and lower ones during the warm period (April – September). The concentrations ratio of the cold period to warm period is obtained 2.4 for SO<sub>2</sub> and 1.4 for particulate sulphate. The higher concentrations during cold period could be explained by the increase in SO<sub>2</sub> emission and by the difference in the meteorological factors, in particular, by a decrease in atmospheric vertical turbulence intensity and increase of inversion events in the region. As for particulate sulphate, a weaker seasonality, in addition to the factors before-mentioned, is likely to be associated with the most rapid conversion from SO<sub>2</sub> to particulate sulphate in summer. Data suggest that the courses of monthly means as well as annual mean of sulphur components concentrations in air are mostly influenced by SO<sub>2</sub> emission in central and west European countries. Fig.7 presents variation in SO<sub>2</sub> and particulate SO<sub>4</sub> concentrations averaged for the eight air mass sectors.

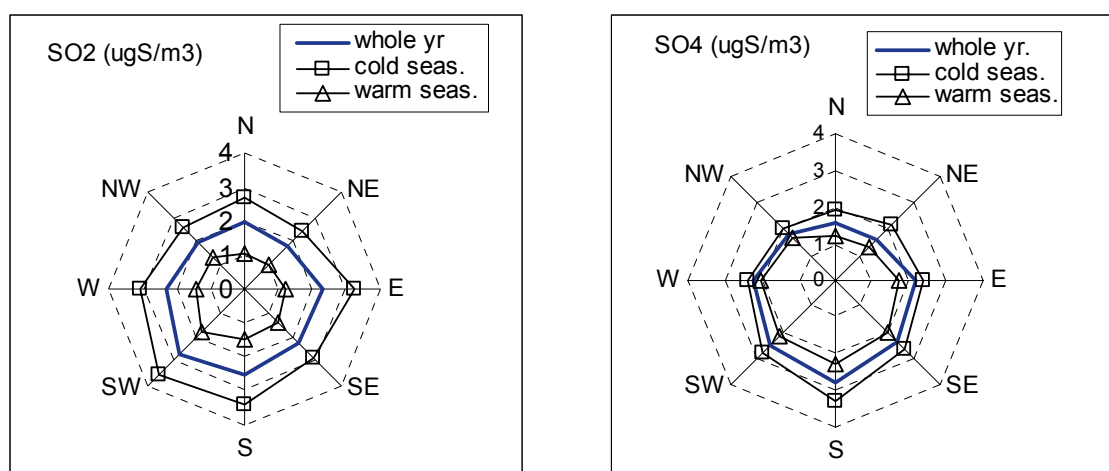


Figure 8. Mean concentrations of sulfur components in 8 sectors in Preila, 1985-2000.

The highest concentrations of both sulphur components were observed when air transport was from the south and southwest, i.e. when the air mass had passed over Central Europe (namely Poland, Czech Republic and partially Germany) before moving in over Lithuania. The lowest levels of SO<sub>2</sub> and particulate sulphate were observed during northerly flows when the air passed over Scandinavia and the Baltic Sea prior to arrival in Preila. The intermediate concentrations of both sulphur components were registered during the northeasterly and easterly air flows reflecting the local emission sources as well the sources in Latvia, Estonia and partially Belarus. Based on the data of the recurrence of air mass from various sectors (Fig.3) and on the averaged concentrations of sulphur components in the corresponding sector, the largest load (almost 21 %) of sulphur components was estimated for the western sector and it increased up to 40 % summing up the inputs of SO<sub>2</sub> from the southern and southwestern sectors.

