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RELATIONSHIP BETWEEN PHYSICO-CHEMICAL PARAMETERS OF PRECIPITATIONS AND WIND DIRECTION AT BULGARIAN COASTAL SITE

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ABSTRACT

Precipitation chemistry has been intensively studied worldwide mainly due to acid deposition, eutrophication, trace metal deposition, damages to forests and vegetation, ecosystem health, and global climate change [1]. The objective of this study is to investigate the relationship between precipitation pH and wind direction for the period of five years (2015-2019) at coast Hydrometeorology station Ahtopol. The pH of bulk precipitation samples, as well as the wind direction are measured in the main synoptic terms (00, 06, 12, 18 UTC). The frequency analysis for pH data showed that 79% are in the acidic range, 14% are weakly acidic and only 3% is neutral and alkaline. The analysis of wind direction in the precipitation cases indicates that 60% of wind directions are from N, NW, NE; 32% are from SW,SE, W, E and 8% of precipitation cases are during wind speed less 0.3 m/s. The acidification potential of precipitation is usually due to the presence of H_2SO_4, HNO_3 and organic acids [2, 3], and the neutralization of these species occurs in the presence of NH_3 and $CaCO_3$. Therefore, daily wet only precipitation samples were collected for chemical analysis for selected period in 2017. Those samples are analyzed immediately for acidity (pH) and conductivity (EC) and further for main anions and cations (Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Ca, Mg, K, Na, Fe, Si, Zn). Mean concentration of analyzed elements in precipitation samples followed the order: $Cl^- > Na > SO_4^{2-} > NO_3^- > Ca > K \sim Mg > NH_4^+ > Zn > Si > Fe > Cu$. For selected periods with elevated concentrations of specific ions, the effect of wind direction, and long-range transport processes are presented and discussed.

Keywords: precipitation chemistry, acidity, wind direction, long-range transport

INTRODUCTION

The problem with acid precipitation has been identified as a major environmental problem in Europe and North America in the 1960s and 1970s associated with significant atmospheric pollution by reactive gases such as sulphur dioxide and nitrate dioxide, and their transformation into acids [1, 2] The deposition of sulfate, nitrogen and ammonium ions has a negative impact on vegetation and water surfaces, as well as on buildings of cultural and historical significance. The study of acid rain (wet deposition of nitrates and sulphates), the deposition of other substances and heavy metals became one of the most significant studies in the last decade [3]. Nowadays, with the sharp reductions of sulfur oxides (SO_x) emissions in Europe, nitrogen oxides and ammonia (NO_x and NH_3) are the main acidifying compounds in Western and Northern Europe, although emissions of SO_x have higher acidifying potential and are still contributing to

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acidification [4]. One of the main reasons is that the reduction of sulfur emissions (mainly from solid fuel power plants) does not lead to the same extent to the reduction of acidification deposits, which has focused the attention of researchers in recent years on transboundary transport of pollutants, emissions from shipping and agriculture and a more in-depth study of the deposition of nitrogen compounds. The emphasis in a several studies on the territory of Bulgaria is often on clarifying only part of the processes that determine the composition of atmospheric air and/or the chemical composition of precipitation. Some studies look only at urban areas where there is a significant impact of pollutants of anthropogenic origin [5-7], while others look at areas remote from large cities - most often mountainous and coastal areas [8-10].

The objective of this study is to investigate the relationship between precipitation pH and wind direction for the period of five years (2015-2019) as well as the precipitation chemical composition at coast Hydro-meteorology station Ahtopol. The selected study area is located in the Strandzha Mountains, the largest nature park in Bulgaria, characterized by rich biodiversity which protection is extremely important.

MATERIALS AND METHODS

Sampling, site location and data analyses

The sampling was carried out at hydrometeorological station (HMS) Ahtopol, located in the south-eastern part of the Bulgarian Black sea coast region (42.084 N and 27.951E), (80 km south-east of Burgas) (Fig.1). The site is about 400 m inland and 30 m in height above sea level located. The HMS Ahtopol is one of the 35 stations of the monitoring precipitation chemistry network in the National Institute of Meteorology and Hydrology. Bulk precipitations samples are collected every 6 hours in the main synoptic hours – 00, 06, 12, 18 UTC and pH is measured on-site at the time of sampling.

