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CHEMICAL COMPOSITION, CONCENTRATION AND SOURCE APPORTIONMENT OF ATMOSPHERIC SUBMICRON AEROSOL PARTICLES AT URBAN AND BACKGROUND SITES

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A quadrupole aerosol mass spectrometer (Q-AMS) was consecutively deployed for 6 months (March–August 2011) at an urban site (vicinity of Vilnius city) and two background sites (Rūgšteliškis, forested area; Preila, seaside area) in Lithuania. Analysis of semi-volatile non-refractory submicron aerosol particles (PM1) was based on measurements of chemical component mass concentration, assessment of long-range air masses and impact of local pollution sources on component concentration and source apportionment. A method for the quantification of nitrate and sulfate contributions to aerosol ammonium compounds was suggested, and results indicated a greater formation of ammonium nitrate than that of ammonium sulfate. The highest average mass concentration of PM1 (7.69 ± 6.83 μg m^{-3}) was found at the Vilnius site, while at the Preila site concentration was 2-fold lower (3.44 ± 2.65 μg m^{-3}). Analysis of chemical compound mass concentrations in the PM1 aerosol volume indicated organics fraction as the dominant at 68.8%, 77.1% and 77.0% for the Preila, Rūgšteliškis and Vilnius sites, respectively. The concentration of nitrate fraction at the Vilnius site was 4-fold higher than at the Preila site (1.84% and 7.68%, respectively) and was attributed to transport-related emissions. Results of Positive Matrix Factorization (PMF) indicated biomass burning organic aerosols (BBOA), hydrocarbon-like organic aerosols (HOA) and semi-volatile oxygenated organic aerosols (SV-OOA) at the urban site; BBOA, low-volatility oxygenated organic aerosols (LV-OOA), SV-OOA at the background forested site, and LV-OOA and SV-OOA at the background seaside site. This study examines PM1 at urban and background sites in Lithuania and suggests a quantification method of ammonium-nitrate and ammonium-sulfate present in ammonium compounds from aerosol particles.

Keywords: aerosol mass spectrometry, PM1 mass concentration, chemical composition, air masses, PMF

PACS: (92.60.hg, 92.60.Mt, 92.60.Ry, 92.60.Sz)

1. Introduction

Ubiquitous atmospheric aerosol particles are important due to their direct and indirect effects on global climate change [1] and the effects of aerosols on ecosystems, human health [2, 3] and climate are well-recognized [4]. Important parameters used to estimate atmospheric aerosol burden and global impact are size distribution [5, 6], chemical composition [5, 7] and concentration. Primary and secondary anthropogenic or/and natural aerosol particles scatter and absorb solar radiation, and act as cloud condensation nuclei (CCN) and/or ice condensation nuclei (IN). The efficiency of solar radiation scattering/absorbing and acting as CCN (which may affect climate) could be estimated by the size distribution and composition of aerosol particles [8]. Estimation of Earth radiative forcing (the difference of received and reflected solar radiation) also requires an ability to distinguish between natural and anthropogenic aerosols [4].

Natural primary aerosol particles mainly originate from volcanoes (mostly sulfur dioxide), sea spray (sea salt and dimethylsulfide oxidation products), desert/soil dust, wildfire smoke and vegetation processes (mostly terpenes and isoprene), whereas anthropogenic sources are mainly vehicles, industry and combustion processes in urban areas. Interaction between natural and anthropogenic aerosol particles, and secondary aerosol particles formed due to this interaction are still the field of active research. Secondary organic aerosol (SOA) particles are usually formed during homogeneous nucleation, condensation and heterogeneous reactions of gas-phase oxidation products from natural (biogenic) as well as anthropogenic volatile and semi-volatile organic compounds [9], while secondary aerosol particles are formed from sulfate and ammonium nitrate compounds [10]. Studies have shown that components of primary aerosol particles (especially semi-volatile) can be desorbed into gas-phase compounds before a secondary aerosol is formed, meaning that compounds undergo oxidation before secondary particles are formed [11]. These findings lead to the conclusion that low-volatility gas phase precursors, including long chain n-alkanes, polycyclic aromatic hydrocarbons (PAHs) and large olefins, are a potentially large source of SOA [12]. However, other secondary aerosol particle components are not yet recognized [13], and the conditions leading to the formation of secondary aerosol particles are unclear [14].

Organics account for 20–90% of the entire aerosol volume in the submicron range (PM1), therefore size distribution, chemical composition and source apportionment are essential to better understanding of aerosol particle processes on a local and global scale [15, 16, 17]. Previous studies in Vilnius have shown that the organics fraction is the dominant component, with a mass concentration ranging between 74.1% and 82.7% of all semi-volatile non-refractory PM1, whereas the nitrate concentration is between 4.6% and 7.7% [18]. Organics account for 60% and 80% of the PM1 at the Preila site (when North-Atlantic air masses are advected), reported by studies [19] and [20], respectively.

The primary aim of this study was to analyze semi-volatile non-refractory PM1 by examining the mass concentrations of chemical compounds, dependence of mass concentration on long-range transport air masses and the source apportionment of the organic matter by using the Positive Matrix Factorization (PMF) method. The secondary objective was to demonstrate that ammonium nitrate formation predominated over ammonium sulfate.

