

CHARACTERIZATION OF AEROSOL SOURCES AT URBAN AND BACKGROUND SITES IN LITHUANIA

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Size and composition real-time measurements of atmospheric submicron aerosol (PM₁) were conducted in the Lithuanian background and urban areas during several months (April–July, 2008) using the Quadrupole aerosol mass spectrometer (Q-AMS). The average mass concentration of non-refractory PM₁ ranged within 8–13 $\mu\text{g m}^{-3}$. Organic compounds of PM₁ were the most abundant constituent ranging from 70 to 83%, nitrate made up 4.0–7.7%, ammonium 1.7–3.9%, sulfate 11–21%, and chloride less than 1%. While sulfate concentrations were comparable at the urban and background sites, concentrations of organic compounds and nitrate in Vilnius city were almost twice as high as those at the background site (Rūgštelėškis). The average aerodynamic diameter for nitrate and organics was about 300 nm at both sampling sites – in Vilnius city and at Rūgštelėškis background site. The average aerodynamic diameter for ammonium was about 355 nm and for sulfate about 400 nm. The main source of organics and nitrates in the city was emission from traffic, however the main source of sulfates at urban and background sites was long-range transport. Positive matrix factorization (PMF) analysis of the unit mass-resolution (UMR) spectra was used to identify sources of organic matter in the urban (Vilnius) and background (Rūgštelėškis) aerosol. Organic aerosol components were identified from AMS spectra for both sites: primary anthropogenic emissions – hydrocarbon-like organic aerosol (HOA), aged oxygenated low volatility organic aerosol (LV-OOA), and less oxygenated, presumably, semivolatile organic aerosol (SV-OOA) at the urban site (Vilnius city) as well as biomass burning organic aerosol (BBOA), aged oxygenated low volatility organic aerosol (LV-OOA), and semivolatile biogenic secondary organic aerosol (SV-OOA) at the background site (Rūgštelėškis).

Keywords: atmospheric submicron aerosol, urban and background sites, concentration, composition, size distribution, sources

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1. Introduction

Aerosol particles are an important component playing a significant role in atmospheric chemistry. They change the energy balance of the climate system by absorbing and scattering the solar radiation and by altering cloud albedo and precipitation. The direct and indirect effects of aerosols on radiative forcing have large uncertainties in both the measurements and modelling of the climate effects of anthropogenic aerosols [1]. Particulate matter (PM) in the air is a complex mixture of organic matter, inorganic salts, mineral dust, elemental carbon, trace elements, and water suspended in the air. Detailed analyses of physicochemical properties and spatiotemporal variability are crucial for understanding the mechanisms of aerosol toxicity and their role in the climate change [2]. Epidemiological studies

have revealed that ambient particulate matter concentrations and negative health impacts such as asthma are very much related [3–5].

Anthropogenic sources of particles in Europe are dominant because of the urbanization and industrialization of many countries. They include coal, oil, gasoline, and wood combustion, chemical processing, and mechanical attrition. Natural sources of primary particles include sea spray, fugitive dust, volcanic and biogenic emissions, and long-range transport of dust. The consistent pattern of geographical variability in Europe is lower concentrations of PM in the far northern countries and higher concentrations in the southern countries [6].

The coarse, fine, and ultrafine PM modes, in general, originate separately, they are transformed separately, and are removed from the atmosphere by various

mechanisms, and have different chemical composition and optical properties [7].

The concentration of urban particles is affected by long-range transported particles [8] as well as by primary and secondary particles produced in the air by local sources such as traffic [9–11], combustion, and others. The concentration of urban particles depends on geographical and meteorological conditions in the city [12]. Dispersion of fine particles is much more affected by the atmosphere mixing height than that of coarse particles.

Physical and chemical characteristics of non-refractory submicron particles (PM₁) with an aerodynamic diameter less than 1 μm were investigated at urban and background sites [13, 14] using the *Aerodyne* aerosol mass spectrometer (AMS) [15]. Size and composition investigations of background, rural, and urban aerosols using mass spectrometry methods are described in [16–20] in which the suitability of the AMS measurement method was confirmed, the mass concentrations and chemically-specified size distributions of submicron particles were characterized *in situ*, and the organic fraction was determined to be most abundant in non-refractory submicron aerosols (NR-PM₁).

