EFFECT OF SAHARAN DUST INTRUSIONS ON PRECIPITATION CHEMISTRY IN BULGARIA

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Abstract: The objective of this work is to investigate the influence of Saharan dust events on the chemical composition of rain samples collected at three sites in Bulgaria during 2017-2018. Saharan dust intrusions were identified through a combination of satellite retrieved aerosol data and results from dust forecasting models and from backward trajectory model. The chemical composition of the samples (acidity pH, conductivity EC, main ions and elements) is analysed in view of the direction of the approaching air masses – "direct" influence (south-west), and "indirect" influence from other directions and regions, already impacted by Saharan dust. All samples were characterised by elevated values of pH (max 7.4), EC (max 202 $\mu S.cm^{-1}$) and Si, Ca, Fe, Mg concentrations. For cases with direct influence Si and Ca values were up to 1.5 and 25 $mg.l^{-1}$. In most of the indirect cases increased concentrations of sulphate, nitrate and ammonium were observed (up to 39.5, 23.1 and 8.3 $mg.l^{-1}$).

Key words: *precipitation chemistry, Saharan dust, field campaigns, dust models, satellite AOD*

INTRODUCTION

Sand and Dust Storms are recognized as hazardous meteorological events that impact the society in many ways – soil and agriculture, ecosystems, air quality and human health, aviation, visibility, solar power production and other socio-economical activities. These events present a unique form of natural hazard in that the source and the impact regions can be separated by great distances (Middleton et al., 2019). Mineral dust particles can be lifted by strong winds from bare dry soils into the atmosphere and being transported downwind affecting regions hundreds to thousand kilometers away. It is estimated that between 1000 and 3000 Tg of mineral dust is uplifted into the atmosphere annually, with Saharan desert being the largest global contributor (Prospero et al., 2002). The atmosphere of the Mediterranean Basin is highly influenced by the Sharan Dust intrusions, as two of the main transport paths of the emitted dust particles is northward to Europe, and eastward to Middle East (Goudie and Middleton, 2006).

The airborne dust particles are removed from the atmosphere by settlement (dry deposition) or are washed out by rains (wet deposition). The last mechanism is prevailing for fine grained particles and distances far-away from the source regions (Stuut et al., 2009). There are various effects of the deposited dust particles: they are capable of modifying the soil properties, can act as fertilizes in marine ecosystems (Maher et al., 2010) and can neutralize atmospheric acidity and reduce acid rains (Rogora e al., 2004).
Although Saharan dust events are detected with higher frequency in the Mediterranean countries and southern Europe, other northern and central parts of the continent are also influenced (Klein et al., 2010, Varga et al., 2013). The Balkans are not regarded as a dusty region, but the location in the so called D1B zone of the Saharan dust-fall map (Stuut et al., 2009) implies that Saharan dust can be incorporated in the soil system and change its structure.

The frequency of Saharan Dust outbreaks for Bulgaria is about 20% over annual days, as estimated by 10 years data for PM10 concentrations at the regional background station Rozhen (Pey et al., 2013). The maximum of Saharan outbreaks towards Bulgaria is in spring and autumn, as found in a recent study based on satellites data for the period 2005-2018 (Dimitrova et al., 2019). This study indicates that on average the days with Saharan outbreaks are 10-13 for the months March, April, May, and can be 20 and more for the same months in specific years. As in Bulgaria during spring also the precipitations are frequent, it could be expected that their chemical composition is influenced by Saharan dust. At the National Institute of Meteorology and Hydrology (NIMH) a monitoring network for acidity of precipitations has been established (Hristova, 2017). In the last years the chemical analysis of the rain water samples was extended (including main ions, macro and microelements) giving thus possibility to investigate also the characteristics of precipitation chemistry during Saharan dust outbreaks in the country.

The purpose of this study is to analyse the influence of Saharan dust on the chemical composition of rain samples collected at three sites in Bulgaria during field campaigns in 2017-2018. Another objective is to discuss precipitation chemistry in view of typical pathways of the dust loaded air masses.

