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Water-soluble inorganic ions in urban aerosols of the continental part of Balkans (Belgrade) during the summer – autumn (2008)

Abstract: Size-segregated aerosol samples were collected using six stages High Volume Cascade Impactor. Aerosol mass and water soluble ions concentrations were determined. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to study the origin of air masses arriving to Belgrade in the investigated period. The obtained results of aerosol mass and water-soluble ion concentrations have been divided into six sub-data sets based on air mass categories. The highest average mass concentration of the fine mode ($D_p \leq 0.49$ µm) was found for air masses coming to Belgrade from the southeast and northwest directions, and of the coarse mode ($3.0 < D_p \leq 7.2$ µm) for air masses arriving from the northwest direction. The highest concentrations of SO_4^{2-} were found in the fine particles transported to the investigated area by air masses from southeast direction. The analysis of contribution of marine aerosol components (Na^+ and Cl^-), the Correlation and Cluster Analysis indicated the influence of marine aerosol on urban aerosol of the central Balkans coming from the Western Mediterranean and northern direction. NH_4^+ and SO_4^{2-} and K+ dominated in the fine mode for all air mass categories. PCA demonstrated the dominant impact of secondary aerosol formation processes on urban aerosols.

Keywords: Urban aerosol, Size-segregated inorganic ions, Balkan region

1 Introduction

An atmospheric aerosol is generally a mixture of species from a number of sources. Gas–particle conversion processes in the atmosphere form sulfate, nitrate and ammonium ions. Sulfates are mainly obtained by the oxidation of SO_2 from burning of fossil fuels, industrial processes, volcanoes, combustion of biomasses or oxidation of lower oxidation state sulfur compounds. The main sources of NO_x are combustion of fossil fuels in high-temperature processes, microbiological activity, combustion of biomass, lightning *etc*. Sulfate and nitrate aerosols can be obtained by neutralization reactions of HNO_3 and H_2SO_4 in the presence of ammonia or salts, and NaCl from marine aerosol [1]. The sulfates in the atmosphere can also originate from other sources: *e.g.*, primary marine aerosol, gypsum $CaSO_4$, resuspended particles or dust from the Sahara [2], *etc*. Ammonia is released in the atmosphere as a result of the decay of vegetation in soils, fertilizer application and production, biomass burning, decay of waste products from domestic animals, wild animals, the seas and the oceans. Total ammonia ($NH_3 + NH_4^+$) is the sum of both, the gaseous and aerosol forms. In many conditions gaseous ammonia is predominant. When the equilibrium favors aerosol forms, the major species are ammonium bisulfate, ammonium sulfate, and ammonium nitrate, depending on the conditions. Seinfeld

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[3] reported that generally ammonia occurs in the form of $(NH_4)_2SO_4$ in the atmosphere, but it can also be found in the form of NH_4NO_3 [4].

The first results in our previous work pointed to the possibility of marine aerosol impacting urban aerosols in the continental part of the central Balkans [5]. Researchers in Spain [6] have shown that Na^+ and Cl^- exhibited slightly higher levels on the Iberian Peninsula in summer, as a consequence of the higher intensity of sea breeze dynamics. In addition, some researchers have developed distribution models of the atmospheric marine salt deposition over the continental Western Europe [7] and in the Central Mediterranean [8].

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [9-12] is a commonly used air modeling program for calculating air mass paths from one region to another [13-15]. The HYSPLIT model (Version 4.8) is a complete system that is designed to support a wide range of simulations related to the regional or long-range transport, dispersion, and deposition of air pollutants.

Investigated region is under influence of Mediterranean Sea [5,15] and industrial zones [5] in surrounding areas.

The purpose of this study is the evaluation of the water-soluble ions contents in the urban aerosol of the continental part of Balkans according to main air masses arriving from different regions. This study is important for identifying influences of remote sources on the contents of some water-soluble ions in urban aerosol of the continental part of Balkans.

2 Experimental procedure

2.1 Aerosol sampling

The aerosol sampling was carried out in downtown Belgrade (Fig. 1) (44°48'N, 20°28'E), Serbia, over the course of 6 months in 2008, from June to December. Samples were collected at a frequency of one sample every sixth day, encompassing all weekdays of the six month sampling period. The sampling duration for each sample set was 48 hours using a six-stage High Volume Cascade Impactor (Model TE-236) for the following particle size ranges: $D_{p1} \leq 0.49$ μm, $0.49 < D_{p2} \leq 0.95$ μm, $0.95 < D_{p3} \leq 1.5$ μm, $1.5 < D_{p4} \leq 3.0$ μm, $3.0 < D_{p5} \leq 7.2$ μm and $D_{p6} \geq 7.2$ μm. The operating flow was 1.13 $m^3\,min^{-1}$. Samples were collected on nitrocellulose fibrous filters and stored at -18°C before analysis. Field blanks, comprising around 20% of all samples, were also collected and followed all handling procedures except for actual sampling.
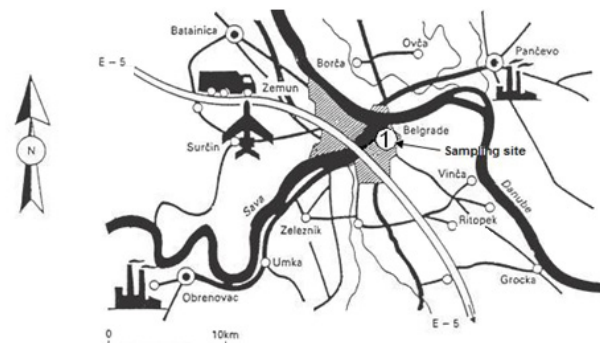

Figure 1: Sampling site 1.

2.2 Gravimetric and chemical analysis

Aerosol mass concentrations are determined by gravimetric measurements (m_{GM}) using a KERN ABT 120-5DM Balance (Accuracy class I and precision of 0.01 mg). The balance and the filters were kept at temperature of 20±5°C and humidity 45±5% controlled nitrogen glove box before and during the weighing procedure [5,16]. The expanded uncertainty of gravimetric mass measurements was 4%.

Samples were extracted in ultra-pure water (resistivity 18.2 MΩ cm at 25°C), using an ultrasonic bath Transsonic T 760 DH (Elma, Germany), at 40 kHz frequency and effective power of 170 W. The samples were subsequently analyzed for Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} by ion chromatography (Metrohm, Switzerland, type 761 Compact IC, with a conductometric detector) [5]. Every analytical run started with calibration standards in order of increasing concentration, followed by water blank and samples. The check calibration standard was analyzed after every ten analysis. In addition to the field blanks and sample filters, a reagent blank was also analyzed. The concentrations of investigated inorganic ions in reagent blank were below detection limit. The expanded measurement uncertainties of ion analysis are the following: 8% for Cl^-, 2% for NO_3^-, 2% for SO_4^{2-}, 3.2% for Na^+, 18% for NH_4^+, 24% for Ca^{2+}, 3% for Mg^{2+} and 8% for K^+. The overall measurement uncertainties were up to 8% for investigated inorganic species except of NH_4^+ and Ca^{2+}.

