ASSESSMENT OF AIR QUALITY IN THE URBAN ZONE OF ŠABAC, SERBIA, BASED ON THE ANALYSIS OF SNOW

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***Abstract**: The aim of this work is to give assessment of air quality in city environment, based on the physical and chemical properties of snow. During January 2017, snow was collected at urban area of Šabac, Serbia. Snow was sampled at four locations in the Šabac, right after the formation of snow cover. In addition, a snow from one location 10 km far from the city in the uninhabited area was also sampled. Electrical conductivity, pH, dry residue, content of organic matter and concentration of chemical species (SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+) were analyzed in snow samples. Comparison of the results obtained in the samples taken in the city with the values measured in the sample of snow from the uninhabited area showed that air quality in the city does not differ significantly from the air quality in the uninhabited area.*

***Keywords**: snow chemistry, Šabac-Serbia, air pollution*

1. INTRODUCTION

Rain and snow carry many polluting substances from the atmosphere with them. Due to the large surface of the snowflake and the lower falling rate in relation to the rain drops, the snow accumulates better and collects the particles from the atmosphere. In addition to effectively collecting pollutants, snow is suitable for analysis because it can be kept longer on the surface of the earth, which makes it easier to sample. Atmospheric trace gases as well as aerosol particles are removed from the atmosphere and accumulated in the snow cover via different deposition processes like the removal by precipitation (wet deposition) or by direct (dry) deposition. During the growth of the flakes, other particles can be collected and additional attachments of chemical impurities may take place by scavenging as the flakes move through the atmosphere.

Natural and anthropogenic sources emit different pollutants into the atmosphere, so they are often part of the snow [1]. The content of pollutants in snow conditions is influenced by several factors: climate, type and purpose of land use, proximity to industrial plants, traffic density [2].

One of the methods for the acquisition of objective information on the transport of natural and human-induced aerosols is studying the chemical composition of snow cover, which accumulates chemical admixtures from the atmospheric air and precipitation over a certain period. The data on the amounts of individual pollutants and their total amount accumulated in snow cover in both the areas adjacent to industrial enterprises and the background areas allow one to assess the environmental impact of various enterprises [3].
Most sulfate in the atmosphere are secondary sulphates formed by the oxidation of gaseous precursors (with SO_2 and dimethyl sulfide as the main contributors), followed by particle formation through nucleation and condensation processes. There are several pathways for sulphate formation such as liquid-phase reactions inside cloud droplets or oxidation of SO_2 with OH via gaseous phase reactions [4]. SO_2 is emitted to the atmosphere from both anthropogenic and natural sources, although it has been estimated that more than 70% of SO_2 global emissions are released by anthropogenic sources [5], and fossil fuel combustion is responsible for the vast majority of these emissions. Other SO_2 sources are biomass burning, shipping, metal smelting, agricultural waste burning, pulp and paper processing, and a modest volcanic source [6, 7].
Nitrogen compounds are mainly of secondary origin and come from the reaction of natural and anthropogenic gaseous precursors. NO_3^- and NH_4^+ are the main nitrogen compounds in atmospheric particulate matter. The main precursor gases emitted by natural and anthropogenic sources are NO, NO_2, N_2O and NH_3, and nitric acid is the main product generated by oxidation in the atmosphere [8]. The anthropogenic production of secondary nitrate precursor gases occurs in the generation of power (gas, fuel–oil and coal combustion) and in other combustion processes involving high temperatures, such as those occurring in the motors of vehicles and in biomass burning [9]. On the other hand, agricultural activities such as land fertilising are the main source of atmospheric NH_3 [10], although it is emitted by other sources, including waste collection, vehicles and a number of production processes [11, 12].
Among the environmental pollutants, organic compounds, many of which are strong toxicants, require the most thorough treatment. Numerous recent investigations show that organic matter (OM) is one of the basic components of aerosols. The "industrial" aerosols are remarkable for a high concentration of C in soot in the form of submicronic particles, which can be transported far away from the source of pollution [3, 13]. Also, an important role in the origin of carbonaceous aerosol play vehicle emissions, coal combustion and biomass burning [14].
In recent years, more and more studies have been carried out on the physical and chemical characteristics of snow, that is, the content of pollutants and the distribution of particle size in melt snow [15, 16]. In our country, research on the composition of snow and the contribution of snowfall to environmental pollution has begun in the last 10-20 years [17, 18].
In this paper we analyzed the snow cover formed in the urban zone of Šabac in January 2017. In order to examine the impact of anthropogenic activities and air quality in the area in Šabac for comparison, a control sample was collected in a the uninhabited area near the village of Vranjska.

