Chemical Characteristics of Precipitation and Cloud Water at High Elevation Site in Bulgaria

Elena Hristova, Blagorodka Veleva, Krum Velchev, and Emilia Georgieva

Abstract The aim of this work is to present and discuss newly obtained data for the chemical composition of precipitation (RW) and cloud water (CW) at a high-elevation site in Bulgaria. Sampling of RW and CW was organized in 2017 and 2018 during field experiments at Cherni Vrah, the highest peak in Vitosha Mountain. Passive collectors designed and constructed at NIMN were used. All collected samples (118) were analyzed for acidity (pH), conductivity (EC), main anions—SO_4^{2-}, NO_3^-, Cl^-, ammonium ions (NH_4^+), macro and micro elements (Na, K, Mg, Ca, Fe, Si, Zn, Cu). The average pH values for both types of samples were in the acidity range (<5.0). The values of EC varied from 5 to 89.2 $\mu S\ cm^{-1}$ for RW and from 0.7 to 202 $\mu S\ cm^{-1}$ for CW. The ion composition was dominated by $nssSO_4^{2-}$, NO_3^-, Ca and NH_4^+ which made up more than 63% of the total ionic content for RW and 75% for CW. The relative contribution of the major compounds to the CW and RW composition is presented and discussed. The volume weighted mean (VWM), fractional acidity and neutralization factor are also calculated. The effect of long-range transport processes is studied for some selected periods of 2018 using HYSPLIT air mass backward trajectory analysis.

Keywords Cloud water · Rain water · Chemical composition · Acidity · Backward trajectories

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E. Hristova (✉) · B. Veleva · K. Velchev · E. Georgieva
National Institute of Meteorology and Hydrology, 66, Tsarigradsko Shose Boulevard, Sofia 1784, Bulgaria
e-mail: elena.hristova@meteo.bg

B. Veleva
e-mail: blagorodka.veleva@meteo.bg

K. Velchev
e-mail: krum.velchev@meteo.bg

E. Georgieva
e-mail: emilia.georgieva@meteo.bg

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1 Introduction

The atmosphere is an important environment in which different gaseous and aerosol species are transported. Clouds and precipitations play important roles in removing particles and dissolved gaseous pollutants from the atmosphere. They also scavenge sulphur dioxide (SO_2), nitrogen oxides (NO_x), and other atmospheric pollutants, which can affect their acidity and chemical characteristics and cause ecological damage to ecosystems [1, 2]. The chemical composition of cloud water (CW) and precipitation (RW) depends on emitted pollutants by sources of anthropogenic and natural origin, the dynamical processes in the atmosphere and on the chemical reactions that occur during both local and long-range transport. Nitrates (NO_3^-), sulphates (SO_4^{2-}) and other ions such as ammonium (NH_4^+), chloride (Cl^-), magnesium (Mg), calcium (Ca), potassium (K), and sodium (Na) are commonly present in the aqueous phase. Some of these species originate from natural sources such as sea spray, soils and forest fires. Other species such as ammonium come from anthropogenic activities, including agricultural fertilizers and biomass burning [3, 4].

Several authors worldwide have explored trends in the chemical composition of cloud and rain water since 1990 [2, 5–9]. At high-elevation environments, cloud and fog liquid water have generally been recognized as being more acidic than precipitation water. In Bulgaria, precipitation chemistry in forest mountain areas was analysed occasionally during field campaigns related to depositions and critical loads to ecosystems [10, 11]. A few studies have focused on analysis of meteorological conditions and the influence of air mass transport on the chemical composition of precipitations at peaks Cherni Vrah and Moussala [12], stations part of the Bulgaria network for precipitations chemistry monitoring.

In the last years, NIMH is conducting research activities on atmospheric depositions in Bulgaria including both numerical simulations and observational campaigns [13–16]. The observational campaigns are organized in areas that could be adversely impacted by the depositions of acidifying and eutrophying compounds, and thus, be exposed to environmental risks (mountain and nature protected areas). The work presented here is part of these recent activities.

The scope of this study is to compare and discuss newly obtained data for the chemical composition of CW and RW at a high-elevation site in Bulgaria—Cherni Vrah (ChV), Vitosha Mountain. Another objective is to analyse the effect of long-range transport processes on the chemical composition that will be briefly outlined for selected case periods.

