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Composition of Precipitations in the Coastal Area of Southeast Bulgaria

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Abstract. The first joint study on air pollution related problems in the cross border area Bulgaria–Turkey, was carried out. Samples of wet only depositions were collect at two sites (Burgas and Kirklareli) during the period from June to November 2014. The samples were analyzed for main cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}), main anions (NO_3^{-}, SO_4^{2-}, Cl^{-}), heavy metals (Co, Cr, Fe, Mn, Mo, Zn, Cd, Cu and Pb), acidity (pH) and conductivity (EC).

The measured acidity of precipitation samples was found to be different at the sampling sites, ranging from alkaline at Kirklareli (6.76) to neutral in Burgas (5.68). The chemical composition of precipitations in Bulgarian site was dominated by Cl^{-} followed by $\mathrm{SO_4^{2-} > NO_3^{-} > Ca^{2+} > Mg^{2+} > Na^{+} > K^{+} > NH_4^{+}}$. The dominated ion in precipitation samples from Turkish site is $\mathrm{SO_4^{2-}}$ followed by $\mathrm{Cl^{-} > Ca^{2+} > NH_4^{+} > K^{+} > Na^{+} > NO_3^{-} > Mg^{2+}}$. The chemical analysis shows that there are no deviations in the content of heavy metals from commonly reported values in Europe.

1 Introduction

Over the last 20-30 years precipitation chemistry has been intensively studied worldwide mainly due to concerns over acid deposition, eutrophication, trace metal deposition, damages to forests and vegetation, ecosystem health, and global climate change [1].

Measurements of the chemical composition of precipitation have been conducted for many years using several networks in different regions. In Europe, precipitation chemistry is measured at about 150 stations of the European Monitoring and Evaluation Programme (EMEP) and Global Atmospheric Watch (GAW) network. The stations are mostly placed in Western and Northern Europe [2]. In Bulgaria and Turkey GAW or EMEP stations measuring the composition of the precipitation on regular basis are not available. In Bulgaria a network for monitoring acidity of precipitations has been established and maintained by the NIMH since 1998. The 34 stations are 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. Only few studies are available on analysis of these data and wet deposition in Bulgaria [3,4]. Acid precipitation studies and wet deposition estimates have been carried out at several locations in Turkey since the 90s, mainly for highly industrialized regions or urban areas and for periods of few years [5,6].

The cross-border region is characterized by rich biodiversity and for its flora and fauna is treated as unique in Europe. The knowledge of the air pollution in the region is important not only for the protection of human health, but also for estimating the threads it poses on the region's main assets – natural parks, tourism, recreation, and cultural heritage places. Important indicators for agriculture and forests, as acidity and chemical composition of precipitation are not routinely measured.

The main objective of this study is to present and analyse precipitation chemistry data, obtained from measurements at two sites in the cross-border area Bulgaria-Turkey during the period from June to December 2014. The acidity of precipitation (pH) was estimated for all collected precipitation (wet) samples (57). The chemical analysis for main cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}), and main anions (NO_3^{-}, SO_4^{2-}, Cl^{-}) was performed on 57 samples. Heavy metals Co, Cr, Fe, Mn, Mo, Zn, Cd, Cu and Pb were analysed in 37 samples.

2 Experimental and Analysis Methods

2.1 Sampling sites and procedures

The cross-border area of Burgas – Kirklareli is located at the south-eastern part of the Balkan Peninsula (Figure 1). The region covers about 10000 km^2 with several protected areas and natural parks as the Strandja Nature Park in Bulgaria and the Saka Lake Nature Reserve with the İğneada Longoz Forests near the Black Sea coast in Turkey.

Atmospheric deposition samples were collected at two sites as indicated in Figure 1.