High time resolution data of the chemical composition of aerosols as provided by the aerosol mass spectrometer have been used in several source apportionment studies. In study [21] a technique for identification of oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA) in AMS mass spectra was developed using mass to charge ratio m/z 44 (CO_2^+) and m/z 57 (C_4H_9^+ , $\text{C}_3\text{H}_5\text{O}^+$) as OOA and HOA tracers. This technique was subsequently modified to a version known as multicomponent analysis (MCA) and 3-component fits have been shown to be applicable to many polluted environments and able to discern variations in the OOA composition [22]. More recently, the application of positive matrix factorization (PMF) [23] has become widespread. It is possible to identify several sources of organic aerosol using this technique. PMF was first used in conjunction with AMS data to quantify main sources of organic matter in Zurich (Switzerland) [24]. The six factors identified were HOA, two types of OOA (a highly-oxygenated, low-volatility type called LV-OOA that correlates well with aerosol sulfate and a less-oxygenated, semi-volatile type called SV-OOA that correlates well with aerosol nitrate), charbroiling, wood burning, and a minor source that may be influenced by food cooking.

The main goal of this study was to identify differences in composition, size, and daily variations of PM₁ in urban versus background areas, to explain the substantial differences in mass spectra, and to determine the main sources of atmospheric submicron aerosol in Lithuania.

2. Methods

2.1. Sampling sites

The background site was located at the Rūgšteliškis integrated monitoring station in North-East Lithuania (Fig. 1), a strict reserve zone of Aukštaitija National Park with mature forest. The highest point of the area was at 188.6 m a. s. l. ($55^\circ 27' 48''$ N, $26^\circ 00' 16''$ E). The climate is moderately cold with high humidity and abundant precipitation. The mean average air temperature is 5.8°C , the mean annual precipitation amount is 680 mm. Coniferous stands are prevailing in the area, mainly Scots pine trees with a mixture of Norway spruce. Our sampling site was located at this station and the measurement period was July 02–24, 2008.

The urban site was located in Vilnius city (Fig. 1). Vilnius is an important industrial and commercial centre with a population of $\sim 550\,000$ and a residential area of about 402 km^2 . The city stretches along both banks of the fast flowing Neris River, and is set among hills and pine woods and further surrounded by the grasslands, forests, and peat bogs. The centre of Vilnius is located in the shallow valley of the confluence of the Neris and Vilnelė Rivers. The width of the valley is about 4–5 km. The altitude varies from ~ 100 m inside the valley to ~ 200 m outside the valley. In Vilnius the majority of the business offices and factories are concentrated in the city centre, while the “sleeping” areas are located around the centre. This feature causes intensive traffic flows to and out of the city centre in the morning and evening, respectively. Vilnius has no fully developed roundabout roads, therefore the city centre is crossed both by local and transit traffic flows. Due to insufficient street capacity, traffic jams became an everyday feature in the Vilnius centre. As a result, during transport peaks, air pollution increases and causes dangerous and unhealthy situation in the city [25].

The first PM₁ sampling site (Žirmūnų St) was located on the outskirts of the city centre with a traffic throughput of about 30,000 vehicles per day. The measurement period was April 21 – May 19, 2008. The second PM₁ sampling site (A. Goštauto St) was located close to the Vilnius city old town, in a relatively