2.3 Air mass trajectories

For investigating the origin of air parcel, the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [9-12] was applied every sixth day from June to December. The trajectory calculation was achieved by time integration of an air parcel position as it is carried by 3D winds [9]. By moving backward in time, the back
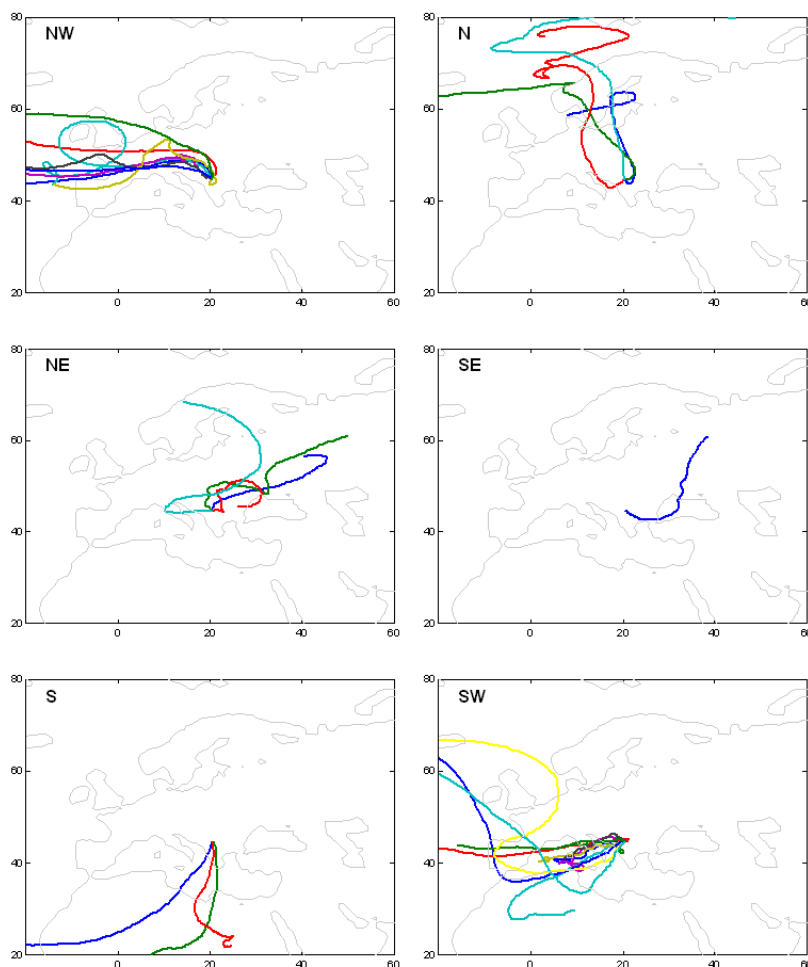
Figure 2: Classification of back trajectories for Belgrade using HYSPLIT model: NW (northwestern Europe), N (northern Europe), NE (northeastern Europe), SE (southeastern Europe), S (southern Europe) and SW (southwestern Europe).

trajectory indicated air masses arriving at a receptor at a particular time, thereby identifying the source region. Six-day back trajectories reaching Belgrade at 500, 1500, and 5000 m were calculated using the NCEP/NCAR (National Centers for Environmental Prediction/National Center for Atmospheric Research) reanalysis meteorological data with a 2.5×2.5° horizontal resolution [17].

3 Results and discussion

A number of studies in Europe regarding urban aerosols were conducted in the last decade [4, 16, 18-22 and others]. This work focuses on the water-soluble ionic content of the size-segregated urban aerosol in the continental area of the Balkans and the influences of characteristic air masses arriving at the study site during the measurement campaign. Table 1 presents aerosol mass concentrations

through six stages and the basic meteorological data for each sample.

The possible air origin was investigated by back trajectories. Air masses trajectories were classified into six trajectory categories by the direction of their approach to Belgrade (Fig. 2). The origins of the air masses are: northwestern Europe (NW), northern Europe (N), northeastern Europe (NE), southeastern Europe (SE), southern Europe (S), and southwestern Europe (SW). NW is a category of air masses arriving from the Atlantic Ocean and Western Europe. N and NE are the categories for air masses that come from areas of northern and northeastern Europe, respectively. SE - a category of air masses originating from southeastern Europe and the Black Sea. S - a category of air masses originating from central Mediterranean or Africa. SW - a category of marine air masses originating from the western Mediterranean, passing over Italy and the Adriatic Sea.

Table 1: Aerosol mass concentrations m_{GM} ($\mu g\ m^{-3}$) of particles distributed through Dp (μm) intervals and air mass category corresponding to each sample, mean values of velocity ($m\ s^{-1}$), humidity (%), and precipitation (mm) for measured intervals.