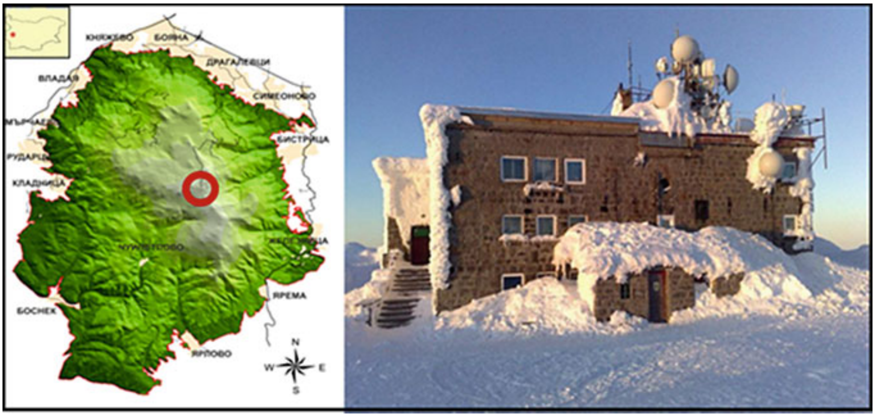

Fig. 1 Map of Vitosha Mountain and synoptic station Cherni Vrah

2 Methodology

2.1 Site Description

Vitosha Mountain is the first national park in Bulgaria and in the Balkan Peninsula. It is located on the outskirts of the city of Sofia, with an area of 270.79 km^2. Cherni vrah is the highest peak where the Meteorological station of NIMH is situated (42.6167 N, 23.2667 E, 2286 m asl), Fig. 1. The CW and RW samples were collected at this site meteorological station from June 2017 to November 2018.

2.2 Sampling Equipment

The cloud water and precipitation were sampled by using a passive collectors designed and constructed in NIMH (Fig. 2). The cloud water sampler was made from plexiglas and the sampling elements were made from fishing lines with length in total 180 m: 100 m–ø1 mm and 80 m–ø0.5 mm. The cloud droplets impact on the vertical strings, combine to larger drops, run down the strings, and drip into a 500 ml polyethylene (PE) bottle. The CW samples were collected on an event basis, resulting in different time duration of typically about several hours. The material of the precipitation sampler is polyethylene terephthalate, the diameter is 20 cm in diameter and the capacity of the bottle is 5 L capacity. The precipitation sampler is washed every day with deionized water (<1 µS cm^{-1}) to avoid dry deposition. The RW samples were taken on daily basis.

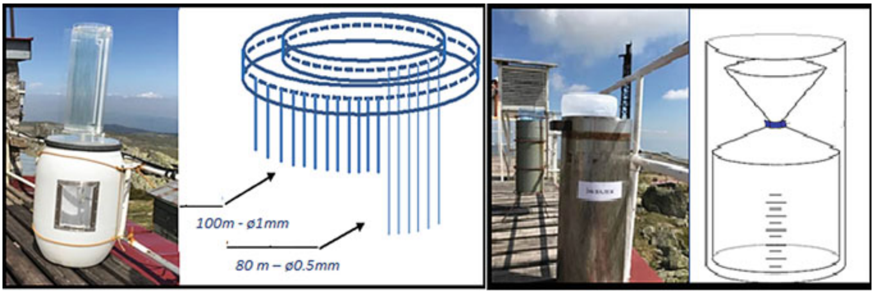

Fig. 2 Samplers for cloud water (left) and precipitation (right)

2.3 Chemical Analysis of Cloud Water and Precipitation Samples

For the studied period, 118 samples were collected in total. All 40 cloud and 78 rainwater samples were analysed for acidity (pH), electro conductivity (EC), Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Ca, Mg, K, Na, Fe, Si, Zn, Cu. Acidity and electro conductivity were measured at the moment of sampling by a portable pH-meter and conductivity meter. The pH meter was calibrated before each measurement using standard buffer solutions of pH 4.00 and 7.01. The conductivity meter was periodically calibrated against KCl standard solutions. Chemical analysis are performed in a certified laboratory in Sofia by Ion Chromatograph (ICS 1100, DIONEX) for Cl^-, SO_4^{2-}, NO_3^-, ICP OES (Vista MPX CCD Simultaneous, VARIAN) for Ca, Mg, K, Na, Fe, Si, Zn, Cu and Spectrophotometer S-20 for NH_4^+.

2.4 Data Analysis

During our field campaign, a total of 118 cloud water and precipitation samples were collected. All samples were tested for ion balance according to the approach proposed in the framework of the European Monitoring and Evaluation Programme (EMEP) for precipitation samples [17]. Statistical analyses were performed with STATISTICA 06 for Windows (StatSoft). Poor ion balance was found in 5% of the cloud water samples and 2% of the precipitation samples and they were excluded from the analysis. The equivalent concentration of H^+ was calculated from measured pH values. Since no direct method is available for the measurement of HCO_3^-, its concentration was estimated from the theoretical relationship between pH and HCO_3^- by an equation proposed by the World Meteorological Organization (WMO) [17].

$$\left[\mathrm{HCO}_3^-\right] = \frac{5.1}{\left[\mathrm{H}^+\right]} \tag{1}$$

