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ORIGIN, CHEMICAL COMPOSITION AND FORMATION OF SUBMICRON
AEROSOL PARTICLES IN THE ATMOSPHERE

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VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRO
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ATMOSFEROS AEROZOLIO SUBMIKRONINĖS FRAKCIJOS DALELIŲ KILMĖ,
CHEMINĖ SUDETIS BEI FORMAVIMASIS

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ABBREVIATIONS

ASR – ammonium to sulfate molar ratio

BB – biomass burning

BBOA – biomass burning organic aerosol

BGOA – biogenic organic aerosol

EC – elemental carbon

HOA – hydrocarbon-like organic aerosol

LV-OOA – low-volatility oxygenated organic aerosol

MOUDI – Micro-Orifice Uniform deposition impactor

OA – organic aerosol

OC – organic carbon

PM₁ – particulate matter with an aerodynamic diameter smaller than 1 μm

PMF – Positive matrix factorization

Q-AMS – Quadrupole aerosol mass spectrometer

SMPS – Scanning mobility particle sizer

SV-OOA – semi-volatile oxygenated organic aerosol

TC – total carbon

VOCs – volatile organic compounds

UTC – Coordinated Universal Time

INTRODUCTION

The effect of aerosol particles on the atmosphere, climate and public health is among the central topics in the current environmental research. Atmospheric aerosol particles have significant local, regional and global impacts. Local impacts include vehicular emissions, wood burning fires and industrial processes that can greatly affect the urban air quality. Regionally, aerosols can be transported from areas of high emissions to relatively clean remote regions. Aerosol particles have the potential to significantly influence the composition of gaseous species in the atmosphere through their role in heterogeneous chemistry in the troposphere and stratosphere, as well as their effect on the Earth's climate as they scatter sunlight and serve as condensation nuclei for cloud droplet formation. At present, the radiative effects of aerosols have the largest uncertainties in global climate predictions to quantify climate forcing due to man-made changes in the composition of the atmosphere. A better understanding of the formation, composition and transformation of aerosols in the atmosphere is of great importance in order to better quantify these effects.

The concentration and composition of aerosol particles in Lithuania were investigated before, but due to lack of the sampling equipment and measuring technique, traditionally more attention was given to the coarse aerosol particle fraction, whereas it is well established that submicron aerosol fraction has a larger impact on the human health and climate. Due to adverse health effects comprehensive studies of submicron aerosol particles composition, concentration and sources become more and more relevant. Thus, this work will give quantitative data for global aerosol and climate model in assessing its impact on the climate change as well as provide information for setting new air quality standards.

THE AIM AND TASKS OF THE WORK

The objective of the work was to investigate physical and chemical properties and sources of the atmospheric aerosol particles in the submicron fraction by combining different analytical techniques.

This aim was achieved by accomplishing the following tasks:

- Determine the dependence of concentrations of organic and elemental carbon in different air masses on the east coast of the Baltic Sea and perform carbonaceous aerosol particle size distribution analysis in background and urban areas.
- Estimate the aerosol particle chemical composition, size distribution in urban and background areas and determine the main sources of atmospheric submicron aerosol particles in Lithuania.
- Analyze physical and chemical aspects of the formation of aerosol particles combining the stable isotope ratio, aerosol mass and size spectrometry methods.
- Evaluate the influence of the long-range air masses transport on the local origin aerosol particle formation and transformation.

STATEMENTS OF DEFENCE

The main carbonaceous aerosol mass is in the submicron range: about 80 % of the mass is in the urban environment and about 60–70 % – in the background areas.

In the urban environment secondary organic submicron aerosol particles are dominating (76 %), while primary organic aerosol particles from the traffic make up 24 % of the total organic aerosol mass.

Secondary biogenic organic material in the aerosol particles comprises 50 % of the total organic mass at the forested site in East Lithuania (Rūgšteliškis), while 15 % of the organic aerosol mass at the coastal site of the Baltic Sea (Preila) was of biogenic origin.

Carbonaceous aerosol sources can be evaluated by combining the stable carbon isotope ratio and aerosol mass spectrometry methods.

Volcanic aerosol particles can be long-range transported (up to 3000km) and can significantly change the chemical composition and size distribution of local aerosol particles in the submicron range.

NOVELTY OF THE WORK

The contribution of the biogenic organic matter to the submicron aerosol fraction was evaluated.

The influence of different sources and photochemical oxidative processes in the atmosphere on the stable carbon isotope ratio of size segregated aerosol samples was determined for the first time by combining the comprehensive aerosol and isotope ratio mass spectrometric techniques.

