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Chemical composition of precipitation in urban area

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Abstract: This paper summarizes one year (July 2015 to June 2016) measurements on precipitation physico-chemical characteristics in the urban environment of Sofia. 53 wet only precipitation samples were collected with wet-only automatic sampler WADOS in the Central Meteorological Observatory (CMO) of NIMH, Sofia. All collected samples were analyzed for acidity (pH), electrical conductivity (EC), chloride (Cl^-), nitrates (NO_3^-), sulphates (SO_4^{2-}), ammonium ions (NH_4^+), calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), iron (Fe), zinc (Zn) and silicium (Si). The measured pH values in precipitation samples collected in the study period are between 4.3 and 7.88. 36 % of the pH values range between 4.3 and 5.0, 31 % in the range 5.0 – 6.0 and 33 % in the range 6.0 – 7.9. Mean concentration of analyzed ions in precipitation samples followed the order: $SO_4^{2-} > NO_3^- > Ca > Cl^- > NH_4^+ > K > Na > Mg > Si > Zn \approx Fe$.

Keywords: acidity, precipitation chemical composition

1. INTRODUCTION

The chemical characteristics of precipitation can be affected by many environment impacts, including anthropogenic emissions, sea spray and terrestrial dust. 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 (Seinfeld and Pandis, 2006). NH_4^+ primarily comes from fertilizers used in agriculture, biomass burning, livestock breeding and even natural activities. Other major elements Cl, Mg^{2+}, K^+ and Na^+ originate mainly from natural sources such as sea spray, soils and forest fires (Mihajlidi-Zelić et., 2006). Air pollution leads to environmental degradation, including the degradation of natural ecosystems. The atmospheric deposition of sulphur and nitrogen compounds has acidifying effects on

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soils and freshwaters, affecting biodiversity and life on land and water. The deposition of nitrogen compounds can also cause eutrophication, an oversupply of nutrients that may lead to changes in species diversity and invasions by new species. The effects of air pollutants on aquatic ecosystems include the loss of biota sensitive to acidification, as well as increased phytoplankton and harmful algal blooms, which may impact on fisheries, water-based recreational activities and tourism (Greaver et al., 2012). Acidification may also lead to increased mobilisation of toxic metals in water or soils, which increases the risk of uptake in the food chain.

The problem of acidity of 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 their transformation into sulphates. The adverse effects of acid rain on the environment cause a wide range of measures to reduce the deposition of pollutants and rainfall. The Geneva Convention of 1979 is the first international legally binding instrument to tackle the problems of long-range transboundary air pollution on a broad regional basis. The European Monitoring and Evaluation Program (EMEP) is a science-based program established for the purpose of international cooperation to address cross-border air pollution problems (EMEP Status Report, 2014).

Several authors have explored long-term trends in the chemical composition of atmospheric deposition in Europe since 1990 (Fowler et al., 2005a,b; Fagerli and Aas, 2008; Torseth et al., 2012; Pascaud et al, 2016). A common decreasing trend has been observed in sulphate and nitrogen concentrations. These trends have been linked to changes in precursor emission quantities, particularly from combustion or industrial processes. After decades of declining sulphur emissions in Europe, acidification is declining or slowing so that some forests and lakes are showing signs of recovery. Due to the considerable SO_x emission reductions over the past three decades, nitrogen compounds emitted as NO_x and NH_3 have become the principal acidifying components in both terrestrial and aquatic ecosystems, in addition to their role causing eutrophication. However, emissions of SO_x, which have a higher acidifying potential than NO_x and NH_3, still contribute to acidification (EEA Report 2017).

In Bulgaria a network for monitoring precipitations chemistry has been established and maintained by the NIMH since 1998. Only few studies are available on analysis of these data and wet deposition in Bulgaria (Iordanova, 2006; Iordanova, 2010; Hristova, et al, 2016 a,b).

The main objective of this study is to summarize one year (July 2015 to June 2016) measurements on physico-chemical characteristics of precipitation in the urban environment of Sofia. The levels of identified elements, their temporal variation and the percentage contribution of each ion to total ionic mass in precipitation samples are presented and discussed. The obtained data significantly contributes to very limited knowledge on precipitation quality in the east Europe.

2. EXPERIMENTAL

2.1. Sampling and chemical analysis

The sampling was carried out at the site Central Meteorological Observatory (CMO) of National Institute of Meteorology and Hydrology. It is placed in the sought-eastern part of the city with coordinates 42.655 N, 23.384 E, at 586 m a.s.l.

24 hour, wet-only samples were collected with automatic collector WADOS (Kroneis GmBH). Period of sampling was from 1.07.2015 to 30.06.2016.