	$Dp{\leq}0.49$	$0.49{\leq}Dp{\leq}0.95$	$0.95{\leq}Dp{\leq}1.5$	$\Sigma_{(fine)}$	$1.5{\leq}Dp{\leq}3.0$	$3.0{\leq}Dp{\leq}7.2$	$Dp{\geq}7.2$	$\Sigma_{(coarse)}$	Air masses corresponding to the sample	48 hour average wind velocity (m/s)	48 hour average humidity (%)	48 hour average Precipitation amount (mm)
21/06/2008	1.0	0.6	1.8	*3.4*	0.7	0.9	0.3	*1.9*	NW	1.6	53	0
27/06/2008	5.4	1.3	1.8	*8.5*	2.5	4.7	1.4	*8.6*	NW	2.7	58	4.0
03/07/2008	9.4	1.5	1.7	*12.6*	2.1	4.8	2.1	*9*	NW	2.1	47	0
09/07/2008	5.7	1.3	0.7	*7.7*	1.3	3.5	0.9	*5.7*	NW	2.1	46	0
15/07/2008	8.1	2.7	2.3	*13.1*	2.0	3.3	1.9	*7.2*	NW	3.0	70	2.0
21/07/2008	7.9	3.4	2.2	*13.5*	3.1	3.5	2.3	*8.9*	SW	2.6	71	12.1
27/07/2008	6.0	2.3	0.9	*9.2*	1.0	2.8	0.8	*4.6*	NE	1.8	67	0
02/08/2008	10.6	1.7	0.3	*12.6*	0.5	2.3	0.3	*3.1*	SE	2.7	53	0
08/08/2088	8.7	2.6	2.2	*13.5*	2.6	3.9	1.3	*7.8*	SW	2.6	70	27.1
14/08/2008	8.7	1.7	1.6	*12*	1.8	3.8	1.2	*6.8*	SW	3.6	39	0
20/08/2008	12.0	1.4	1.2	*14.6*	1.9	4.2	1.5	*7.6*	NW	2.2	46	0
26/08/2008	4.4	1.6	1.7	*7.7*	2.5	4.8	1.8	*9.1*	NW	1.2	50	0
01/09/2008	14.3	2.0	1.5	*17.8*	1.8	4.2	1.6	*7.6*	N	2.2	49	0
07/09/2008	11.1	4.0	5.1	*20.2*	5.7	7.2	3.3	*16.2*	SW	2.6	45	0.1
13/09/2008	7.1	2.7	1.9	*11.7*	2.2	2.4	2.2	*6.8*	SW	2.2	85	34.6
19/09/2008	9.7	2.4	1.4	*13.5*	1.3	1.6	1.0	*3.9*	NE	1.9	78	0
25/09/2008	5.9	2.1	0.9	*8.9*	0.6	1.3	0.1	*2*	NE	2.3	90	0
01/10/2008	3.9	2.6	1.8	*8.3*	2.4	4.6	1.9	*8.9*	NE	2.3	58	0
07/10/2008	15.8	4.3	3.3	*23.4*	3.1	7.6	2.7	*13.4*	NW	1.7	65	0
13/10/2008	25.3	5.6	3.5	*34.4*	4.4	7.4	2.9	*14.7*	NW	1.1	76	0
19/10/2008	9.5	6.2	2.3	*18*	2.3	4.6	1.1	*8*	SW	1.6	67	0
25/10/2008	12.0	5.4	1.4	*18.8*	2.9	1.6	0.7	*5.2*	SW	1.7	82	0
31/10/2008	5.8	1.6	2.8	*10.2*	3.3	4.0	0.8	*8.1*	SW	3.4	56	0.2
06/11/2008	7.5	4.7	3.2	*15.4*	2.7	5.0	1.7	*9.4*	SE	4.9	62	0
12/11/2008	11.7	4.5	2.5	*18.7*	2.4	3.4	1.8	*7.6*	SW	3.1	68	0
18/11/2008	10.1	3.3	2.0	*15.4*	1.8	2.3	1.0	*5.1*	N	2.1	78	0
24/11/2008	4.2	3.5	1.6	*9.3*	1.2	1.3	0.7	*3.2*	N	4.4	72	35.2
30/11/2008	0.7	1.1	0.9	*2.7*	1.5	2.1	0.5	*4.1*	SW	4.9	62	0
06/12/2008	1.7	1.6	0.8	*4.1*	0.6	0.5	0.2	*1.3*	SW	3.1	76	22.0
12/12/2008	0.9	0.7	0.2	*1.8*	0.4	0.3	0.4	*1.1*	S	6.7	73	3.4
18/12/2008	2.9	2.3	1.4	*6.6*	1.1	1.1	0.7	*2.9*	S	4.2	84	6.2
24/12/2008	4.6	2.4	1.2	*8.2*	0.8	0.6	0.1	*1.5*	N	2.4	71	0.4

Table 2: Aerosol mass concentrations m_{GM} (µg m^{-3}) of particles distributed through D_p (µm) intervals for the total data set and for the sub-sets for considered air masses origins.

		$Dp≤0.49$	$0.49≤Dp≤0.95$	$0.95≤Dp≤1.5$	$\Sigma_{(fine)}$	$1.5≤Dp≤3.0$	$3.0≤Dp≤7.2$	$Dp≥7.2$	$\Sigma_{(coarse)}$	Total Σ
Total data set	Mean ± σ	7.9 ± 5.0	2.7 ± 1.5	1.8 ± 1.0	12.4 ± 6.6	2.0 ± 1.2	3.3 ± 2.0	1.3 ± 0.8	6.6 ± 3.7	**19.0 ± 9.7**
	% of total mass	41.6	14.2	9.5	65.3	10.5	17.4	6.8	34.7	**100**
N segment $N*=4$	Mean ± σ	8.3 ± 4.8	2.8 ± 0.7	1.6 ± 0.3	12.7 ± 4.7	1.4 ± 0.5	2.1 ± 1.5	0.9 ± 0.6	4.4 ± 2.6	**17.4 ± 7.2**
	% of total mass	48.7	16.4	9.3	74.4	8.1	12.4	5.1	25.6	**100**
NE segment $N*=4$	Mean ± σ	6.4 ± 2.4	2.4 ± 0.2	1.2 ± 0.4	10.0 ± 2.4	1.3 ± 0.8	2.6 ± 1.5	1.0 ± 0.7	4.8 ± 2.9	**14.8 ± 3.1**
	% of total mass	43.0	15.9	8.3	67.3	8.9	17.3	6.4	32.7	**100**
SE segment $N*=2$	Mean ± σ	9.0 ± 2.2	3.2 ± 2.1	1.7 ± 2.0	14.0 ±2.0	1.6 ± 1.6	3.6 ± 1.9	1.0 ± 1.0	6.2 ± 4.5	**20.2 ± 6.4**
	% of total mass	44.8	15.8	8.5	69.1	7.8	18.0	5.0	30.9	**100**
S segment $N*=2$	Mean ± σ	1.9 ± 1.4	1.5 ± 1.2	0.8 ± 0.9	4.2 ± 3.4	0.8 ± 0.5	0.7 ± 0.6	0.5 ± 0.2	2.0 ± 1.3	**6.2 ± 4.8**
	% of total mass	30.5	24.3	13.0	67.7	12.2	11.4	8.5	32.2	**100**
SW segment $N*=11$	Mean ± σ	7.7 ± 3.7	3.2 ± 1.7	2.2 ± 1.2	13.1 ± 5.8	2.6 ± 1.3	3.4 ± 1.8	1.4 ± 0.9	7.4 ± 3.7	**20.4 ± 8.7**
	% of total mass	37.8	15.4	10.6	64.0	12.7	16.4	7.0	36.0	**100**
NW segment $N*=9$	Mean ± σ	9.7 ± 7.3	2.2 ± 1.6	2.0 ± 0.9	13.9 ±9.6	2.3 ± 1.1	4.6 ± 2.0	1.7 ± 0.8	8.6 ± 3.8	**22.0 ± 8.2**
	% of total mass	43.0	10.0	8.8	61.9	10.1	20.3	7.7	38.1	**100**

Back trajectories showed that the dominant air mass origin was from southwestern and northwestern Europe (Table 1).