The Bulgarian sampling site in Burgas ($42°29'$N, $27°28'$E) is situated near the Black Sea coast, at the NIMH meteorological observatories. The

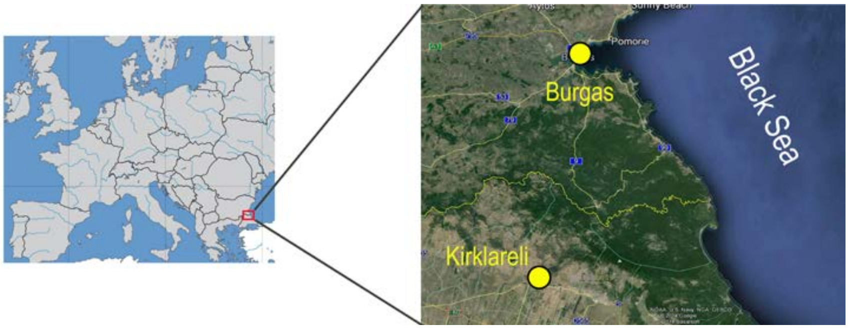

Figure 1: The sampling sites in the cross-border.

Turkish sampling site in Kirklareli ($41°42'$N, $27°12'$E) is located at the premises of the Atatürk Soil and Water Resources Research Institute at the southern edge of the town.

The measurement campaigns were organized in the period from June to December 2014. Manual sampling systems have been assembled by NIMH and the University of Kirklareli, and have been installed at the selected locations at a height of about 1.5 m a.g.l. Common for all samplers was their ability to collect wet (precipitation), dry, and bulk (wet plus dry) atmospheric deposition, although the design of the samplers by the two groups was different. The sampling was carried out by trained meteorological technicians, available at the sites all the time. The procedure with cleaning and storage of the samples was similar for both sites. All sampling instruments and equipment have been washed and rinsed with deionised water before and after each sampling.

2.2 Chemical analysis

Acidity (pH) and electro conductivity (EC) of the precipitation samples were determined on spot immediately after the collection using portable pH/EC/TDS meters, HI9811-5 Hanna Instruments. The samples were then stored in a refrigerator at 4°C, without access to sunlight, before their transportation to the chemical laboratories.

The Bulgarian samples were analysed in the Water Lab at the University "Prof. Dr. Asen Zlatarov" – Burgas by using standard cuvettes of Hach LANGE photometric equipment for Cl^-, SO_4^{2-} , NO_3^-, NH_4^+ and Inductively Coupled Plasma (ICP) technique for K^+, Na^+, and heavy metals as cobalt, chromium, iron, manganese, molybdenum, zinc, cadmium, copper and lead (Co, Cr, Fe, Mn, Mo, Zn, Cd, Cu and Pb).

The analysis of the Turkish samples was carried out in the laboratory of the Atatürk Soil, Water and Agricultural Meteorology Research Station in Kırklareli. Ion chromatography (DIONEX ICS-5000) was used for Cl^-, SO_4^{2-} , NO_3^-, NH_4^+, analysis and ICP- OES (SPECTRO ARCOS) apparatus for the analysis of Ca^{2+}, Mg^{2+}, K^+, Na^+ and heavy metals.

3 Results and Discussions

3.1 pH in precipitation samples

The pH values for the period from June to November 2014 ranged between 4.7 and 6.8 for the Bulgarian samples and from 6.29 to 7.43 for the Turkish samples.

The frequency analysis of observed pH values at all sampling sites is shown in Figure 2. Values of pH greater than 6.0 were observed in all samples from Kirklareli, while such high pH values were observed in 34% of the samples from Burgas. pH less than 5.6 were observed only in samples from the coastal site of Burgas – in 44% of the samples.

Table 1 shows average, minimum and maximum values of pH, conductivity and ion concentrations in wet deposition samples from both sampling sites. Low pH values (< 5.6) in the samples from Burgas can be explained by the higher concentrations of SO_4^{2-} and NO_3^-. It is known that the acidity of rain is controlled mainly by strong acids, e.g. H_2SO_4 and HNO_3. The average value (5.68) is comparable to values (5.8) for the same period obtained from the Bulgarian network for monitoring of precipitation acidity, where bulk precipitations samples are collected.

The mean pH values of samples from Kirklareli (6.76) indicate alkaline character of the precipitations in the study period. These values are similar to results from previous field campaigns in the period from June to December 2011, when the mean pH for Kirklareli town and a rural site nearby were reported, respectively, as 6.26 and 6.24 [8]. The alkaline character of precipitation samples in Kirklareli could be due to the neutralizing effect of soil dust particles or ammonium.

