Proceeding of 1st International Conference on Environmental Protection and Disaster RISKs

Part One

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Part One of the proceeding book presents texts on the following topics: *Air Pollution, Climate and Health; Biodiversity; Informatics, Remote Sensing, High Performance Computing and GIS for Environmental Monitoring and Management*.

In Part Two of the proceeding book will be presented texts on the following topics: *Natural Hazards and Risks; Water Resources, Human Activities and Management.*

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Air Pollution, Climate and Health

CLOUD AND RAIN WATER CHEMICAL COMPOSITION AT PEAK CHERNI VRAH, BULGARIA

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Abstract. The purpose of the work is to present and discuss newly obtained data for the chemical composition of cloud water (CW) and rain water (RW) at a high-elevation site in Bulgaria. Sampling of CW and RW 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 NH_4^+, Ca, $nssSO_4^{2-}$ and NO_3^-, 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 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

INTRODUCTION

The atmosphere is an important environment in which different gaseous and aerosol species are transported. Cloud water (CW) and rain water (RW) 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 composition and cause ecological damage to ecosystems (Seinfeld and Pandis, 2006, Gioda et al., 2013). The chemical composition of CW and RW depends on pollutants emitted by sources of anthropogenic and natural origin, the dynamical processes in the atmosphere and 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 (Hůnová, et al., 2017, Mihajlidi-Zelić et., 2006).

Several authors worldwide have explored trends in the chemical composition of cloud and rain water since 1990 (Weathers, et al., 1988, Anderson, et al., 2006, Aleksic et al., 2009, Gioda et al., 2013 Schwab et al., 2016). At high-elevation environments, cloud and fog liquid water have generally been recognized as being more acidic than rainwater. In Bulgaria, precipitation chemistry in forest mountain areas was analysed occasionally during field campaigns related to depositions and critical loads to ecosystems (Zeller et al., 1998, Ignatova & Damyanova, 2012, Ignatova & Fikova, 2007). A few studies have focussed on analysis of meteorological conditions and the influence of air mass transport on the chemical composition of precipitations at peaks Cherni Vrah and Moussala (Iordanova & Blaskova, 2011).

In the last years, NIMH is conducting research activities on atmospheric depositions in Bulgaria including both numerical simulations and observational campaigns (Georgieva et al., 2015, Georgieva et al., 2018, Hristova et al, 2016, Hristova, 2017, Hristova &Veleva, 2015). 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.

METHODS

Site description

Vitosha Mountain is the first national park in Bulgaria and in the Balkan Peninsula. It is located on the outskirts 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 meteorological station from June 2017 to November 2018.

The cloud water is sampled by using a passive collector designed and constructed in NIMH (Fig.2a). All construction is made from plexiglas and sampling elements are made from fishing lines with length in total 180 m: 100m - ø1mm 80 m – ø0.5mm. 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

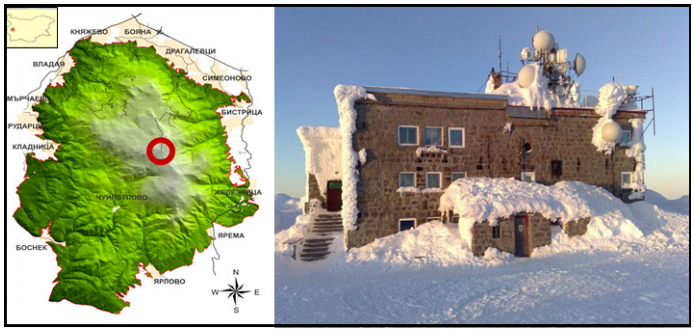
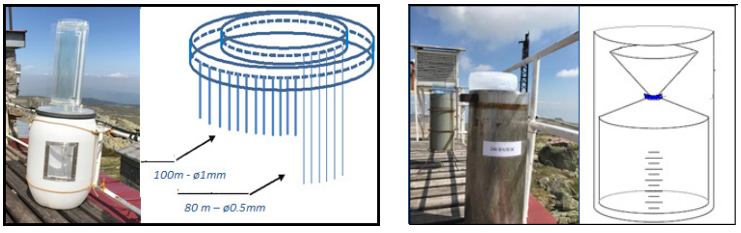


Figure 1. Map of Vitosha Mountain and synoptic station Cherni Vrah

samples were collected on an event basis, resulting in different time duration of typically about several hours.



a) b)

Figure 2. Samplers for (a) cloud water and (b) rain water

Manual (bulk) rain water sampler is used for sampling of rainwater samples (Fig.2b). The material of the collector is polyethylene terephthalate funnel of 20 cm in diameter and bottle with 5l capacity. The bulk sampler is washed every day with deionized water (<1μS.cm^{-1}) to avoid dry deposition. The RW samples were taken on daily basis.