Table 2 shows average particle mass concentrations, including the mean values and standard deviations (σ) of six sub-sets obtained by dividing the total data set according to characteristic air mass origins. The number of days for each corresponding category ($N*$), based on directions of trajectories, is also shown in Table 2. The two prevailing directions were from southwestern - 11 cases (34.4%) and northwestern Europe - 9 cases (28.1%). The highest average mass concentration of the fine mode ($D_p ≤ 0.49$ µm) was found for the SE and NW air mass categories and for the coarse mode (3.0 < Dp ≤ 7.2 µm) was found for the NW air mass category (Table 2, Fig. 3). With respect to the total particle mass concentration of the corresponding air mass category, the highest average mass concentration of the fine mode was found for the N (74.4%) and SE (69.1%) segments (Table 2, Fig. 3). A similar investigation of urban aerosols in Seville [19] has shown 50% share of fine mode. In Athens, the particle fraction <0.95 µm, accounted for 62% and 36% of the total PM in winter and summer period, respectively [23].

The average concentration of the water-soluble ions for the characteristic air masses is presented in Fig. 4. Sulfur dioxide is the predominant anthropogenic sulfur-containing air pollutant. The highest average concentration of SO_4^{2-} (2505.0±787.0 ng m^{-3}) was found in the fine particles ($D_p ≤ 0.49$ µm) arriving at the investigated area by air masses from southeast direction (SE air mass category). An origin of sulfur could be the mining and smelting complex in the city of Bor, located about 200 km southeast of Belgrade. The average content of sulfur in crude ore is up to 15% [24]. Also, in the SE directions are two Coal-Fired Power Plants, Drmno and Kostolac, about 150 km from Belgrade. Coal combustion is significant source of SO_2. The old technologies in southeastern part of Europe exploiting fossil fuels with high sulfur content could also be source of sulfate coming to the receptor. But, although the concentrations of SO_4^{2-} from the SE direction are the highest (Figs. 5a$_1$-5a$_6$), the total contribution is negligible (Figs. 5b$_1$-5b$_6$) due to frequency of days with air masses coming from southeast direction being less than 10%.

Furthermore, highest average contents of NH_4^+ were found in the size range $D_p ≤ 0.49$ µm for each air mass category (Fig. 4). The obtained high average concentrations for NH_4^+ are indicating that the gas-phase chemical reactions were responsible for gas–particle conversion of ammonia with acid oxides in the air. In addition, for Cl$^-$ and K$^+$ high concentrations were also found in all air masses categories in the fine mode ($D_p ≤ 0.49$ µm).
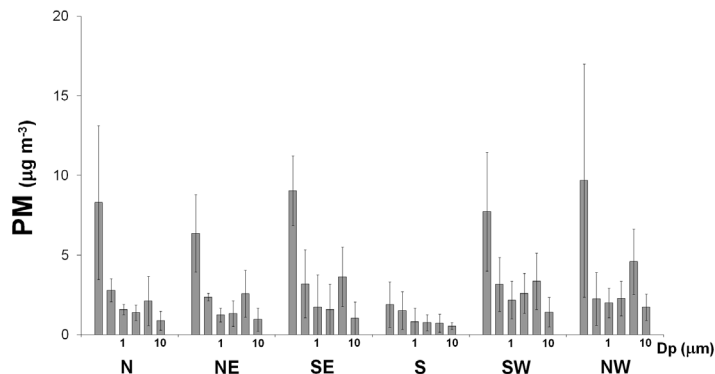
Figure 3: Average mass concentrations and standard deviations of size-segregated aerosols for each of the characteristic air mass categories.
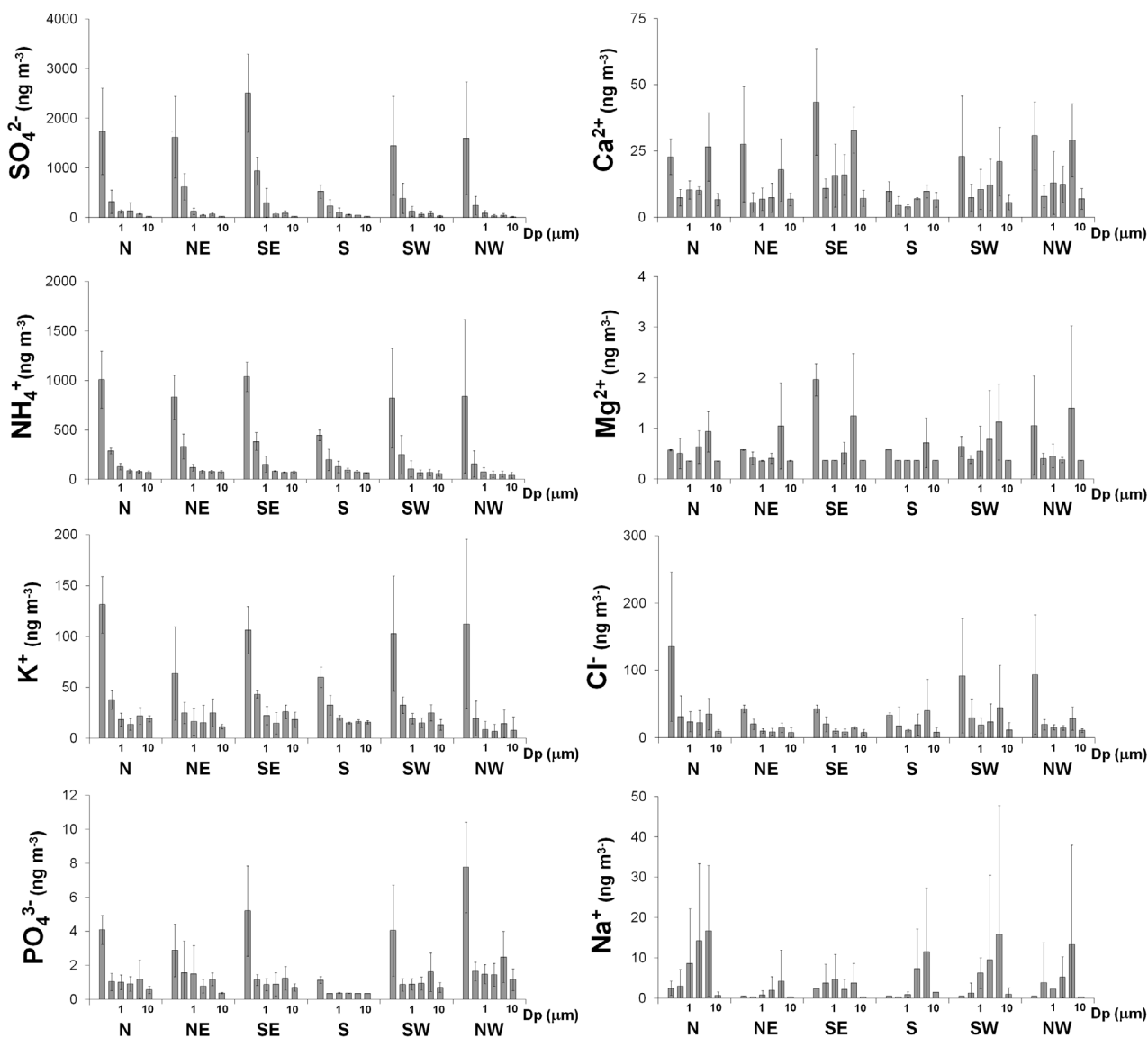