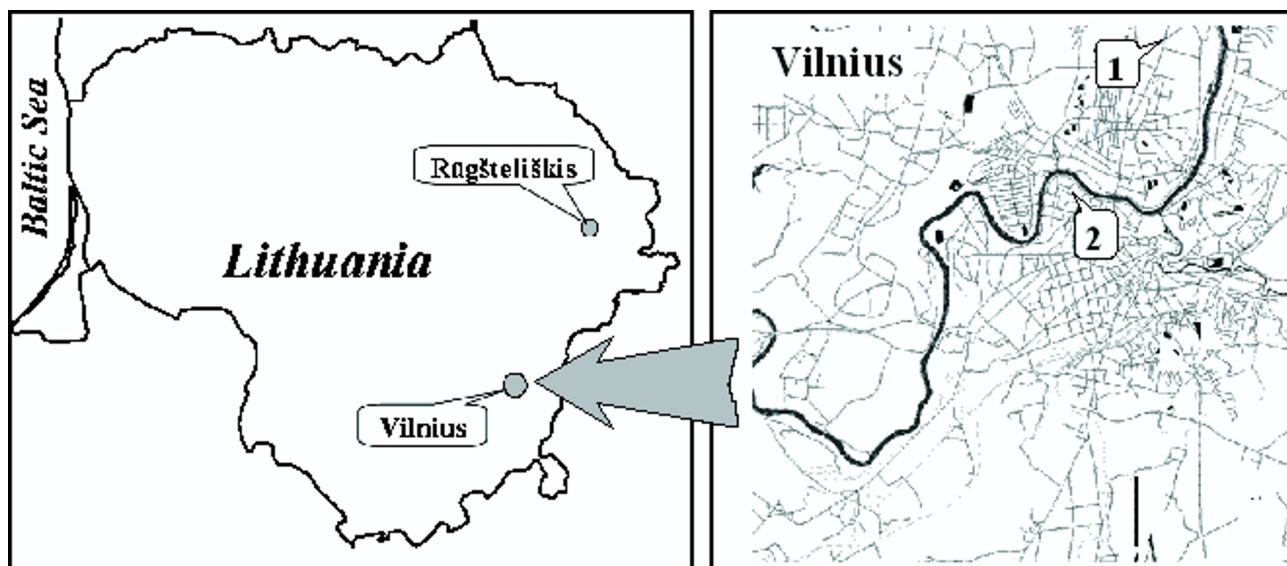


Fig. 1. Location of the sampling sites in Vilnius city (1 Žirmūnų St, 2 A. Goštauto St) and in the background area (Rūgštelėškis).

quiet location with a traffic throughput of about 25,000 vehicles per day. The measurement period was May 22 – June 10, 2008.

2.2. Instruments

The submicron aerosol (PM₁) concentration and chemical composition were measured with the *Aerodyne Research, Inc.* (ARI) Quadrupole aerosol mass spectrometer (Q-AMS). The ARI Q-AMS provides a real-time size resolved composition analysis of volatile and semi-volatile particulate matter. The instrument combines standard vacuum and mass spectrometric techniques with aerosol sampling techniques. Detailed description of the AMS and its operation is given in [17, 26].

The time of flight (TOF) between the chopper and the detector is used to measure the particle velocity as well as the particle vacuum aerodynamic diameter (D_{va}). The particles passing through the flight chamber are directed onto the resistively heated surface. Upon collision with this heated surface, non-refractory particles flash vaporize under high-vacuum conditions. The vaporization process occurs directly inside an electron impact ionizer where vaporized constituents are converted to positive ions, which can be detected with the Q-AMS. The AMS does not efficiently detect low-volatility materials such as black carbon, NaCl, crustal oxides, and certain metals. However, higher volatility species adsorbed on such materials can be detected.

The ionization efficiency calibration, also called the mass or nitrate calibration, evaluates the ionization and ion transmission efficiency of ammonium nitrate. The

ionization efficiency was calibrated at the beginning and at the end of the measurement campaign according to the method described in [27]. Specific description of the calibration procedure was presented in [20]. Measurements were accomplished with a time resolution of 5 min, with a vaporizer temperature of about 600°C. For the whole measurement period the collection efficiency of aerosols $CE = 1$.

The *Environment S.A* model CO11M (infrared gas absorption method) analyzer was used to measure CO concentrations, and nitrogen oxides (NO_x) were measured using model AC31M NO-NO₂-NO_x analyzer (chemo-luminescent method).

2.3. PMF model description

Positive matrix factorization [23, 28] (PMF) was conducted based on unit mass resolution (UMR) spectra. It is a well-established program to solve functional mixing models. PMF results were analysed using the Igor Pro-based PMF evaluation tool (PET) developed for rapid and comprehensive exploration of the PMF solution space [29]. The application of PMF to AMS organic aerosol spectra has been described in [24, 29].

To analyse the diurnal variation of PM₁, the atmosphere mixing height was calculated using the Hybrid Single Particle Lagrangian (HYSPLIT) model from the National Oceanic and Atmospheric Administration (NOAA) [30].

Table 1. Concentrations of PM1 and its constituents at the sampling sites of Vilnius city and Rūgšteliškis during the investigation period.

Concentration, $\mu\text{g m}^{-3}$					
	Ammonium	Nitrate	Sulfate	Organics	PM1
Vilnius, Žirmūnų St (April 21 – May 19, 2008)					
Minimal	0.004	0.011	0.01	0.08	0.17
Median	0.258	0.508	0.99	5.26	6.33
Average	0.387	0.764	1.36	7.40	9.98
Maximum	2.04	4.89	6.12	26.0	30.5
Vilnius, A. Goštauto St (May 22 – June 10, 2008)					
Minimal	0.001	0.045	0.03	0.71	0.73
Median	0.190	0.330	1.27	7.49	7.60
Average	0.214	0.573	1.33	10.3	12.4
Maximum	1.09	3.46	3.69	37.2	39.6
Rūgšteliškis site (July 2–24, 2008)					
Minimal	0.001	0.070	0.41	0.89	1.02
Median	0.211	0.253	1.39	4.44	4.93
Average	0.294	0.325	1.73	5.68	8.05
Maximum	1.20	1.55	5.28	33.0	35.3