Chemical analysis of cloud and rain water samples

All 40 cloud and 78 rainwater samples were analysed for acidity (pH), electro conductivity (EC), Cl-, SO_4^{2-}, NO_3^-, Ca, Mg, K, Na, Fe, Si, Zn, Cu, NH_4^+. 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 certified laboratory by Ion Chromatograph (ICS 1100, DIONEX)

for SO_4^{2-}, NO_3^-, Cl^- ICP OES (Vista MPX CCD Simultaneous, VARIAN) for Ca, Mg, K, Na, Fe, Si, Żn, Cu and Spectrophotometer S-20 for NH_4^+.

Table 1. Detection limits (*DL*) for all analysed elements

	Cl^-	NO_3^-	SO_4^{2-}	*Ca*	*K*	*Mg*	*Na*	*Fe*	*Si*	*Zn*	NH_4^+
DL, mg.l^{-1}	0.10	0.10	0.10	0.002	0.1	0.002	0.1	0.005	0.10	0.005	0.05

The detection limits for all analysed elements are presented in Table 1. The concentration of nss_SO_4^{2-} has been estimated by correction based on assumption that sodium is a sea salt tracer: $[nss\_SO_4^{2-}] = [SO_4^{2-}]-(0.25\times [Na])$, according to WMO GAW, 2004.

Trajectory analysis for long range effects

The origin of the air masses back-ward analysis was conducted using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT), (Stein et al, 2015, Rolph et al., 2017). Three different arrival heights were used: 500, 1000, 1500 m a.g.l (above ground level). The calculations were made for 72h using meteorological input from NCEP GDAS with horizontal resolution of 0.5° x 0.5°.

RESULTS AND DISDUSIONS

Physico-chemical parameters

The CW and RW pH values in this study ranged from 3.5 to 5.7 and the conductivity values from 0.7 to 202 μS cm^{-1}. The distribution of the relative pH and EC frequency for both types of samples are presented in Figure 3. This frequency analysis shows that 100 % of the cloud and 98% of the rain samples have pH value in the acidity range (Figure 3a). The highest percentage of pH values are in the range of 4.0 – 4.5 for both CW and RW (58% and 56%). Only 1.5% of the collected rain water samples are in the neutral range (5.5-6.0), there are not cloud water sample with pH value higher than 5.3. Around 10% of CW and RW samples have pH in the slightly acidic range (5.0 – 5.5), and 28% of RW pH and 18% of CW are in the 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 Figure 3b 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 have higher conductivities (0.7 – 202 μS cm^{-1}) than rain water (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 (Gioda et

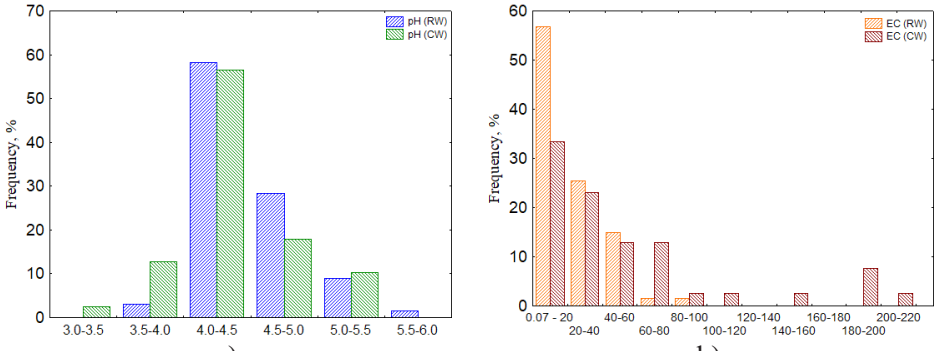


Figure 3. Frequency of pH (a) and EC (b) for cloud and rain water samples

al., 2013). The average EC values for CW and RW are 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. The total ionic content (TIC) of cloud and rain water samples is 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 is 16.5 mg l^{-1} and for RW samples is 6.2 mg l^{-1}. As