Figure 1. Map with the sampling location (HMS Ahtopol) and automatic sampler WADOS

Because the fact that the acidification of precipitation is primarily related to the emissions of acidic species such as SO_2 and NO_x in the atmosphere, as these gases are the precursors of major acids H_2SO_4 and HNO_3 [1], investigation of chemical composition of precipitation is very important. That is why in this work we have analyzed the data from the chemical composition of precipitation for the period June to December 2017. In this period, 24 hour, wet-only samples were collected with automatic sampler WADOS (Kroneis GmBH). After every rain episode, the sampling set was cleaned with deionised water, and the bottle was replaced with a new one. The collected samples are further analyzed 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^+. The pH and conductivity (EC) are measured in the HMS Ahtopol with portable pH and EC meters Hanna Instruments.

RESULTS AND DISCUSION

Relationship between precipitation pH and wind direction

In this section five years (2015 to 2019) data for precipitation pH and wind directions are summarized. During the study period 595 precipitation samples were collected and analyzed for pH. As a first step in the analysis, the frequency of pH for different groups depending on the type: acidic, neutral or alkaline was made. The scale for the acid-alkaline composition of the precipitations is evaluated as follows: pH 4-5.0 - acid, 5 - 5.6 slightly acid, pH = 5.6 - neutral, pH> 5.6-6 slightly alkaline, pH> 6 – alkaline. The spatial distribution of pH frequency in precipitation samples in HMS Ahtopol for the study period is presented on Fig. 2. More than 79% of the precipitation samples have pH value in the acid range, 14% are in the range 5.0 - 5.6 (slightly acid), 3% of the samples are between 5.6 – 6.0 and under 6% are in the range > 6 (alkaline range).

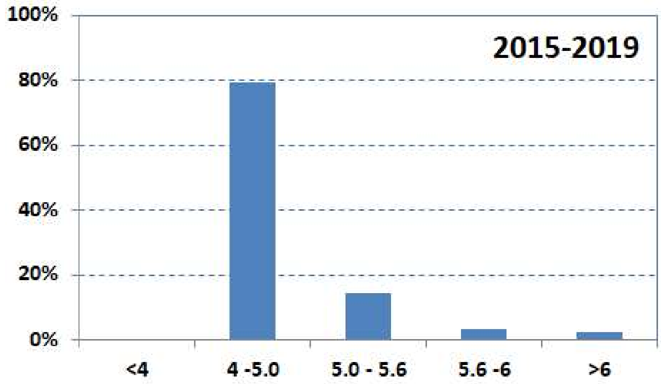

Figure 2. Distribution of pH frequency in precipitation samples in HMS Ahtopol for the period 2015 – 2019

Distribution of the frequency of the wind direction during precipitation events as well as the average value of precipitation pH for all wind directions in HMS Ahtopol for the period 2015 – 2019 are illustrated on Fig. 3.

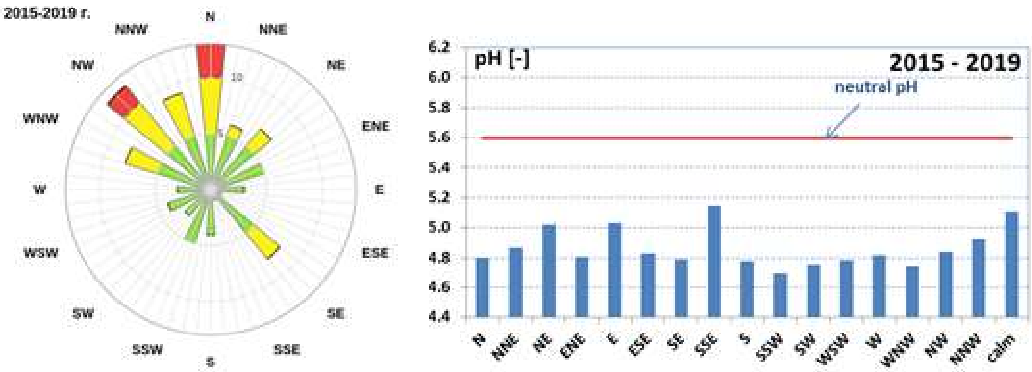

Figure 3. Distribution of the frequency of the wind direction in case of precipitation (right) and average values of precipitation pH for all wind directions (left) in HMS Ahtopol for the period 2015 – 2019