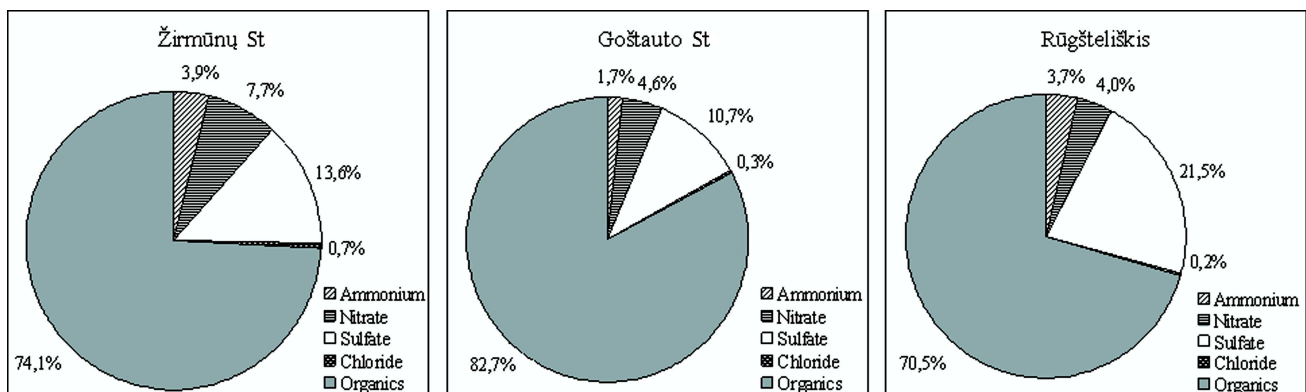


Fig. 2. Averaged chemical composition of PM1 at all three sampling sites.

3. Results and discussion

3.1. Concentration, aerodynamic diameter, and chemical composition of PM1 particles

Concentrations of PM1 and its constituents (ammonium NH_4^+ , nitrate NO_3^- , sulfate SO_4^{2-} , and organics) are presented in Table 1.

The data in Table 1 show that the difference between concentrations of ammonium is negligible at all three sites, however, concentrations of nitrate in the city are about twice as high as those at the background site (Rūgšteliškis). Similarly for the organics, concentrations are higher in the city, especially in A. Goštauto St, which is located along the river valley surrounded by buildings and local meteorology conditions lead to poorer mixing capabilities. Organics in the city

is emitted mainly from vehicles, whereas organics in Rūgšteliškis is the products of natural re-emission from forest and wood burning [31]. Although sulfate concentrations were comparable, the background site had slightly higher values, probably, due to different measurement periods and predominant air masses.

The chemical composition of PM1 particles from all three sampling sites is presented in Fig. 2. Organic compounds dominated at all three sampling sites and made up 70–83%, while sulfate concentration varied from 11 to 21% of the total non-refractory PM1. Diurnal sulfate variations (discussed in the next paragraph) indicated its regional origin (Fig. 3), therefore, higher sulfate contribution to the background site aerosol was an anticipated result. Nitrate and ammonium made

small contributions to the total mass at all sites, but slightly higher at the urban ones.

The determined average aerodynamic diameter for nitrate and organics was about 300 nm at both sampling

sites of Vilnius city and at a background site. The average aerodynamic diameter for ammonium was about 355 nm and for sulfate it was about 400 nm. It is well known that particles originated from local combustion