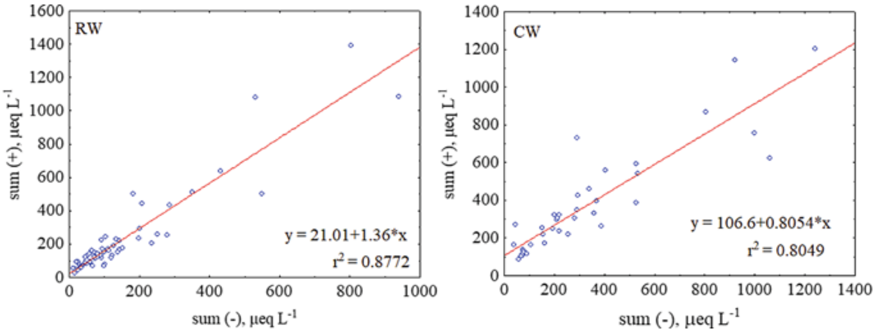

Fig. 3 Equivalence ratio of the total anions and cations for precipitation (left) and cloud water (right) samples

The equivalence ratio of the total anions (sum of Cl^-, $SO_4{}^{2-}$, $NO_3{}^-$, $HCO_3{}^-$) to the total cations (sum of Ca, Mg, K, Na, $NH_4{}^+$, H^+), presented in Fig. 3, showed a good correlation ($r^2 = 0.88$ and 0.81) and suggests that the ions are accurately quantified.

The concentration of the studied species in rainwater is dependent not only on the amount of the component, but also on sample amount. Larger amount tend to dilute ionic concentrations while smaller amount tend to be more concentrated. To avoid this effect, the Volume Weighted Mean (VWM) concentrations were calculated to by Eq. 2:

$$C_{VWM} = \frac{\sum_{i=1}^{N}(C_i \times P_i)}{\sum_{i=1}^{N} P_i} \tag{2}$$

where C_i is the concentration of a particular ion in the ith sample (mg L^{-1}), P_i is the precipitation amount collected within the ith sampling period (mm), and N is the total number of precipitation events. In the case for cloud samples the P_i is amount of cloud water sample.

To estimate the amount of $SO_4{}^{2-}$ in the samples deriving from anthropogenic sources, the non-sea-salt sulphate ($nssSO_4{}^{2-}$) concentration was calculated from the measured $SO_4{}^{2-}$ and Na^+ concentrations with Eq. 3 proposed in WMO Report 160 [17]

$$\left[\mathrm{nssSO_4^{2-}}\right] = \left[\mathrm{SO_4^{2-}}\right] - (0.25 \times [\mathrm{Na}]) \tag{3}$$

Furthermore, we calculated the fractional acidity (FA), as proposed in. [18], to represent the ratio of non-neutralized H_+ in liquid water (Eq. 4):

$$FA = \frac{\left[\mathrm{H^+}\right]}{\left[\mathrm{nssSO_4^{2-}}\right] + \left[\mathrm{NO_3^-}\right]} \tag{4}$$

To assess the neutralization reaction of precipitation by various alkalies, the neutralization factor (NF) for Ca, Mg and NH_4^+ was calculated according to the Eq. 5:

$$NF_X = \frac{[X]}{\left[\mathrm{nssSO}_4^{2-}\right] + \left[\mathrm{NO}_3^-\right]} \quad (5)$$

where $[X]$ is the concentration of chemical component of interest.

2.5 Back-Trajectory Analysis for Long Range Effects

The back-ward trajectory analysis was conducted using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model, [19, 20] for all day with precipitation and cloud water samples. Three different arrival heights were used: 500, 1000, 1500 m a.g.l (above ground level). The calculations were made for 72 h using meteorological input from the Global Data Assimilation System GDAS with horizontal resolution of 0.5° × 0.5°.

3 Results and Discussion

3.1 Physico-Chemical Parameters

The pH values of cloud water and precipitation in this study ranged from 3.5 to 5.7 and the conductivity values from 0.7 to 202 µS cm^{-1}. The frequency distribution of the relative pH and EC frequency for both types of samples are presented in Fig. 4. This frequency analysis shows that 100% of the cloud and 98% of the precipitation