The Excel template MAKESENS (EMEP, 2003) was applied to the annual means of SO<sub>2</sub> and particulate sulphate for the period 1981-2000 to evaluate the change in concentrations as well as significance levels of the changes. Statistically significant downward trends for SO<sub>2</sub> were calculated for the whole year as well for the cold season, while the downward trend with a less significance level was obtained for the warm period (Table 3). The decrease in particulate sulphate is statistically significant for the whole year as well as for the cold and warm seasons. The trend analyses have also been performed using the annual averages of sulphur components in air mass having different origin for the time period 1985-2000. Statistically significant decreasing trends for SO<sub>2</sub> with Sen's

slope ranging from  $-0.20$  to  $-0.27 \mu\text{gSm}^{-3}\text{year}^{-1}$  were obtained in air mass from northern, northwestern and western sectors, i.e. from western and northern Europe.

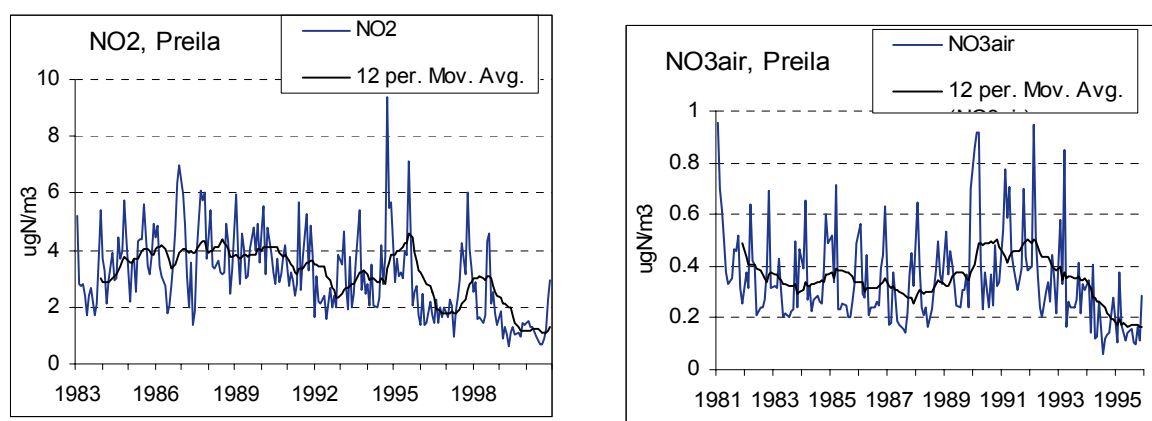
*Table 3. Trend analysis results for sulphur dioxide and particulate sulphate.*

Pollutants	Period	Trend sign.	Sen's slope, $\mu\text{gSm}^{-3}\text{yr}^{-1}$			Total change per period, %
			est.	min 95	max 95	
<b>SO<sub>2</sub></b>	<b>1981-2000</b>					
	Whole year	***	-0.15	-0.22	-0.09	-79
	Cold season	***	-0.26	-0.35	-0.14	-86
	Warm season	*	-0.06	-0.10	-0.01	-65
<b>Particulate SO<sub>4</sub></b>	<b>1981-2000</b>					
	Whole year	***	-0.12	-0.16	-0.09	-75
	Cold season	***	-0.14	-0.18	-0.09	-75
	Warm season	***	-0.10	-0.13	-0.06	-76

\*\*\*=0.001 level of significance, \*\*=0.01 level of significance, \*=0.05 level of significance, blank cell > 0.1 level of significance.

#### *Nitrogen dioxide, particulate nitrate and total nitrates.*

Time series of monthly mean concentrations (Fig.9) fluctuated in the interval from 2 to  $6 \mu\text{gNm}^{-3}$  and from 0.2 to  $0.9 \mu\text{gNm}^{-3}$  for  $\text{NO}_2$  and particulate nitrate, respectively.