METHODOLOGY

The procedures used for the collection of precipitation samples and their chemical analysis, as well as the methods applied for identification of Saharan dust intrusions are briefly outlined.

Precipitation samples and their chemical analysis

The collection of precipitation samples was organised during field campaigns in 2017-2018 at three meteorological stations located in different environment (Fig. 1). Two of the stations are in the western part of the country: urban one - Sofia-NIMH (42.655 N, 23.384 E, 586 m asl), and a mountain one – peak Cherni Vruh (42.6167 N, 23.2667 E, 2286 m asl). The third station is rural one in southeast Bulgaria near the Black Sea coast - Ahtopol (42.084 N, 27.952 E, 26m asl). Daily precipitation samples in Sofia and Ahtopol were collected with an automatic wet only device (WADOS), at Cherni Vruh a passive bulk sampler was operated, made of polyethylene terephthalate funnel that was washed every day with deionized water to avoid dry deposition.

Figure 1. Geographical map of Bulgaria with sampling sites
(orange square – Sofia, blue triangle – Cherni vruh, red circle – Ahtopol)

The collected samples were further analysed for acidity-pH, conductivity-EC, main anions Cl^-, SO_4^{2-}, NO_3, cation NH_4^+ and elements Na, K, Mg, Ca, Fe, Si, Zn, Cu. More details and detection limits for the analysed elements are given in Hristova et al., 2020.

Identification of Saharan Dust intrusions

A combination of modelling results and observational data were used in order to identify the days characterised by Saharan dust outbreaks in Bulgaria in 2017 and 2018. For all the dates with available precipitation chemistry data at the three stations, an analysis was carried out, involving the following information:

a) Results for dust optical depth, dust surface concentrations, dust dry and wet depositions forecasted by the models at the Barcelona Supercomputing Centre (BSC) - BSC-DREAM8b (Basart et al., 2012) NMMB/BSC-Dust (Pérez et al., 2011), horizontal resolution 0.3° x 0.3°;

b) Results for aerosol optical depth and dust surface concentrations, forecasted by the ensemble model at the World Meteorological Organization Sand and Dust Storm Warning Advisory and Assessment System (WMO SDS-WAS) Regional Center for Northern Africa, Middle East and Europe on a grid with resolution 0.5° x 0.5°;

c) Results for the dust and total aerosol optical depth at 550nm, and PM10 concentrations forecasted by the global CAMS-ECMWF model (Benedetti et al., 2009), over Europe on a grid resolution 0.125° x 0.125°, available through the Copernicus Atmosphere Monitoring Service (CAMS);

d) Result for dust and PM10 over Europe by the CAMS regional air quality ensemble model, with horizontal resolution 0.1°x0.1° (Marécal et al., 2015);

e) Maps based on multi-model results at global scale with resolution 0.1°x0.1° at the Marine Meteorology Division of the Naval Research Laboratory, USA (NRL), (Xian P. et al., 2019);
f) HYSPLIT air mass backward-trajectories (Stein et al, 2015, Rolph et al., 2017) calculated at three arrival heights (500, 1500 and 3000m agl.) for 96 hours, using NCEP GDAS meteorological input with resolution 0.5° x 0.5°, and reanalysis data ;
g) Satellite data for AOD (level 3 MODIS Terra&Aqua globally on a grid 0.1° x 01°), for Aerosol absorbing index and Dust optical depth from MetOP satellites;
h) Observed particulate matter (PM10) concentrations at two background rural stations in mountain areas in BG – Kopitoto (BG0070A) and Rozhen (BG0053R).

RESULTS AND DISCUSSION

Selected dates and samples

The analysis of the origin of the dust loaded air masses indicated that the daily precipitation samples can be grouped into two main categories – with "direct" influence, i.e. approaching flow from southern directions, mainly from south-west, and with "indirect" influence, associated with other directions and respective regions, already impacted by Saharan dust. Table 1 presents details for the samples analysed in this study and the type of influence attributed to them.