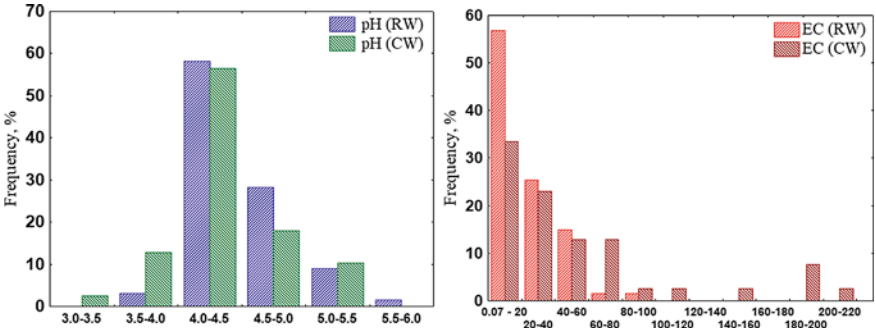

Fig. 4 Frequency of pH (left) and EC (right) for cloud water and precipitation samples

samples had pH value in the acidity range. The highest percentage of pH values were in the range of 4.0–4.5 for both CW and RW (58 and 56%). Only 1.5% of the collected precipitation samples are in the neutral range (5.5–6.0), there were not cloud water samples with pH value higher than 5.3. Around 10% of CW and RW samples had pH in the slightly acidic range (5.0–5.5), and 28% of RW pH and 18% of CW were in the rage 4.5–5.0. In the very acidic range (3.5–4.0) are 13% of the CW pH values and 5% of the RW pH values. The frequency analysis of electrical conductivity presented in Fig. 4 shows 57% of RW EC values and 33% of CW EC values in the range 0.07–20 μS cm^{-1}.

The percentage of EC values in the range 20–40 μS cm^{-1} is very close for both type of samples (23 and 25%). The percentage with EC values in the range >60 μS cm^{-1} is very different: 3% for RW and 31% for CW. Cloud water samples had higher conductivities (0.7–202 μS cm^{-1}) than precipitation (4.7–89 μS cm^{-1}) due to dilution factors in the rain, i.e., cloud droplets have lower water content than rain droplets; therefore the ionic concentrations were higher in cloud water [2]. The average EC values for CW and RW were 56 μS cm^{-1} and 23 μS cm^{-1}, respectively.

The CW and RW pH parameter is the result of acid-base reactions in the cloud droplets. Sulphates and nitrates are the main ions that increase the concentration of H^+ ion in rainwater, while NH_4^+, Ca (usually in the form of $CaCO_3$), Mg, K are the main neutralizing ions.

3.2 Chemical Composition

Statistical information as Volume Weighted Mean (VWM), average, minimum, and maximum concentrations of all studied elements and the number of the samples (N) with concentrations above detection limit are summarized in Tables 1 and 2 for precipitation and cloud water, respectively. The following trend in VWM concentration was obtained: for anions: $nssSO_4^{2-} > NO_3^- > Cl^-$ for both type of samples and Ca > K > NH_4^+ > Na > Si > Mg > Zn > Fe > Cu (RW) and Ca > NH_4^+ > K > Mg > Na > Si > Zn > Fe > Cu (CW).

The VWM total ionic content for cloud water samples (23.1 mg L^{-1}) was around three times higher than this for precipitation samples (7.23 mg L^{-1}). The major anion for both types of samples was sulphate with contribution to the total ionic concentration (TIC) above 30%. The second element is Ca for precipitation samples (18%) and NO_3^- for cloud water samples (25%). The VWM total ionic content for cloud water samples (23.1 mg L^{-1}) was around three times higher than this for precipitation samples (7.23 mg L^{-1}). The major anion for both types of samples was sulphate with contribution to the total ionic concentration (TIC) above 30%. The second element is Ca for precipitation samples (18%) and NO_3^- for cloud water samples (25%).

The total ionic content (TIC) of precipitation and cloud water samples as frequency distribution is presented on Fig. 5.

Table 1 Volume weighted mean (VWM), average, minimum, and maximum concentrations and number of the samples (N) for precipitation samples

mg L^{-1}	Precipitation				
	VWM	Average	Min	Max	N
Cl^-	0.89	1.36	0.05	26.94	63
NO_3^-	1.21	2.12	0.18	15.83	67
SO_4^{2-}	2.26	3.35	0.32	20.28	67
nss_SO_4^{2-}	2.23	3.30	0.32	19.70	67
Ca	1.28	1.85	0.08	15.83	67
K	0.73	0.92	0.10	8.87	62
Mg	0.09	0.14	0.01	1.40	67
Na	0.30	1.27	0.10	15.64	23
Cu	0.01	0.01	0.01	0.05	28
Fe	0.01	0.01	0.01	0.06	33
Si	0.06	0.25	0.06	1.33	20
Zn	0.06	0.08	0.01	0.81	67
NH_4^+	0.42	0.59	0.03	3.90	64
TIC	7.27	10.72	1.13	68.29	67