After every rain episode, the sampling set was cleaned with deionised water, and the bottle was replaced with a new one.

The collected samples were divided into two aliquots: one for the analysis of EC and pH, and the other for the further chemical analysis. The samples for the chemical analysis were refrigerated at 4 °C. Values for pH and electro conductivity (EC) were measured in the Precipitation Chemistry Laboratory at NIMH with pH meter 7110 WTW and Cond 7110 WTW. The chemical analysis was performed in certified laboratory 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, Zn, Si and by Spectrophotometer S-20 for NH_4^+.

3. RESULTS AND DISCUSION

3.1. Spatial distribution of precipitation acidity (pH)

The network for monitoring precipitations chemistry of NIMH consists of 34 stations, co-located with the synoptic stations. 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. The spatial distribution of precipitation acidity (pH) for Bulgaria for the study period is presented on Fig. 1. For the spatial analysis of precipitation acidity is used Surfer 11 software. The scale with which the acid-alkali composition of the precipitations is evaluated is as follows: pH <5 - acid, 5 ÷ 5.6 slightly acid, pH = 5.6 - neutral, pH> 5.6 slightly alkaline, pH> 6 – alkaline.

The average precipitation pH values for the period July 2015 – June 2016 for all 34 stations vary from 4.9 to 6.5.

The results on the Fig. 1 show that slightly acid precipitations are mainly distributed along the western and south-eastern (Elhovo and Ahotol stations) regions of Bulgaria. Slightly alkaline and alkaline precipitations are distributed mainly over the northern area (Danubian Plain) and Upper Thracian Plain in Bulgaria, where the biggest agricultural areas are located. CMO, Sofia is also part from the network for monitoring precipitations

chemistry. The obtained mean pH value for Sofia station during the study period is 5.2 (slightly acid range).

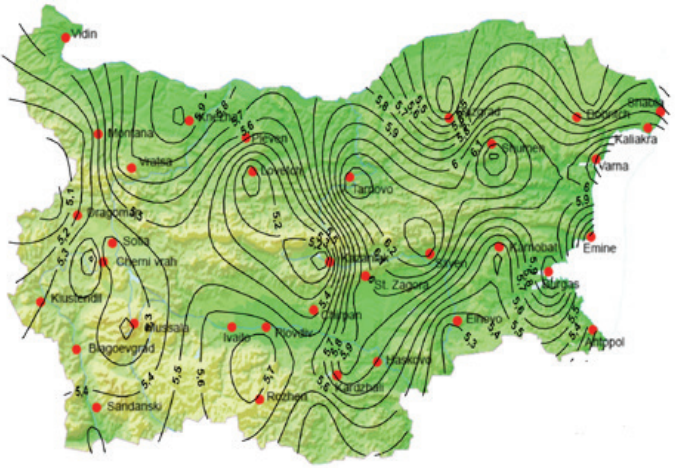

Fig. 1. Spatial distribution of precipitation pH for the period July 2016 – June 2016

3.2. pH, frequency analysis and acidity neutralization

53 wet only precipitation samples were collected and measured for pH and conductivity during the study period. Variation in pH values and the frequency analysis are illustrated in Fig. 2.

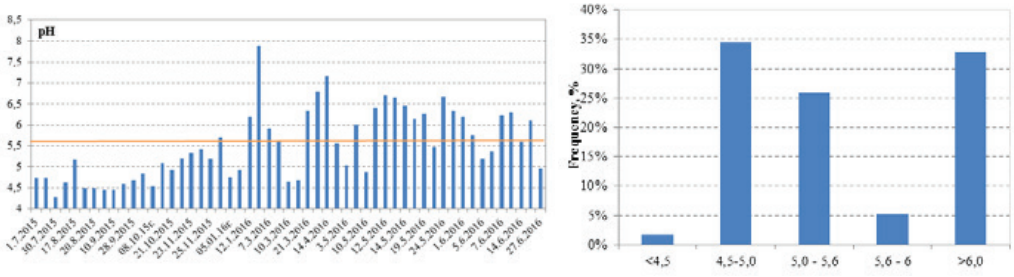

Fig .2. Variation in pH values (left) and frequency analysis of pH (right) in wet-only precipitation samples for the period July 2015 –June 2016

The measured pH values vary between 4.3 and 7.9. During the studied period the mean value of pH is 5.51. That value is close to the 5.6 (the orange line on the Fig.2) which is the pH value resulting from equilibrium between atmospheric CO_2 and pure distilled water (Seinfeld and Pandis, 2006). Natural precipitation acidity can be

generated by atmospheric CO_2, NO_x, SO_2 and other acidifying trace gases emitted by natural sources and dissolved in cold droplets.

