



Assessment report on the Latvian EMEP data 1985–2000

Riga 2004-02-10

Latvian Hydrometeorological Agency

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1. Introduction

The aim of the present report is to scrutinise the air quality and deposition in Latvia during the period 1985-2000 based on data series available under the EMEP programme and to evaluate the progress of international activities in abatement of pollution emissions under the Convention on Long-range Transboundary Air Pollution.

The present report employs the emission data provided by the Latvian Environment Agency. The ambient air and precipitation quality data have been obtained from the EMEP stations maintained by the Latvian Hydrometeorological Agency, Rucava (LV10) for 1985-2000 and Zoseni (LV16) for 1994-2000.

The Republic of Latvia has ratified the 1979 Geneva Convention on Long-range Transboundary Air Pollution by Resolution 63 of 7 July 1994 of the Cabinet of Ministers of Latvia. Later on, the following protocols to the Convention have been signed:

- the 1998 Protocol on Heavy Metals;
- the 1998 Protocol on Persistent Organic Pollutants (POPs);
- the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone.

As follow-up to the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, the Cabinet of Ministers of Latvia passed on 09.09.2003 Regulation N507 on national total maximum permitted emission into ambient air. On 16 January 1997, the Cabinet of Ministers issued Resolution 13 on adhesion of Latvia to the 1984 Protocol on Long-term Financing of Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP).

2. Monitoring stations

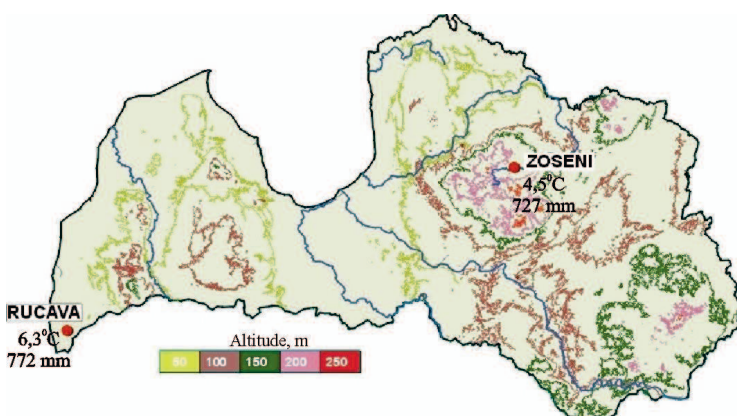


Figure 1 EMEP stations in Latvia

The observations under the EMEP programme started at Rucava station (LV10) in 1985 followed by the station Zoseni (LV16) in 1994.

The stations have provided for the assessment of ambient air and precipitation quality at sites under different physico-geographical conditions (Fig. 1).

The Rucava station is located in the south-western part of Latvia, some 10 km east from the Baltic Sea and 50 km south from the town of Liepaja with a

population of 95000. The Zoseni station is situated in the north-eastern part, some 30 km southeast from the town of Cesis with 20000 inhabitants.

The GAW programme works have been performed at the same stations. For the assessment of the impacts of transboundary transmission of air pollutants on the ecosystem of Latvia the integrated monitoring polygons, Rucava (LV01) and Zoseni (LV02), and ICP –Waters stations are placed 15 km from the regional GAW/EMEP stations.

3. Emissions

Generally, the total emissions were decreasing from 1990 till 2000. Thus SO_x emissions decreased from 119 kt in 1990 to 18 kt in 2000 (85% reduction). The NO_x emissions fell from 92 to 37 kt (60% reduction), NH₃ emissions from 44 to 12 kt (73% reduction) and NMVOC emissions from 143 to 69 kt (52% reduction).

A steady decline in the emission of SO_x was caused by changing to the use of natural gas at heating installations, and reduction in the number of industries. A decline in the NO_x emission had been observed until 1996; since 1997, the emission has been stable. Emissions of NH₃ do not seem to have changed since 1994. The NMVOC emissions have increased slightly since 1994 (Fig. 2).