2. Methodology

2.1. Sampling sites

Geographic locations of the sites are shown in Fig. 1. The Rūgšteliškis sampling site is located in a national park in Aukštaitija, and is surrounded by a boreal and Scots pine trees forest (55°27’48”N, 26°03’60”E). The mean average air temperature is 5.8 °C, the highest point is 188.6 m a. s. l. and there are no considerable point pollution sources. The Preila sampling site is located near the Baltic Sea (55°22’34”N, 21°01’52”E, 5 m a. s. l.), and the closest possible pollution sources are the village of Preila (2.5 km away to the East), but due to low population (~300 inhabitants) its effect is negligible and not considered, Nida (~1,200 inhabitants) 10 km to the South and the city of Klaipėda (~160,000 inhabitants) 40 km to the North. The Rūgšteliškis and Preila sites are considered to be background sites. The urban sampling site is located near the city of Vilnius,

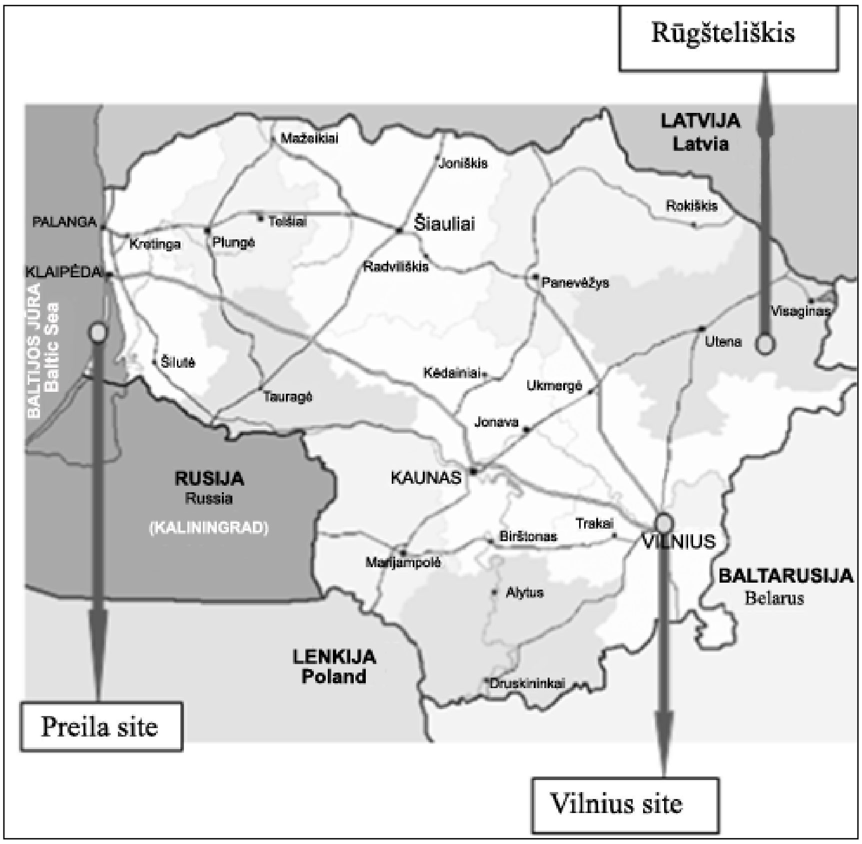

Fig. 1. Locations of sampling sites.

an industrial center with a population of over 520,000 and a residential area of 400 km^2. There are two power stations near the sampling site, one to the North-West and the other to the East, while in the South and West there are no important sources of pollution. A more detailed description of the three sites can be found in [18, 19, 21].

The 2011 measurements were performed in the vicinity of Vilnius city from March 23 to June 5, at the Rūgšteliškis site from June 17 to July 1 and at the Preila site from July 3 to August 24.

2.2. Instrumentation and methods

Q-AMS (Aerodyne Research, Inc.) was used to obtain quantitative real-time size resolved distribution and chemical composition of ambient non-refractory PM1 components, sulfate, chloride, ammonium, nitrate and organics. The measurements were performed every 5 min at every sampling site, yielding 21 million measurement values, which were examined.

The Q-AMS does not efficiently detect low-volatility materials such as black carbon, crustal oxides and certain metals, but provides information on volatile and semi-volatile aerosol particles with limited single-particle information. The instrument combines vacuum and mass spectrometric techniques with aerosol sampling techniques. After entering the sampling inlet, aerosol particles are focused into a collimated beam while passing through an aerodynamic lens system [22], the stream of particles impacts on the vaporizer heated up to ~600 °C and non-refractory particles are flash vaporized. The vapor plume is ionized by the 70 eV electron impact ionization source and analyzed with a quadrupole mass spectrometer with a mass-to-charge (*m/z*) resolution. The total mass concentration C for a particular species s can be expressed using the following equation [23]:

$$C_s = \frac{10^{12} MW_s}{IE_s Q N_A} \sum_{alli} I_{s,i}, \qquad (1)$$

where C_s is expressed in μg m^{-3}, IE_s is the ionization efficiency of species s expressed in ions/molecule, $I_{s,i}$ are ions s^{-1}, N_A is the Avogadro's number, MW_s is the molecular weight of species s, and Q is the speed of ambient air flow into the Q-AMS in cm^3 s^{-1}. Detection limit is 32 ng m^{-3}, flow rate is 0.85 l min^{-1}, m/z = 1–300. A detailed description of instrument performance is available in study [24].

Instrument ionization efficiency was calibrated using 300 nm dry ammonium nitrate particles before and after the measurements, owing to its ability of being reasonably well-focused by the aerodynamic lens system and high collection efficiency. The collection efficiency value (CE) was set at 0.5 [25], and calibrations for the quadrupole mass, resolution and electron multiplier were performed. A detailed description of the performed calibrations before and after our experiments by using Q-AMS is given in studies [18, 20, 21].

