

Letter to Editor

Major Ions and Their Relationship in Rime and Hoarfrost Samples from Highly Urbanized Regions

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Abstract

Rime and hoarfrost samples were collected in Gdańsk in northern Poland, and Działdowo in central Poland during winter 2003/2004 and analyzed for major ions. Analysis of the correlations between co-occurring ions confirmed the significant impact of the location of the sampling site (sea coast). For all analyzed ions, the concentrations of hoarfrost samples collected in Gdańsk were higher than those of hoarfrost samples collected in Działdowo at the same time. The concentrations of ions in rime were observed to be less than the ion concentrations in the hoarfrost samples. The high levels of pollution concentration present in the hoarfrost samples compared to the other forms of precipitation are related to the hoarfrost crystalline lattice texture.

Keywords: rime, hoarfrost, environmental analysis, anions, cations

Introduction

Atmospheric precipitation is the result of condensation of atmospheric water vapour due to adiabatic cooling. Rain, snow, drizzle, snow pellets and hail, together with water, bring a number of solutes and suspended solids, captured dust and aerosol particles. A quantitatively less important kind of wet deposition is horizontal deposition: cloud, fog, dew, rime, and hoarfrost. Environmental protection begins with identification and definition of the kind and degree of pollution and its analysis and monitoring.

In recent years an increased interest is observed in the chemistry of atmospheric precipitation and deposits, as the impurities and pollutants undergo complicated chemical and biochemical reactions in the aquatic and soil ecosystem due to which they enter the biogeochemical circulation, disturbing the environmental balance. For this reason, the pollution of atmospheric air, as well as the pollution

of atmospheric precipitation and deposits, which follows, constitute a problem on an international scale, requiring constant monitoring. The settles can be good indicators of the atmospheric pollution's degree in a given geographical region, because of the types and quantity of the substances transported by them and the range of their interactions.

The deposited precipitation can represent an important portion of total precipitation [1]. Those more related to the pollution detected in deposited precipitation have been investigated in the literature. Comparison of pollutant concentrations between differently polluted regions, comparison of pollutant concentrations between fog and rime water and relationship between the chemical and physical properties of rime was described in literature [2-6].

In this paper, stress will be put on the comparison of pollutant concentrations between the samples of rime and hoarfrost. This study presents the results of determination of cation (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , NH_4^+) and anion (F^- , Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-}) concentrations collected from November 2003 to February 2004 in two large urban agglomerations in Poland: Gdańsk and Działdowo. The paper also

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Fig. 1. Location of the sampling sites.

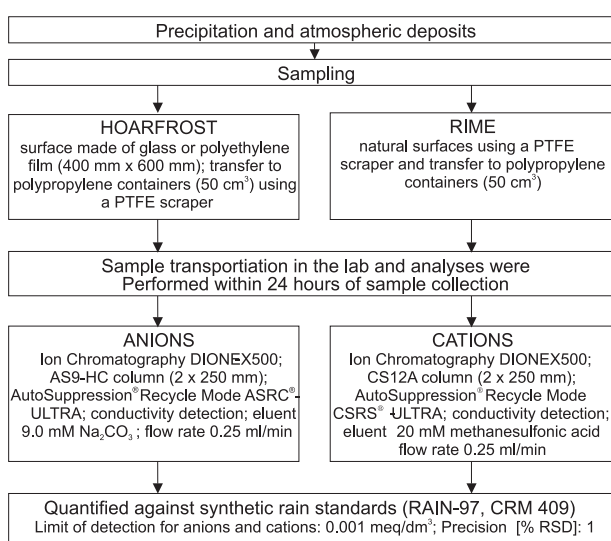


Fig. 2. Schematic diagram of the analytical procedure applied in analyzing the collected samples.

provides detailed information on the correlations of concentration of cations and anions commonly monitored in rime and hoarfrost.