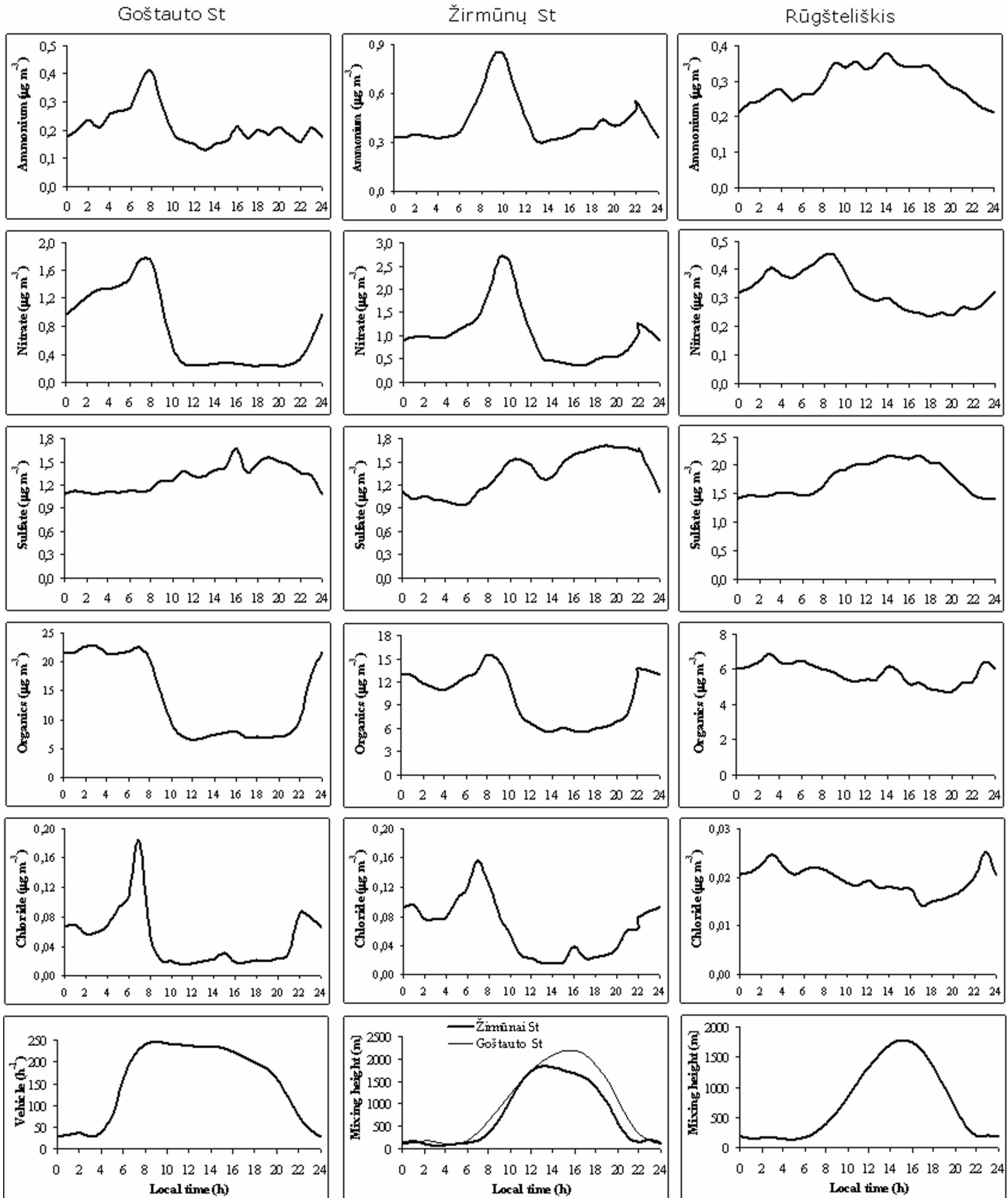


Fig. 3. Diurnal variation of PM1 components and atmosphere mixing heights at all three sampling sites. Averaged diurnal variation of the number of vehicles per hour is presented only for A. Goštauto street.

processes have a smaller modal diameter than particles advected with long-range transport. During the transportation from distant areas the particles are growing due to condensation and accumulation processes in the atmosphere.

The concentration of PM1 in the air is determined by both local and long-range emissions in Vilnius city and in the background site. However, in the city area local sources of aerosols are dominant, while in the background area the long-range transport makes a larger impact.

3.2. Diurnal variation

A very clear diurnal concentration variation of nitrates, organics, and chlorides in both locations of Vilnius city can be seen from Fig. 3. The concentration variation of nitrates, chlorides, and organic components is determined by the atmosphere mixing height and by emissions from traffic (see graphs at the bottom of Fig. 3). The nitrates, chlorides, and organic components are emitted by combustion sources and their diurnal cycles have a peak early in the morning during the rush hours.

At midday, the concentration of nitrates, chlorides, and organic matter decreases because the atmosphere mixing layer height rises causing dispersion of this accumulated species that is much faster than the rate of emission at that time. Emitted PM1 components during the day tend to accumulate at the nighttime because of frequent temperature inversions in the atmosphere during the nighttime. Early in the morning the increasing atmospheric turbulence and mixing height tend to reduce the concentration of PM1 components. Nitrate variations at a background site did not show such pronounced variations, therefore the long-range transport should dominate over the local sources.

Diurnal variation of sulfates in the city was similar to that at the background site, however, this variation was different from that of nitrates or organics in both areas. The concentration variability of sulfates at all three sampling sites was almost opposite as compared with the above mentioned components: the concentration maximum was observed from 8 AM to 10 PM. The source of sulfates in this case was SO₂ oxidation and the long-range transport from neighbouring regions. Possibly, higher amounts of sulfates can penetrate through the boundary layer from the troposphere to the atmosphere surface level when the temperature inversion layer is broken in the early morning. Diurnal variation of ammonium concentration is not expressed

clearly and possibly can be caused by local and distant sources.