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The results show that the wind directions with highest percentage are from north (N) and northwest (NW) - (12-13%), followed by north-northwest NNW - 9%, calm (wind speed < 0.2), west-northwest (WNW) and southeast (SE) - 8%. The lowest percentage values are for wind with directions east-southeast (ESE) and south-southeast (SSE) - 1%. The analysis of the average precipitation pH values in relation with wind direction for the entire study period showed that in the range of weakly acidic (from 5.0 to 5.6) are the precipitation during wind direction from E, NE, and SSE. The precipitations during cases with wind direction ENE, ESE, N, NNE, NNW, NW, S, SE, SSW, W, WNW and WSW are with pH in the acidic rage (below 5.0).

Relationship between precipitation physic-chemical composition and wind direction

This part presents the results of the analysis of physicochemical parameters of precipitation in Ahtopol for a selected period June - December 2017. The obtained data and statistical information from chemical analysis are summarized in Table 1. It can be seen that Cl^- have the highest average concentration, followed by Na > SO_4^{2-} > NO_3^- > Ca > K ~ Mg > NH_4^+ > Zn > Si > Fe > Cu. The influence of marine aerosol on the precipitation composition is significant and is expressed in high concentrations of the elements Na and Cl^-. The concentration of SO_4^{2-} is also affected from the marine aerosol and requires a sea salt correction. The concentration of sulphates from anthropogenic origin (nss_SO_4^{2-}) was obtained by the following equation: $[nss\_SO_4^{2-}] = [SO_4^{2-}] - (0.25\times [Na])$ [11]. The results showed that 29% of the sulphate samples in HMS Ahtopol are from marine origin.

Table 1. Concentrations of the analyzed elements (mg.l^{-1}), pH (-), EC (μS.cm^{-1}), standard deviation (SD) and number of samples (n) with concentration above detection limit (DL)

	Min	Max	Mean	SD	n, >DL
pH	4.40	7.30	5.73	0.75	21
EC	11.30	87.80	32.35	18.57	19
Cl^-	0.25	35.74	6.11	9.58	21
NO_3^-	0.35	5.41	1.65	1.30	21
SO_4^{2-}	0.59	9.15	2.58	2.22	21
nss_SO_4^{2-}	0.52	7.68	1.84	1.60	21
Ca	0.11	2.40	0.84	0.75	21
K	0.10	1.11	0.46	0.30	19
Mg	0.04	2.17	0.46	0.60	21
Na	0.11	16.99	2.97	4.77	21
Cu	0.01	0.02	0.01	0.01	3
Fe	0.01	0.03	0.02	0.01	12
Si	0.07	0.14	0.11	0.03	7
Zn	0.01	0.78	0.15	0.19	18
NH_4^+	0.06	2.30	0.45	0.54	20

Distribution of the frequency of the wind direction and wind seed during precipitation events in the period June-December 2017 are illustrated on Fig. 4. It shows that the highest frequency of wind direction (19%) is from north-northeast (NNE), followed by WNW, NW, SW (14%), NNW, WSW and NE (10%).

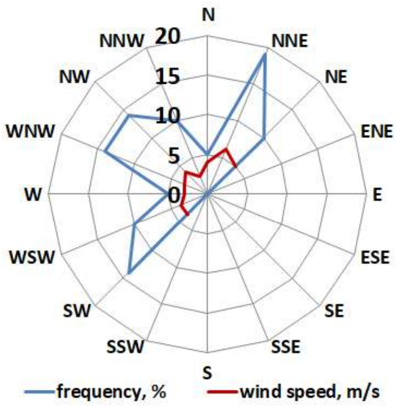

Figure 4. Wind rose for the precipitation events during period June-December 2017

The concentrations of NO^{3-}, SO_4^{2-}, $nssSO_4^{2-}$ (left) and Cl, Na (right) in relation with wind direction are presented in Fig. 5. The highest average concentrations for all elements are obtained for precipitation during wind directions from north-northeast (N-NE). On the next figure (Fig.6) are given the average concentrations of elements (left - calcium and ammonium ions; right - silicon) that could neutralize precipitation or will make it alkaline.