SHORT SUMMARY OF THE THESIS

1. Methods of the work

Experiments were carried out in background (Preila, Rūgšteliškis, Mace Head) and urban (Vilnius) areas. Aerosol particles were collected on filters and with the Micro-Orifice Uniform deposition impactor (MOUDI) (Model 110, MSP corporation, USA). The quadrupole aerosol mass spectrometer (Q-AMS), developed at Aerodyne Research (ARI, USA), was used to obtain real-time quantitative information on the chemical composition and mass size distribution of non-refractory chemical components present in ambient

aerosol particles [1]. Positive matrix factorization (PMF) analysis of the unit mass resolution spectra was used to identify sources of organic matter in submicron aerosol particles [2]. Thermal–optical analytical technique (Sunset Lab, USA) was used for determination of organic and elemental carbon [3]. The investigations of the carbon isotopic ratio in different size aerosol particles were carried out with the stable isotope ratio mass spectrometer (*ThermoFinnigan Delta Plus Advantage*) [4]. Aerosol size distributions were measured by a scanning mobility particle sizer (SMPS). Radon (^{222}Rn) isotope concentrations were determined using the active deposit method.

2. Results and discussions

2.1. Carbonaceous aerosol particles

2.1.1. Organic and elemental carbon in coastal aerosol at the Baltic Sea

The investigation of carbonaceous compounds was performed at the Preila Environmental pollution research background station located on the Curonian Spit, on the coast of the Baltic Sea in the period of 19–28 June, 2006. The results of carbonaceous compound investigation are presented in Table 1.

Table 1. Concentrations of carbonaceous compounds ($\mu\text{g m}^{-3}$), air mass backward trajectories, and wind directions.

Date	TC	OC	EC	EC/TC	Air mass trajectory	Wind direction
2006.06.19	0.80	0.75	0.05	0.06	SE	W, SW
2006.06.20	3.20	3.06	0.14	0.04	SW	S
2006.06.21	2.82	2.66	0.16	0.06	SW	S
2006.06.22	2.14	2.05	0.09	0.04	SW	S
2006.06.23	0.16	0.09	0.07	0.43	N	W
2006.06.24	0.65	0.56	0.09	0.14	NW	W, NW
2006.06.25	1.32	1.22	0.10	0.08	NW, W	W
2006.06.26	1.92	1.85	0.07	0.04	NW, W	W, SE
2006.06.27	0.75	0.64	0.11	0.15	NW, W	W
2006.06.28	0.10	0.06	0.04	0.40	N	W
Mean	1.39	1.29	0.09	0.14		
Std. dev.	1.09	1.06	0.04	0.15		

The concentrations of organic carbon (OC) and elemental carbon (EC) differed even 10 times at the same place. A reliable correlation ($r = 0.73$, $p < 0.1$) between organic and elemental carbon indicates that both carbonaceous substances reach the Preila background station mostly from the same sources of pollution.

The highest concentrations of carbonaceous pollutants were determined on 20, 21, and 22 of June, when southwestern air masses from the “black triangle”, which includes some part of the Czech Republic, Germany, and Poland or industrial region of Silesia (Fig. 1a), and southern winds from Nida and Kaliningrad region were prevailing. On 19 June air mass arrived from the northwestern part of Ukraine via Belarus (Fig. 1b) and passed the Preila background station when western wind was prevailing. A relatively low concentration of carbonaceous compounds was observed during this period, though these air masses were of continental origin. Similar concentrations were observed on 25 and 26 June with air masses transported from the northern part of West Europe with a minor influence of southern mining regions (Fig. 1 c). The EC/TC ratio varied between 0.04 and 0.06 and was typical of background areas during these analyzed periods [5]. Lowest concentrations of EC and OC were determined at the background station on 23 and 28 of June, when air masses were passing the investigation site from the Atlantic Ocean via England, the North Sea, and the Baltic Sea (Fig. 1d). An exclusively high EC/TC ratio observed during this period indicated the anthropogenic origin of carbonaceous pollutants. A low amount of organic carbon carried to the recipient site with the northern air masses indicated an intensive washout process of OC in the marine atmosphere.

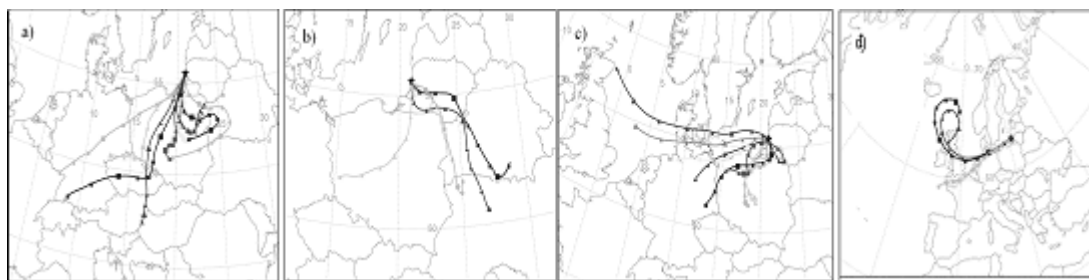


Fig. 1. Air mass backward trajectories at the Preila background station on (a) 20–22, (b) 19, (c) 25–26, (d) 23 of June 2006.

