Pollutant Concentrations in Rime and Fog Water

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Abstract: The present study deals with a comparison between the pollutant concentrations in the samples of rime and of fog water (so-called deposited or occult precipitation) collected at the Milešovka Observatory. Although rime can be observed during a limited part of the year, it still has an important share in the total amount of precipitation and can contribute significantly to a local increase in pollutant loads. The total sum of the selected free ions in the rime water represents approximately a half of the total sum of the selected free ions in the fog water. The relative contents of free ions in the mean sample were different in rime and fog water with the exception of K^+, Mg^{2+} and F^- that did not show any significant variations.

Keywords: fog water; rime water; pollutant concentration

The observed precipitations from fog can occur in solid (rime water) and liquid (fog water) phases. It has been recognised that the precipitation from fog can represent an important share in the total precipitation amounts in the middle and high altitudes.

Fog and rime water have attracted a significant attention since the 80ties of the last century. We can recognise three main streams of studies; in particular, (i) the use of the deposited precipitation as potable water or in watering (Edwards *et al.* 2001; Henderson & Falk 2001; Muselli *et al.* 2001), (ii) environmental impacts of the pollutants contained in the deposited precipitation (see e.g. Li & Aneja 1992; Arends *et al.* 1994; Woodbrock *et al.* 1994; Acker *et al.* 1995, 2001; Kalina *et al.* 1998; Elbert *et al.* 2000; Klemm 2001; Bridges *et al.* 2002; Lange *et al.* 2003; Holder 2004; Zapletal *et al.* 2007), (iii) sampling facilities capable to collect the deposited precipitation (see e.g., Daube *et al.* 1987; Straub *et al.* 2001; Moore *et al.* 2002; Straub & Collet 2002, e.t.c.). The investigation of pollutants in the deposited precipitations comprises a very broad range of problems. For instance, they include long-term changes in the pollutant concentrations or the effects of physical parameters which determine the evolution of a single deposited precipitation type and affect the pollutant concentrations in a sample.

In the Institute of Atmospheric Physics of the AS CR (IAP), the attention has been focused on the fog research since 1998. Four basic topics, related to the pollution revealed in the deposited precipitations, were investigated in the IAP in the past years:

(i) Comparison between the pollutant concentrations in two types of differently polluted regions; we compared the pollutant concentrations in the

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fog water samples coming from the so-called black triangle with the samples collected in the Šumava mountainous region, the latter representing a relatively clean area in the CR. (Fišák & Řezáčová 2001; Fišák *et al.* 2002a).

(ii) Comparison of the pollutant concentrations in fog and rime water; we processed samples of fog and rime water and compared the concentrations of several significant pollutant components. The water samples were collected at the Milešovka station during the time period of 1999–2000 (Fišák & Řezáčová 2001).

(iii) Relationships between the chemical and physical properties of water samples in fog and low clouds; the attention was primarily paid to the fog type, liquid water content (LWC), and the sampling timing with respect to the duration of the fog event (Fišák *et al.* 2002b).

(iv) Dependence of the pollutant concentrations on the prevailing air flow patterns; we applied the classification of synoptic circulation at the 850 hPa level (Fišák & Řezáčová 2001; Fišák *et al.* 2002a, 2004).

In this paper, we pay attention to a comparison between of the pollutant concentrations in the samples of deposited solid and liquid deposited precipitations collected at the Milešovka Observatory. Although the deposited solid precipitation can be observed during a limited part of the year only, it still has an important share in the total amount of precipitation and can contribute significantly to the local increase in the pollutant loads.

SITE DESCRIPTION

The collection of rime and fog water was implemented at the meteorological observatory, situated at the top of Milešovka, a conical isolated mountain (50°33'17''N, 13°55'57''E, 837 m a.s.l.). Milešovka lies in a close vicinity of the North Bohemian brown coal basin, which is considered to be a region strongly affected by the air pollution. Several power plants are situated close to the Krušné Hory mountain chain which represents the north-western border of the opencast lignite mine area. There is a road with heavy traffic of both truck and public transport near Milešovka. The position of the meteorological observatory is shown in Figure 1.

In the majority of cases, the fog occurrence is connected with a low cloudiness at the Milešovka top where good conditions exist for fog water sampling. During winter months, numerous rime events evolve there as well.