3.3. Organic aerosol sources

The positive matrix factorization technique was used to identify the origin of organic matter in the urban (Vilnius city) and background (Rūgšteliškis) aerosol. Organic aerosol components were identified from AMS spectra for both sites: HOA, LV-OOA, and SV-OOA at urban (Vilnius) site, as well as BBOA, LV-OOA, and SV-OOA at a background site (Rūgšteliškis).

The HOA mass spectrum in Vilnius city is similar to the previously reported urban spectra [21], showing characteristic ion groups of refined hydrocarbons, $\Delta = 0$ (m/z 41, 55, 69, 83) and $\Delta = 2$ (m/z 43, 57, 71, 85) with little signal from m/z 44 (Fig. 4(a)). The Δ values are defined as $\Delta = \text{peak mass} - 14n + 1$ (where n is the “nominal” number of CH₂ groups in the fragment) and are used to determine general classes of organic compounds [32]. Diurnal variations of HOA show strong morning emissions during rush hours (Fig. 5(b)). The afternoon traffic jams sometimes occurred, but often to a smaller extent, presumably due to the elevated atmosphere boundary layer height and mixing volume typically seen later in the day. The HOA mass concentration shows a high correlation in time with NO_x ($R^2 = 0.67$) and CO ($R^2 = 0.68$), which is consistent with the identification of HOA as being dominated by combustion-related urban sources such as transport.

The primary emission mass spectrum at the Rūgšteliškis site (Fig. 4(d)) is the factor with a significant contribution from m/z 60 (1.5% of total), which is used as a tracer for levoglucosan and an indicator of biomass burning. Peaks were also observed at m/z 43, with minor peaks at 41, 55, and 57, which is consistent with HOA from combustion. It is interesting to note high wood burning organic aerosol concentrations ($7 \mu\text{g m}^{-3}$) during the national fiesta on 6–7 July, due to an old tradition of making bonfires all over Lithuania. The peak in diurnal profiles tends to occur in the late evening, going into the night (Fig. 5(a)), which would be consistent with fire burning during the evening and night.

The LV-OOA mass spectra recorded in Vilnius city and at Rūgšteliškis site were dominated by m/z 44, indicating strongly oxidized organic matter typical of the regional source (Fig. 4(b,e)). While an urban site still had a contribution from m/z 43, the background LV-OOA tended to have even higher degree of oxidation without any contribution from semivolatile