Table 2 Volume weighted mean (VWM), average, minimum, and maximum concentrations and number of the samples (N) for cloud water samples

mg L^{-1}	Cloud water				
	VWM	Average	Min	Max	N
Cl^-	1.17	1.17	0.10	8.05	40
NO_3^-	5.69	5.69	0.15	23.13	40
SO_4^{2-}	9.13	9.13	0.59	39.52	40
nss_SO_4^{2-}	9.10	9.10	0.59	39.33	40
Ca	3.55	3.55	0.32	24.95	40
K	0.82	0.91	0.11	8.68	36
Mg	0.29	0.29	0.04	1.37	40
Na	0.29	0.50	0.06	3.20	23
Cu	0.01	0.01	0.01	0.03	15
Fe	0.02	0.03	0.01	0.14	21
Si	0.16	0.24	0.06	1.45	27
Zn	0.15	0.15	0.01	1.77	39
NH_4^+	1.86	1.91	0.11	8.28	39
TIC	23.10	23.10	3.93	90.14	40

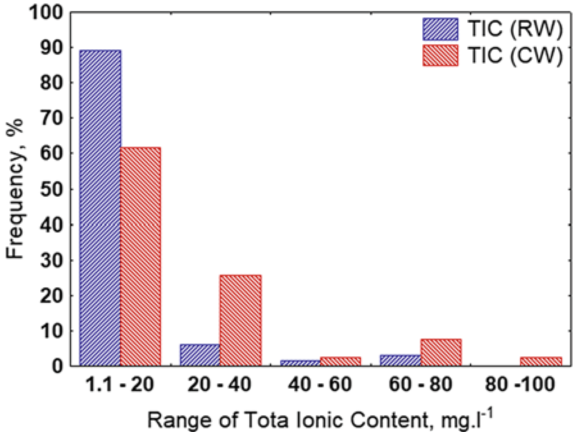

Fig. 5 Frequency distribution of total ionic content in cloud and rain water samples

The total ionic content in CW and RW was in the ranged from 1.1 to 68 mg L^{-1} and from 4 to 90 mg L^{-1}, respectively. The median of TIC in CW samples was 16.5 mg L^{-1} and 6.2 mg L^{-1} for RW samples. As shown by the frequency distribution of TIC, a fraction of cloud and precipitation samples have concentrations between 1 and 20 mg L^{-1} (89% of the RW and 62% of the CW). The percentage of samples in the concentration range 20–40 mg L^{-1} was higher for the CW than for the RW (25% and 6%, respectively). Only 2.6% of the CW samples had TIC in the range 80–100 mg L^{-1}.

The variation in the concentrations of all studied elements is shown as Box Plot presented in Fig. 6. The ion composition of RW and CW was dominated by NH_4^+, Ca, nss_SO_4^{2-} and NO_3^-, which made up more than 63% and 75% of the total ionic content. As expected, concentrations of analyzed elements were higher in cloud water than in precipitation samples.

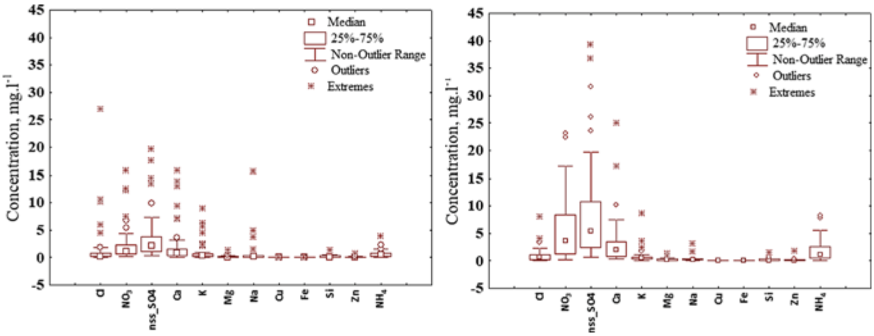

Fig. 6 Concentrations of the studied elements in RW (left) and CW (right) samples

The concentrations of the main acidifying ions—nssSO_4^{2-} for the study period ranged from 0.6 to 39 mg L^{-1} for CW and from 0.3 to 20.3 mg L^{-1} for RW. Concentrations of NO_3^- vary from 0.15 to 23.1 mg L^{-1} for CW and from 0.18 to 15.8 mg L^{-1} for RW. NH_4^+ ion concentrations for CW and RW samples are ranged from 0.01 to 8.3 mg L^{-1} and from 0.03 to 3.9 mg L^{-1}. The lowest variations in concentrations were observed for Fe, Cu and Zn. Their concentration is ranged from 0.005 to 1.8 mg L^{-1}. High variation in Cl and Na concentrations are observed in RW samples. The obtained Cl concentration ranged from 0.05 to 27 mg L^{-1} and for Na from 01 to 15.6 mg L^{-1}.