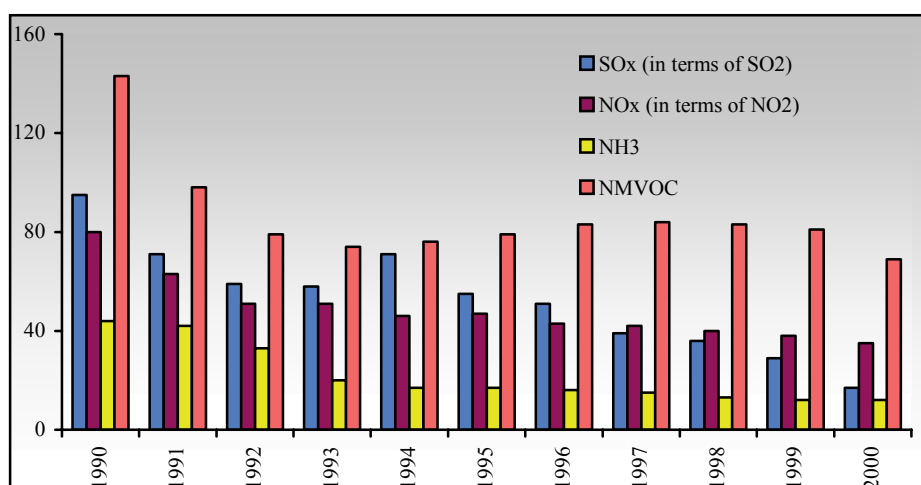


Figure 2. Dynamics of the total emission of pollutants (kt/yr) in Latvia

The Cabinet of Ministers' regulation N507 on national total maximum permitted emissions into ambient air of 09.09.2003 sets the following standards to be effective from 2010:

- 101 kt/yr for sulphur dioxide;
- 61 kt/yr for nitrogen dioxide;
- 44 kt/yr for ammonium;
- 136 kt/yr for NMVOC.

The emissions of the specified substances in 2000 are not in excess of the national total maximum permitted emissions into ambient air on 2010.

4. Sampling and analytical methods and air quality control

Sampling techniques

In 1985-1993 daily observations covered gases and aerosols at Rucava stations. From 1994 the observation programme also comprised the sum of gases and aerosols at Rucava. Daily observations have been performed at Zoseni since 1994. The heavy metal measurements with weekly exposure started at both stations in 1994.

The implemented air sampling technique implies passing of the pumped ambient air through filters or other sorbents. In 1993 the glass tube with the absorption solution for SO₂ was substituted by sampling on the filter.

Precipitation sampling at Rucava had been performed with daily exposure. Daily sampling at Zoseni commenced in 1996. Monthly exposure was used at both stations for heavy metal measurements over the period under assessment. Precipitation is collected with home-made bulk samplers and Wet-only samplers. Collection of samples at the station in Rucava has been made with a Wet-only sampler since July 1996.

The tropospheric ozone measurements have been performed at Rucava from 1994, with an UV-absorption ozone monitor (ozone analyser O₃41M, Environment S.A., France).

Analytical methods

Spectrophotometry is used for analysis of sulphur- and nitrogen-containing compounds, ion chromatography (since 1997) for nitrates and chlorides in precipitation, and for trace elements both atomic spectrophotometry in a graphite furnace and flame spectrophotometry.

During 1985-1992, samples from the Rucava station were analysed at the Latvian Hydrometeorological Agency's (LHMA) laboratory in Ventspils; 1993-1997 – at the LHMA's laboratory in Liepaja, and since 1998 - at the LHMA's central laboratory in Riga. The EMEP station at Zoseni started to operate in 1994; analyses of samples from the station have been performed at the LHMA's central laboratory in Riga.

Quality control

The above developments should be born in mind in assessing the homogeneity of the observation data series, as should be the "human" factor and the changes in the sampling equipment, analytical techniques, and transportation of samples.

Checking of data series and statistics is based mainly on a comparison of current and earlier measurement results and knowledge of the seasonal and temporal variations.

The EMEP Data Check programme for quality control of the EMEP data has been implemented in 1996, and the data checking procedure has been documented. The historical measurement data used in the present EMEP assessment have been evaluated, involving:

- checking of the digitised historical data against the data available on paper media; the erroneous values and measurement units were amended;
- the use of the updated system of data flags introduced in 1996-1997; wherever possible, the historical data were flagged;
- individual checking and evaluation of extreme values; if the extreme values were assumed to be due to contamination, the values were rejected. Such values were frequent among the heavy metal values.

The data sets with completeness above 50% were used for statistical calculations.

5. Air and precipitation concentrations and deposition

Sulphur dioxide and sulphate in air

The observations at the Rucava station show the statistically significant decrease ($\alpha=0.01$) of the mean concentration of sulphur dioxide in the cold period. The significance of the negative trend in the mean annual concentration is very poor, only 10 % (Fig. 3).