The long-range air masses were defined by using a backward trajectory model for a Hybrid Single Particle Lagrangian Integrated Trajectory Model – HYSPLIT model [26] provided by the National Oceanic and Atmospheric Administration (NOAA). The advected air mass trajectories were calculated every 6 hours with the backward duration of 72 hours at 50 m, 500 m and 1500 m above the ground level (AGL). Generally, the air masses were depicted as North (N), East (E), South (S), West (W), North-West (NW), North-East (NE), South-East (SE) and South-West (SW). Advected long-range air masses can have a noticeable influence on local mass concentration and particle size distribution up to 3000 km away from the emission source, thus the assessment of long-range transport air masses implications is important [27].

Positive Matrix Factorization (PMF), a method for solving functional mixing models [28, 29], was applied to the organics component to obtain the organics source apportionment. Calculations were performed using the PMF Evaluation Tool (PET) in the Igor-Pro software [30]. This technique assigns organics to their origin, but the drawback to this technique is the subjective apportionment which depends (in part) on the user. The PMF was run by altering the number of factors up to 7, as the residual error matrix decreases when the number of factors increases, hence yields greater accuracy for the results. However, it was crucial to assess the uniqueness of results after every step of factor increase. During analysis, a number of factors were chosen based on the stability of the solution and uniqueness [20].

3. Results and discussion

3.1. The average mass concentration of PM1 chemical components

The highest average semi-volatile non-refractory submicron particle mass concentration of 7.69 ± 6.83 μg m^{-3} was observed at the Vilnius site, while concentrations were 4.19 ± 2.91 μg m^{-3} at Rūgšteliškis and 3.44 ± 2.65 μg m^{-3} at the Preila site. The average mass concentration of PM1 components at all three sites is shown in Fig. 2. Organics was a dominant

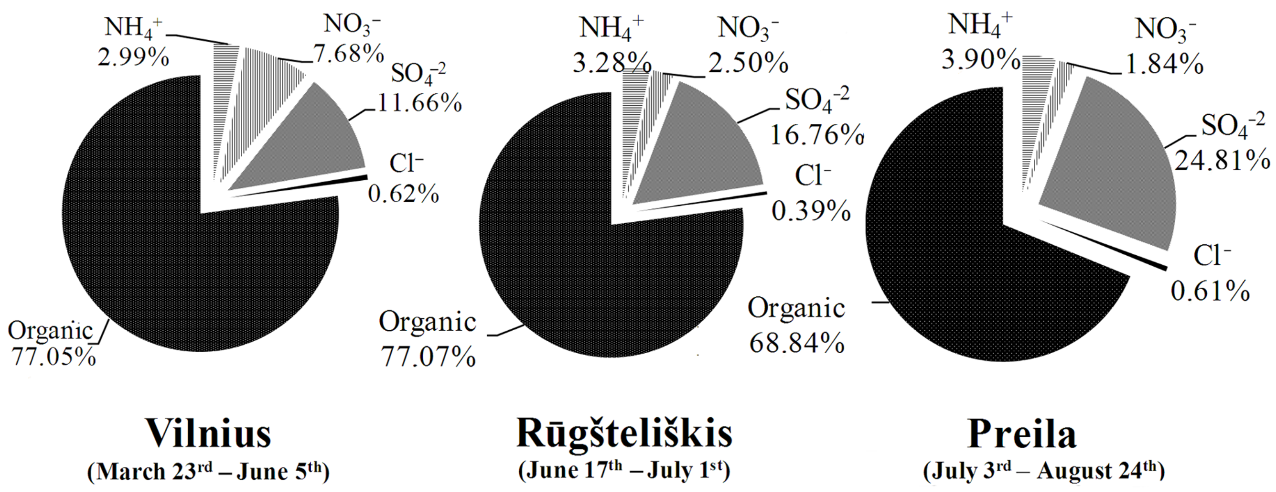

Fig. 2. Average PM1 concentrations at the Vilnius, Rūgšteliškis and Preila sites.

component (68.8–77.1%) of the entire semi-volatile non refractory PM1 aerosol volume at all three sites, which was consistent with previous studies [18, 19, 20] where organics made up from 74.1% to 82.7%, 60% and 80% of the total semi-volatile non refractory PM1 mass, respectively. These data indicated that organics accounted for ~70% of all PM1 in the aforementioned sampling sites under usual conditions.

It was assumed that organics at background sites was advected with air masses or emitted from biogenic sources such as sea spray at the Preila site or reactive terpenes at the Rūgšteliškis site [31, 32]. In urban areas, PM1 were composed mainly of primary particles of anthropogenic origin and secondary particles produced by secondary formation from ambient pollutants [18, 33]. The mass concentration of nitrate in Vilnius was three-fold higher than at Rūgšteliškis and four-fold higher than at the Preila site.

One of explanations for this difference in mass concentration may be due to negligible dissipation resulting from stagnant conditions and low mixing height due to the low wind speed (up to 3 m s^{-1}) during the sampling period in Vilnius. Secondly, the increased nitrate concentration in Vilnius was observed with a North-East wind, while the mass concentration was reduced with a North-West wind, suggesting an influence for nitrates from transportation sources [34]. Moreover, Vilnius city has local pollution sources such as the power plant situated to the East of the sampling site.