3.3 Acidification and Neutralization Potentials

The acidification potential of precipitation is usually due to the presence of H_2SO_4, HNO_3 and organic acids [1, 9, 21], and the neutralization of these species occurs in the presence of NH_3 and $CaCO_3$. The analysis of linear regression applied to the set of variables with acidification (SO_4^{2-} and NO_3^-) and neutralization potential (Ca^{2+} and NH_4^+) is presented in Fig. 7. The correlation coefficient for precipitation samples (0.74) was higher than one found for cloud water samples (0.66), indicating that the contribution of other ionic species in the neutralization and acidification processes in the samples of atmospheric precipitation was not significant.

The mean values of fractional acidity (FA) and the neutralization factor, calculated by Eqs. 4 and 5, for the precipitation and cloud water samples are summarized in Table 3. The fractional acidity (FA) ratio indicates whether the acidity generated by strong acids (H_2SO_4 and HNO_3) is neutralized or not, with the value of 1 for non-neutralized precipitation.

Deviations from unity quantify the percentage of neutralization. The FA for the precipitation samples is 0.77 and for cloud water is 0.36, which is indicates that

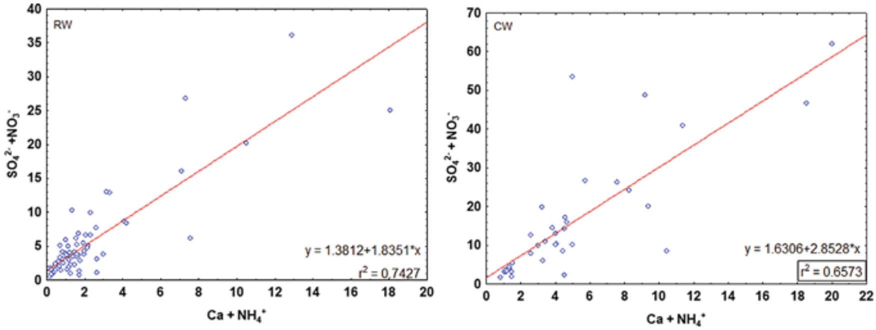

Fig. 7 Linear regression of sum (SO_4^{2-}, NO_3^-) and sum (Ca^{2+}, NH_4^+) in mgL^{-1} for RW (left) and CW (right) samples

Table 3 Mean fractional acidity (FA) and neutralization factor (NF) for precipitation (RW) and cloud water samples (CW)

	FA	NF_{Ca}	$NF_{NH_4^+}$	NF_{Mg}
RW	0.77	0.35	0.18	0.03
CW	0.36	0.52	0.16	0.03

there is not full neutralization of acidifying substance by alkaline constituents. This explained lower value of pH in this study.

The neutralization factors (NF) of Ca, NH_4^+, and Mg for RW samples were 0.35, 0.18, and 0.03 and for CW samples 0.52, 0.16, and 0.03, respectively. From these data it is obvious that the major neutralizing element is Ca followed by NH_4^+.

3.4 Long Range Transport Effects for Some Selected Periods

The origin of the air masses was examined by using back-trajectories from the model HYSPLIT for three periods: 19–20 March 2018, 30 June–4 July 2018 and 27-th of August 2018.

The synoptic situation during the period 19–20 March 2018 is characterised by Saharan outbreak towards the Balkans, associated with coloured rain and orange snow in many parts of Eastern Europe. At Cherni Vrah the arriving air masses were from south (S)-southwest (SW) (Fig. 8) on 19.03 (precipitation sample) and from West (W) on 20.03 (cloud water sample) (Fig. 8). From all analysed samples collected in 2018, the highest concentrations of Cl and Na were obtained in the precipitation samples from 19 March. The TIC of the precipitation sample was 64.1 mg L^{-1} with

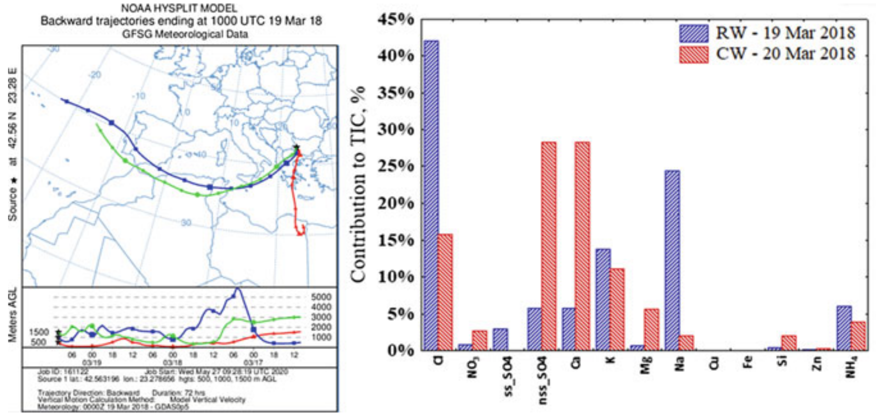

Fig. 8 Back-trajectories and contribution of different elements in precipitation and cloud waters samples for the period 19–20 March 2018

42% contribution of Cl, 24% of Na, 3% ss_SO_4^{2-} (sea salt SO_4^{2-}) and only 6% of the sulphates from anthropogenic source (nss_SO_4^{2-}) (Fig. 8). A significant difference in the SO_4^{2-} concentrations between RW and CW was observed.