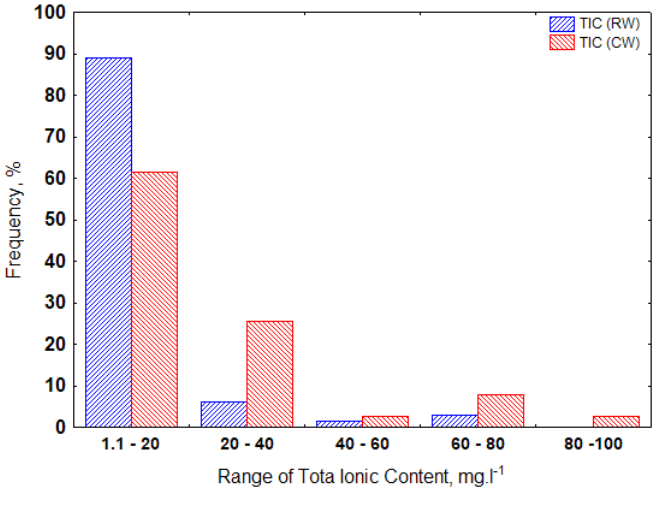
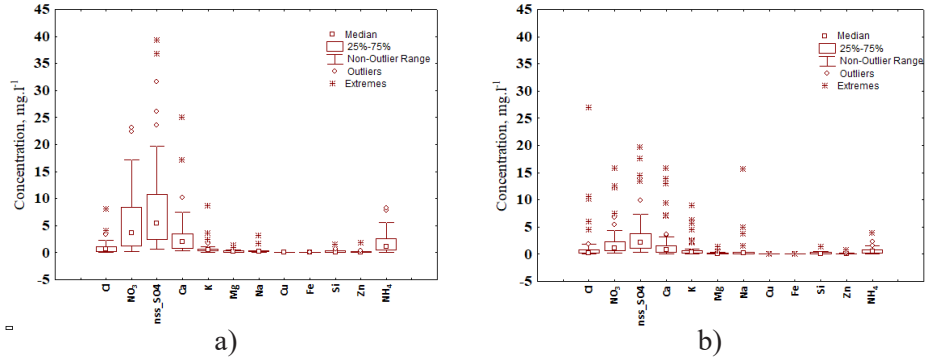


Figure 4. Frequency distribution of Total Ionic Content in cloud and rain water samples

shown by the frequency distribution of TIC in Fig. 4, a fraction of cloud and rain 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} is higher for the CW than for the RW (25% and 6%, respectively). Only 2.6% of the CW samples have TIC in the range 80-100 mg l^{-1}.

The variation in the concentrations of all studied elements is seen on the Box Plot presented in Fig.5. 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 are higher in cloud water than in rain water samples.



a) b)

Figure 5. Concentrations of the studied elements in (a) cloud water and (b) rain water samples

The concentrations of the main acidifying ions - SO_4^{2-} for the study period ranged from 0.6 to 39mg.l^{-1} for CW and from 0.3 to 20.3mg.l^{-1} for RW. Concentrations of NO_3^- vary from 0.15 to 23.1mg.l^{-1} for CW and from 0.18 to 15.8mg.l^{-1} for RW. NH_4^+ ion concentrations for CW and RW samples are ranged from 0.01mg.l^{-1} to 8.3mg.l^{-1} and from 0.03mg.l^{-1} to 3.9mg.l^{-1}. The lowest variations in concentrations were observed for Fe, Cu and Zn. Their concentration is ranged from 0.005 to 1.8mg.l^{-1}. High variation in Cl and Na concentrations are observed in RW samples. The obtained Cl concentration ranged from 0.05mg.l^{-1} to 27mg.l^{-1} and for Na from 01 mg.l^{-1} to 15.6mg.l^{-1}.

Long range transport effects for some selected periods

The origin of air masses was examined by using back-trajectories from the model HYSPLIT (Stein et al, 2015, Rolph et al., 2017) for two periods: 19 – 20 March 2018 and 30 June – 4 July 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 ChV the arriving air masses were from South (S)-Southwest (SW) (Fig. 6) on 19.03 (rain water sample) and from West (W) on 20.03 (cloud water sample) (Fig. 6). From all analysed samples collected in 2018, the largest concentrations of Cl and Na were obtained in the rain water samples on 19 March. The TIC of the rain sample is 64.1mg.l^{-1} with 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.6). A very large difference in the SO_4^{2-} concentrations between RW and CW is observed. The TIC of the cloud water sample on 20 March 2018 is 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.