3.2. Mass concentration dependence on the origin of air mass

Air mass backward trajectories were calculated using the HYSPLIT model (described in the Instrumentation and methods section). The trajectories of air masses were divided into 8 sectors, and those with uncertain origin (3 or more directions) were rejected. Figure 3 depicts the distribution of PM1 components (chloride, ammonium, nitrate, sulfate and organics) which were dependent on air mass trajectories at the three sites (note – ammonium and organics concentration is shown by half of it). The peak mass concentration for all PM1 components was observed in the presence of air masses from the South and South-East (Fig. 3). However, during the same period, local wind directions from the East and North-East were dominant at the Vilnius site, and the pollution input could not be clearly quantified, either it was due to air masses or wind direction at the Vilnius site. The peak concentration at the Rūgšteliškis site was observed with advected air masses from the South, while increased concentrations were observed with North-East and South-East air masses at the Preila site. Sulfate was the exception at Preila, as the concentration increased with air masses from the sea (South-West, West and North-West), suggesting the increased concentration of sulfates was due to marine aerosol particles.

3.3. Nitrate and sulfate contributions to total ammonium

The mass concentration of ammonium was similar at Rūgšteliškis and Preila (0.14 μg m^{-3} and 0.13 μg m^{-3}, respectively), nevertheless, the median diameter for the accumulation mode of ammonium was higher at the Preila site (Fig. 4) than at Vilnius, hence suggested different particles sources and formation processes at the background and urban sites [35]. Water

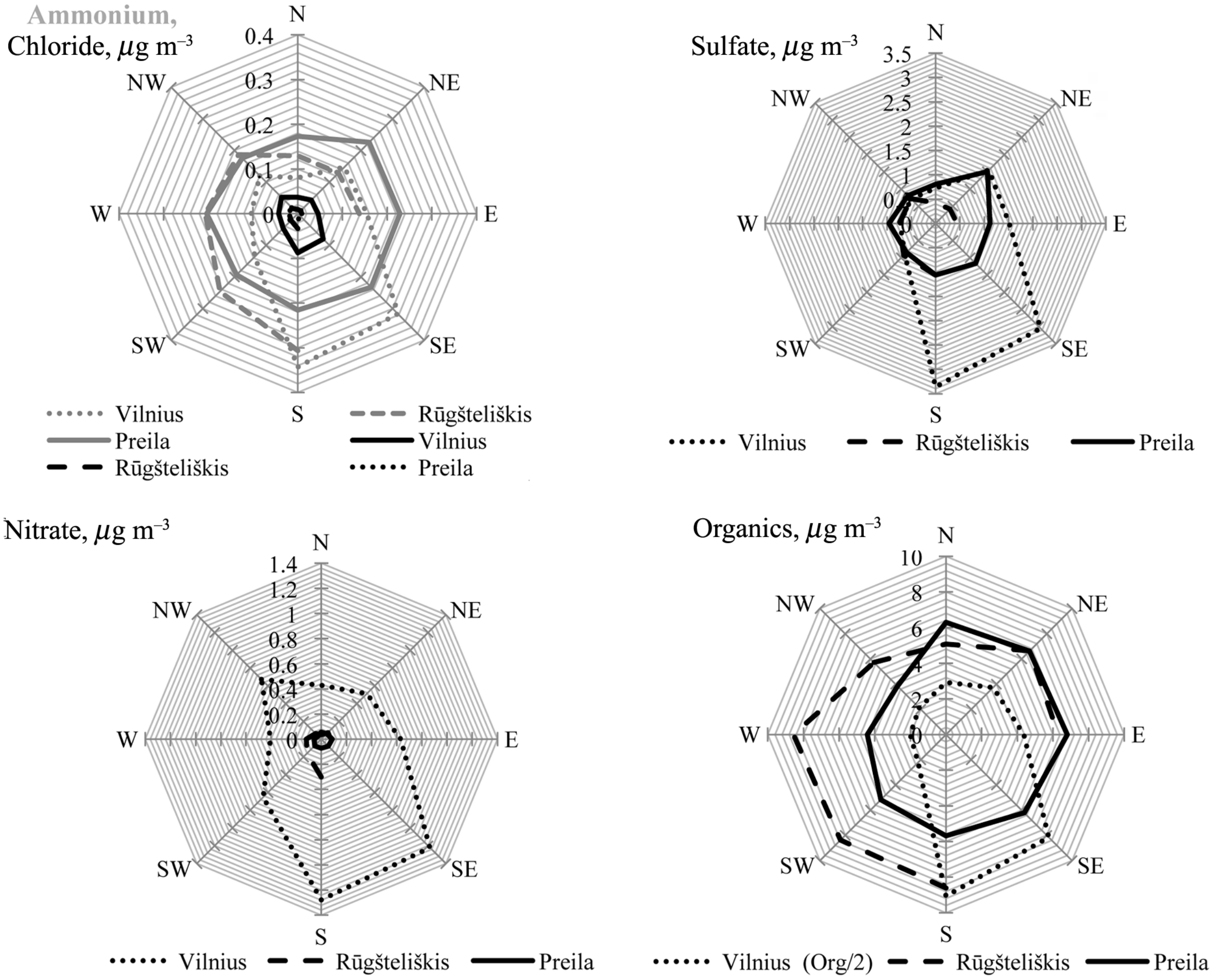

Fig. 3. Dependence of ammonium, chloride, sulfate, nitrate and organics mass concentrations on backward air mass trajectories.

uptake promoted growth of ammonium particles at the Preila background site, which was consistent with the data reported in study [36], where increasing relative humidity induces an increase in the secondary aerosol mass. Furthermore, particle formation is also enhanced by water uptake of fine particles [37], as some compounds forming secondary aerosol particles are water-sensitive [38].