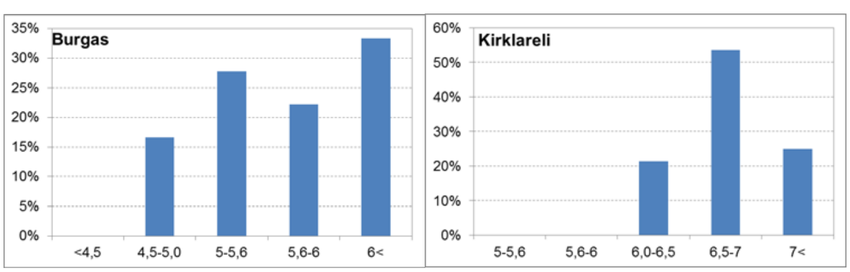

Figure 2: Frequency analysis of pH in precipitation samples for the period June-November 2014.

Table 1: Average, minimum and maximum concentrations and standard deviation of various species (mg/l) in precipitation samples

	Burgas				Kirklareli			
	Average	**Min**	**Max**	**SD**	**Average**	**Min**	**Max**	**SD**
pH	5.68	4.70	6.80	0.62	6.76	6.29	7.43	0.30
EC	92.94	10.00	330.00	97.12	38.22	11.90	97.10	23.65
$\mathbf{Ca^{2+}}$	4.20	2.00	12.02	2.26	1.52	0.06	7.78	1.93
$\mathbf{Mg^{2+}}$	3.02	0.30	6.38	1.77	0.15	0.01	0.71	0.16
$\mathbf{NH_4^+}$	0.08	0.04	0.42	0.08	1.47	0.04	2.93	0.67
$\mathbf{NO_3^-}$	5.03	0.20	16.60	4.41	0.48	0.03	1.96	0.44
$\mathbf{SO_4^{2-}}$	6.45	1.40	16.81	3.70	5.93	1.43	31.71	6.09
$\mathbf{Cl^-}$	14.20	1.42	63.81	14.18	1.69	0.01	5.72	1.50
Na	0.72	0.06	2.35	0.68	0.66	0.12	2.62	0.53
K	0.68	0.03	4.10	0.89	0.77	0.04	2.20	0.63

3.2 Ion concentration

The average concentration of anions in Kirklareli in descending order is as follows $SO_4^{2-} > Cl^- > NO_3^-$ with mean anions values 5.93, 1.69, 0.48 mg/l. The concentration of cations follows general pattern $Ca^{2+} > NH_4^+ > K^+ > Na^+ > Mg^{2+}$. The mean values of those cations are 1.52, 1.47, 0.77, 0.66, 0.15 mg/l.

The mean concentration of anions in precipitation samples from the Burgas can be ordered in a descending order as follows $Cl^- > SO_4^{2-} > NO_3^-$ with mean values 14.20, 6.45, 5.03 mg/l for Burgas. The order of mean cations concentration for Burgas is $Ca^{2+} > Mg^{2+} > Na^+ > K^+ > NH_4^+$ with mean cations concentrations 4.20, 3.02, 0.72, 0.68, 0.08 mg/l

The prevailing ions with respect to the total ionic mass for both sites can be seen in Figure 3.

Generally, SO_4^{2-} was found to be the dominant anion in precipitation samples from Kırklareli (46.8%) and Cl^- the dominant anion in wet samples from Burgas (41.3%). The predominant cation in Kırklareli and Burgas is Ca^{2+} representing 12% of the total ionic content. The contribution of ammonium is different in Burgas (0.3%) and in Kiklareli (11%).

The ion concentrations analysis indicates that the station in Kırklareli was affected by sources of Ca and NH_3, while the ions composition at Burgas station was influenced by the Black Sea during the study period [7,8]. The contribution of chloride ions in precipitation samples (38.45%) is high, while ammonia concentrations (NH_4^+) in all wet samples are practically equal for both stations (average value of 0.08 mg/l, and without any variability during the study period.

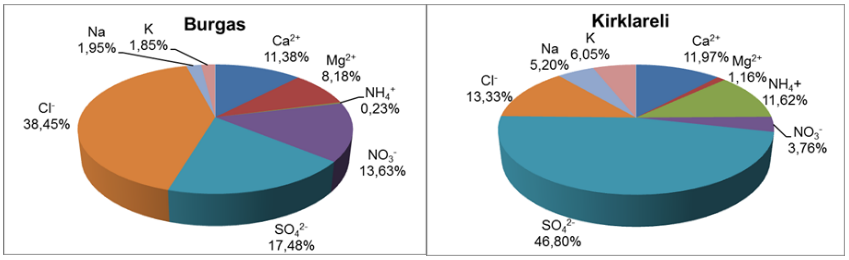

Figure 3: Percentage contribution of each ion to total ionic mass in precipitation samples.