Table1. Date, location and type of influence for the precipitation samples used in this study, A- direct influence, B – indirect influence

No	Date	Sofia	ChVruh	Ahtopol	Type
1.	04.06.2017			+	A
2.	06.06.2017		+		A
3.	03.07.2017		+		B
4.	04.07.2017			+	B
5.	20.09.2017		+		A
6.	07.02.2018	+			A
7.	08.02.2018			+	A
8.	02.03.2018	+			A
9.	05.03.2018			+	A
10.	06.03.2018	+			A
11.	19.03.2018		+		A
12.	20.03.2018		+		A
13.	20.03.2018			+	A
14.	21.03.2018	+			A
15.	22.03.2018	+			A
16.	23.03.2018	+			B
17.	23.03.2018			+	B
18.	28.03.2018			+	A
19.	06.04.2018	+			A
20.	16.04.2018	+			A
21.	24.04.2018	+			B
22.	24.04.2018		+		B
23.	05.05.2018	+			B
24.	10.06.2018	+			B
25.	15.06.2018			+	B
26.	30.06. 2018		+		B

Examples for type A and type B of Saharan Dust outbreaks

Some of the analysed maps and precipitation chemistry data are shown as example for two cases for the types A and B influence of dust loaded air masses. The first case (16.04.2018) is characterized by Saharan flow from south-west (Fig. 2). The second case (30.06.2018) is a situation with north and north-westerly intrusion towards Bulgaria, but the regions in Central and Western Europe were impacted by Saharan dust few days before (Fig. 4). The chemical composition for precipitation samples for these cases is shown in Fig. 3 and Fig. 5.