Q-AMS is a quantitative instrument for measurements of non-refractory ammonium, even though Q-AMS cannot distinguish and quantify the contribution of different compounds to the total concentration of certain components (e. g. which part of the ammonium was from ammonium nitrate and which was from ammonium sulfate). The variance in mass concentration was used to evaluate the contributions of ammonium nitrate and ammonium sulfate to the total quantity of ammonium in ambient air. As the concentrations of nitrate and sulfate correlated with the concentration of ammonium in most studies, nitrate, sulfate and ammonium concentration could be used to determine the quantity of ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3) in ambient air. The calcula-

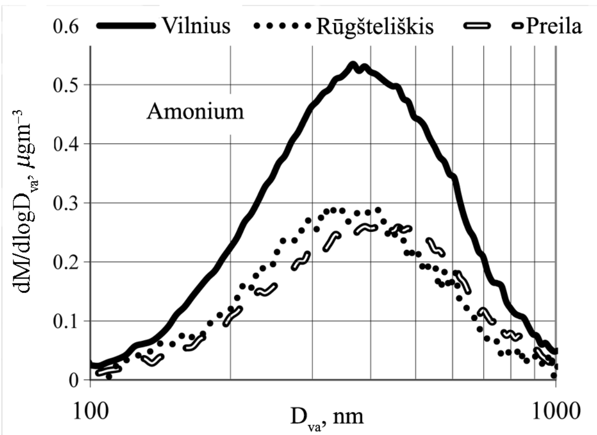

Fig. 4. Modes of ammonium at the sampling sites.

tions were made by applying the least squares method to the ammonium concentration as a combination of nitrate and sulfate concentrations (Eq. (2)).

$$C_{\mathrm{NH_4^+}} = AC_{\mathrm{NO_3^-}} + BC_{\mathrm{SO_4^{2-}}}; \qquad (2)$$

$$\begin{cases} A\sum_{i=1}^{n} C^2_{\mathrm{NO_3^-}} + B\sum_{i=1}^{n} C_{\mathrm{NO_3^-}} C_{\mathrm{SO_4^{2-}}} = \sum_{i=1}^{n} C_{\mathrm{NH_4^+}} C_{\mathrm{NO_3^-}} \\ A\sum_{i=1}^{n} C_{\mathrm{NO_3^-}} C_{\mathrm{SO_4^{2-}}} + B\sum_{i=1}^{n} C^2_{\mathrm{SO_4^{2-}}} = \sum_{i=1}^{n} C_{\mathrm{NH_4^+}} C_{\mathrm{SO_4^{2-}}}. \end{cases} \qquad (3)$$

Solving Eq. (3) yielded coefficients A and B, which denoted the concentration of nitrate and sulfate, respectively. Chloride was not considered due to its relatively low concentration compared to sulfate, and ammonium nitrate formation was dominant compared to ammonium chloride [39]. Figure 5 depicts the period of April 2–8 at the Vilnius sampling site and the percent contribution of ammonium nitrate (of all nitrates) and the ammonium sulfate (of all sulfates) to the total quantity of ammonium (Table 1). Initially, it was expected that ammonium-sulfate would make a relatively larger contribution to the overall quantity of ammonium compared to ammonium-nitrate, which would confirm a commonly-accepted statement that nitrate aerosols were formed only if sulfate aerosols were fully neutralized. However, this study indicated that ammonium nitrate (on average 61% at the Vilnius and Rūgšteliškis sites and 80% at the Preila site) made a greater contribution than ammonium sulfate (37%, 44% and 36% for the Vilnius, Rūgšteliškis and Preila sites, respectively). It is worth noting that sulfuric acid is indicated as the main component (but not the only factor) in aerosol formation [40], thus the role of other components should be examined in greater detail considering the influence of local conditions.

Ammonia is in the gas phase in the boundary layer and is converted into particulate matter at higher altitudes, where the dissociation constant of ammonium nitrate is decreased due to lower ambient temperatures [41]. Ternary H_2SO_4-NH_3-H_2O nucleation is important to secondary aerosol formation in the boundary layer [42], but according to study [43] H_2SO_4-H_2O nucleation is insignificant in the boundary layer due to uniformly-distributed oxidized sulfuric compounds, however, H_2SO_4-H_2O nucleation is dominant in the mid-troposphere. Nucleation and secondary aerosol formation processes are not fully understood and are still under discussion [42]. Our observations could be explained as follows: i) the reaction between single-phase components (Eq. (4)) was much more likely to occur than between multiphase components; ii) the growth of particles favours ammonium nitrate; iii) nucleation processes; iv) the uptake of ammonia into acidic aerosols contributes to the formation of ammonium nitrate; and v) local conditions strongly influence nitrate aerosol formation as a result of abundant precursor gases in ambient air [44].