Materials and Methods

Sampling

Samples were collected from winter 2003/2004. The sampling site was located in two large urban agglomerations: the Gdańsk-Sopot-Gdynia Tricity in northern Poland and Działdowo in central Poland. The Gdańsk area is a large municipality in the eastern part of the Baltic coast in Poland. The population of the region is about 500,000 in the three cities of Gdańsk, Gdynia and Sopot. Major point sources of pollution in the region include harbours, shipyards, an oil refinery, power plants and a phosphate fertilizer plant. Traffic and combustion of coal and oil in small residential furnaces are the main diffuse sources of

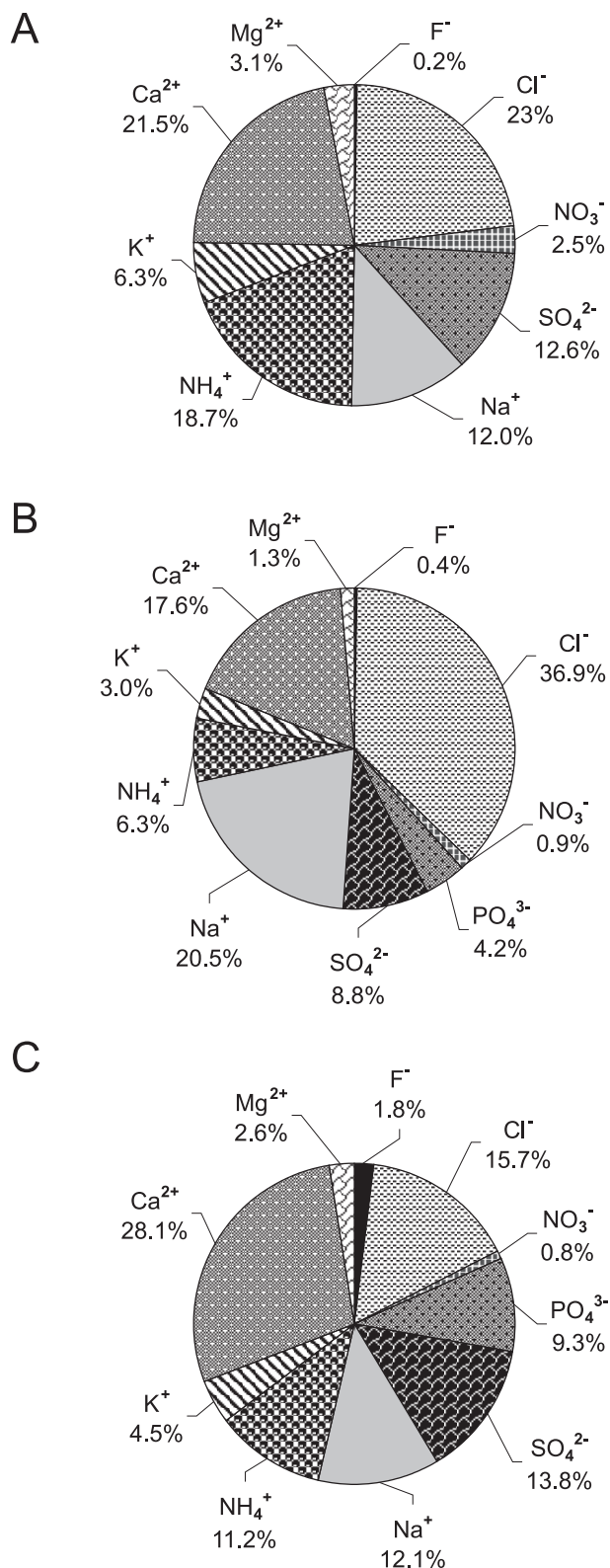


Fig. 3. Mean pollutant distribution in rime and hoarfrost samples: A - rime, Gdańsk; B - hoarfrost, Gdańsk; C - hoarfrost, Działdowo.

air pollution in the region. The Działdowo area is called the Green Lungs of Poland. The population of the city is about 23,000 people. Major point sources of pollution in the region include road (the E7 international road) and

Table 1. Basic statistics parameters obtained during analysis of rime and hoarfrost samples.