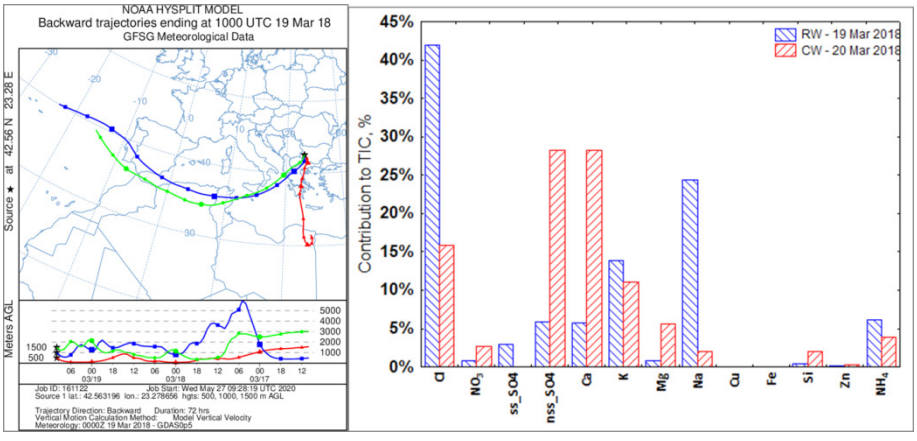


Figure 6. Back-trajectories and contribution of different elements in rain water and cloud waters samples for the period 19 – 20 March 2018

The synoptic situation for the second period, 30 June – 4 July 2018, is 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 (Monthly bulletin, 06 & 07, 2018). The TIC in rain 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 ChV is from North while they are from W, NW on 3 of July (Fig.7). 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

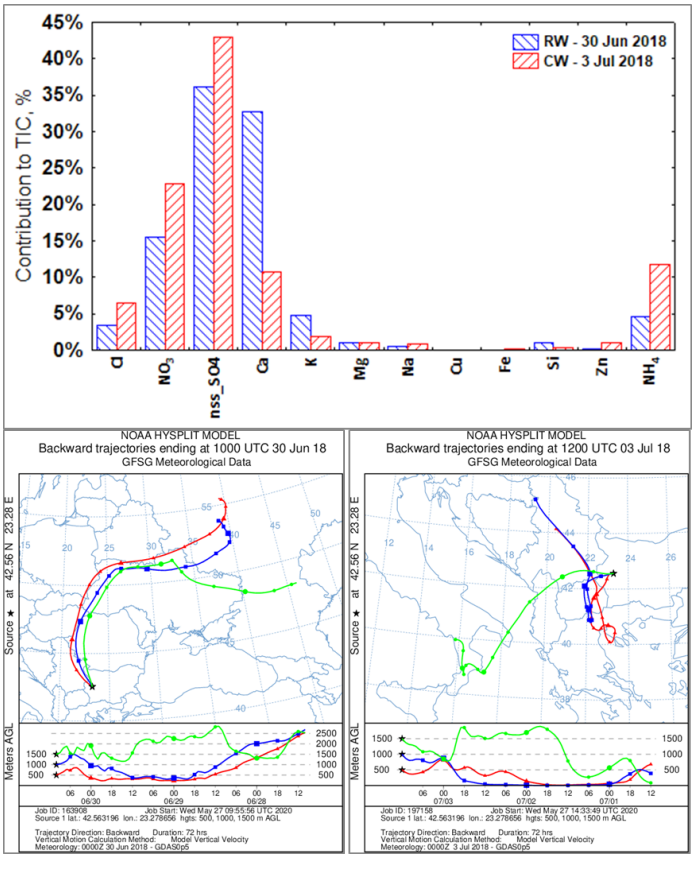


Figure 7. Back-trajectories and contribution of different elements in rain water (30 Jun) and cloud water (3 Jul) samples

(23% and 12%) are 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%).

CONCLUSIONS

New results for the chemical composition of cloud water (CW) and rain water (RW) 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 cloud and rain water presents 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 rain 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 various mountain sites by Marinoni et al., 2004, Schwab et al., 2016 and Gioda et al., 2013. The mean concentrations of NO_3^- and NH_4^+ in the CW samples are lower than ones derived in Marinoni et al., 2004 and Gioda et al., 2013. The study of the origin of the air masses contributed to better understanding of variations in the chemical composition and concentration levels in two specific cases in 2018.

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