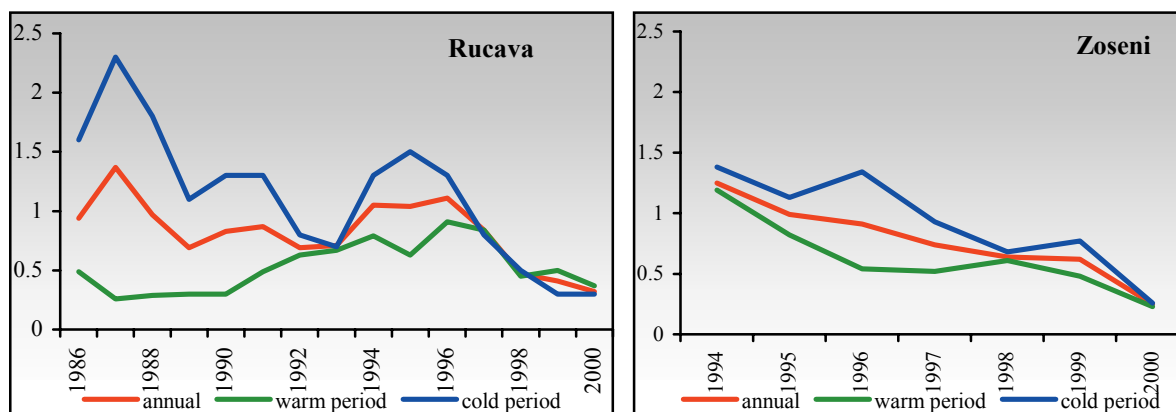


Figure 3. Mean annual and mean concentration of SO_2-S ($\mu g/m^3$) in the cold and warm periods of 1986-2000

The trend in the concentration of SO_2-S at Rucava was non-monotonous. During the years 1986-1993 and 1998-2000, annual mean concentrations were decreasing, while concentrations increased a bit in the years 1994-1997. This behaviour was a result of changes in analytical laboratory and the measurement technology but also the effect of the meteorological conditions in those periods.

The monotonous and statistically significant decrease ($\alpha<0.05$) in the annual mean concentration of sulphur dioxide was observed at both stations during the 1994-2000 observation period.

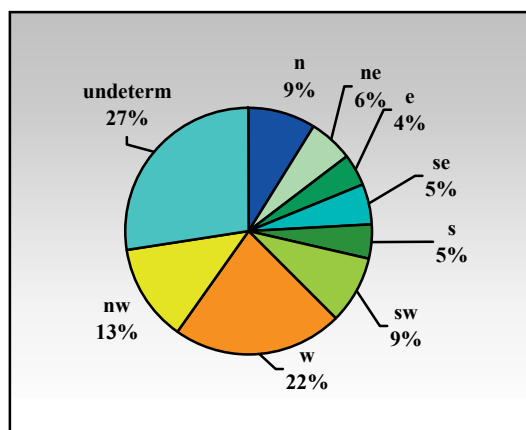


Figure 4. Air mass transport (in %) for the period 1985-2000

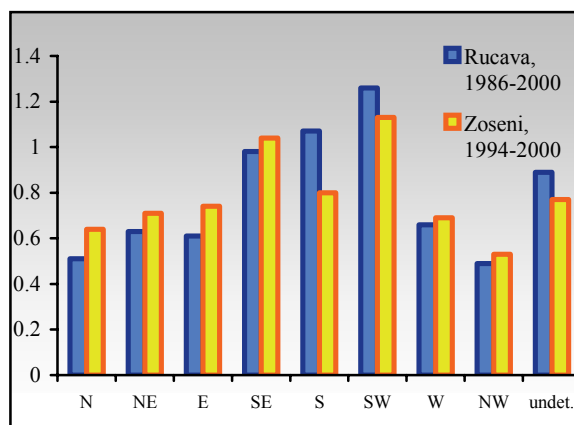


Figure 5. SO_2-S concentration of different origin, ($\mu g/m^3$)

An analysis of the trajectories of air mass transport over the Latvia's territory in 1986-2000 showed predominance of W, NW transport (35% of the wind direction events); the determination of wind directions was hampered in 27% of cases (Fig. 4).

The concentrations of SO₂-S at stations would be on average 2 times higher when the air trajectory originated from the S, SW directions (Fig. 5). The annual mean maximum of SO₂-S was 2.70 µg/m³ under such conditions (1988, Rucava), and the annual mean maximum concentration was 4.12 µg/m³ in the cold period (1994, Rucava). Higher concentrations were measured at stations in SE transport as well. The lowest concentrations occurred when the trajectory originated in N, NE and NW directions.

The results of the sectorial trend analysis of SO₂-S has shown the negative slope of the trend for SW, S, SE, NE, E directions of air transport at the both stations and the statistically significant for the SW and undetermined sectors at the Rucava station. Practically, no changes in the concentrations were observed for the N, W and NW sectors.