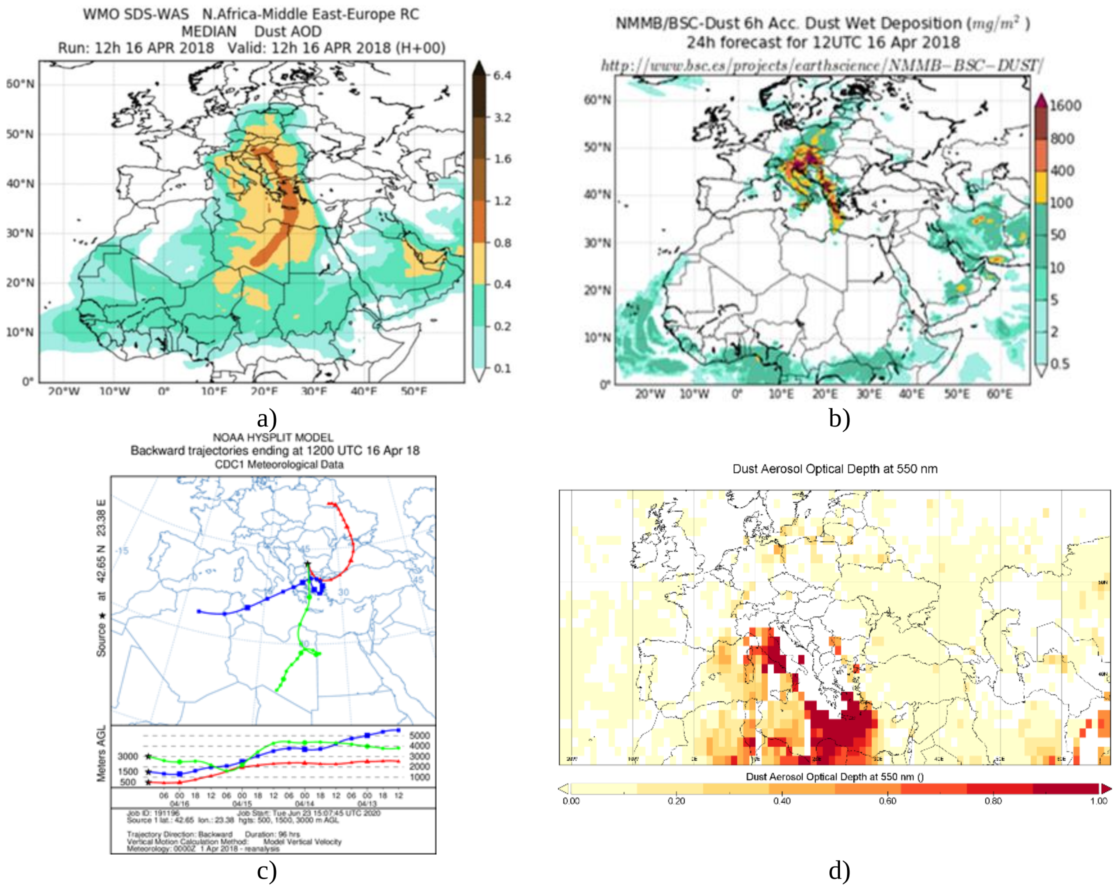

Figure 2. Case 16.04.2018 a) Dust AOD from SDS-WAS ensemble model; b) Dust wet deposition from NMMB/BSC-Dust model; c) HYSPLIT back trajectories, and d) Dust AOD a from IASI instrument on MetOpA

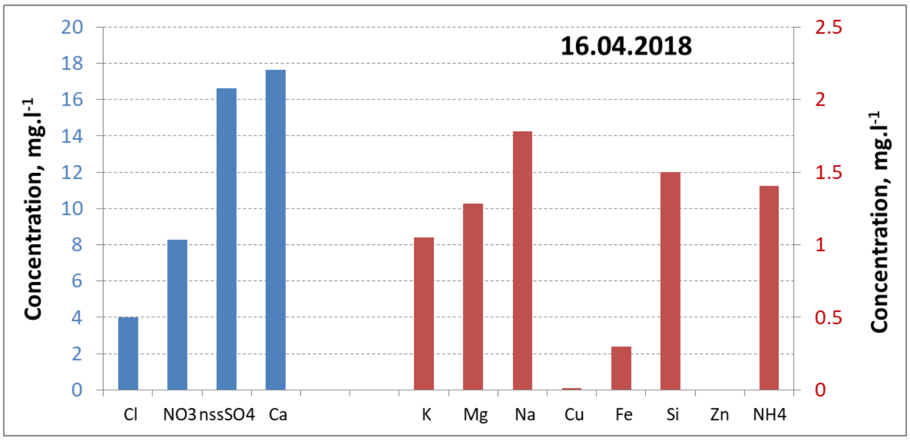

Figure 3. Concentrations of elements in precipitation sample from Sofia on 16 April 2018

For the first case the total ionic concentration (TIC) in the precipitation sample is 54.1 $mg.l^{-1}$, and consisted from 79% of elements: $nssSO_4^{2-}$, NO_3^- and Ca. The pH and EC values of this sample are very high (7.4 and $132.7 \mu S.cm^{-1}$). The most abundant element is Ca followed by $nssSO_4^{2-}$ and NO_3^-. The concentrations of Si, K and Mg are also high with contribution to the TIC of 3%, 2% and 2%, respectively. The contribution of NH_4^+ is 3%.

The second case (30.06.2018) was characterised by more complex synoptic situation some days before. The models suggest that dust might has been transported the preceding days towards the Black Sea. Satellite data are limited in Eastern Europe due to cloudiness, Fig. 4.