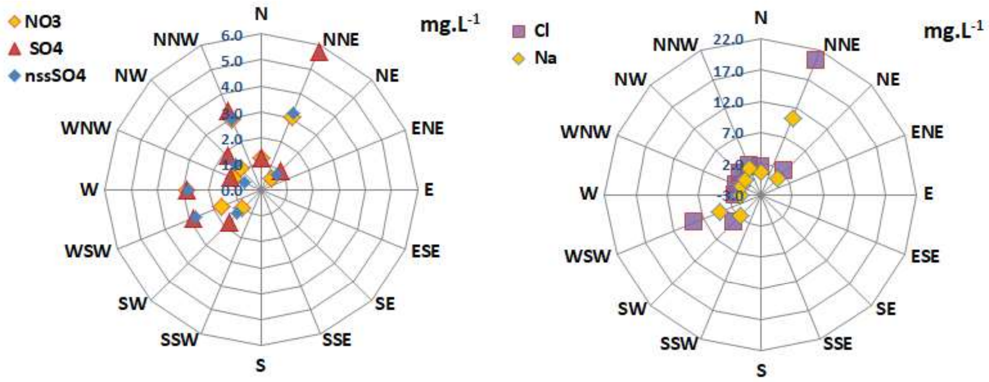

Figure 5. Concentrations of NO^{3-}, SO_4^{2-}, $nssSO_4^{2-}$, (left) and Cl-, Na (right) in relation with wind direction

On the next figure (Fig.6) are given the average concentrations of elements (left - calcium and ammonium ions; right - silicon) that could neutralize precipitation or will make it alkaline. The highest concentration of ammonium ions is obtained for the cases when the wind direction is from north-northwest (where the agricultural areas of Ahtopol are located). The main source of ammonium ions in the air are agricultural activities. Ammonium ions are also part of the secondary aerosols in the form of $(NH_4)_2SO_4$, NH_4NO_3, which can be transported on long distances [1, 12]. The highest concentration of ammonium ions was determined in the precipitation sample from 19 November 2017. The same sample has high concentrations of sulfates and nitrates.

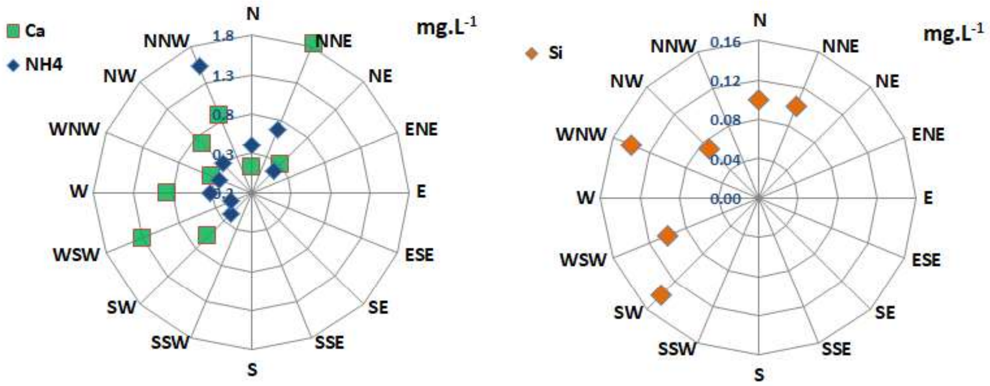

Figure 6. Concentrations of Ca and NH_4^+ (left) and Si (right) in relation with wind direction

The analysis of the backward trajectories of the air masses with the model of the American Oceanic and Atmospheric Agency HYSPLIT [13] (Fig.7) shows local and regional transport from areas where the industrial zones of Burgas city, TPP Maritsa and megacity Istanbul are located. The highest average concentration for Si is obtained for precipitation with wind directions, south-west (SW) on 12 November 2017. The main source of Si in the atmosphere is from resuspension of dust, soil, sand. It is one of the main elements of terrestrial origin that is found in precipitation affected by the Sahara intrusion.