*Figure 9. Monthly means of nitrogen dioxide and particulate nitrate in air.*

The annual means of  $\text{NO}_2$  showed a relatively stable period with values between  $3.0 - 4.0 \mu\text{gNm}^{-3}$  in 1983-1995 and then a decrease up to  $1.3 \mu\text{gNm}^{-3}$  beginning with 1996. The annual means of particulate nitrate varied from  $0.3$  to  $0.5 \mu\text{gNm}^{-3}$  in 1983-1992 and they decreased up to  $0.2 \mu\text{gNm}^{-3}$  in 1995. The seasonal variation with lower concentrations in spring and summer, like for sulphur components, is obtained for  $\text{NO}_2$  (Fig.10). Nitrogen dioxide concentrations for different sectors (Fig.11) averaged for the period 1985-2000 showed the highest values of  $\text{NO}_2$  in air mass from southwestern and western sectors, i.e. when air mass passed over the highly industrialized countries in

Western Europe. The largest contribution (23%) to the mean NO<sub>2</sub> concentration was estimated from western sector, i.e. from Germany, Denmark and UK.

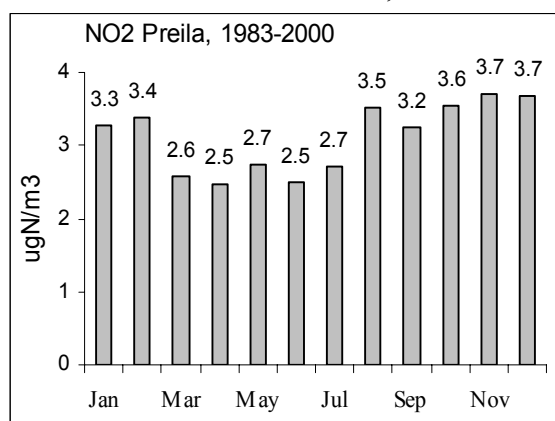


Figure 10. Annual cycle for NO<sub>2</sub>

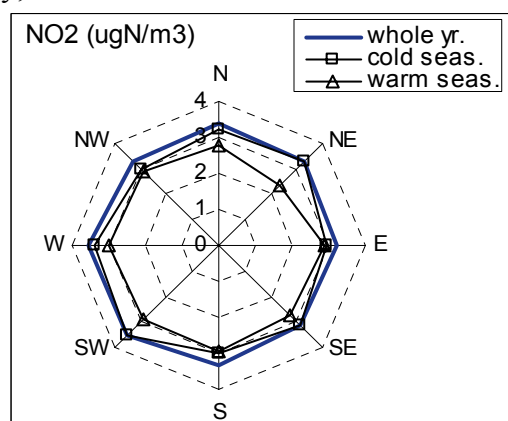


Figure 11. Mean concentrations of NO<sub>2</sub> in 8 sectors in Preila, 1985-2000

Trend analysis data (Table 4) indicate the significant decreasing trends for NO<sub>2</sub> both for the whole year and cold season. The Mann-Kendall test also gives a decreasing trend for particulate nitrate, but with the significance level >0.1.

Table 4. Trend analysis results for nitrogen dioxide and particulate nitrate.

Pollutants	Period	Trend sign.	Sen's slope, $\mu\text{gNm}^{-3}\text{yr}^{-1}$			Total change per period, %
			est.	min 95	max 95	
<b>NO<sub>2</sub></b>	<b>1983-2000</b>					
	Whole year	**	-0.11	-0.19	-0.05	- 46
	Cold season	**	-0.16	-0.24	-0.08	- 61
	Warm season	*	-0.11	-0.17	-0.01	- 49
<b>Particulate NO<sub>3</sub></b>	<b>1981-1995</b>					
	Whole year		-0.004	-0.023	0.006	- 17
	Cold season		-0.005	-0.026	0.005	- 47
	Warm season		-0.008	-0.017	0.006	- 32

\*\*\* = 0.001 level of significance, \*\* = 0.01 level of significance, \* = 0.05 level of significance, blank cell > 0.1 level of significance.