The TIC of the cloud water sample on 20 March 2018 was 3.9 mg L^{-1} containing 28% nss_SO_4^{2-}, following by 28.3% Ca, 15.9% Cl and 11.1% K. These results indicated aged air masses with sea salt aerosols (Cl and Na) and mineral dust (Ca and Si) associated with Saharan origin. The coefficient of neutralization suggested Ca (0.36) as major neutralizing element in CW samples while the NH_4^+ ion (1.77) is for the precipitation sample.

The synoptic situation for the second period, 30 June–4 July 2018, was characterized by the influence of the slowly moving Mediterranean cyclone "Nefeli" crossing the country from south to northeast. The atmospheric conditions in the first part of the period were highly unstable with heavy rains and thunderstorms in many places in Bulgaria, while the end of the period was marked by increased surface pressure and occasional convective precipitations [22].

The TIC in precipitation sample collected on 30 June (48.5 mg L^{-1}) is higher than this for cloud water sample collected on 3 July (36.7 mg L^{-1}). The trajectory analysis shows that on 30 of June the transport of air masses to the Cherni Vrah is from north while they were from W, NW on 3 of July (Fig. 9). Generally, nss_SO_4^{2-} was found to be the dominant ion in both samples: RW (36%) and CW (43%). The contribution of NO_3^- and NH_4^+ ions in the CW sample (23 and 12%) were higher than in the RW sample (16 and 5%). The contribution of Ca is three times higher in the RW sample than observed in the CW sample. For this selected period the TIC is consisted mainly of nss_SO_4^{2-}, NO_3^-, NH_4^+ and Ca (RW-83% and CW-88%). The analysis of neutralization factors for precipitation samples showed that Ca is the most dominant neutralized element (0.63). This analysis for cloud water samples presented lower neutralization from NH_4^+ (0.18) followed by Ca (0.16).

The back-trajectory analysis for the 3rd case (27 of August 2018) shows that the transport of air masses to the sampling site were mainly from E, SE presenting influence from local or regional pollution sources. The synoptic situation for the country was characterized by a low-pressure system with very unstable atmospheric conditions. Frequent precipitations, somewhere also intense, were observed over the whole country. The TIC in this case is 5.5 and 63.3 mg L^{-1} for precipitation and cloud water samples, respectively. The most dominant ion in both types of samples was nss_SO_4^{2-} with very high contribution to the TIC (49.8% for CW and 36.2% for the RW). This high contribution of the sulphates is related probably to the main point emission sources of SO_2 located in south-east of Bulgaria. The second ion with high contribution to the TIC in RW was NO_3^- (26%) followed by Ca (15%). The contribution of NO_3^- to the TIC of CW is almost the same (27%). The contribution of NH_4^+ to the TIC of CW (2.7%) was lower than one for RW (9.9%). The analysis of neutralization factors in this case showed that Ca is the dominant neutralized element for RW and CW (Fig. 10).