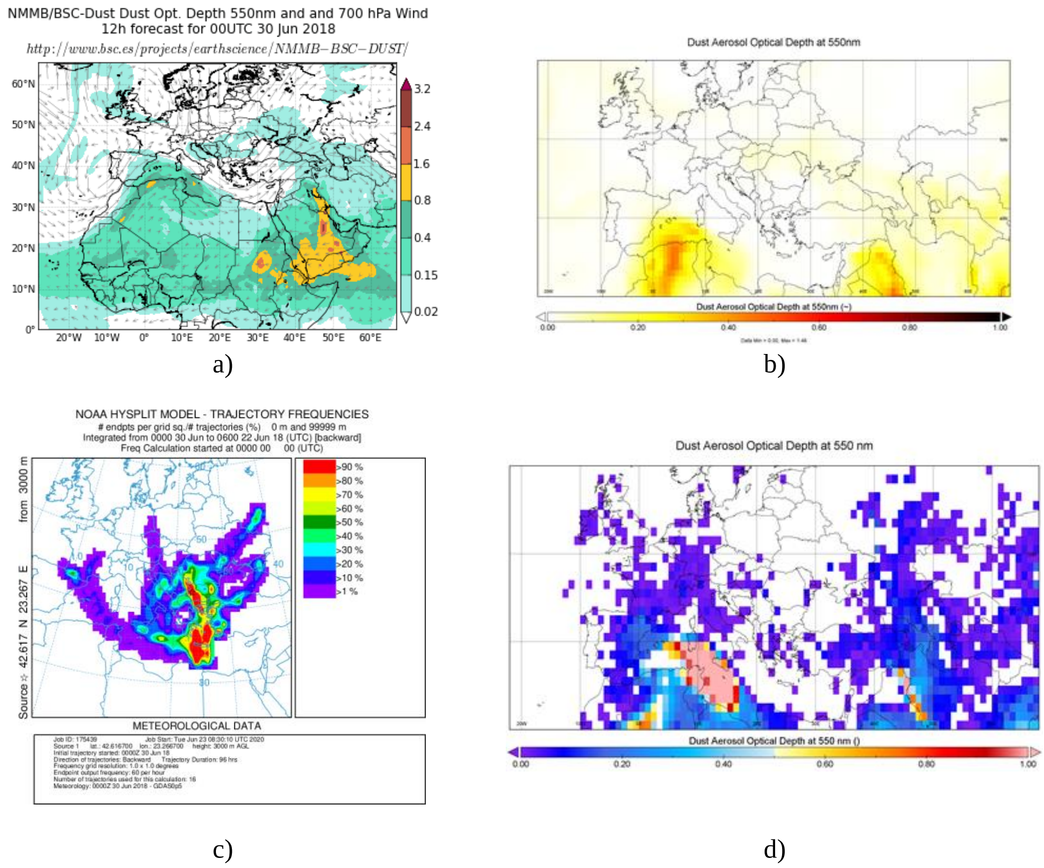

Figure 4. Case 30.06.2018 (type B) – a) Dust AOD from NMMB/BSC-Dust model; b) Dust AOD from CAMS-ECMWF model on 29.06.18 at 18h; c) HYSPLIT frequency of back trajectories (22-30.06.18), and d) Dust AOD from IASI instrument on MetOpA on 30.06.2018

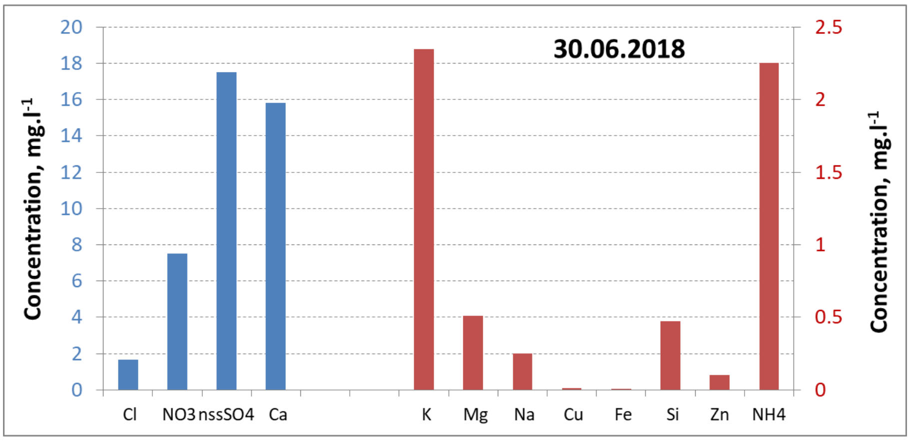

Figure 5. Concentrations of elements in precipitation sample from Cherni Vrah on 30 June 2018

The chemical analysis of the precipitation sample in this case shows high concentrations of $nssSO_4^{2-}$, Ca, K and NH_4^+. The measured pH and EC are 4.9 and 50μS.cm^{-1}. The TIC is 48.5 mg.l^{-1} composed from 84% of elements: $nssSO_4^{2-}$, NO_3^- and Ca. The contribution of NH_4^+ is 5% and Si is only 1%.