Total nitrate measurement was started in 1996, and the time series of monthly averages are presented in Fig.12. Although total nitrate has comparatively short period of monitoring, its concentration shows the tendency to decrease. From 1996 to 2000, the annual mean of totNO<sub>3</sub> declined from 1.12 to 0.62  $\mu\text{gNm}^{-3}$ . This component in air also shows the seasonal cycle with the lower concentration (0.67  $\mu\text{gNm}^{-3}$ ) during the warm period and with maximum (1.02  $\mu\text{gNm}^{-3}$ ) in winter.

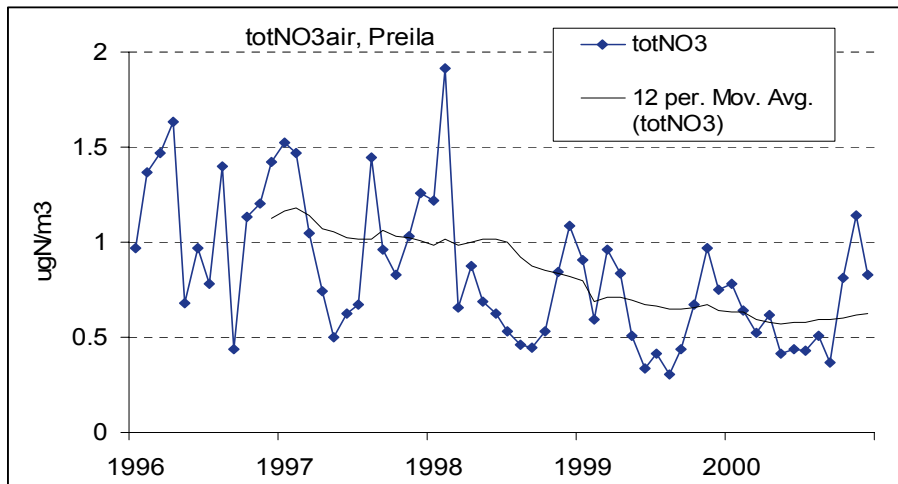


Figure 12. Monthly means of total nitrate in air

#### Particulate ammonium and total ammonium

Wide amplitude (from 0.4 to 3.7  $\mu\text{gNm}^{-3}$ ) of variation of monthly means is obtained (Fig.13) for particulate ammonium in air. Despite the fact that different tendencies of change in its concentrations can be seen over the period, the annual means of particulate ammonium indicate a decreasing trend with the slope  $0.077 \mu\text{gNm}^{-3}\text{year}^{-1}$  at the 0.001 significance level. Particulate ammonium concentrations show seasonality with a similar pattern as for particulate sulphate and nitrate.

Time series of total ammonium indicate a decreasing trend during the period 1996-2000. Annual concentration declined from 3.1  $\mu\text{gNm}^{-3}$  in 1996 to 1.7  $\mu\text{gNm}^{-3}$  in 2000. Based on the data from air mass sector analysis, the highest concentrations of total ammonium as well as particulate ammonium (3.2 and 2.1  $\mu\text{gNm}^{-3}$ , respectively) were measured during southerly air flows and the lowest ones (0.9 and 0.8  $\mu\text{gNm}^{-3}$ , respectively) during northerly air flows.