The trend analysis of the sulphate data series at Rucava has shown a statistically weak tendency of the ambient SO₄-S to decrease ($\alpha=0.1$) in the cold period. The trend was non-monotonous. An increasing tendency was observed at Rucava in 1986-1996 though it was not statistically confirmed. (Fig. 6).

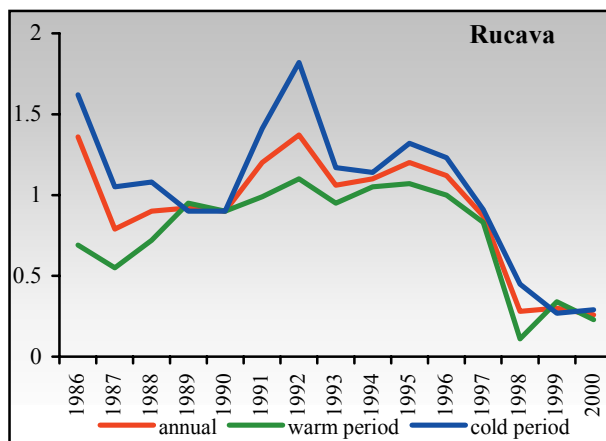


Figure 6. Annual mean and mean concentrations of SO₄-S (µg/m³) in the cold and warm periods of 1986-2000

The trend analysis has shown the statistically significant decrease ($\alpha < 0.05$) in the annual means of SO₄-S of 1994-2000 at both stations.

Like for SO₂-S, concentration of SO₄²⁻-S at both stations would increase 2 times on average in SW and S air mass transport. At Zoseni, the concentration is 2 times higher in SE and E transport as well.

The results of the sectorial trend analysis of SO₄-S have shown the negative slope of the trends for all directions of air transport, and statistically significant for the S, E, SE and undetermined sectors (Rucava).

Sulphate in precipitation

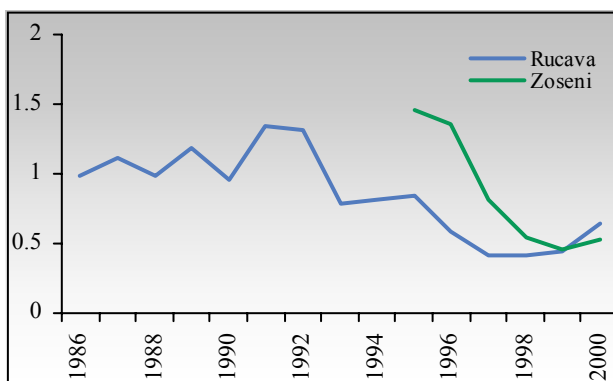


Figure 7. Annual mean concentrations of SO₄-S (µg/l) in precipitation

The statistically evident trends ($\alpha < 0.05$) in the annual mean sulphate concentrations shown in Fig. 7 were also observed in the concentrations corrected for the sea-salt effect.

Data at Rucava station show that sulphate from sea-salt particles on the average constituted between 2 and 8% of the total precipitation sulphate.

Nitrogen compounds in air and precipitation

The observations at the Rucava station show statistically significant decreases ($\alpha=0.001$) in the annual mean concentrations during 1986-2000. The statistically significant decrease in the $\text{NO}_2\text{-N}$ mean concentrations has been revealed for all directions of air mass transport (Fig. 8). The significance of the negative trend in annual mean concentrations at the Zoseni station was very poor, only 10 %.

As for directional dependence concentrations of $\text{NO}_2\text{-N}$ were observed to be higher by a factor of 1.5 at both stations when the air trajectories originated from the SW and S directions. Lower concentrations occurred when the trajectories originated in the N, NW, NE directions.