2. EXPERIMENTAL

2.1. Study area

Šabac is a well-known medium-sized industrial city of north-west Serbia. Its coordinates are: 44°45'20.88" N, 19°41'38.04" E. Šabac is one of the industrial hub in north-west Serbia comprising, large industries (production of mineral fertilizers, ceramic tiles, pharmacy…), small scale industries, enterprises. The industrial zone is located on a former chemical industry HI "Zorka", which exists today in the form of independent companies with similar activities. Šabac municipality covers an area of 795 km^2 and having a population of 115 884 (Census, 2011) inhabitants. In the city and in the suburbs, has a population of 70 000 inhabitants. In this paper environmental monitoring in urban zone of Šabac, was performed using snow cover. Snow samples were collected at the urban site located in Šabac during winter in 2017 (Fig. 1).
The sampling site represents urban area that is affected by different types of anthropogenic sources (fuel combustion, industrial processes, and minor role of heavy traffic). From January 9 until January 11, 2017, snow was collected at four locations across Šabac and one location from uninhabited area (village Vranjska, 10 km fare away from the city). The snowfall started on January 4 and continued intermittently until January 11. The snow depth was in the range of 7–16 cm. The snow cover persisted about ten days due to cold weather, with temperatures constantly below 0 °C, from -6ºC up to -19ºC. The cold wave which occurred during the period 6 January to 11 January 2017 was characterized by extremely low temperatures in the whole of Serbia. According to the data of the Republic Hydrometeorological Service of Serbia, the average air temperature measured from December 1, 2016 to January 12, 2017, for two grades is lower compared to the same period from 1981 to 2010. Since the beginning of winter 2016/2017, the average air temperature for Serbia was -2.5 ºC, while the average for the same period from 1981 to 2010 was -0.5ºC.