Ions [meq/dm ³]	GDAŃSK					DZIAŁDOWO					C _R /C _H	C _G /C _{DZ}		
	Rime		Hoarfrost			Rime		Hoarfrost						
	Mean	Median	Range	Frequency of occurrence (%)	Mean	Median	Range	Frequency of occurrence (%)	Mean	Median			Range	Frequency of occurrence (%)
F ⁻	0.0020	0.0011	n.d.-0.006	75	0.020	0.0053	n.d.-0.11	77	0.072	0.045	n.d.-0.27	94	0.36	0.28
Cl ⁻	0.22	0.22	0.13-0.32	100	1.9	0.28	0.071-21	100	0.62	0.18	0.063-3.8	100	1.2	3.1
NO ₃ ⁻	0.024	0.021	0.015-0.040	100	0.049	0.025	0.014-0.29	100	0.033	0.027	n.d.-0.090	94	1.2	1.5
SO ₄ ²⁻	0.12	0.11	0.068-0.18	100	0.45	0.16	0.050-3.1	100	0.55	0.24	0.058-2.9	100	1.1	0.83
Na ⁺	0.11	0.10	0.041-0.21	100	1.06	0.11	0.048-11	100	0.48	0.12	0.015-2.6	100	0.61	2.2
K ⁺	0.060	0.056	0.11-0.29	100	0.16	0.078	n.d.-1.7	92	0.18	0.075	n.d.-1.8	67	0.86	0.73
NH ₄ ⁺	0.18	0.16	0.036-0.092	100	0.33	0.21	0.011-0.94	100	0.44	0.23	0.002-0.81	100	3.4	0.87
Ca ²⁺	0.20	0.20	0.12-0.32	100	0.91	0.51	0.23-2.5	100	1.11	1.09	0.44-2.2	100	1.3	0.82
Mg ²⁺	0.030	0.029	0.021-0.039	100	0.069	0.057	0.030-0.14	100	0.10	0.068	0.039-0.36	100	0.53	0.66

n.d.- no detected

railway (main railway junction in Poland) traffic. The specific character of the climate in this city is connected both with marine and continental influences. Fig. 1 illustrates the locations of the sampling sites.

Chemical Analysis

Samples were collected during or immediately after a precipitation event. They were stored at low temperatures (4-7°C) in a dark room, with no preservatives added. In general, all analyses were performed within 24 hours of sample collection. Due to the high contents of solid particles (sand, dust, etc.) in the samples, inclusion of a filtration stage was necessary in some analyses (0.45 mm, Millex®-HV). Fig. 2 presents a schematic diagram of the analytical procedure for samples [7, 8].

Results

In the winters from 2003/2004, the chemical analyses of the total 88 samples (rime – 20 samples, hoarfrost from Gdańsk – 34 samples, hoarfrost from Działdowo – 34 samples) were completed. The mean and range concentration of selected components are shown in Table 1.

Fig. 3 demonstrates the mean relative content of the main ions in rime and hoarfrost collected in Gdańsk and Działdowo. The total sum of selected free ions in rime (3.8 meq/dm³) collected in January represents approximately half of the sum of these ions in hoarfrost (8.3 meq/dm³). According to Fisak et al. [3], the total sum of selected free ions in rime represents approximately half of the sum of these ions in fog collected in the same time. Obviously the relative content of Cl⁻ and Na⁺ was lower in rime than in hoarfrost, while the content of F⁻ did not show any significant change. The other ion concentrations were higher in rime than in hoarfrost (Mg²⁺, K⁺, NH₄⁺ and NO₃⁻; more than twice).

The results were subjected to statistical evaluation. The calculations were performed from C_R/C_H ratios (concentration of a compound in rime collected in Gdańsk, January / concentration of a compound in hoarfrost collected in Gdańsk, January). Due to the considerable scatter of the individual data and the not normally distributed data, different results were obtained for averages and medians (Table 1). Higher C_R/C_H ratios were found for chloride (1.2), nitrate (1.2), calcium (1.3) and ammonium (3.4). The higher ratio might be an artifact due to the low concentrations in hoarfrost. The lowest rime/hoarfrost ratio (0.36) is found for fluoride.

Figure 4A shows the distribution function of C_R/C_H for sulfate. The function is bimodal, but the distribution functions for the components Ca²⁺ and Na⁺ are considerably different (no maxima appear in the graphs – see Figs. 4B and 4C). This means that the composition of rime with respect to crustal or “sea salt” elements (Na⁺, Ca²⁺) is not dependent on the concentration of these components in