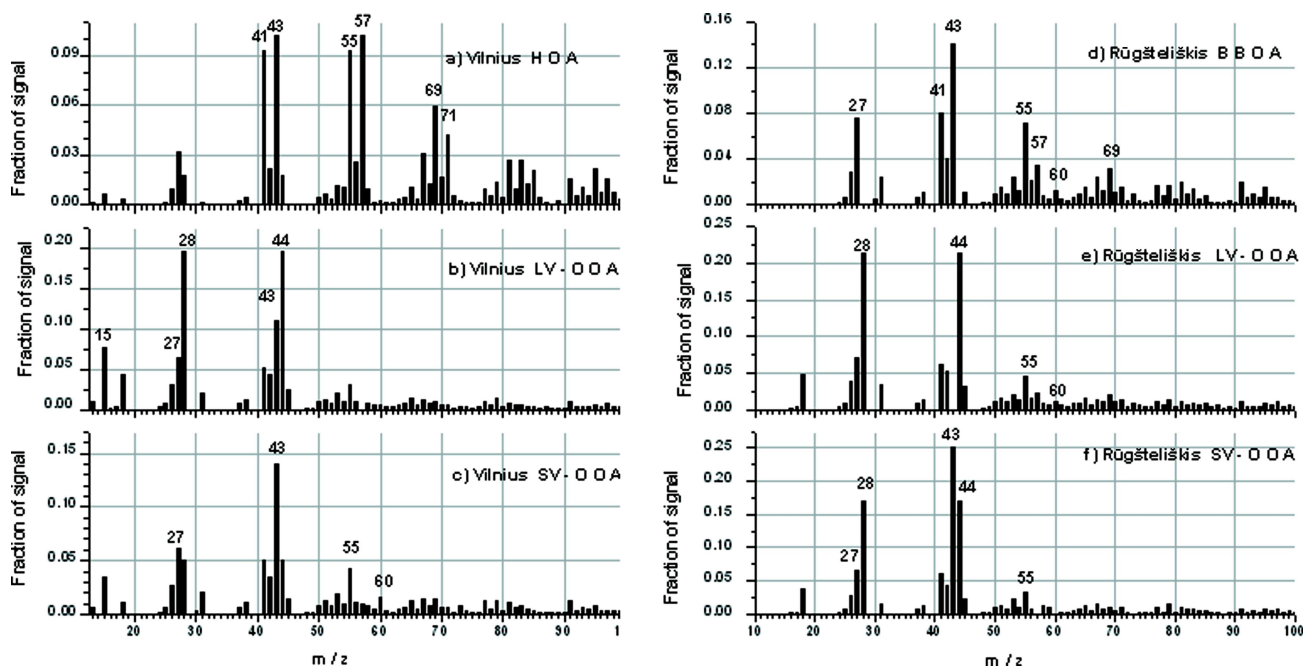


Fig. 4. Mass spectra of the PMF components from campaigns in Vilnius city and Rūgštelėškis site.

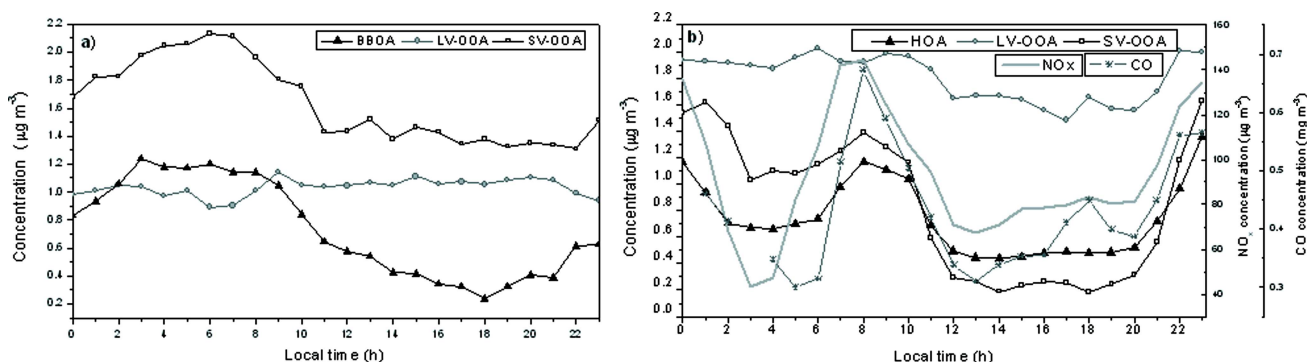


Fig. 5. Diurnal concentration course of aerosol components: (a) at Rūgštelėškis site, (b) in Vilnius city (Žirmūnų St). NO_x and CO concentration data are from monitoring station in Vilnius city (Žirmūnų St).

species. The LV-OOA time series correlated with particulate sulfate ($R^2 = 0.5$) and with air mass transport passing over industrial regions from the west/southwest of Europe. This factor does not show any strong diurnal cycle (Fig. 5(a,b)), which is consistent with a regional source and domination by atmospheric transport. Moreover, LV-OOA factor at the Rūgštelėškis site contains negligible contribution from m/z 60 ($\sim 1\%$) (Fig. 4(e)), probably formed from regional biomass burning (BB) emissions: during the nights of 6 and 7 July, which follow a period of the intense fire impact and have a higher OOA concentration, probably due to secondary organic aerosol formed from BB emissions. Formation of humic-like substances (have a notable signal at m/z 44) from biomass burning is determined in [33] and supports the suggestion that the LV-

OOA in this period can be additionally produced from biomass burning emissions.

The SV-OOA spectrum in Vilnius city showed less-oxygenated organics than that of LV-OOA, with smaller impact from m/z 44 (5% for the SV-OOA and 19% for the LV-OOA) but dominated by m/z 43, with little signal at 41, 55, and 57 (Fig. 4(c)). This factor is widely reported as fresh oxygenated OOA [24]. As shown in Fig. 5(b), the SV-OOA time series correlates well with NO_x ($R^2 = 0.52$) and CO ($R^2 = 0.51$) though less than with HOA, suggesting combustion related secondary organic aerosol production. However, NO_x and CO are also emitted by biomass burning and industrial sources. The notable contribution from m/z 60 (1.5%) is a strong indication that the SV-OOA factor is also influenced by BB emissions. The mass spectrum of SV-OOA at the Rūgštelėškis site (Fig. 4(f)) does

not contain marker peaks for anthropogenic (m/z 57) and BB emission (m/z 60), but has similarities with spectra obtained from α -pinene oxidation products [34] and from the particle growth event at Hyytiälä [16]. Higher SV-OOA concentrations were observed when the wind direction was from the south, southwest (notably forested areas). This further supports the biogenic source of the SV-OOA at the Rūgšteliškis site, formed through the secondary aerosol formation from the VOCs emitted over the forested area.