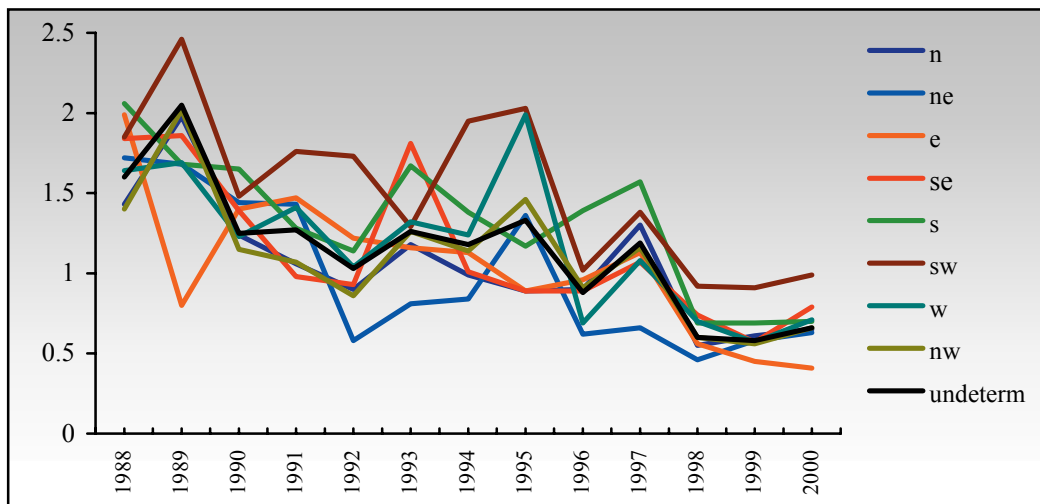


Figure 8. Trends in $\text{NO}_2\text{-N}$ ($\mu\text{g}/\text{m}^3$) at Rucava of different origin

SW and S air mass transport brought about higher concentrations of total $\text{NO}_3\text{-N}$ and total $\text{NH}_4\text{-N}$ at both stations. At Rucava, higher concentrations of total $\text{NO}_3\text{-N}$ were observed in W transport as well. Higher concentrations of these substances would be recorded at Rucava, in the various air transport trajectories (Fig. 9).

A significant decrease ($\alpha=0.05$) in the annual mean concentrations of total $\text{NH}_4\text{-N}$ can be noted in the SE directions at Rucava.

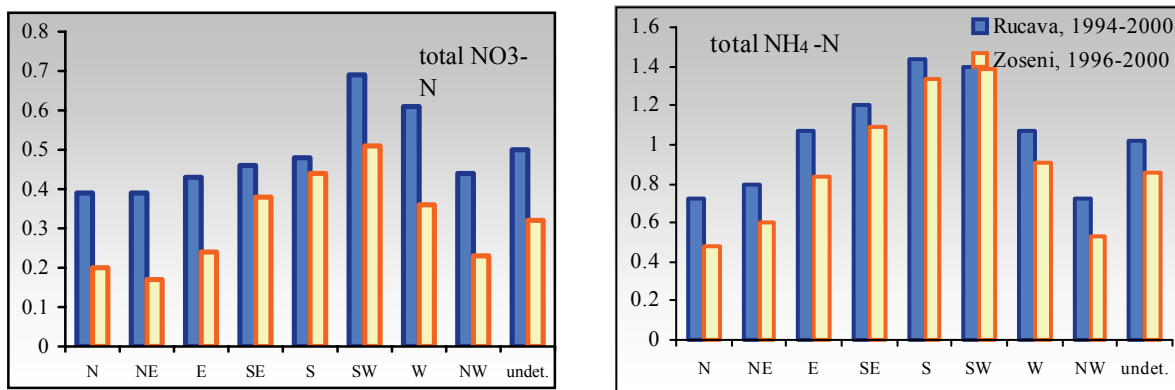


Figure 9. Concentration of total $\text{NO}_3\text{-N}$ and total $\text{NH}_4\text{-N}$ ($\mu\text{g}/\text{m}^3$) of different origin

The trend analysis of the $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ data series in precipitation has in general revealed a slightly expressed decreasing tendency ($\alpha=0.1$) in the annual mean concentrations of nitrate (Fig.

10). The decrease is more obvious in the cold period ($\alpha=0.01$). No statistically significant reduction in the annual mean concentrations of ammonium has been ascertained for both stations (Fig. 11).

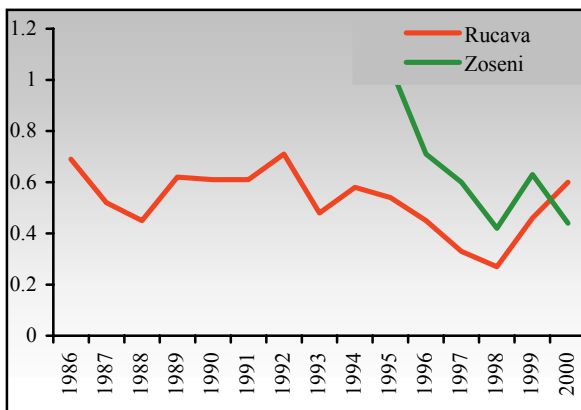


Figure 10. Annual mean concentration of $\text{NO}_3\text{-N}$ ($\mu\text{g/l}$) in precipitation