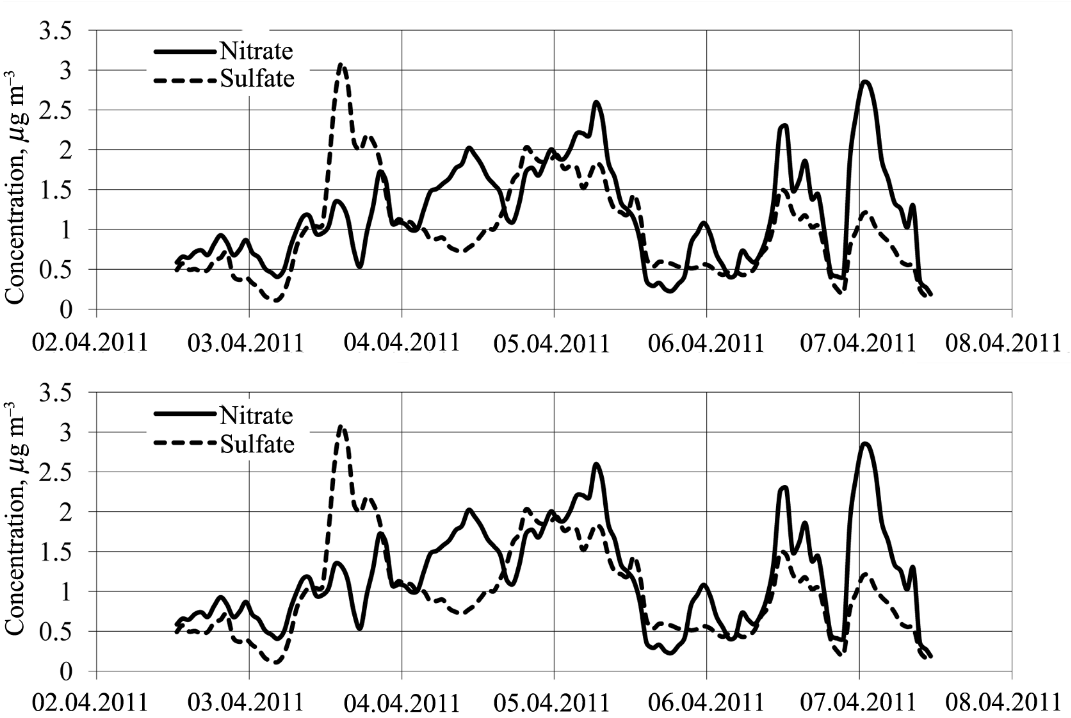

Fig. 5. Ammonium nitrate and ammonium sulfate concentrations.

Table 1. Nitrate and sulfate contributions to ammonium aerosol particles, and the average molar concentrations of nitrate, sulfate and ammonium.

Date and location	NH_4NO_3, %	$(NH4)_2SO_4$, %	NO_3^-, μmol m^{-3}	SO_4^{-2}, μmol m^{-3}	NH_4^+, μmol m^{-3}
Vilnius					
23.03/28.03.2011	63	44	0.0031	0.0026	0.0043
28.03/01.04.2011	70	44	0.0138	0.0080	0.0166
02.04/07.04.2011	66	38	0.0193	0.0104	0.0206
07.04/18.04.2011	70	33	0.0155	0.0092	0.0165
18.04/22.04.2011	54	40	0.0076	0.003	0.0063
22.04/04.05.2011	56	37	0.0149	0.0256	0.0274
04.05/13.05.2011	44	38	0.0071	0.0081	0.0092
13.05/19.05.2011	70	30	0.0039	0.0075	0.0071
24.05/26.05.2011	57	33	0.0008	0.0096	0.0067
Average	**61**	**37**	**0.0096**	**0.0093**	**0.0127**
Rūgšteliškis					
17.06/24.06.2011	65	45	0.0026	0.0098	0.0107
24.06/01.07.2011	58	43	0.0009	0.0053	0.0051
Average	**61**	**44**	**0.0017**	**0.0075**	**0.0079**
Preila					
03.07/16.07.2011	100	35	0.0011	0.0106	0.0089
16.07/27.07.2011	55	39	0.0009	0.0100	0.0084
31.07/08.08.2011	34	36	0.0011	0.0084	0.0064
08.08/18.08.2011	66	34	0.0009	0.0065	0.0050
18.08/24.08.2011	100	39	0.0011	0.0090	0.0085
Average	**80**	**36**	**0.0010**	**0.0089**	**0.0074**

$$NH_{4(g)} + HNO_{3(g)} \leftrightarrow NH_4NO_3 . \qquad (4)$$

During the period presented in Fig. 5, local wind conditions were stagnant (average wind speed of 0.7 m s^{-1}) and a Western wind direction was predominant. The mean average temperature was 6.3 °C with a 73% relative humidity (RH). The long-range air masses of April 2–8 were unstable (NW, W, SE, S, W, NW and NW), and the influence of long-range air masses was rejected as negligible. The molar concentrations for nitrate, sulfate and ammonium are presented in Table 1. The nitrate molar concentration was nine-fold lower at the Preila site compared to the Vilnius site, sulfate molar concentration was comparable at all three sampling sites and the ammonium molar concentration was ~2-fold less at background sites compared to the urban site. The method was evaluated on the data from all three sampling sites, the local conditions of the other sampling sites showed no influence on the applied method and the coincidence was approved for all the data.

3.4. Positive Matrix Factorization analysis for organic matter

The Positive Matrix Factorization (PMF) method developed in study [28] was used to obtain organics source apportionment. A solution of 3 factors was consistent with the chosen criteria (stability and uniqueness) at the Vilnius and Rūgšteliškis sites ($Q/Q_{exp} = 1.3$, $Q/Q_{exp} = 0.56$, respectively), and a solution of 2 factors at the Preila site ($Q/Q_{exp} = 0.92$).