Data of investigation indicate that the main part of carbonaceous compounds is carried to the Preila background station by air masses from the southwestern part of Europe. Carbonaceous compounds in southwestern air mass may comprise more than 50 % of total carbonaceous compounds reaching the background station with air masses from different directions.

2.1.2 Size segregated carbonaceous aerosol particles

In this subchapter results of experimental investigation dedicated to the analysis of size segregated carbonaceous aerosol particles at the background and urban sites are presented. Variation of the carbonaceous aerosol particle mass size distribution in different background and urban areas was experimentally observed by analyzing data of samples collected in Rūgšteliškis, Preila (background site), Vilnius city and Vilnius suburban background areas. Aerosol particles were collected with the MOUDI for measurements of the total carbon (TC) mass size distribution.

Fig. 2 presents the TC mass size distribution in the particle size range of 0.056–18 μm . For all sites, almost all aerosol particle mass was below 1 μm . As shown in Fig. 2 the main mode diameter of TC mass size distribution differed significantly. The submicron particle mass was centred at around 0.18–0.32 μm in the urban environment. In background areas the mass size distribution peaked in the size range of 0.32–0.56 μm . Accumulation mode particles shifted to the smaller sizes in Vilnius due to the impact of primary carbonaceous aerosol particle sources (vehicle exhaust). Meanwhile long range transported and cloud processed aerosol particles in background areas tend to be in a larger size range (0.32–0.56 μm). The results indicate that submicron aerosol particles at an urban site (Vilnius) made up about 80 % and at background and urban background sites – 60–70 % of the total TC concentration.