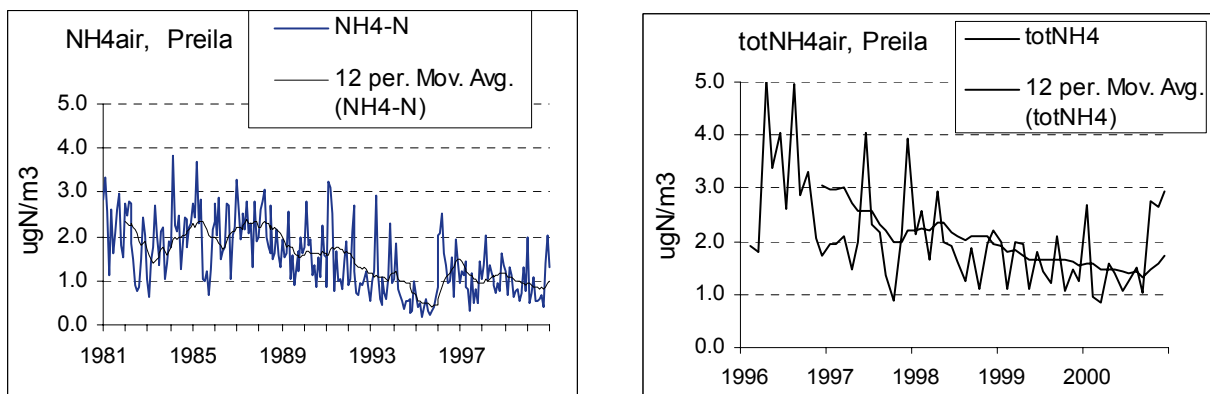
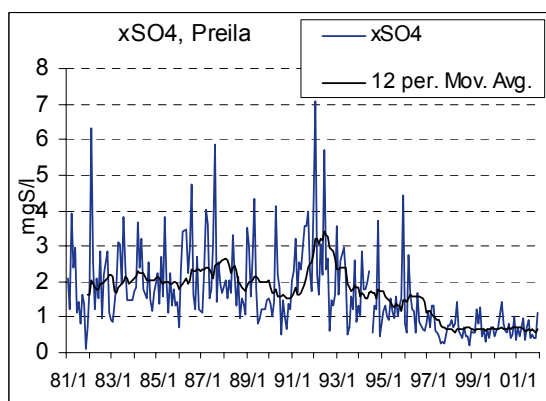


Figure 13. Monthly means of particulate ammonium and total ammonium in air.

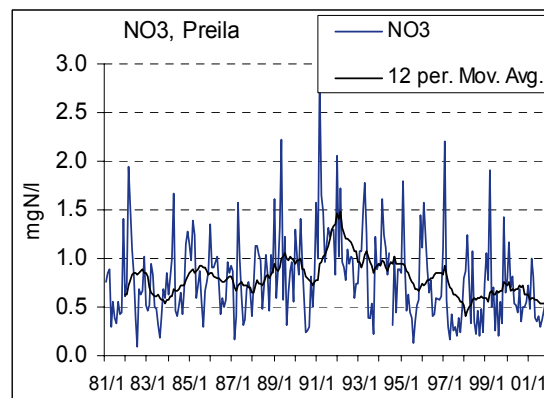


#### 4. Wet deposition.

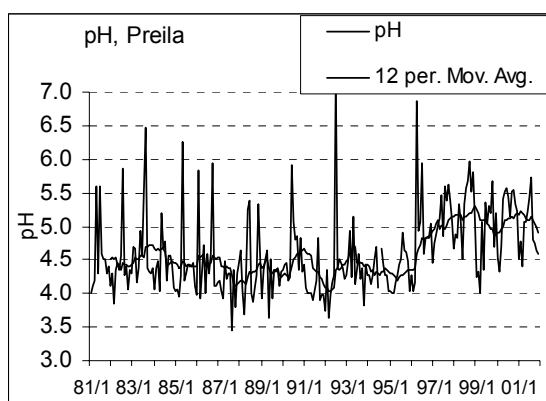
Time series of v/w monthly means for the major ions in precipitation in Preila for the period 1981-2001 are presented in Fig.14, 15, 16 and 17.