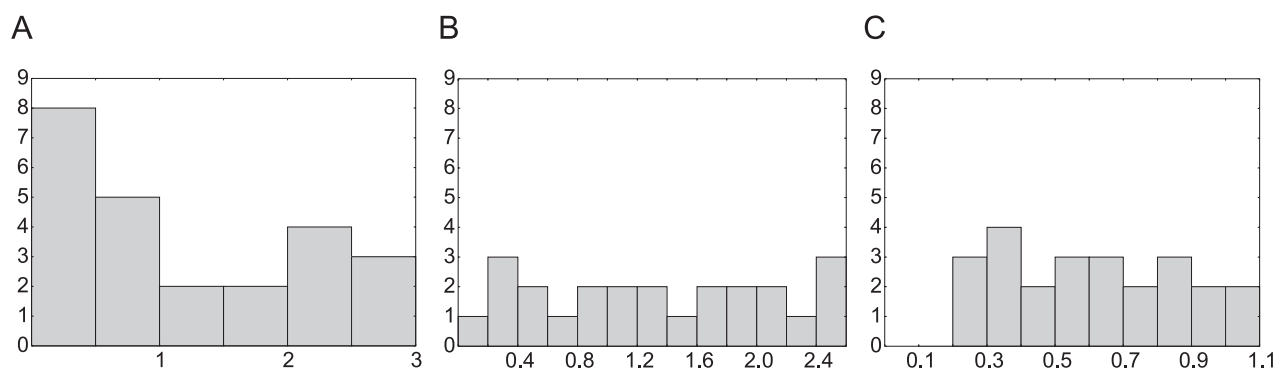


Fig. 4. Frequency distribution of the CR/CH ratios for sulfate (A), sodium (B), calcium (C).

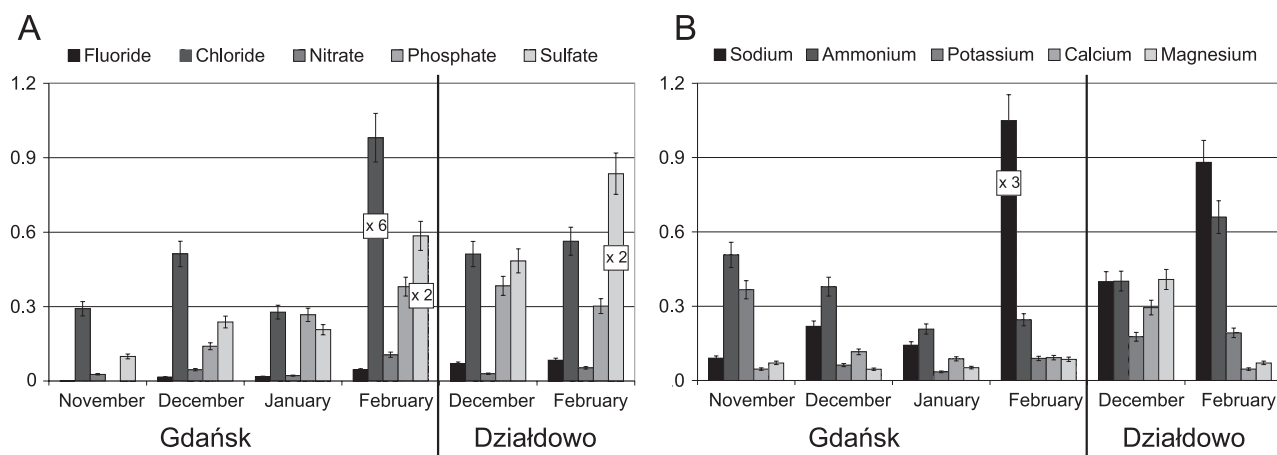


Fig. 5. Concentration (meq/l) of anions (A) and cations (B) in hoarfrost samples collected in Gdańsk and Działdowo.

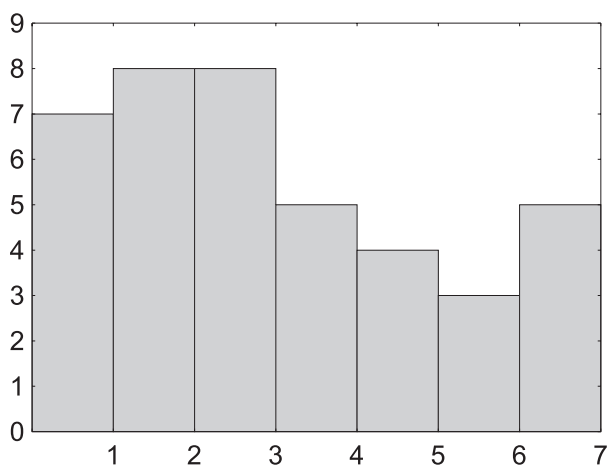


Fig. 6. Frequency distribution of the C_G/C_{Dz} (concentration of a compound in hoarfrost collected in Gdańsk/ concentration of a compound in hoarfrost collected in Działdowo) ratios for chloride.

the hoarfrost. This can be explained by the fact of localization of the sampling sites in the coastal areas of the Baltic Sea (marine aerosols).