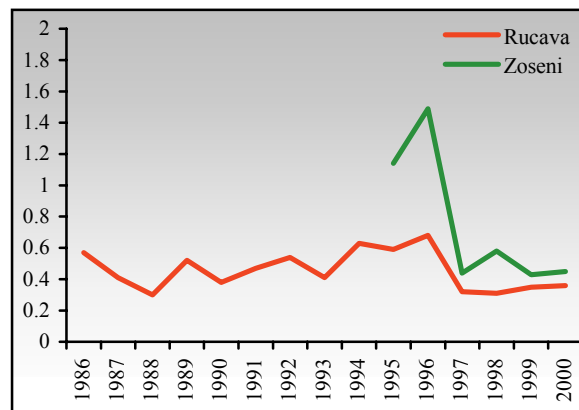


Figure 11. Annual mean concentrations of $\text{NH}_4\text{-N}$ ($\mu\text{g/l}$) in precipitation

Basic cations and pH in precipitation

Generally, basic cations in the precipitation at Zoseni are ordered in decreasing concentrations: $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ and Mg^{2+} and are in correspondence with the order of the concentrations for the most of Latvia. At Rucava, the order is different: $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$. This is attributable to the proximity of the Baltic Sea.

The trend analysis of the annual values of basic cations has shown negative significant trends for calcium and potassium at both stations (Fig. 12). The long-term mean pH in precipitation was 4.53 at Rucava and 5.20 at Zoseni. As natural precipitation has pH 5.3-6.5, the precipitation at Rucava is classed as acidic and at Zoseni as neutral.

No significant trend has been found for the pH annual values at both stations; the upward trend at the significance level 0.05 was ascertained for the cold period at Rucava.

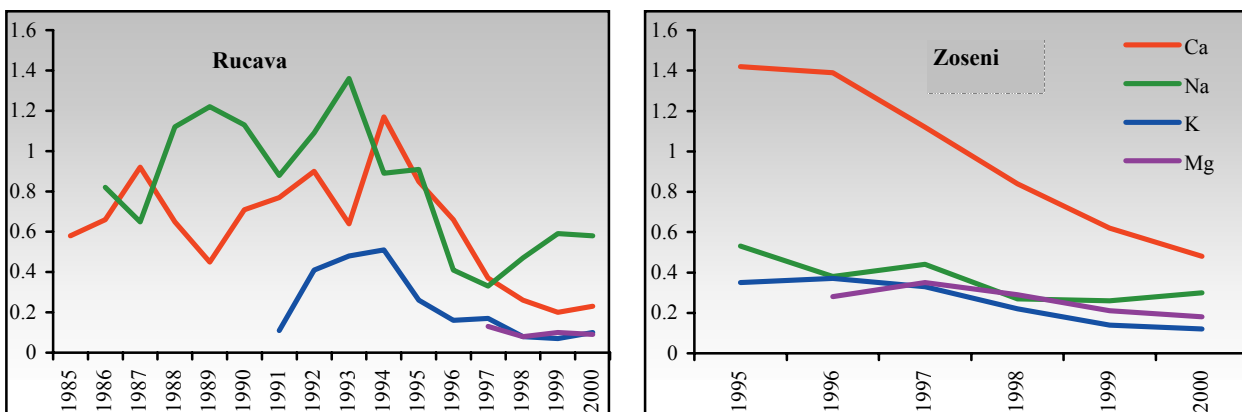


Figure 12. Annual mean concentrations of basic cations (mg/l) in precipitation

Heavy metals

Both precipitation and aerosols at Rucava station would show higher concentrations of Cd and Pb than at Zoseni station (Fig.13 and Fig.14). A significant decreasing tendency ($\alpha=0.05$) has been found at both stations for annual values of Pb in precipitation.

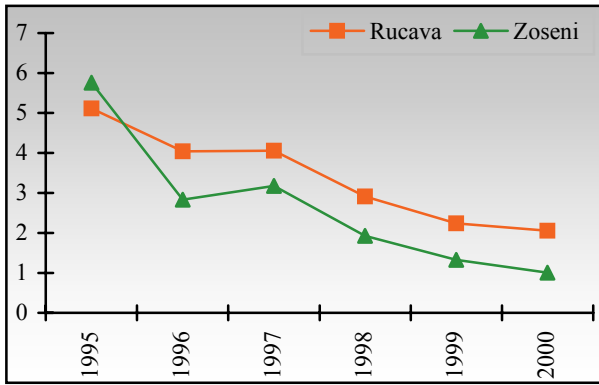


Figure 13. Annual mean concentrations of Cd, µg/l, in precipitation

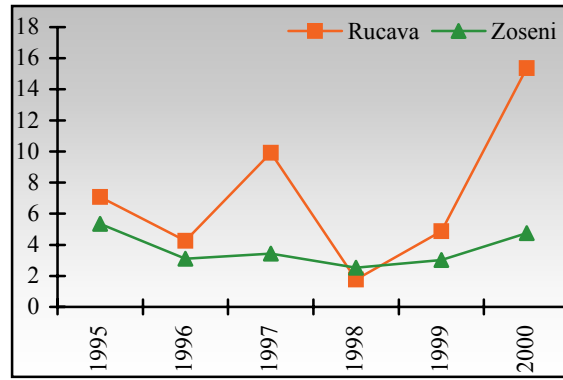


Figure 14. Annual mean concentrations of Pb, ng/m³, in air

No significant trends have been found for the annual concentrations of Pb and Cd in air at any of the stations.