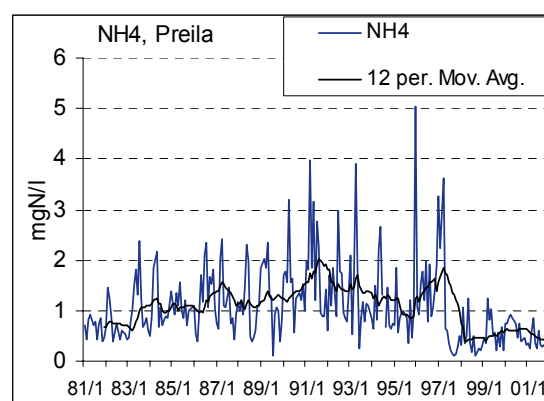
*Figure 14. Monthly means of sulphate*



*Figure 15. Monthly means of nitrate*



*Figure 16. Monthly means of pH*



*Figure 17. Monthly means of ammonium*

Despite a large variation in concentrations of all components from month to month which in the most cases reflects the changes of meteorological factors (such as precipitation amount, air flows sector, components concentration in air), data indicate a tendency of a decrease in sulphate and ammonium ions concentrations and an increase in the pH value. Annual mean of sulphate ion concentration was of the order of 2.0 – 3.0 mgS/l during the 1980s, but after 1992 it showed a sharp decrease and dropped below 1.0 mgS/l at the end of the 1990s. Annual concentration of nitrate ions has gradually decreased to the value 0.5 mgN/l since 1995. Different tendencies of change can be seen for annual ammonium concentration during 1981-1997, but an obvious decrease in ammonium concentrations started in 1997. The annual pH value ranged from 4.0 to 4.5 up to 1997 and it steadied at a value of about 5.0 at the end of the 1990s.

Fig.18 presenting the data of annual wet deposition of sulphur and nitrogen components clearly shows the decreasing trends. A distinct decline of sulphur wet deposition from about 1500 to 350 mgSm<sup>-2</sup> over the period under review is calculated. During the 1990s, a decrease of annual wet deposition of both nitrogen components was also observed.

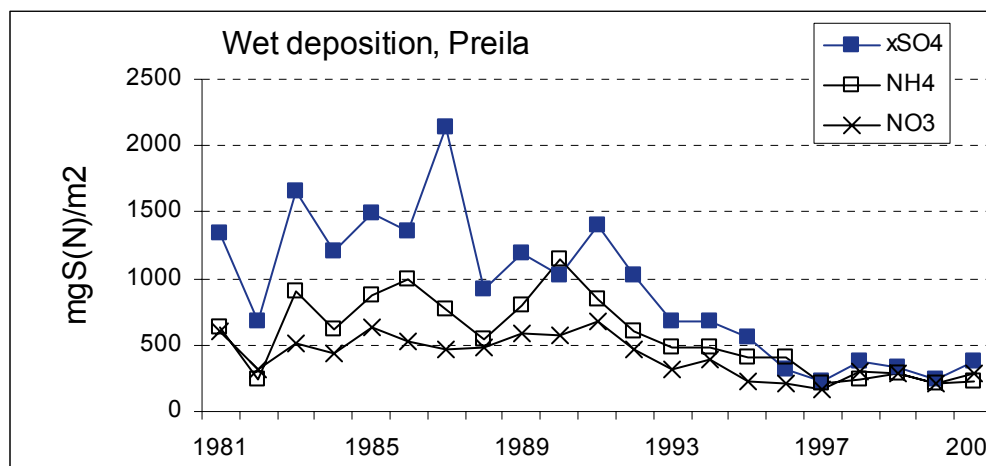


Figure 18 Annual wet deposition of sulphate, nitrate and ammonium.

The trend analysis for the annual concentrations and wet depositions of the major components has been performed using Excel template MAKESENS and the obtained data are presented in Table 5.