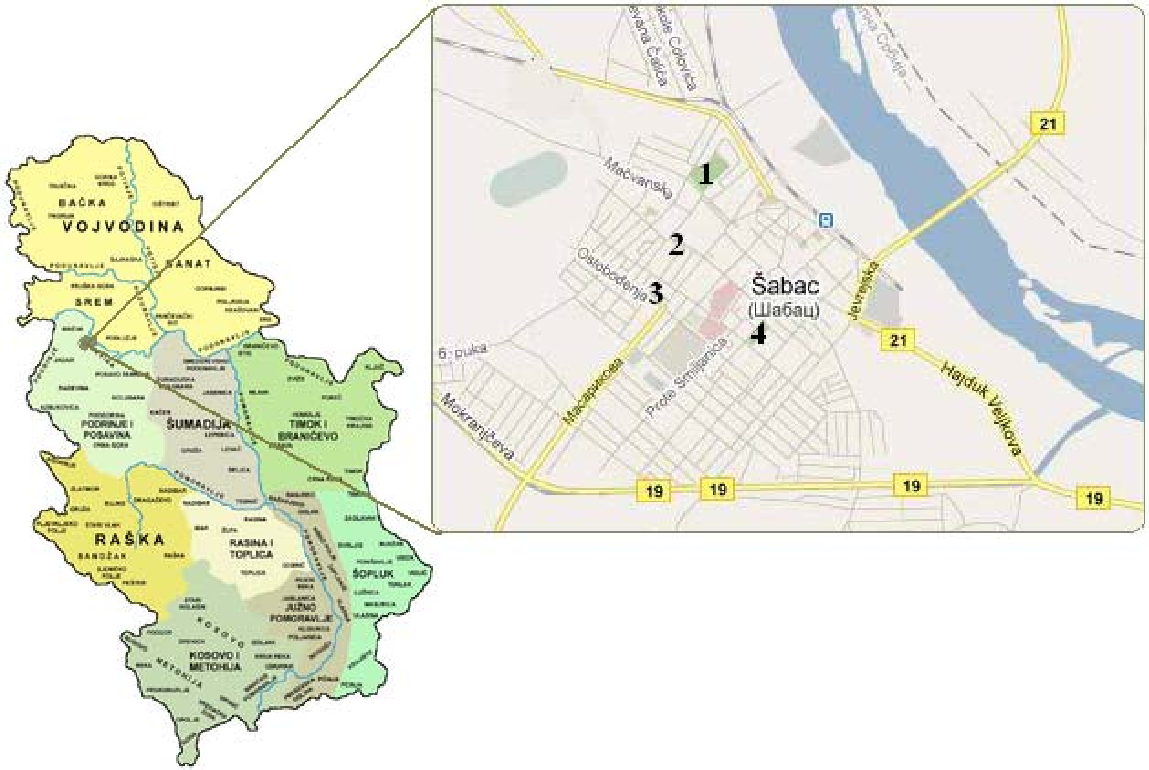

Figure 1: Location sampling sites in Šabac.

2.2. Snow sampling and chemical analysis

Plastic bags and gloves were used so as to avoid negative artifacts during snow sampling. The snow cover was collected through the use of a plexiglas device and a plate. Samples placed in a polyethylene bag, and subsequently transported to the laboratory [19]. Ten individual samples of snow were taken at each location and a composite sample was prepared which was further analyzed.

In the laboratory samples were analysed immediately after thawing. Conductivity and pH were determined electrochemically at 25 °C on the unfiltered liquid samples, using a conductometer 4310 Jenway and pH –meter HANNA instruments HI8314. For analysis the melted samples were filtered. Anion (NO_3^-, NO_2^- and SO_4^{2-}) and cation (NH_4^+) concentrations were determined by spectrophotometer ThermoScientific Evolution 60S UV-Visible-Spectrophotometer [20]. Blank values were recorded in the subtracted from the analysed ion concentrations in the redistilled water. The dry residue was determined by gravimetric evaporation of 100 ml of the melted snow sample. Organic matter was determined volumetrically, titration with standard solution $KMnO_4$.

3. RESULTS AND DISCUSSION

Analytical results of the concentrations of selected ions (NO_3^-, NO_2^- , SO_4^{2-} and NH_4^+), conductivity, pH values and content of organic matter in melted snow samples from Šabac and in the uninhabited area near village Vranjska (control) are summarized in Table 1 and 2.

The data on the amounts of individual pollutants and their total amount accumulated in snow cover in urban area of Šabac, Serbia and the background area allow one to assess the environmental impact of various anthropogenic activities. In this paper the concentrations of selected ions, conductivity, pH values and content of organic matter in samples from Šabac were compared with the control sample (village Vranjska).

In three of five melted snow samples, pH values were homogeneous and ranged between 5.83 and 5.99 (Table 2). One sample (sample **1**) and control (sample **5**) showed higher pH values 6.20-6.48. On the basis of the measured pH values of the melted snow, cannot be classified as acid precipitation.

The conductivity in all snow samples was low in the range 21.0 - 44.4 $\mu S/cm^{-1}$, demonstrating that pure snow samples had been collected with small content of ions.

The dry residue is in the range of 49 (sample **5**) to 67 mg / l for sample **1**. These results also indicate a small content of the dissolved matter. The obtained results are in line with the results presented in the paper Ilić et al. [20].

Table 1: Location of sampling of snow, snow density, conductivity and dry residue of melted snow samples from Šabac, samples **1-4** and in control sample **5**.