MATERIAL AND METHODS

Passive fog collectors were employed to sample the deposited solid precipitation. The modified Grunow samplers (Figure 3), constructed at the Institute of Atmospheric Physics (IAP), were used. After the collection, the samples of rime water were melted in a closed vessel at the temperature of +5°C to prevent the possible contamination. After melting, the samples were kept in darkness in a

Figure 1. The location of the Milešovka Observatory

Figure 2. The active fog water collectors used in the Institute of Atmospheric Physics of the AS CR (IAP)

fridge at a temperature below +5°C. Conductivity and pH were measured at the site immediately after the sample melting. The samples that had been contaminated by snow, freezing rain or other falling atmospheric precipitation particles, were not processed.

The samples of fog water were collected by means of an active fog collector (Figure 2), which was described in Daube *et al.* (1987) or Tesař *et al.* (1995). The samples were kept in darkness at the temperature of +5°C. The passive and active water collectors are placed in a meadow area, the distance between them being about 10 m. Chemical analyses were performed in the accredited laboratories of the Czech Geological Survey. An overview of the techniques, which were employed in assessing the concentrations of the individual components, and the detection limits are summarised in Table 1. Attention was focused on the following components: conductivity (cond.), acidity (pH), cations Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, and anions F^-, Cl^-, NO_3^-, SO_4^{2-}.

RESULTS AND DISCUSSIONS

In the period of 2000–2003, chemical analyses of 77 fog water samples were completed. Similarly, 14 samples of rime water were analysed in winter 2000/2001 and 2003/2004. Figure 4 demonstrates the mean relative contents of the main ions in rime and fog water. Table 2 indicates that the total sum of the selected free ions in the mean rime water

Table 1. Analytic methods and instrumentation utilised in fog and rime water analyses

Components	Methods and instrumentation	Detection limits
Na^+, Mg^{2+}, K^+, Ca^{2+} (mg/l)	flame atomic absorbtion spectrometry – FAAS; PE-3100	0.01
NH_4^+ (mg/l)	spectrometry; PE 200 Hitachi	0.02
NO_3^- (mg/l)	high pressure liquid chromatography – HPLC; Schimadzu LC-6A	0.15
SO_4^{2-} (mg/l)		0.3
Cl^- (mg/l)		0.5
F^- (mg/l)	ion selective electrode – ISE; ION 85	0.02
pH	pH-meter; PHM-62 + electrode GK 2401C	2
Conductivity (µS/cm)	conductivity-meter; CDM-83	8

Table 2. Basic characteristics of several components analysed (ΣIA – sum of the ion amount, a – mean, b – minimum, c – maximum)

Components		Conductivity (μS/cm)	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}	ΣIA
				(mg/l)									
Rime	a	122.54	4.74	0.17	3.57	18.16	9.70	2.37	1.19	6.00	0.48	2.84	44.49
	b	41.00	3.79	0.05	0.97	6.34	0.97	0.60	0.28	1.22	0.08	0.77	11.29
	c	249.00	6.32	0.39	8.45	38.39	28.18	6.00	3.16	16.93	2.07	11.77	115.34
Fog	a	177.35	4.73	0.34	2.48	32.21	26.19	1.63	2.13	13.91	0.62	3.17	82.69
	b	47.30	3.64	0.0	0.34	0.25	3.87	0.06	0.12	0.02	0.01	0.07	4.72
	c	589.00	7.84	2.82	14.69	146.92	117.69	11.49	49.94	60.06	6.87	26.56	437.04
Rime/fog		0.69	1.00	0.50	1.44	0.56	0.37	1.45	0.56	0.43	0.76	0.90	0.54

sample (44.5 mg/l) represents approximately a half of the corresponding sum in the mean fog water sample (82.7 mg/l). Obviously, the relative contents of SO_4^{2-} and NH_4^+ were lower in rime water than in fog water while the contents of K^+, Mg^{2+}, and F^- did not show any significant differences. The other ion concentrations were higher in rime water than in fog water (Ca^{2+} and Cl^- more than twofold). In Table 2 the mean, minimum and maximum values of the selected components are also shown. Furthermore, the last column in Table 2, marked ΣIA, gives the summed values of the mean, minimum, and maximum concentrations, respectively. The numbers in Table 2 indicate that the conductivity of the samples decreases while the acidity remains constant over the period studied. Except for SO_4^{2-}, the minimum concentration values of all ions considered are higher in rime water than in fog water. On the contrary, the maximum concentration values are higher in fog water without any exception. In particular, markedly higher maximum concentration values in fog water were found for NO_3^-, SO_4^{2-}, and K^+. Consequently, the range of values in the fog water significantly exceeds the variability of the rime water components.