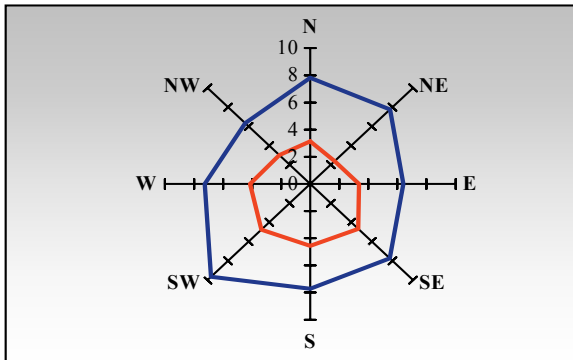


Figure 15. Pb concentration rose (ng/m³)

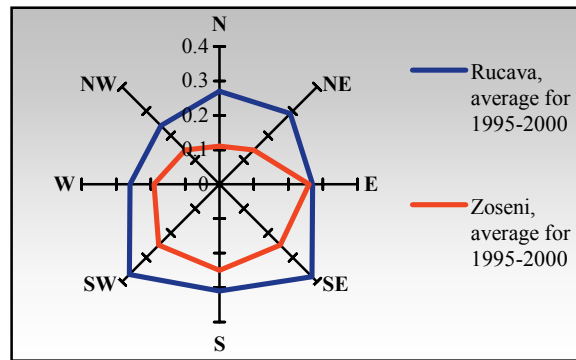


Figure 16. Cd concentration rose (ng/m³)

The concentrations of Pb in air at Rucava were 1.5 times higher in SW transport than in E and NW transport. At Zoseni, lead concentrations in SW, S and SE air transport were 1.5-2 times as high as in N, NW and NE transport (Fig. 15).

The sectorial analysis showed higher Cd values in winds from the SE, S and SW sectors at Rucava and in winds from the E, SE, S and SW sectors at Zoseni (Fig. 16).

Ground-level ozone

The annual mean concentrations of ozone at Rucava station varied between 41 µg/m³ and 54 µg/m³. The decrease of the mean annual concentrations of ozone and daily maximums during 1994-2000 is statistically insignificant.

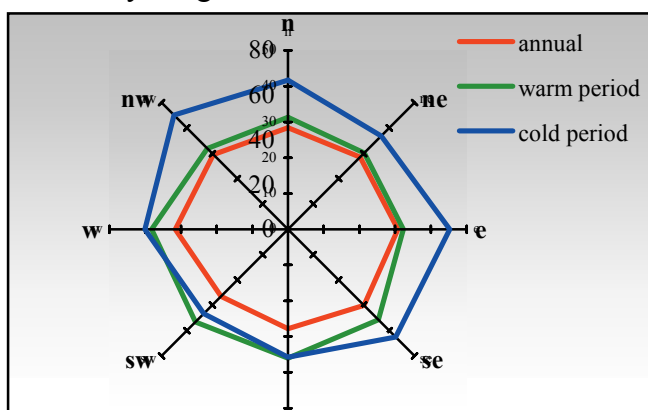


Figure 17. Distribution of the ground-level ozone concentrations (µg/m³) by the wind sectors

The sectorial analysis showed lower annual means ozone concentrations in south-westerly winds. For other sectors, the concentrations are distributed evenly.

The situation is similar in the cold period of the year; higher concentrations have been reported in north-westerly, easterly and south-easterly winds.

This contrasts with the warm period of the year, with increased concentrations measured in prevailing westerly and south-westerly winds (Fig. 17).

Deposition

Deposition from the atmosphere is the major indicator of precipitation and ambient air quality, and of ecosystems.

Table 1 on the whole, sulphur and nitrogen compounds and basic cations deposited in larger amounts at Zoseni, except for Na wet deposition that was higher at Rucava due to the likely effect of the seawater. Rucava would show higher depositions of heavy metals.