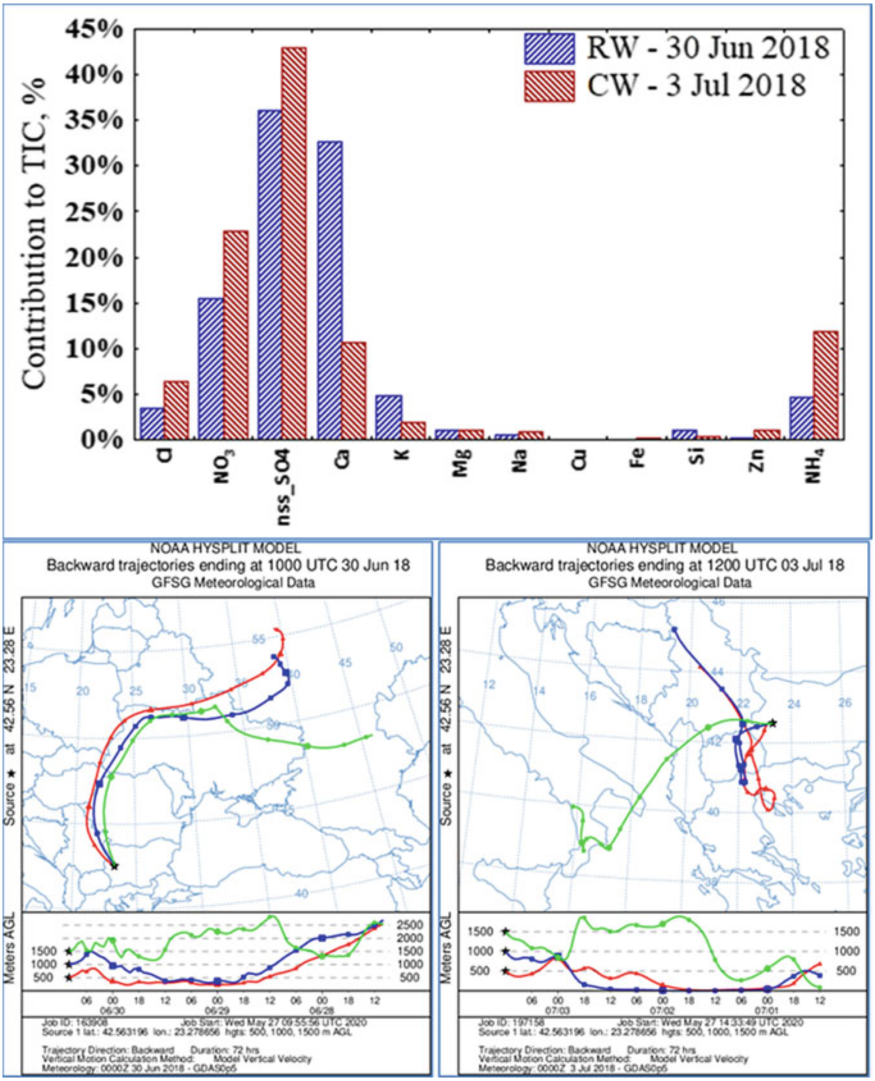

Fig. 9 Back-trajectories and contribution of different elements in precipitation (30 Jun 2018) and cloud water (3 Jul 2018) samples

4 Conclusions

New results for the chemical composition of precipitation (RW) and cloud water (CW) at the high-elevation site Cherni Vruh were presented. The results were based on 40 cloud and 78 rainwater samples collected and analysed in the period June 2017–November 2018. The comparison of the chemical content of the precipitation

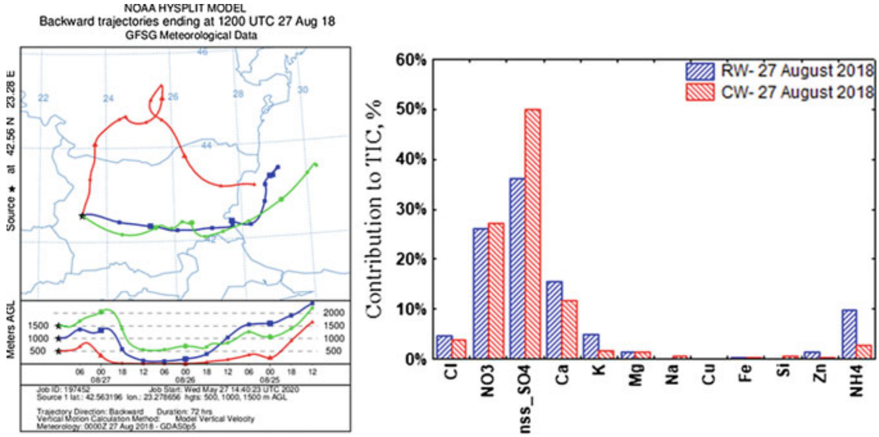

Fig. 10 Back-trajectories and contribution of different elements in precipitation and cloud water samples on 27 August 2018

and cloud water presented systematic differences concerning the pH, the electric conductivity, and concentrations of most elements. The frequency analysis showed that 100% of the cloud and 98% of the precipitation samples have pH value in the acidity range (<5.0).

Mean concentrations were generally higher in cloud water than in rainwater samples. The ion composition of RW and CW was dominated by NH_4^+, Ca, nss_SO_4^{2-} and NO_3^- accounting for more than 63 and 75% of the total ionic content. The obtained concentrations of nss_SO_4^{2-} in the cloud water samples are two times higher than those reported for mountain sites worldwide [2, 5, 8, 23]. The mean concentrations of NO_3 and NH_4^+ in the CW samples are lower than ones derived in [2, 23]. According the neutralization factors (NF) the dominant neutralizing acidity species were Ca and NH_4^+.

The study of the origin of the air masses contributed to better understanding of variations in the chemical composition and concentration levels for three specific cases in 2018. The cases were representative for different origin of the air masses approaching the sampling site, and were characterized by completely different total ionic concentration and concentration of all studied elements.

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