4. Conclusions

The average mass concentration of PM₁ at all sampling sites ranged within 8–13 $\mu\text{g m}^{-3}$. The organic constituent was the most abundant, PM₁ ranging from 70 to 83%, while sulfate contributed only 11–21%. Other constituents comprised ammonium (1.7–3.9%), nitrate (4.0–7.7%), and chloride (less than 1%). The concentrations of organics and nitrate in Vilnius city were almost twice as high as those at a background site, although the sulfate contribution to the total PM₁ mass was higher in the latter. The main source of organics and nitrates in the city was emission from traffic, and this was clearly seen from diurnal variation of both constituents: the maximum of the atmosphere mixing height almost coincided with the traffic maximum and with the concentration minimum. However, the main source of sulfates was long-range transport with air masses from neighbouring countries and this is seen from diurnal variation of sulfate at all sampling sites: the concentration peak coincided with the atmosphere mixing height maximum, and this means that air masses enriched with sulfate are transferred into the atmosphere surface layer. The average aerodynamic diameter for nitrate and organics was about 300 nm at both sampling sites – in Vilnius city and at a background site (Rūgšteliškis). The average aerodynamic diameter for ammonium was about 355 nm and for sulfate about 400 nm.

Three organic aerosol components were identified from AMS spectra using PMF analysis for both sites, though their factors were different. Primary anthropogenic emissions of HOA, LV-OOA, and SV-OOA were identified at an urban (Vilnius) site. The major source types at the background (Rūgšteliškis) site were BBOA, LV-OOA and SV-OOA. Different diurnal variations and distinct correlation with gaseous pollutants and other aerosol constituents such as sulfate or nitrate indicated a primary combustion source of HOA,

while SV-OOA and LV-OOA were produced by secondary processes from local and regional pollutants, respectively. The lack of anthropogenic markers in the SV-OOA mass spectrum from the Rūgšteliškis site and correlation of this organic aerosol with the wind direction from the forested areas confirmed the SV-OOA biogenic origin.

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AEROZOLIO DALELIŲ ŠALTINIŲ APIBŪDINIMAS MIESTO IR FONINĖSE VIETOVĖSE LIETUVOJE

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Santrauka

Submikroninės frakcijos (PM₁) atmosferinio aerozolio dalelių pasiskirstymo pagal dydį ir cheminės sudėties tyrimai realiaame laike Vilniaus mieste ir Rūgšteliškio foninėje vietovėje, naudojant kvadrupolinį aerozolio masės spektrometrą (AMS), atlikti 2008 m. balandį–liepą. Vidutinė PM₁ aerozolio dalelių masės koncentracija kito nuo 8 iki 13 μg m⁻³. Organinė PM₁ aerozolio dalelių komponentė buvo vyraujanti ir kito nuo 70 iki 83 %, nitratai sudarė 4,0–7,7 %, sulfatai – 11–21 %, amonis – 1,7–3,9 %, chloridai – mažiau negu 1 %. Sulfatų koncentracijos buvo tos pačios eilės abiejose vietovėse, tuo tarpu organinės komponentės ir nitratų koncentracijos aerozolio dalelėse Vilniaus mieste buvo daugiau nei dvigubai didesnės. Vidutinis organinės komponentės ir nitratų aerodinaminis aerozolio dalelių skersmuo abiejose vietovėse buvo ~300 nm,

amonio ~355 nm, sulfatų ~400 nm. Pagrindinis organinės komponentės ir nitratų šaltinis mieste buvo autotransportas, o sulfatų šaltinis ir mieste, ir foninėje vietovėje – tolimoji oro masių pernaša.

Organinės medžiagos, esančios aerozolio dalelėse iš miesto (Vilniaus) ir foninės vietovės (Rūgšteliškio), kilmei nustatyti panaudotas teigiamos matricų faktorizacijos metodas, pritaikytas vietinės masės skyros spektrams. Vilniaus mieste iš AMS spektro identifikuotos trys organinio aerozolio komponentės: pirminės antropogeninės emisijos angliavandenilio dariniai (HOA), senesnės oksidacijos mažai lakus (LV-OOA) ir mažai oksiduotas pusiau lakus (SV-OOA) aerozoliai. Foninėje vietovėje (Rūgšteliškyje) aptiktas biomasės degimo procese susidaręs organinis aerozolis (BBOA), senesnės oksidacijos mažai lakus (LV-OOA) ir mažai oksiduotas pusiau lakus (SV-OOA) aerozoliai.