Figure 4: Average concentrations and standard deviations of ions in size-segregated aerosols for each of the characteristic air mass categories.
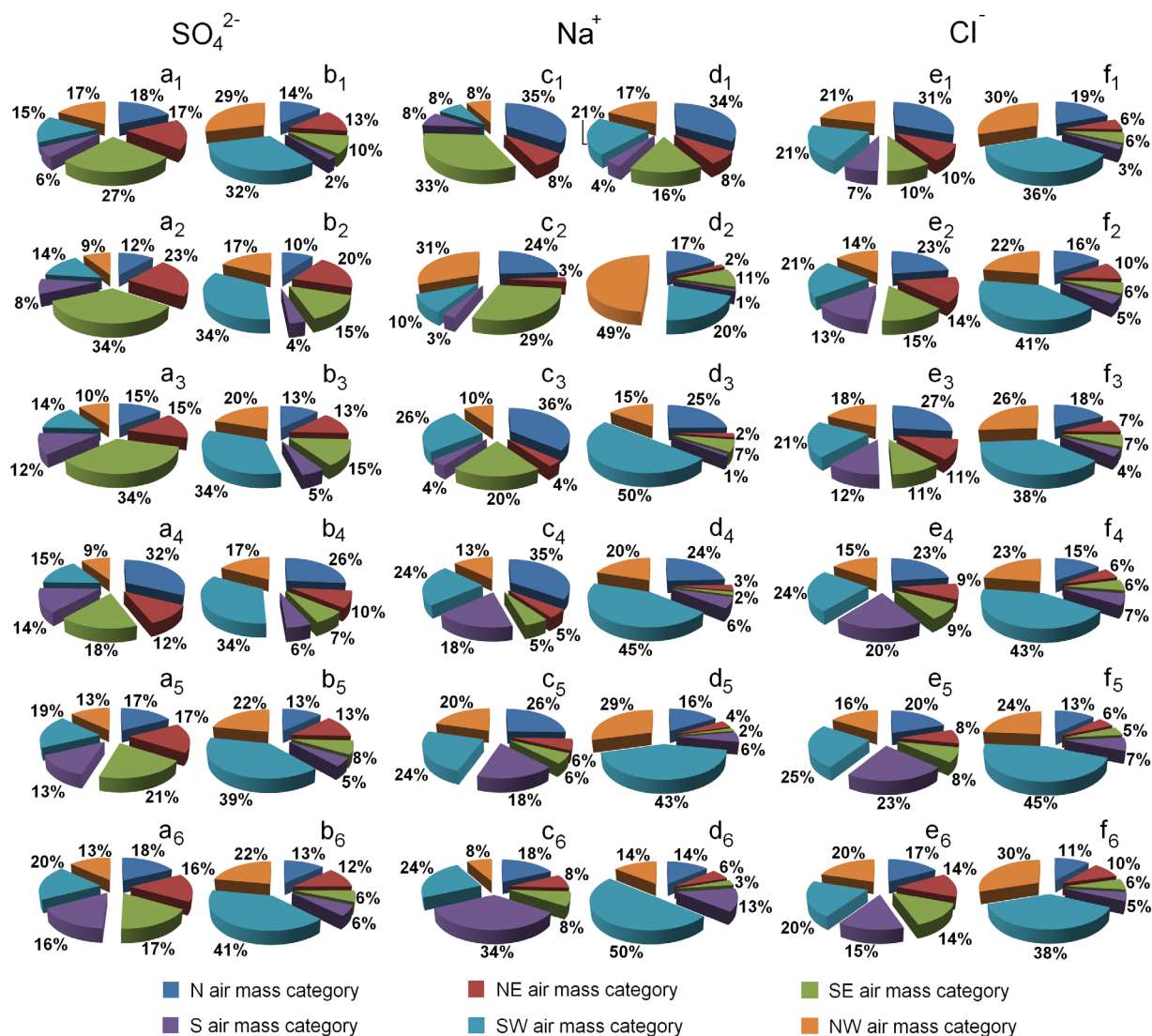
Figure 5: The average concentrations (a, c and e) and total contributions (b, d and f) of SO_4^{2-}, Na^+ and Cl^- according to air mass trajectories and *Dp* intervals 1: *Dp* ≤ 0.49 μm; 2: 0.49 < *Dp* ≤ 0.95 μm; 3: 0.95 < *Dp* ≤ 1.5 μm; 4: 1.5 < *Dp* ≤ 3.0 μm; 5: 3.0 < *Dp* ≤ 7.2 μm; 6: *Dp* > 7.2 μm.

Fertilizer plant located in the industrial zone of the nearby city of Pančevo (Fig. 1) is producing mineral fertilizers [25] that could be one of the important sources of NH_4^+ and K^+. The origin of Cl^- in the nuclei mode could be from the electrolysis utility, a part of Petrochemical plant which is located in the same Pančevo industrial zone [5]. Industrial emissions as sources of Cl^- in the fine mode have already been reported in Thessaloniki [22]. Other sources of K^+ in the fine mode could be wood and biomass burning. The additional origin of Cl^- but in the coarse mode could be long-range transport of marine aerosols.

In our previous work we indicated the possibility of marine aerosol influence on urban aerosols in the continental part of the central Balkans [5]. In this work we tried to verify this assumption by analyzing the origin of

air masses and the content of marine aerosol components, primarily Cl^- and Na^+. The highest average concentrations of Na^+ were found in the coarse mode, (Figs. 4 and 5) in air masses coming from the north direction (N air mass category), Western Mediterranean region (SW air mass category) and south direction (S air mass category) (Fig. 2). The highest average concentrations of Cl^- in the coarse mode were found in the SW air masses coming over the Mediterranean region (Figs. 2, 4 and 5). The main emission source of NaCl from SW direction is the Mediterranean Sea.

The larger contribution of sea salt was also found in the coarse mode roughly in the interval 0.6 μm < Dp ≤ 6 μm, in northwestern Italy [18], corresponding to our results related to air masses coming from the

Table 3: Correlations between Na⁺ and Cl⁻ in air masses from the SW segment.

		Na⁺				
	Correlation (Significance)	$0.49 \leq Dp \leq 0.95$ µm	$0.95 \leq Dp \leq 1.5$ µm	$1.5 \leq Dp \leq 3.0$ µm	$3.0 \leq Dp \leq 7.2$ µm	$Dp \geq 7.2$ µm
Cl⁻ $1.5 \leq Dp \leq 3.0$ µm	r (p)	0.746 (0.008)	0.900 (0.000)	0.991 (0.000)	0.964 (0.000)	
$3.0 \leq Dp \leq 7.2$ µm	r (p)	0.866 (0.001)	0.958 (0.000)	0.962 (0.000)	0.994 (0.000)	0.683 (0.021)
$Dp \geq 7.2$ µm	r (p)	0.929 (0.000)	0.970 (0.000)	0.880 (0.000)	0.957 (0.000)	0.795 (0.000)

Table 4: Correlations between Na⁺ and Cl⁻ in air masses from the N segment.