The frequency distribution for the pH of all considered raining events shows that 36% of the samples have pH value in the acidity range, 26 % are in the range 5.0 – 5.6 (slightly acid), 5% of the samples are between 5.6 - 6 and 33 % are in the range 6.0 – 7.9 (alkaline range).

The most acidic precipitation event (pH of 4.29) occurred on 30.07.2015. This was the result of air mass originating from west-southwest Europe (NIMH-Bulletin, 2015). The concentrations of the main acidifying components SO_4^{2-} and NO_3^- are 3.76 and 1.99 $mg.l^{-1}$, respectively.

The precipitation event with the highest pH value (7.88) is obtained on 29.02. 2016. The country is under the influence of the Mediterranean Cyclones. The air mass transport is from south and in the country is relatively warm. In some places in Bulgaria there are weak precipitations. The air masses carried by the cyclone are colored due to the presence of dust and sand from Sahara (NIMH-Bulletin, 2016). The influence of Sahara dust in the precipitation compositions is also confirmed by the presence of Si (0.55 $mg.l^{-1}$) and the large amount of Ca (8.9 $mg.l^{-1}$).

Neutralization factor (NF_{Xi}) values were calculated to quantify the neutralization of precipitation by Ca^{2+}, Mg^{2+} and NH_4^+ as follows: $NF_{Xi}=[Xi]/([NO_3^-] + [SO_4^{2-}])$, were *Xi* is the chemical components of interest in $mg.l^{-1}$. The NF values calculated for Ca^{2+}, NH_4^+ and Mg^{2+} in the precipitations sampled in this study are 0.258, 0.128 and 0.0265 respectively, indicating that $Ca^{2+}$is the dominant neutralizing cation with lower contribution from NH_4^+ and Mg^{2+}.

3.3. Time series of main ionic concentrations and conductivity

Variation of main anion and cation concentrations ($mg.l^{-1}$) and conductivity is presented on Fig. 3. The measured concentrations of SO_4^{2-} in the samples range from 0.49 $mg.l^{-1}$ to 6.68 $mg.l^{-1}$ with mean concentration 2.26 $mg.l^{-1}$. NO_3^- concentrations vary from 0.39$mg.l^{-1}$ to 1.78 $mg.l^{-1}$ and Ca values from 0.068 to 8.99$mg.l^{-1}$. The concentrations of Mg ranged from 0.007$mg.l^{-1}$ to 0.11$mg.l^{-1}$. The results show very good correlation between concentrations of SO_4^{2-}, NO_3^- and values of EC. The highest concentration of sulfates (6.68$mg.l^{-1}$) is observed on 14.04.2016. Concentrations of NO_3^- (3.22$mg.l^{-1}$) and Ca (6.13 $mg.l^{-1}$) are also high. The measured pH and EC values are 7.16 and 48.2 $\mu S.cm^{-1}$, respectively.

There is a very good correlation in the concentrations of Ca and the EC values. The highest measured concentration of Ca and the highest value of EC and pH in the study period were measured on 29.02.2016.

Seasonal variability in NH_4^+ concentrations relevant the maximum value is recorded during the spring (1.12$mg.l^{-1}$) and the summer (1.01$mg.l^{-1}$). The increases in ammonium concentrations in the spring and summer might result from the volatilizations of NH_3

from fertilizer applications during crop growth (spring) and the spread of manure in the late summer (Pascaurd, 2016). The mean concentration of NH_4^+ in the study period is 0.45mg.l^{-1}.