Fig. 5 shows diagrams of the anion and cation concentrations in the hoarfrost collected in Gdańsk and Działdowo in particular months. The concentrations of chloride (C_G/C_{Dz}

$C_{Dz} = 3.1$) and sodium ($C_G/C_{Dz} = 2.2$) in hoarfrost collected in Działdowo were observed to be less than the ion concentrations in the samples collected in Gdańsk. The higher levels of concentration in a single analysis of a hoarfrost sample taken within the Gdańsk area are attributed to the different character of sampling places (Gdańsk – the Tricity centre, Działdowo – a residential area). In addition, the climatic conditions of the two regions are different (Gdańsk – proximity to the Bay of Gdańsk, marine aerosols). Fig. 6 shows the distribution function of C_G/C_{Dz} for chloride. The distribution of ratios for chloride exhibits an intermediate behavior between the groups of the “sea salt” compounds. The lowest values of $nss-SO_4^{2-}/SO_4^{2-}$ were observed at a lowland urban station localized close to the Baltic Sea coast line (the proportion of mean values of $nss-SO_4^{2-}$ to SO_4^{2-} was approximately 74% in hoarfrost and 73% in rime in Gdańsk, 94% in hoarfrost in Działdowo).

Table 2 presents the results of correlation matrices for ion pairs in the rime and hoarfrost. A strong positive correlation between Na^+ and Cl^- in rime and hoarfrost was found in Gdańsk. Similar results were obtained by other researchers determining selected cations and anions in precipitation samples collected close to the seashore [9-11]. Hansen and Nielsen [12] suggested that the correlation was the strongest at the coastal heath showing the dominance of sea salts in atmospheric deposition. On the basis of the results of statistic

Table 2. Ion pair correlations.

	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
GDAŃSK, RIME									
F ⁻	1.00								
Cl ⁻	0.60	1.00							
NO ₃ ⁻	-0.33	0.55	1.00						
SO ₄ ²⁻	0.42	0.98	0.70	1.00					
Na ⁺	0.45	0.99	0.69	1.00	1.00				
NH ₄ ⁺	0.81	0.19	-0.68	0.03	0.02	1.00			
K ⁺	0.45	0.98	0.69	0.99	1.00	0.02	1.00		
Mg ²⁺	0.81	0.93	0.27	0.84	0.87	0.37	0.87	1.00	
Ca ²⁺	0.45	0.98	0.69	1.00	1.00	0.02	1.00	0.86	1.00
GDAŃSK, HOARFROST									
F ⁻	1.00								
Cl ⁻	0.41	1.00							
NO ₃ ⁻	0.56	0.98	1.00						
SO ₄ ²⁻	0.97	0.41	0.57	1.00					
Na ⁺	0.42	1.00	0.98	0.42	1.00				
NH ₄ ⁺	-0.01	-0.21	-0.19	0.05	-0.21	1.00			
K ⁺	-0.18	-0.06	-0.06	-0.13	-0.07	0.84	1.00		
Mg ²⁺	0.28	0.20	0.21	0.27	0.20	0.70	0.72	1.00	
Ca ²⁺	0.60	0.49	0.58	0.68	0.49	0.56	0.56	0.63	1.00
DZIAŁDOWO, HOARFROST									
F ⁻	1.00								
Cl ⁻	0.14	1.00							
NO ₃ ⁻	0.38	0.28	1.00						
SO ₄ ²⁻	0.23	0.97	0.37	1.00					
Na ⁺	-0.21	-0.08	0.29	-0.07	1.00				
NH ₄ ⁺	-0.09	0.10	0.28	0.16	0.93	1.00			
K ⁺	-0.03	0.11	0.14	0.16	0.89	0.97	1.00		
Mg ²⁺	-0.01	-0.05	0.12	-0.01	0.93	0.93	0.96	1.00	
Ca ²⁺	-0.28	0.27	0.13	0.39	0.55	0.68	0.65	0.60	1.00

analysis, it was assumed that the concentrations of Cl⁻ ions in hoarfrost decreased with increasing distance from the Baltic Sea. At the same time, it was observed that a decrease in the concentration of Cl⁻ in hoarfrost was accompanied by an increase in the concentrations of Mg²⁺ and Ca²⁺[8].