Three factors were revealed at the urban sampling site in Vilnius: BBOA, HOA and SV-OOA (Fig. 6). The most distinctive tracers of BBOA were $m/z = 60$ ($C_2H_4O_2^+$) levoglucosan and $m/z = 73$ ($C_3H_5O_2^+$). The f_{60} value 0.01 (f_{60} is the $m/z = 60$ ratio to the total organics in the mass spectrum of the factor) was higher when compared to its value for other factors, thus the BBOA factor was recognized suggesting the influence of biomass burning emissions in Vilnius. The HOA factor was recognized due to the presence of f_{57}, acknowledged as the most valuable indicator of HOA. The f_{57} value was close to the reference spectrum value ($f_{57} = 0.04$), while other m/z values for the standard HOA spectrum at 27, 41, 43, 55, 57, 69, 71, 83, 85, 97 were observed and correlated with the tracers of nitrate ($r = 0.65$, $N = 1370$) and sulfate ($r = 0.14$, $N = 1370$) particulate matter. The SV-OOA profile had an f_{44} value of 0.05, the same f_{44} value reported in study [45]. The f_{44} value was highest in the SV-OOA spectrum when compared to other factors, indicating SV-OOA consisted of more-oxygenated organics than HOA ($f_{44} = 0.04$) and BBOA ($f_{44} = 0.03$). The SV-OOA profile correlated with its tracer, particulate nitrate (Fig. 6) ($r = 0.76$, $N = 1370$), indicating a relatively higher contribution

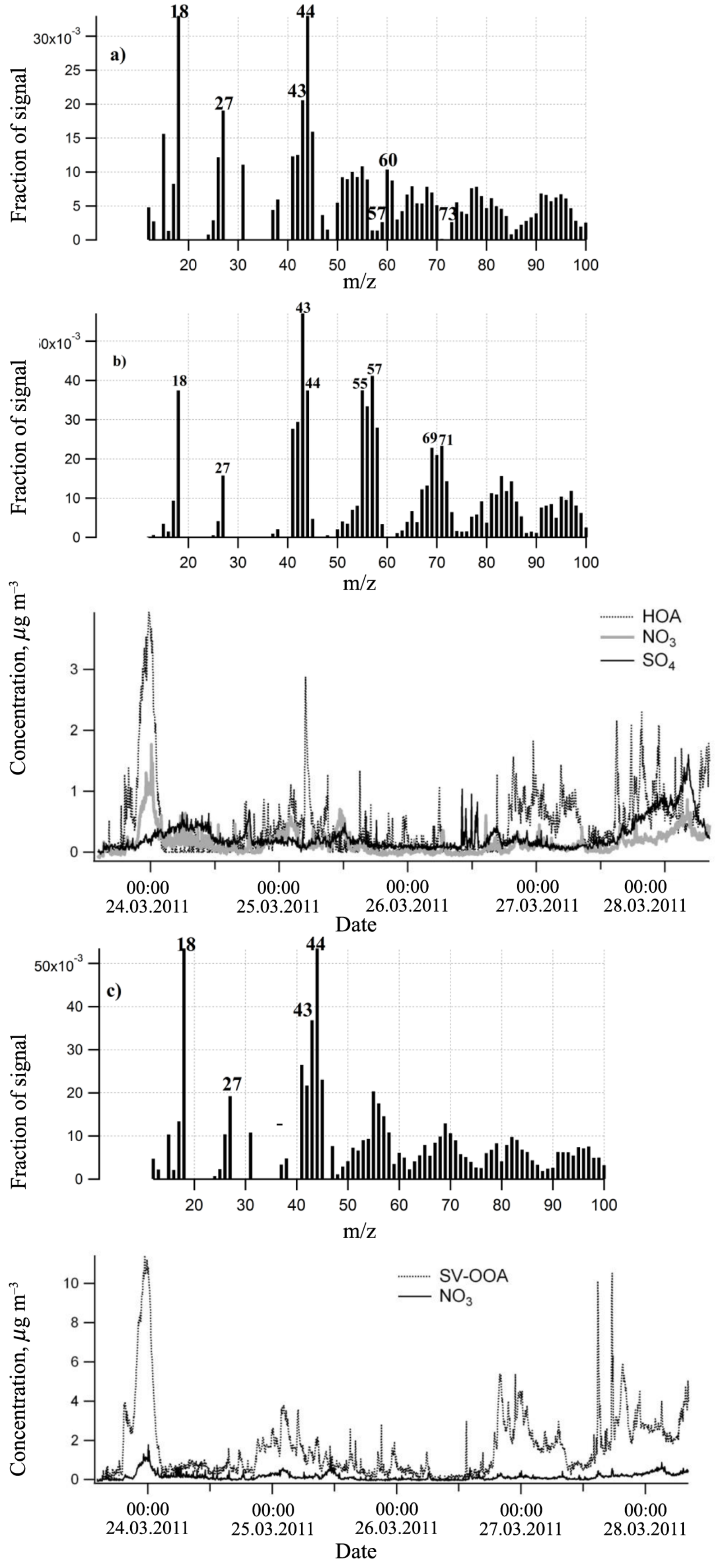

Fig. 6. (a) BBOA factor *m*/*z* spectra, (b) HOA factor *m*/*z* spectra and time series with tracers and (c) SV-OOA factor *m*/*z* spectra and time series with tracer at the Vilnius site.

for fresher secondary aerosol particles than aged secondary aerosol particles (r (SV-OOA – SO_4) = 0.14, N = 1370) [30].

During the June 17–24 period, 3 factors (BBOA, LV-OOA, SV-OOA) were indicated at the Rūgšteliškis background sampling site (Supplementary material, Fig. 1). It was likely that the BBOA factor was increased due to the bonfires in Lithuania and neighbouring Latvia during the national holidays (June 21–24). The f_{44} values for SV-OOA and LV-OOA were 0.02 and 0.18, respectively, relatively close to the values of 0.05 and 0.16 reported in [45]. The lower contribution of m/z = 44 suggested the SV-OOA at Rūgšteliškis was less-oxygenated and fresher than the urban site, which confirmed Rūgšteliškis was a background site. The LV-OOA time-series correlated with the sulfate particulate (r = 0.42, N = 2043), which was similar to that reported in [18], while the SV-OOA time series correlated with particulate nitrate (r = 0.25, N = 2043) (Supplementary material, Fig. 1 (b), (c)). The biogenic m/z = 27 tracer was observed for BBOA and SV-OOA, with f_{27} = 0.01 for both factors.