Precipitation chemistry analysis

We present here some statistical parameters for pH and EC, precipitation chemistry elements and TIC, for samples defined as A and B (Table 2).

Table 2 Statistics (mean, standard deviation, minimum and maximum) for the samples in A (N=16) and B (N=10)

Element mg.l^{-1}	Mean A	SD A	Min A	Max A	Mean B	SD B	Min B	Max B
pH [-]	5.5	0.9	4.1	7.4	5.5	0.5	4.7	6.2
EC [uS/cm]	38.7	34.1	16.4	132.7	29.8	22.5	7.4	76.0
Cl	4.55	7.04	0.44	26.94	1.67	1.93	0.11	6.41
NO3	3.09	3.96	0.17	15.83	4.52	4.84	0.88	15.75
SO4	5.91	5.54	1.67	20.28	5.93	5.45	0.41	17.55
nssSO4	5.64	5.40	1.59	19.70	5.88	5.44	0.41	17.52
Ca	3.89	4.66	1.07	17.66	4.59	5.03	0.75	15.83
K	1.20	2.37	0.08	8.87	0.79	0.74	0.23	2.35
Mg	0.46	0.42	0.14	1.40	0.34	0.24	0.06	0.86
Na	2.40	4.27	0.11	15.64	0.48	0.86	0.10	2.60
Cu	0.02	0.02	0.01	0.05	0.01	0.00	0.01	0.01
Fe	0.06	0.09	0.01	0.30	0.02	0.02	0.00	0.05
Si	0.28	0.36	0.06	1.50	0.24	0.16	0.07	0.55
Zn	0.11	0.24	0.01	0.81	0.05	0.04	0.01	0.11
NH4	0.90	1.00	0.13	3.90	0.92	0.80	0.06	2.33
TIC	22.28	22.28	6.58	68.87	18.72	16.95	2.53	48.50

The pH values ranged from 4.1 to 7.4. The analysis of the distribution of the relative pH frequency for both categories (A and B) showed that 40% of the precipitation samples in A are in the acidity range (pH < 5.0), 6.7% are in the slightly acidic range (5.0 – 5.5) and 6.7% are in the alkaline range (> 7.0). The pH frequency analysis for B samples showed that in 30% pH was in the range 4.5-5.0, 10% were in the slightly acidic range, and 20% were in slightly alkaline range. pH value higher than 6.2 were not observed for B samples. pH values in the neutral range are observed in 40% for B samples, and in 33% for A samples. The mean pH value for both groups of samples from Sofia is 6.05 and is higher than the average multiyear pH (5.12) estimated from the precipitation chemistry network for the period 2002-2019. The same is observed for the samples from Ahtopol – mean for both groups pH is 5.34, while the multiyear one is 5.16.

The contribution of different elements in both A and B samples to the total ionic concentration is presented in Fig. 6. The most abundant ionic species for samples in both categories was $nssSO_4^{2-}$, followed by Cl and Ca for A category, and Ca and NO_3^- for B category.