Conclusion

Statistical analysis revealed significant differences between the results obtained for different sampling site

locations and characteristics (region of Poland, form of deposits).

The total sum of selected free ions in rime was approximately half of the total sum of selected free ions in hoarfrost. The relative content of free ions in the mean sample was different in rime and hoarfrost with the exception of F⁻ that did not show any significant variations. The high levels of pollution concentration present in the hoarfrost samples compared to the other forms of precipitation are related to the hoarfrost crystalline lattice texture.

The differences in concentration of pollutants in hoarfrost samples can be explained by the different sampling location. The hoarfrost samples gathered within the Gdańsk area are characterized by higher average sodium and chloride ion concentrations than the samples from the Działdowo area, which may be attributed to the proximity of the Bay of Gdańsk.

Although solid deposited precipitation can develop in a relatively short part of the year, they still have an important share on the total amount of precipitation and they can contribute significantly to the local increase in the load with pollutants.

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References

1. BŁAŚ M., SOBIK M., Natural and Human Impact on Pollutant Deposition in Mountain Ecosystems with the Sudetes as an Example, [in:] Pyka J.L., Dubicka M., Szczepankiewicz-Szmyrka A., Sobik M., Błaś M. (ed.), *Man and Climate in the 20th Century, Acta UWrat. 2542, Stu. Geo.*, **75**, 411, **2003**.
2. BERG N., DUNN P., FENN M., Spatial and temporal variability of rime ice and snow chemistry at five sites in California, *Atmos. Environ.*, **25A**, 915, **1991**.
3. FISAK J., REZACOVA D., Comparison between pollutant concentration in the samples of fog and rime water collected at the Milesovka Mt., *Studia Geophysica et Geodaetica*, **45**, 319, **2001**.
4. DUNCAN L.C., Chemistry of rime and snow collected at a site in the central Washington Cascades, *Environ. Sci. Technol.*, **26**, 61, **1992**.
5. FERRIER R.C., JENKINS A., ELSTON D.A., The composition of rime ice as an indicator of the quality of winter deposition, *Environ. Pollut.*, **87**, 259, **1995**.
6. BARANOWSKI S., LIEBERSBACH J., The intensity of different kinds of rime on the upper tree line in the Sudety Mountains, *J. Glaciol.*, **19**, 489, **1978**.
7. SKARŻYŃSKA K., POLKOWSKA Ż., NAMIEŚNIK J., Samples handling and determination of physico-chemical parameters in rime, hoarfrost, dew, fog and cloud water samples – a review, *Pol. J. Environ. Stud.*, **15**, 185, **2006**.
8. POLKOWSKA Ż., ASTEL A., WALNA B., MAŁEK S., MĘDRZYCKA K., GÓRECKI T., SIEPAK J., NAMIEŚNIK J., Chemometric analysis of rainwater and through-fall at several sites in Poland, *Atmos. Environ.*, **39**, 837, **2005**.
9. SAXENA A., KULSHRESTHA U.C., KUMAR N., KUMARI K.M., SRIVASTAVA S.S., Characterization of precipitation at Agra, *Atmos. Environ.*, **30**, 3405, **1996**.
10. JACOB D.J., WALDMAN J.M., MUNGER J.W., HOFFMANN M.R., Chemical composition of fogwater collected along the California Coast, *Environ. Sci. Technol.*, **19**, 730, **1985**.
11. ASMAN W.A.H., SLANINA J., BAARD J.H., Meteorological interpretation of the chemical composition of rainwater at one measuring site, *Water, Air, Soil Pollut.*, **16**, 159, **1981**.
12. HANSEN B., NIELSEN K.E., Comparison of acidic deposition to semi-natural ecosystems in Denmark – coastal heath, inland heath and oakwood, *Atmos. Environ.*, **32**, 1075, **1998**.