*Table 5. Trend analysis results for sulphate, nitrate, ammonium, calcium and acidity in precipitation, 1981-2001.*

	Pollutants	Trend sign.	Sen's slope, $\text{mg l}^{-1}\text{yr}^{-1}$			Total change, %
			est.	min 95	max 95	
Concentration	xSO <sub>4</sub> -S	**	-0.07	-0.10	-0.04	-71
	NO <sub>3</sub> -N		-0.01	-0.02	0.00	-27
	NH <sub>4</sub> -N		-0.01	-0.05	0.01	-27
	xCa		0.00	-0.02	0.02	0.7
	Pollutants	Trend sign.	Sen's slope, $\text{mg m}^{-2}\text{yr}^{-1}$			Total change, %
			est.	min 95	max 95	
Deposition	xSO <sub>4</sub> -S	***	-70.5	-89.5	-52.4	-93
	NO <sub>3</sub> -N	**	-17.9	-26.8	-8.4	-62
	NH <sub>4</sub> -N	***	-36.7	-48.2	-17.3	-81

\*\*\* = 0.001 level of significance, \*\* = 0.01 level of significance, \* = 0.05 level of significance, blank cell > 0.1 level of significance.

The statistically significant negative trends for the whole period are calculated both for concentration and deposition of sulphate. The Mann-Kendal test shows the decreasing trends for concentrations of both nitrogen components, but the slopes are obtained with a low significance level, i.e. greater than 0.1. Annual concentrations of calcium in precipitation did not indicate any change during the period 1981-2001.

The results of trend analysis showed that a significance level for the decreasing trends both for SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> wet deposition is greater than that for NO<sub>3</sub><sup>-</sup> wet deposition.

## 5. Conclusions

- In Lithuania, sulphur dioxide emissions have been markedly reduced. A total SO<sub>2</sub> emission was reduced by 87 % between 1980 and 2000.
- The largest reduction of NO<sub>x</sub> emissions occurred in 1992 and it remained almost at the same level till the end of the 1990s. From 1980 to 2000, NO<sub>x</sub> emissions declined by 68 %.
- Emission of ammonia in Lithuania dropped by 55 % between 1980-1995 and it remained relatively stable till the end of the 1990s.
- A remarkable reduction in sulphur components both in air and precipitation was detected in the period 1981-2000.
- Both sulphur components in air show high seasonality.
- Statistically significant decreasing trends for SO<sub>2</sub> have been obtained in air mass from northern, northwestern and western sectors, i.e. from West and North Europe.
- Decreasing trends for NO<sub>2</sub> have been observed both for the whole year and cold period. The Mann-Kendall test also gives a decreasing trend for particulate nitrate, but with a low level of significance.
- Western and northwestern sectors are prevailing for the monitoring site, whereas the southerly and southeasterly air flows exhibit the lowest percentage of recurrence.
- The largest contribution (almost 21 %) to the mean concentration of SO<sub>2</sub> was estimated for the western sector and it increased to 40 % summing up the inputs of SO<sub>2</sub> from the southern and southwestern sectors.
- The pH value increased from 4.0 to 5.0 in the period under review.
- The statistically significant negative trends for the 1981-2001 are estimated both for the concentration and deposition of sulphates. The decreasing trends for concentrations of both nitrogen components are obtained with a low significance level, i.e. greater than 0.1. Annual concentration of calcium in precipitation did not indicate any change during the period 1981-2001.

## 6. References

1. EMEP, 2003. <http://emep.int>. Pages for Assessment Report.
2. Salmi T., Määttä A., Anttila P., Ruoho-Airola T., Amnell T., 2002. Detecting trends of annual values of atmospheric pollutants by the Mann-Kendall test and Sen's slope estimates –the Excel template application MAKESENS. Finnish Meteorological Institute. Publications on Air Quality, No. 31.
3. Sopauskiene D. and Budvytyte D., 1994. Chemical characteristics of atmospheric aerosol in rural site of Lithuania. Atmospheric Environment vol. 28, No. 7, pp.1291-1296.
4. Sopauskiene D., Jasineviciene D. and Stapcinskaite S., 2001. The effect of changes in European anthropogenic emissions on the concentrations of sulphur and nitrogen components in air and precipitation in Lithuania. Water, Air, and Soil Pollution 130, pp. 517-522