Sample	Location	ρ (snow) (kg/m^3)	conductivity at 22ºC ($\mu S/cm^{-1}$)	dry residue (mg /l)
1	"Large park"	114.1	44.4	67
2	Park in Partizan street	110.2	21.0	54
3	Park in Masarikova street	111.9	36.9	56
4	Park in Hilandarska street	103.4	30.1	54
5	village Vranjska	-	36.7	49

Major ion in the snow samples was sulfate ranged 8.63 mg/l up to 22.53 mg/l (Table 2). The obtained values are several times higher than the control sample **5** (2.46 mg/l), indicating some pollution in the urban environment due to anthropogenic activities such as combustion of fossil fuels, traffic and industry.
Nitrate was the dominating N ion, surpassing ammonium by a factor of 2 expect for the control sample number **5** (Vranjska). In this sample factor is 8. In all snow samples (from the urban area) nitrate were homogeneous ranged from 2.84 up to 3.35 mg/l. In control sample nitrate is 2.64, it is very close to the values of the samples **1-4**.
The concentration in nitrite ion in sample **3** ($0.49 \cdot 10^{-3}$ mg/l) is very close to control $0.42 \cdot 10^{-3}$ mg/l. In others samples concentration of nitrite is in the range 1.48-2.28 $\cdot 10^{-3}$ mg/l.
In all samples in urban area concentration of ammonium ions were homogeneous, too. The obtained values are in the range 1.32 to 1.84 mg/l. Ammonium ion in the control sample is 0.33 mg/l. A significantly higher concentration of ammonium ions in the samples (**1-4**) compared to the control sample **5** is probably due to the burning of fossil fuels or the emission of a mineral fertilizer plant in the industrial zone of Šabac. Human activities have more than doubled inputs of nitrogen to terrestrial ecosystems worldwide in recent decade [21]. Until recently, most of this increase was focused in the developed regions. Presently, fertilizer consumption and fossil-fuel emissions increase most rapidly in less developed regions; thus sources of anthropogenic nitrogen as well as N deposition now occur globally [22].

Table 2: Concentrations NO_3^-, NO_2^- , SO_4^{2-} and NH_4^+, pH values and organic matter in the melted snow samples

Sample	pH	NO_3^- (mg/l)	NO_2^- $\cdot 10^{-3}$ (mg/l)	NH_4^+ (mg/l)	organic matter (mg KMO_4/l melt water)	SO_4^{2-} (mg/l)
1	6.20	2.91	1.48	1.33	14.19	22.53
2	5.99	2.84	2.28	1.32	15.19	8.63
3	5.83	3.35	0.49	1.84	21.66	20.99
4	5.87	2.86	1.55	1.53	24.75	9.39
5	6.48	2.64	0.42	0.33	7.56	2.46

The content of organic matter is determined volumetrically and expressed as the volume of consumed $KMnO_4$ per 1 melted snow. In samples of the urban area the content is in the range 14.19-24.75 mg KMO_4/l. In all samples, two or three times more $KMnO_4$ solutions were consumed than the control sample (7.56 mg KMO_4/l). These results indicate that there is more organic matter in the samples of melted snow from the urban environment as a result of combustion of fossil fuels and traffic.

4. CONCLUSIONS

Within this work, during January 2017 the snow was sampled at four locations at urban area of Šabac and from a one location 10 km far from the city in the uninhabited area. Based on the results of the measured pH values in all five samples of the melted snow cannot be classified as acid precipitation. The measured values conductivity, dry residue and concentration of nitrates in the control sample was very close to the values measured in samples of four urban locations. Ammonium ion concentration was higher in all samples in urban area compared to a control sample probably due to the burning of fossil fuels or the emission of a mineral fertilizer plant in the industrial zone of Šabac. The higher concentration of sulfate and organic matter in all samples in urban area compared to a control sample could be associated with the cold wave that fused Serbia in the period from 6 January to 11 January 2017 which resulted in higher consumption of fossil fuels for household heating in the city.

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