Table 1. Wet deposition of substances at EMEP stations

Amounts, mg/m ²	Rucava (1986-2000)	Rucava (1995-2000)	Zoseni (1995-2000)
SO ₄ -S	300 - 970	300-630	320 - 1100
NO ₃ -N	200 - 590	200-410	270 - 800
NH ₄ -N	210- 480	210 - 450	270 - 860
Ca	140- 810	140-650	320-1080
Na	210 - 1040	210-710	190 - 400
K		56-200	80-270
Mg		50-90	120-270
Pb		1.25-4.01	0.68-4.42
Cd		0.07-0.15	0.03-0.11

Statistically significant decreasing trends were observed for wet deposition of sulphate, as well as for nitrate, calcium, potassium and lead (Fig. 18).

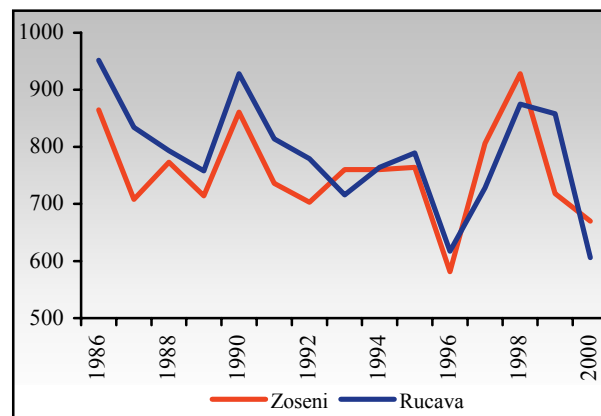
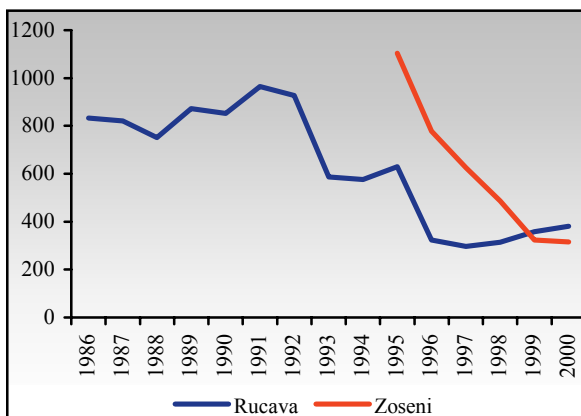


Figure 18. Variation tendency in sulphur wet deposition, mg/m²

Figure 19. Precipitation amount (mm)

The downward trend of SO₄-S, NO₃-N, Ca, K and Pb deposition is attributed to the decreasing precipitation concentrations and, though less clear ($\alpha=0.1$), decreasing precipitation amount (Fig. 19).

6. Conclusions

1. Significant reductions in sulphur dioxide and nitrogen dioxide emissions have been observed over Europe and in Latvia during the recent 15 years. Accordingly, the Latvian EMEP stations showed statistically significant decreases in the mean concentrations of SO₂-S and NO₂-N in air and in the weighted mean concentrations of SO₄²⁻-S, NO₃⁻-N, K⁺, Ca²⁺ and Pb in precipitation. No significant trend has been found for the pH annual values at both stations.
2. Higher sulphur and nitrogen concentrations have been measured in air and precipitation in the cold period of the year; and the downward trend was more pronounced in that period.
3. Analyses of the trajectories of air mass transport over the Latvia's territory in 1986-2000 have shown the predominance of W-NW transport (35% per year). In SW and S transport, both stations reported 2 times higher concentrations of sulphur- and nitrogen-containing substances than in N and NW transport. Higher concentrations were measured at the stations in E and SE transport as well.
4. The sectorial trend analysis of the SO₂-S and NO₂-N concentrations for 1986-2000 has shown negative slope of trends in different air mass transport, with statistical significance for the SW sector for SO₂-S and for all sectors for NO₂-N.
5. Statistically significant decreasing trends were observed for the deposition of sulphate and nitrate, as well as for calcium and potassium during 1986-2000 and for Pb for 1995-2000.
6. The effect of transboundary transmission of air pollutants on ecosystems manifested itself in lower pH and higher heavy metal concentrations in south-western Latvia (IM station Rucava) compared to its continental region (IM station Zoseni). Sulphate concentrations in precipitation have in general decreased significantly ($\alpha < 0.05$) at the IM stations at Rucava and Zoseni. The tendency for decrease has been ascertained for the groundwater and stream water of both IM stations. Long-running (1946-2000) observations performed at the ICP-Waters stations have shown increasing sulphate concentrations since the mid-1980-ies; in the years 1985-2000, the sulphate concentration was stable.

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