		Na⁺				
	Correlation (Significance)	$0.49 \leq Dp \leq 0.95$ µm	$0.95 \leq Dp \leq 1.5$ µm	$1.5 \leq Dp \leq 3.0$ µm	$3.0 \leq Dp \leq 7.2$ µm	$Dp \geq 7.2$ µm
Cl⁻ $0.95 \leq Dp \leq 1.5$ µm	r (p)	0.967 (0.033)	0.952 (0.048)	0.956 (0.044)		
$1.5 \leq Dp \leq 3.0$ µm	r (p)	0.998 (0.002)	0.998 (0.002)	0.987 (0.013)		0.980 (0.020)
$3.0 \leq Dp \leq 7.2$ µm	r (p)	0.966 (0.034)	0.976 (0.024)	0.983 (0.017)	0.957 (0.043)	0.991 (0.009)

Western Mediterranean region. In the Finokalia Aerosol Measurement Experiment in 2008 [20] was shown that in the coarse fractions dominated crustal matter (50%) and sea salt (24%), while sulfate and organics accounted for 55% and 28% of the fine particle mass, respectively. An investigation of physical and chemical characteristics of the atmospheric aerosol at Mt. Cimone (Italy) has shown that regressions between K⁺, Mg²⁺, Ca²⁺, and SO₄²⁻ on one side, and Na⁺ on the other side, indicated a sea spray as a common source of Na⁺ and Mg²⁺ [4]. Our previous work [5] has shown the existence of significant correlations in associations of Mg²⁺ – Na⁺ and Na⁺ – Cl⁻ indicating an influence of sea spray on urban aerosols. The correlations among sea salt components found in this study, have shown that the best significant correlations are between coarse Na⁺ and Cl⁻, for the SW and N air mass categories respectively from the Mediterranean sea and northern Europe or north seas (Tables 3 and 4).

The calculation of sea salt fractions of Na⁺, SO₄²⁻ and Mg²⁺ and the sea salt contribution according to 3 models [1,26,27] have shown domination of sea salts contribution for southwestern (SW) and northern (N) categories (Table 5). The significant contribution of ssNa⁺ in the coarse mode fractions ($1.5 \leq Dp \leq 3.0$ µm and $3.0 \leq Dp \leq 7.2$ µm) is also found by the sea salt calculation (Table 5). The air masses coming from southwest (Western Mediterranean) and north directions have 40-60% share of to the Na⁺ and Cl⁻ average concentrations in the coarse mode comparing to all air masses (Figs. 5c₄-5c₆, Figs. 5e₄-5e₆), while the total contributions are up to 70% for Na⁺ in the coarse mode (Figs. 5d₄-5d₆, Figs. 5f₄-5f₆) because of the highest frequency of SW direction.

Cluster analysis (CA), a widely used multivariate statistic method, was applied on the sub-data sets in this study. This method is often used to validate correlation between variables. CA can further elucidate the existing associations between variables in the data set and give more information on source identification. The calculation results of cluster analysis can be seen on a figure, called dendrogram. The cluster analysis was performed using average linkage between groups based on Pearson's correlation coefficients. In this work, the role of CA was to verify the assumption that marine aerosol affects the contents of marine components (Na⁺,Cl⁻, Mg²⁺) in urban aerosols of Central Balkans.

The cluster analysis of the sub-data set for the SW (Fig. 6) and N air mass categories (Fig. 7) showed a group of marine origin characterized by Na⁺, Cl⁻ and Mg²⁺ indicating the contribution of marine aerosol coming from the West Mediterranean and the north seas. Another group was characterized by Mg²⁺ and Ca²⁺ representing a crustal contribution. The cluster analysis also revealed that SO₄²⁻ is strongly associated with NH₄⁺, and there is a weaker association with K⁺. A group associated with marine contribution was not found for the sub-data sets corresponding to other air mass categories.

In order to identify the sources responsible for the formation of aerosols with respect to size, principal component analysis (PCA) was carried out on the total data set, separately for each aerosol fraction. Principal component analysis is a multivariate statistical technique commonly used in environmental studies to identify sources from data taken at receptors. PCA is based on the correlations among variables, which are assumed

Table 5: Average sea salt fractions of Na$^+$, SO$_4^{2-}$ and Mg^{2+} and average sea salt contribution (ng m^{-3}) of the size segregated aerosol samples for the considered air mass origins.