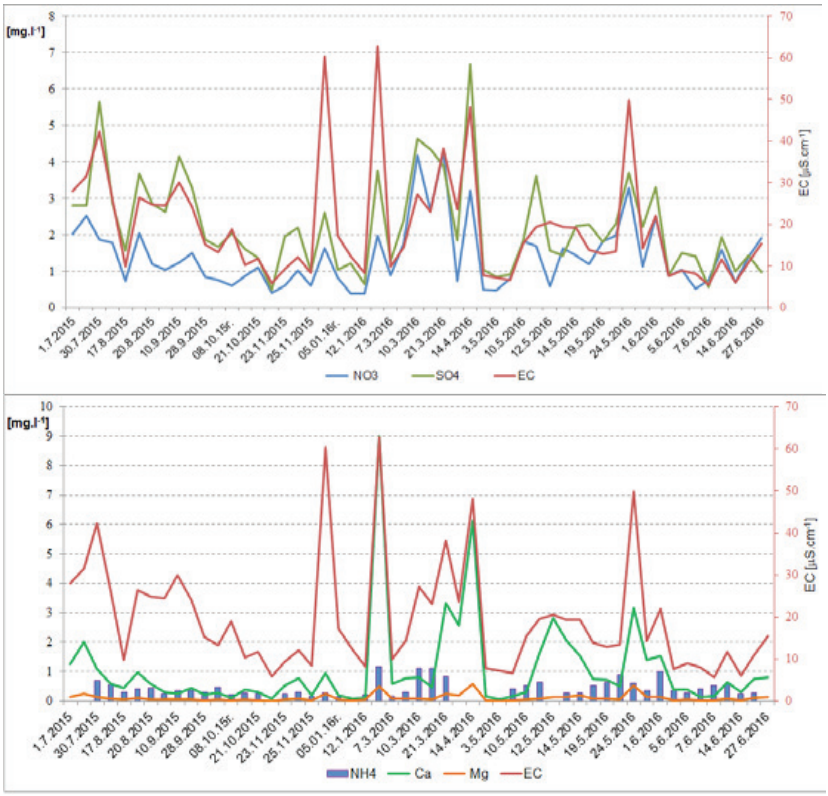

Fig .3. Time series of ionic concentrations (SO_4^{2-}, NO_3^- - above and Ca, Mg, NH_4^+ - below) and conductivity (EC)

The comparison with the results for the precipitation composition from 2014 in Sofia, published in (Hristova & Veleva, 2015), indicates that the obtained results for the all elements in this study are lower. This can be explained by the sampling method when the precipitation is collected in a permanently open vessel (bulk sampler) that allows the contribution of the dry atmospheric deposition.

3.4. Percentage contribution of each ion to total ionic mass in precipitation samples

The prevailing ions with respect to the total ionic mass can be seen in Fig.4. Generally, SO_4^{2-} is found to be the dominant anion in precipitation samples (31.4%), followed by

NO_3^- (21.5%) and Cl^-(10.3%). The predominant cation is Ca^{2+} representing 16% of the total ionic content.

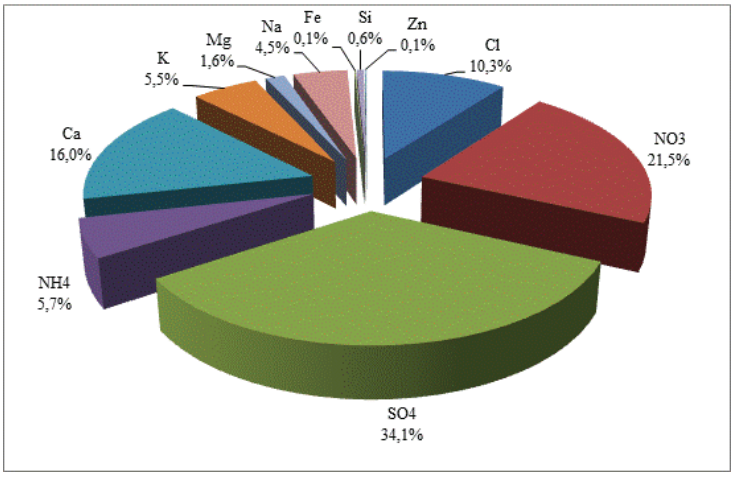

Fig 4. Percentage contribution of each ion to total ionic mass in precipitation samples

In the general trend of different elements, SO_4^{2-} ions contribute most to the total ion concentration, followed by NO_3^- > Ca > Cl^- > NH_4^+ (5.7%) > K (5.5%) > Na (4.5%) > Mg (1.6%) > Si (0.6%) > Zn ≈ Fe (0.1%).

4. CONCLUDING REMARKS

This work reports on variation of the precipitation chemical composition during one year (July 2015 – June 2016) in Sofia. The analysis of 53 wet-only precipitation samples shows that 36% of the samples have pH value in the acidity range, 26 % are in the range 5.0 – 5.6 (slightly acid), 5% of the samples are between 5.6 - 6 and 33 % are in the range 6.0 – 7.9 (alkaline range).

Results from chemical analysis show very good correlation between concentrations of SO_4^{2-}, NO_3^-, Ca and EC values. Seasonal variability in NH_4^+ concentrations relevant the maximum value is recorded during the spring and the summer. Mean concentration of analysed ions in precipitation samples followed the order: SO_4^{2-} > NO_3^- > Ca > Cl^- > NH_4^+ > K > Na > Mg > Si > Zn ≈ Fe.

The obtained data significantly contributes to very limited knowledge on precipitation quality in the east Europe. Continued studies on precipitation chemistry with more extensive spatial and temporal variations, relation of some elements concentration to the meteorological parameters, source apportionment study are necessary to better understand the main sources of the acidifying compounds.

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