Two factors (LV-OOA and SV-OOA) were identified at the background site of Preila, which accounted for 64% and 34.4% to the total organic mass, respectively (Supplementary material, Fig. 2). Factor BBOA was negligible due to the seasonal conditions. LV-OOA and SV-OOA factors were similar to those reported in [20], however, one must be cautious when evaluating the contribution of factors due to the contrary results reported for this site, where LV-OOA contributed 22% and SV-OOA 63% to the total organic mass [20]. LV-OOA correlated with particulate sulfate (r = 0.63, N = 1657) and SV-OOA correlated with particulate nitrate (r = 0.62, N = 1657). It should be noted that SV-OOA factors with values of m/z = 18, 27, 41, 43, 44, 55, 58, 60, 69, 79, 83, 91 were very similar to those reported/defined as the BGOA factor in [20, 46]. The SV-OOA f_{44} values at the Preila and Rūgšteliškis sites were 0.18, suggesting this ratio was a typical SV-OOA f_{44} value for background sites, however, further experiments would be required to confirm this prediction.

4. Conclusions

This study revealed organics as the most abundant component at all three sampling sites, which accounted for 68.8–77.1% of the PM1, and suggested that under typical conditions, organics account for ~70% of the measured semi-volatile non-refractory submicron particle mass concentration PM1 in Lithuania.

The concentration of nitrates in the urban Vilnius site was four-fold higher than in the background Preila site and three-fold higher than in the background Rūgšteliškis site (7.68%, 2.50% and 1.84%, respectively). The increased PM1 concentration in Vilnius correlated with a North-East wind direction (directly from the city center), while a rapid increase in PM1 concentration was observed when air masses prevailed from the East in Rūgšteliškis and for North-East/South-East air masses in Preila. These indicated that Vilnius city was under the influence of traffic-related nitrates, whereas Preila and Rūgšteliškis were influenced by advected long-range air masses.

The variances in component mass concentrations (ammonium, sulfate and nitrate) indicated which part of sulfates and nitrates in aerosol particles is ammonium-sulfate and ammonium-nitrate. Ammonium nitrate (on the average 61%, 80% and 61% in Vilnius, Preila and Rūgšteliškis sites, respectively) formation was dominant compared to ammonium sulfate (on the average 37%, 44% and 36% in Vilnius, Rūgšteliškis and Preila sites, respectively), due to uniformity in the components phase, particle growth processes, particle nucleation and local conditions.

PMF analysis at Rūgšteliškis and Preila confirmed them to be background sites, where less-oxygenated and fresher particles dominated. The typical value of f_{44} in SV-OOA at backgrounds sites should be about 0.18, but it must be confirmed by further investigation.

This study partially characterized atmospheric submicron aerosol particles and their sources in urban and background sites. However, additional measurements are needed to better understand the processes on-going in atmospheric submicron aerosol particles.

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SUBMIKRONINĖS FRAKCIJOS ATMOSFEROS AEROZOLIO DALELIŲ ŠALTINIAI, CHEMINĖ SUDĖTIS IR KONCENTRACIJA MIESTO IR FONINĖSE VIETOVĖSE

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Santrauka

Vilniaus mieste, Rūgšteliškio ir Preilos foninėse matavimų stotyse 2011 m. kovo–rugpjūčio mėn. naudojant kvadrupolinį aerozolių masės spektrometrą (Q – AMS) buvo atliekami pusiau lakių (amonio, sulfato, chloro, nitrato, organinių junginių) submikroninės frakcijos atmosferos aerozolio dalelių (PM1) koncentracijos, pasiskirstymo pagal chemines komponentes bei jų kilmės šaltinių identifikavimo tyrimai. Analizė ir vertinimas remiasi cheminių komponenčių koncentracijos matavimo rezultatais, tolimųjų pernašų duomenimis, vietinių taršos šaltinių įtakos vertinimu pagal PMF metodą. Pasiūlytas nitratų ir sulfatų kiekybinio indėlio į aerozolio dalelių amonio junginius metodas parodė, jog esant tam tikroms sąlygoms gali dominuoti amonio nitrato, o ne amonio sulfato aerozolio dalelių susidarymas. Didžiausia vidutinė PM1 koncentracija (7,69 μg m^{-3} ± 6,83 μg m^{-3}) nustatyta Vilniaus mieste, o Preiloje – dvigubai mažesnė (3,44 μg m^{-3} ± 2,65 μg m^{-3}). Nustatyta, jog organinių junginių dalis sudarė didžiąją dalį visos pusiau lakių PM1 koncentracijos, atitinkamai 68,8, 77,1 ir 77,0 % Preilos, Rūgšteliškio ir Vilniaus matavimo stotyse. Pažymėtina, kad Preiloje submikroninės frakcijos aerozolio dalelių nitratų komponentės koncentracija (1,84 %) buvo 4 kartus mažesnė nei Vilniaus mieste (7,68 %), kur didžiausias nitratų šaltinis – transporto priemonių išmetamųjų medžiagų emisija. Pagal PMF analizės metodą buvo identifikuoti BBOA, HOA, SV-OOA šaltiniai Vilniaus mieste ir BBOA, LV-OOA, SV-OOA miškingoje Rūgšteliškio stotyje bei LV-OOA, SV-OOA Preilos matavimų stotyje. Šiame darbe pateikiama PM1 analizė miesto ir foninėse vietovėse bei amonio nitrato ir amonio sulfato kiekybinio indėlio į amonio aerozolio daleles metodas.