3.3 Heavy metals

The precipitation samples were also analyzed for heavy metals as Co, Cr, Fe, Mn, Mo, Zn, Cd, Cu and Pb. A recent problem of metal particulate air pollution is their role in the oxidation of sulphur dioxide and the formation of acidic aerosols involved in global acid rain [9]. Some of the heavy metals (Fe, V, Ca, Pb, Br, and Cl) also contribute to the formation of photochemical smog. As a result of increased emissions from industrial and transport the release of metal particulates into the environment is now under strict control in air quality regulations [10]. The average concentrations, the standard deviation, minimum and maximum values of some metals in the collected precipitation samples are reported in Table 2.

Table 2: Concentration of heavy metals (μg/l) in precipitation samples (June – December 2014).

Station		Fe	Mn	Cu	Zn	Mo	Co	Cr	Pb
Burgas n = 9	Average	16.97		9.8^a	20.02				15.35^b
	Min	5.8			13.2				14.1
	Max	37.4			33.3				16.6
	SD	13.56			7.55				
DL		5	10.1	1.1	10.3	10.3	9.8	4.9	5.3
Kirklareli n = 28	Average	3.66	5.45	2.50		0.81	0.13	0.64	
	Min	0.95	0.2	0.33		0.45	0.01	0.15	
	Max	10.65	23.59	6.09		1.31	0.54	2.54	
	SD	2.49	6.41	1.38		0.20	0.10	0.56	

SD – standard deviation; ^{a} – based on two samples; ^{b} – based on single samples; DL – detection limit.

Mean concentrations of Mn, Fe, Cu, Co, Cr and Mo in wet deposition samples from Kirklareli are 5.45, 3.66, 2.50, 0.13, 0.64 and 0.81 μg/l. Comparatively high Fe concentrations were detected in the samples from Burgas.

It was found that the average concentrations of Fe and Zn in Burgas (16.97 and 20.02 μg/l) are higher than the average concentrations of the same metals in Kirklareli. It is usually though that Fe is bound to soil particles and, thus, the content is not solely due to atmospheric deposition, however, iron is also emitted during combustion of fossil fuels, such as coal. Zn levels can be explained by the corrosion of exposed zinc surfaces, as a direct consequence of more acidic character of precipitations in Burgas. There are many old buildings with galvanized steel sheets on the roof around Burgas stations. The measured concentration of zinc in the collected Bulgarian samples varies from 13.2 to 33.3 μg/l. Mn, Co and Mo were under detection limit in wet samples.

4 Conclusions

Atmospheric deposition sampling was carried out from June to December 2014 at two locations: one coastal site Burgas and one inland location in Northern Turkey – Kirklareli. 57 precipitation samples were collected in total. While pH was measured for all of them, chemical analysis was performed on selected samples – on 57 samples for main anions and cations, and on 37 samples for heavy metals.

The measured acidity of precipitation samples has been found to be different at the two sampling sites, ranging from alkaline at Kirklareli (6.76) to neutral in Burgas (5.68). The chemical composition of precipitations at both sides of the border is also different. While Ca^{2+} is dominant in the selected samples in Kirklareli, Mg^{2+} is more evident in the samples from the Bulgarian samples, while NH_4^+ is more evident in the samples from the Turkey (effect of agriculture). The influence of the Black Sea is expressed also in the higher Cl^- concentrations at the Bulgarian site.

For both sampling sites, deviations in the content of heavy metals from commonly reported values in Europe were not observed. For Kirklareli dominant heavy metals in wet samples were Mn, Fe and Cu; for Burgas – Fe, Cu and Zn.

Some of the uncertainties of the presented results are related to different methodologies for sampling and analysis. The collected new data on precipitation chemistry in the cross-border region Burgas – Kirklareli contribute to filling in the gap on this topic in the studied area. However, for better understanding of atmospheric processes and deposition phenomena more observational data are needed.

Acknowledgements

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