		$Dp \leq 0.49$ µm			$0.49 \leq Dp \leq 0.95$ µm			$0.95 \leq Dp \leq 1.5$ µm			$1.5 \leq Dp \leq 3.0$ µm			$3.0 \leq Dp \leq 7.2$ µm			$Dp \geq 7.2$ µm		
		a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
ssNa$^+$	N	2.5	2.5	/	3.1	3.1	1.6	8.6	8.6	6.2	14.3	14.3	10.1	16.7	16.7	8.6	0.8	0.8	/
	NE	0.6	0.6	/	0.4	0.4	/	0.9	0.9	/	2.0	2.0	/	4.2	4.2	/	0.4	0.4	/
	SE	2.4	2.4	/	3.7	3.7	/	4.7	4.7	/	2.2	2.2	/	3.8	3.8	/	0.4	0.4	/
	S	0.6	0.6	/	0.4	0.4	/	0.9	0.9	/	7.3	7.3	4.9	11.5	11.5	7.8	1.5	1.5	/
	SW	0.6	0.6	/	1.3	1.3	0.3	6.3	6.3	4.0	9.6	9.6	6.6	15.9	15.9	11.8	1.0	1.0	0.3
	NW	0.6	0.6	/	3.9	3.9	2.9	2.3	2.3	0.9	5.2	5.2	1.8	13.3	13.3	5.4	0.4	0.4	/
ssSO$_4^{2-}$	N	0.6	0.6	/	0.8	0.8	0.4	2.2	2.2	1.5	3.6	3.6	2.5	4.2	4.2	2.2	0.2	0.2	/
	NE	0.1	0.1	/	0.1	0.1	/	0.2	0.2	/	0.5	0.5	/	1.1	1.1	/	0.1	0.1	/
	SE	0.6	0.6	/	0.9	0.9	/	1.2	1.2	/	0.5	0.5	/	1.0	1.0	/	0.1	0.1	/
	S	0.1	0.1	/	0.1	0.1	/	0.2	0.2	/	1.8	1.8	1.2	2.9	2.9	2.0	0.4	0.4	/
	SW	0.1	0.1	/	0.3	0.3	0.1	1.6	1.6	1.0	2.4	2.4	1.7	4.0	4.0	3.0	0.3	0.3	0.1
	NW	0.1	0.1	/	1.0	1.0	0.7	0.6	0.6	0.2	1.3	1.3	0.4	3.3	3.3	1.4	0.1	0.1	/
ssMg^{2+}	N	0.3	0.3	/	0.4	0.4	0.2	1.0	1.0	0.7	1.7	1.7	1.2	2.0	2.0	1.0	0.1	0.1	/
	NE	0.1	0.1	/	/	/	/	0.1	0.1	/	0.2	0.2	/	0.5	0.5	/	/	/	/
	SE	0.3	0.3	/	0.4	0.4	/	0.6	0.6	/	0.3	0.3	/	0.5	0.5	/	/	/	/
	S	0.1	0.1	/	/	/	/	0.1	0.1	/	0.9	0.9	0.6	1.4	1.4	0.9	0.2	0.2	/
	SW	0.1	0.1	/	0.2	0.2	/	0.8	0.8	0.5	1.1	1.1	0.8	1.9	1.9	1.4	0.1	0.1	/
	NW	0.1	0.1	/	0.5	0.5	0.3	0.3	0.3	0.1	0.6	0.6	0.2	1.6	1.6	0.7	/	/	/
sea salt	N	8.3	139.1	/	10.0	36.4	16.1	28.1	36.4	20.0	46.6	43.6	31.7	54.6	59.8	37.2	2.6	10.6	/
	NE	1.9	43.8	/	1.2	20.7	/	2.8	11.4	/	6.7	11.9	/	13.9	21.0	/	1.2	8.3	/
	SE	7.9	88.9	/	12.2	29.1	/	15.4	24.8	/	7.2	22.4	/	12.5	32.7	/	1.2	11.0	/
	S	1.9	34.3	/	1.2	18.4	/	2.9	12.1	/	24.0	30.2	22.6	37.7	57.1	48.0	4.9	10.6	/
	SW	1.9	92.6	/	4.3	31.5	3.4	20.4	27.7	13.5	31.3	37.7	25.4	52.0	68.1	51.2	3.4	13.1	4.6
	NW	1.9	94.6	/	12.8	25.4	5.8	7.4	19.0	5.1	17.2	22.7	8.5	43.6	48.1	17.6	1.2	11.8	0.9

[a] [Na$^+$]= [ssNa$^+$], sea salt = 3.27[Na$^+$], [ssSO$_4^{2-}$] = 0.25[Na$^+$], [ss Mg^{2+}] = 0.12[Na$^+$], [1].

[b] [Na$^+$]= [ssNa$^+$], sea salt = 1.47[Na$^+$]+[Cl$^-$], [26], [ssSO$_4^{2-}$] = 0.25[Na$^+$], [ss Mg^{2+}] = 0.12[Na$^+$].

[c] [ssNa$^+$]= [Na$^+$] − 0.61[Ca^{2+}], sea salt = 1.47[ssNa$^+$]+[Cl$^-$], [27], [ssSO$_4^{2-}$] = 0.25[ssNa$^+$], [ssMg^{2+}] = 0.12[ssNa$^+$].

to be caused by certain underlying structures (sources). PCA uses the correlation matrix to calculate a suite of principal components which could explain the variability of most of the original data. Principal components are then subjected to rotation to generate a matrix of factor loadings for variables in the factors. After rotation of the factor-loading matrix, the factors can be interpreted as origins or common sources [28,29].

The results of the PCA, presented as factor loadings of the varimax rotated matrix of sub-data sets, each corresponding to one of the six aerosol fractions, are given in Table 6. For almost all aerosol fractions three principal components were extracted, which explained 63 - 80% of the total variance (σ^2). The origins of aerosols, identified by PCA, are summarized in Table 7. The results of PCA indicated that processes of formation of secondary aerosol (PC1) had the dominant impact on urban aerosols, since the representatives of secondary aerosols had