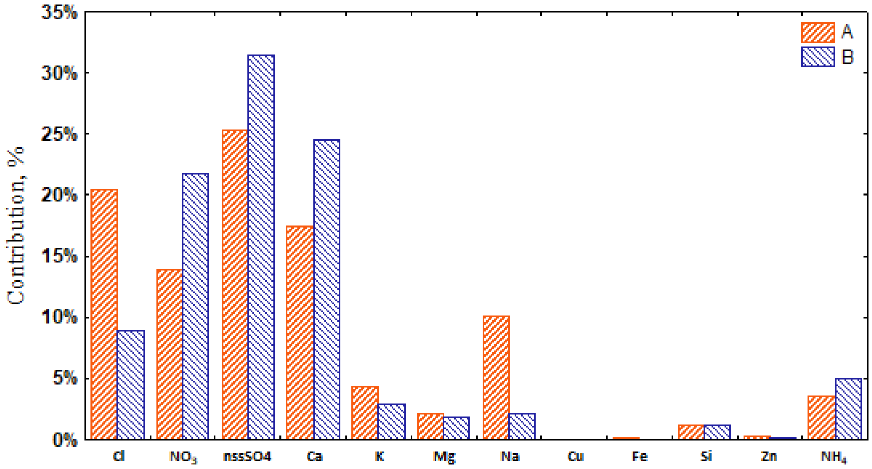

Figure 6. Contribution of different elements in precipitation samples for both categories (A and B)

The total ionic concentration in both A and B samples consist mainly of $nssSO_4^{2-}$, NO_3^- NH_4^+ (A - 44% and B - 58%). For A (flow mainly from south-west) the air masses passing over the Mediterranean Sea are enriched with sea salt aerosol. The evident high correlation of the elements Cl and Na (0.99) conferred this. 31% of the TIC consist of Cl and Na. The percentage of terrigenous elements (Ca, K, Mg and Si) of the TIC in the A samples is 23.3%. High correlation is obtained also for Ca/Si (0.90) and Ca/Fe (0.84).
The higher contribution of sulphates, nitrates and ammonium ions in B samples can be explained by the enrichment of air masses with substances of anthropogenic origin. Very high correlations were found for $nssSO_4^{2-}$ and Ca (0.91) and Ca/K (0.95), indicating that the main source of those ions are from terrigenous origin (e.g. gypsum - CaSO4) (Conradie et al., 2019). 30.4% of the TIC consist of Ca, K, Ma and Si.
The t-test performed for the mean elemental contributions in the two groups returned a value of 0.035 for the two-tailed p- value indicating, thus, to statistically significant differences between the two groups. Having in mind that the samples are low in number, we recognize that more robust statistical tests should be based after collecting and analyzing more precipitations samples in different synoptic situations.
The chemical analysis of all samples confirms that the precipitation associated with dust intrusions is characterized by higher concentrations of terrigenous elements. In both types of intrusions the correlation between $nssSO_4^{2-}$ and Ca is relatively high, indicating similar source of origin. For B samples this correlation ($nssSO_4^{2-}$/Ca) is lower, but correlations between $nssSO_4^{2-}$ and NH_4^+ (0.7) , and NO_3^- and NH_4^+ (0.9) indicate contribution from secondary formed aerosols ($(NH_4)_2SO_4$ and NH_4NO_3).

CONCLUSIONS

We have analysed the influence of Saharan dust events on the chemical composition of 26 rain samples collected at three sites in Bulgaria during 2017-2018. The samples were divided into two groups with respect to the direction of the approaching dust loaded masses: A (direct influence) and B (indirect influence). Common features for all samples were elevated values of pH (max to 7.4), EC (max to 202 $\mu S.cm^{-1}$) and Si, Ca, Fe, Mg concentrations. The concentrations of Si and Ca were significantly higher (up to 1.5 and 25 $mg.l^{-1}$) for A samples. In B samples higher concentrations of sulphates, nitrates and ammonium ions suggest enrichment of air masses with anthropogenic pollutants. The preliminary results, presented here, show that the trajectory of the air masses is an important factor for the chemical composition of precipitations in Bulgaria. Additional data from samples are needed to extend the analysis and perform more robust statistical estimates.

ACKNOWLEDGMENTS

This study was inspired by COST16202 "inDust", and was partially funded by the Bulgarian National Science Fund trough contract N. DN-04/4-15.12.2016, and the European Space Agency through contract No. 4000124150/18/NL/SC. The Copernicus Atmosphere Monitoring Service is acknowledged for providing analysed and forecasted model data on atmospheric chemistry. We are thankful also to Barcelona Supercomputing Center, WMO SDS-WAS NA ME E Center and the Marine Meteorology Division of U.S. Naval Research Laboratory for providing archives of modelled dust products.

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