Figure 3. The passive fog water collectors employed in the Institute of Atmospheric Physics of the AS CR (IAP)

CONCLUSIONS

The deposited precipitation, especially rime, represents an important fraction of the total precipitation amount in the middle and higher altitudes (generally above 800 m a.s.l.). The concentrations of the selected components in fog water corresponded to the results presented in Fišák *et al.* (2002a, b, 2004). The total sum of the selected free ions in rime water represents approximately a half of that in fog water. The relative contents of free ions in the mean samples were different in rime and fog water with the exception of K^+, Mg^{2+}, and F^- that did not show any significant differences. These results correspond to the conclusions derived by Fišák and Řezáčová (2001). In the above-mentioned paper, the resultant conclusions followed the analysis of the fog and rime water samples collected during the period of 1999–2000.

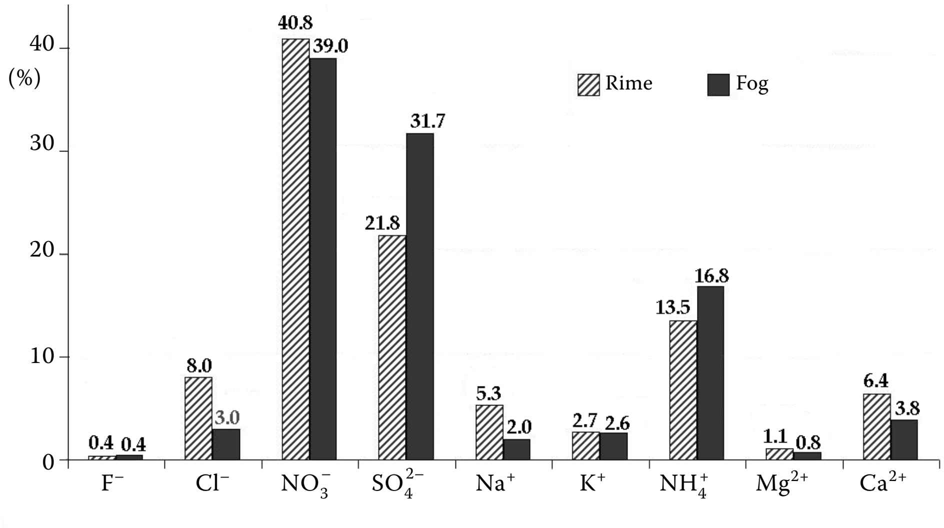

Figure 4. Mean pollutant distribution in rime and fog water

In comparison with the former sampling period, the contents of the selected ions decreased in fog water from 217.0 mg/l to 82.7 mg/l and in rime from 178.0 mg/l to 44.5 mg/l.

The differences in the concentrations of pollutants in rime and fog water cannot be explained solely by the different sampling methods. The sample phase state at the collection time and other factors may play a certain role. The decrease in the contents of the majority of the selected ions could be caused by a lower content of dust particles in the atmosphere (snow cover, wet soil, the reduction of organic particles in the winter atmosphere). The salt treatment of roads in the winter season might be responsible for the significant increase of Na^{2+} and Cl^- contents in the samples.

The number of the rime water samples was significantly smaller than, that of the fog water samples. This is due to the shorter duration of the periods of the rime occurrence. There are additional factors affecting the rime evolution, like negative temperatures close to 0°C, the fog occurrence, or a high relative humidity. Therefore, further verification with an extended data set is needed as well as a future long-lasting investigation. In the nearest future, we plan to focus on the dependence of the rime water pollution on the liquid water content (Elbert *et al.* 2000) and, possibly, on the droplet size distributions in fogs. We intend to continue in studying the dependence of the pollutant concentrations on the direction of the flow patterns, which may lead to the identification of the pollution sources, and which also requires a substantially extended data set.

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