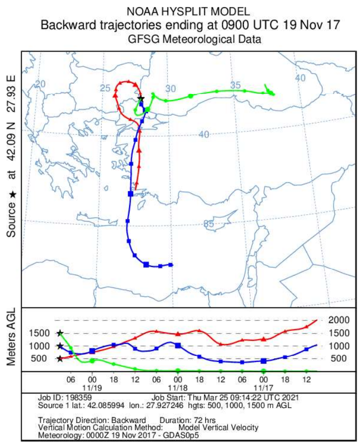

Figure 7. HYSPLIT backward trajectories for 19 November 2017

An example of such a case is the precipitation from 12 November 2017. On this day, the air masses over the Balkan Peninsula, including Bulgaria, are affected by Saharan dust. This can be seen from the analysis of the backward trajectories as well as from the model of the Barcelona Dust Forecast Center [14] (https://dust.aemet.es/forecast/) shown in Fig. 8. Due to the small amount of precipitation, it can be assumed that the high concentrations of Si in the precipitation samples are mainly through the washout process.

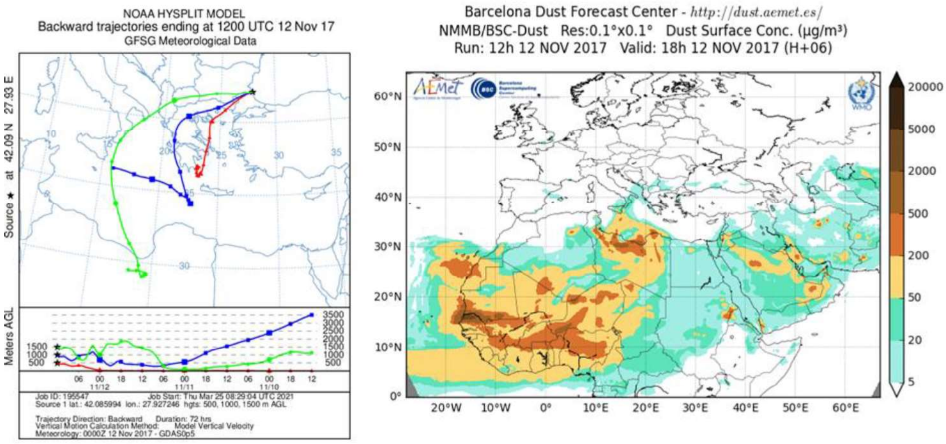

Figure 8. HYSPLIT Backward trajectories (right) and map of dust concentrations in the atmosphere from the NMMB / BSC-Dust model (left)

CONCLUSION

The relationship of the precipitation physicochemical parameter, as pH and wind direction for the period of five years (2015-2019) at coast Hydrometeorology station Ahtopol was studied. The data for precipitation pH and wind direction for 595 events were analyzed. The frequency analysis for five years pH data showed that 79% are in the acidic range, 14% are weakly acidic and only 3% is neutral and alkaline. The analysis of wind direction in the precipitation cases indicates that 60% of wind directions are from N, NW, NE; 32% are from SW, SE, W, E and 8% of precipitation cases are during wind speed less 0.3 m/s.

In order to investigate the relationship between precipitation chemical composition and wind direction, daily wet only precipitation samples were collected for chemical analysis in 2017. Mean concentration of analyzed elements in precipitation samples followed the order: Cl^{-}> Na > SO_4^{2-} > NO_3^{-} >Ca > K ~ Mg > NH_4^{+} > Zn > Si > Fe > Cu. Analysis of precipitation chemistry and wind direction shows that the highest frequency of wind direction (19%) is from the north-northeast (NNE), followed by WNW, NW, SW (14%), NNW, WSW and NE (10%). The highest average concentrations for NO^{3-}, SO_4^{2}, $nssSO_4^{2-}$, Cl, Na, Zn and Cu were obtained for precipitation during wind directions from north-northeast. The highest concentration of ammonium ions was measured for the cases when the wind direction is from north-northwest. The highest average concentration of Si and Ca (the main elements of terrestrial origin which are found in the precipitation affected by the Saharan intrusion) were received for the cases of precipitation with wind direction from SW. The backward trajectory analysis of the air mass in cases with elevated concentrations of acidifying compounds show local and regional influence, while in the case of high concentrations of Si and Ca show long-range transport.

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