moderate to high factor loadings in component 1 (PC1) for almost all particle size ranges (Tables 6 and 7). Submicron particles ($D_p \leq 0.49$ µm, $0.49 < D_p \leq 0.95$ µm) additionaly originated from mineral dust. PCA also implied impact of sea spray (PC2) and industrial emission (fertilizer plant) (PC3) on aerosol fraction $0.95 < D_p \leq 1.5$. For the data related to aerosol fraction $1.5 < D_p \leq 3.0$ µm applied PCA extracted two components. Component that explains the highest variance, PC1, had high factor loadings for species associated with sea salt particles indicating the influence of marine aerosol. The second component (PC2) is characterized by moderate to high factor loadings for representatives of secondary aerosols, hence it demonstrates the impact of secondary aerosol formation processes on aerosol fraction $1.5 < D_p \leq 3.0$ µm. On the contents of investigated water soluble ions in aerosol fraction $3.0 < D_p \leq 7.2$ µm the formation of secondary aerosols and industrial emission – fertilizer plant (PC1)
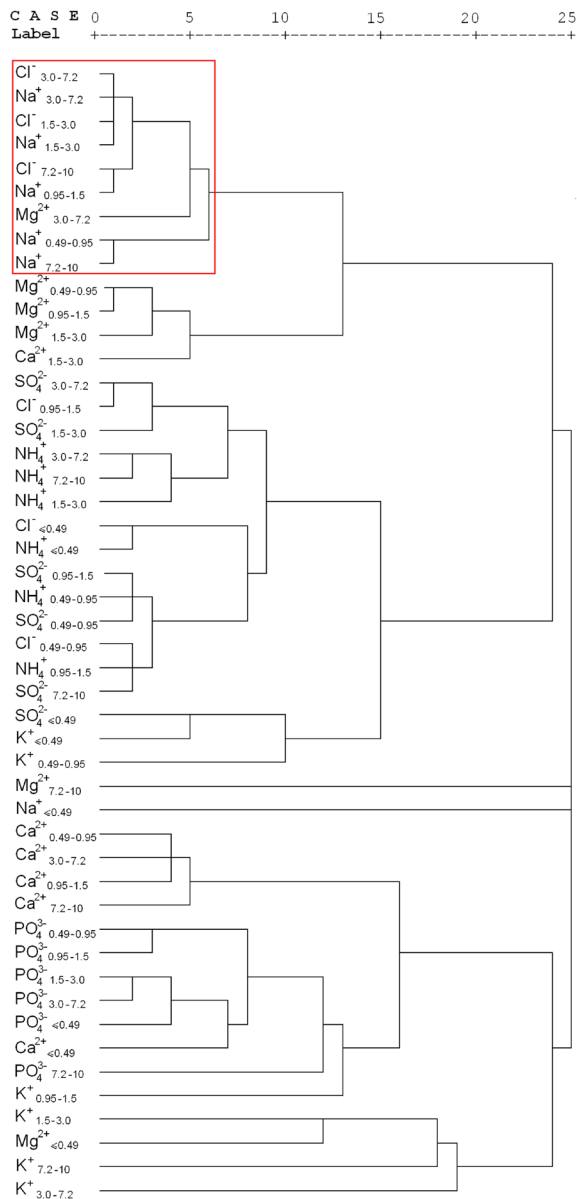
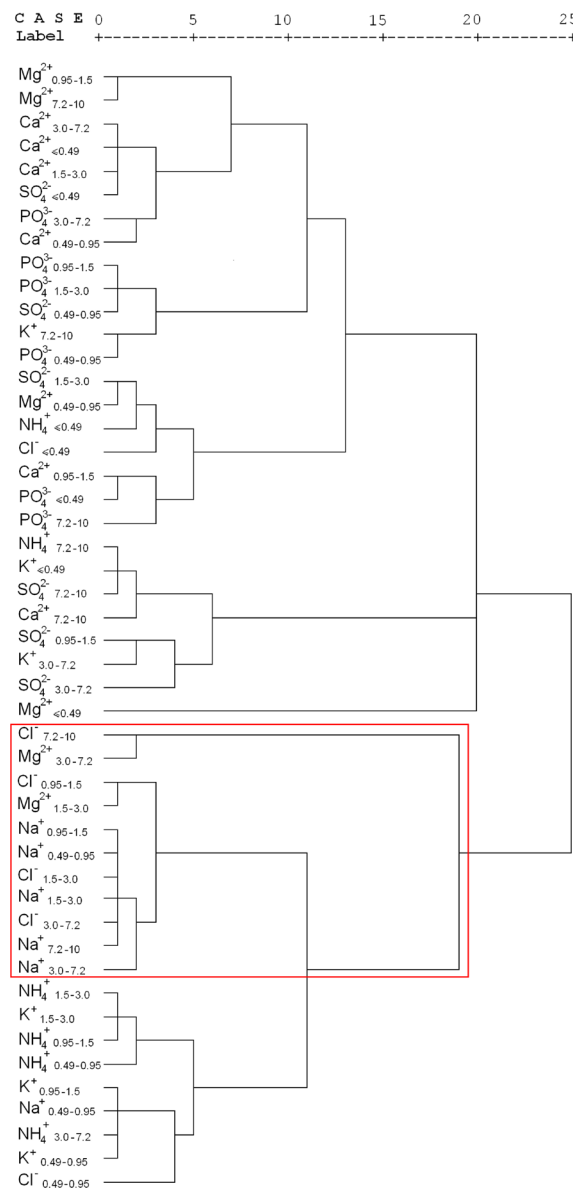**Figure 6:** Dendrogram of the Cluster Analysis for the SW segment.

Figure 7: Dendrogram of the Cluster Analysis for the N segment.

have significat influence. The impact of sea spray (PC2) and mineral dust (PC3) on this aerosol fraction can also be observed. For the coarsest fraction, PCA revealed the influences of secondary aerosol, mineral dust (PC1), sea spray (PC2) and industrial emission (PC3).

4 Conclusions

The samples of size-segregated urban aerosol collected in the city of Belgrade (central Balkans) in the period June-December 2008 have been analyzed for Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} according to air

masses coming to the investigated area. Air trajectories were classified into six categories by the direction of their approach to Belgrade. The two prevailing directions were from southwestern and northwestern Europe. In general, ions formed from gas precursors (NH_4^+ and SO_4^{2-}) and K^+ dominated in the fine mode of all air mass categories. The high contents of sulfates in the fine mode found in air masses coming from the southeast direction are indicating old technologies, like the mining and smelting basin in the city of Bor located about 200 km southeast from Belgrade and others in region and south-eastern Europe using fossil fuels with high sulfur content, as key sources. The highest contribution of components of marine aerosol (Na^+ and

Table 6: Factor loadings (varimax normalized) for the eigenvalues > 1 for each aerosol fraction.

Component	$D_{p1} \leq 0.49$ µm 1	2	3	$0.49 < D_{p2} \leq 0.95$ µm 1	2	3	$0.95 < D_{p3} \leq 1.5$ µm 1	2	3
σ^2 (%)	41.1	23.9	15.3	36	15.8	14.9	27.7	22	18.5
SO_4^{2-}	0.879			0.881			0.925		
PO_4^{3-}		0.695			-0.632	0.439			-0.656
Cl^-	0.859			0.798				0.643	
Na^+			0.898					0.781	
NH_4^+	0.966			0.969			0.912		
K^+	0.846			0.701					0.657
Ca^{2+}		0.890				0.904	0.518		
Mg^{2+}		0.691			0.745			0.759	

Component	$1.5 < D_{p4} \leq 3.0$ µm 1	2	$3.0 < D_{p5} \leq 7.2$ µm 1	2	3	$D_{p6} \geq 7.2$ µm 1	2	3
σ^2 (%)	39.1	23.1	31.4	28.5	20.4	28	21.6	18.9
SO_4^{2-}		0.415	0.673			0.766		
PO_4^{3-}		-0.704						0.785
Cl^-	0.915			0.940			0.932	
Na^+	0.898			0.960			0.892	
NH_4^+		0.824	0.888			0.866		
K^+		0.684	0.655			0.412		-0.550
Ca^{2+}	0.722				0.952	0.781		
Mg^{2+}	0.852			0.532	0.630			0.613

Table 7: Sources of aerosols identified by PCA.

Particle size	PC1	PC2	PC3
$D_{p1} \leq 0.49$ µm	secondary aerosol	mineral dust	
$0.49 < D_{p2} \leq 0.95$ µm	secondary aerosol		mineral dust
$0.95 < D_{p3} \leq 1.5$ µm	secondary aerosol	sea spray	industrial emission (fertilizer plant)
$1.5 < D_{p4} \leq 3.0$ µm	sea spray	secondary aerosol	
$3.0 < D_{p5} \leq 7.2$ µm	secondary aerosol + industrial emission (fertilizer plant)	sea spray	mineral dust
$D_{p6} \geq 7.2$ µm	secondary aerosol + mineral dust	sea spray	Industrial emission

Cl^-) in the coarse mode was found in air masses from the Mediterranean region and northern direction. The best correlations between Na^+ and Cl^- were found in the sub-data set corresponding to the air masses coming from the Western Mediterranean region and northern direction indicating the influence of marine aerosol on continental urban aerosols in the Balkans. The CA confirmed the presence of marine contribution. PCA indicated that processes of formation of secondary aerosols had the dominant impact on urban aerosols. Furthermore, the influence of marine aerosol was observed for the coarse particles.

model and/or READY website (http://www.arl.noaa.gov/ready.php) used in this publication.

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