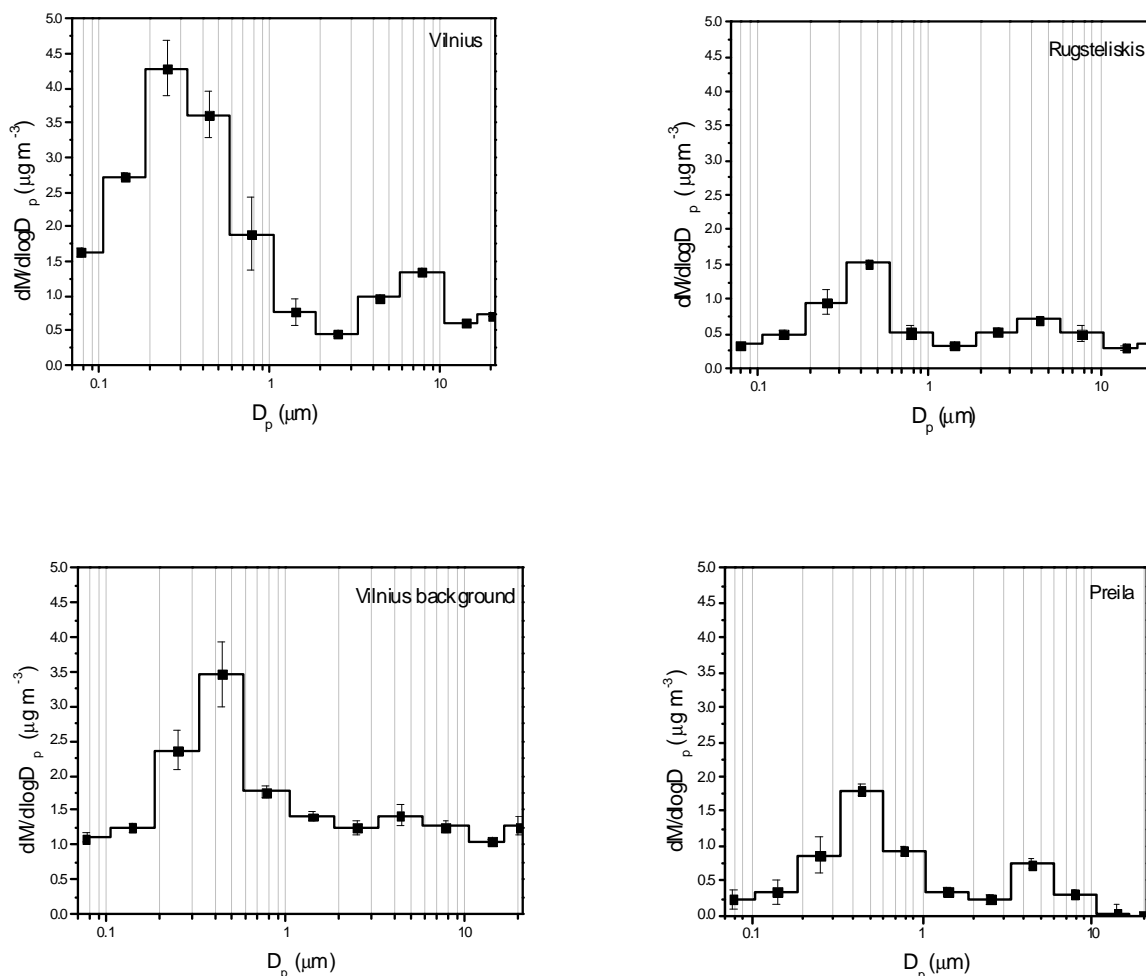


Fig. 2. Total carbon mass size distribution at urban (Vilnius), background (Preila, Rūgšteliškis) and suburban (Vilnius) sites.

2.2. *Biogenic and anthropogenic organic matter in aerosol over continental Europe: source characterization in the east Baltic region*

The measurements of chemical composition of submicron aerosol particles (PM_{10}) were performed at the Air Pollution Research Station in Preila during 3–15 September, 2006. The average concentrations of ammonium, nitrate, sulfate, chloride and organic compounds during the observation period were 0.94, 0.43, 2.35, 0.07, 3.28 $\mu\text{g m}^{-3}$, respectively. The organic aerosol fraction dominated in the total aerosol particle mass in all air masses and reached ~80 % in the North Atlantic air masses (Fig. 3b). Organic matter and sulfate

concentrations were well correlated ($r=0.83$, $N=267$, $P<0.0001$) (Fig. 3a) in the continental air masses indicating that the organic matter was derived from regional production and long-range transport. However, in the clean North Atlantic air masses the organic matter concentration was higher than that of sulfate and did not correlate ($r = 0.102$, $N = 96$, $P < 0.31$) indicating that biogenic organic compounds were of different origin, most likely marine and/or secondary biogenic and they significantly contributed to the total aerosol particle mass.

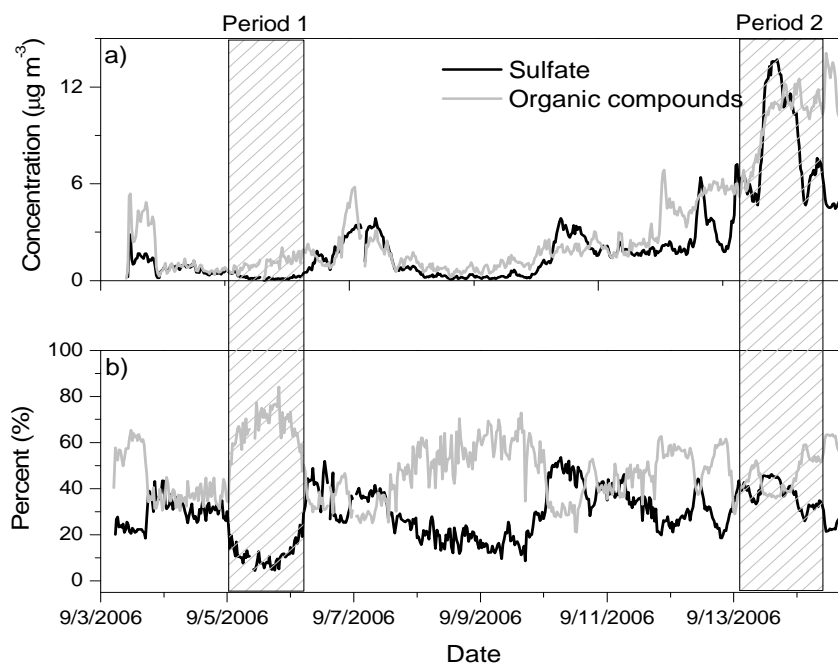


Fig. 3. Time series of sulfate and organic compound mass loadings (a) and mass fraction (b). Periods 1 and 2 are sampling periods of the North Atlantic and Southern European air masses accordingly.

Size distributions of chemical components varied significantly during the campaign leading to important insights into the source origin and mixing state of the particles. The main mode diameter of sulfate (295 nm) and organic matter (118 nm) in the clean marine air masses (Fig. 4a) demonstrated that organic-containing particles were fresher particles of the sampled aerosol compared to sulfate-containing particles. It is likely that organic species in clean marine air masses originated through the secondary aerosol formation from the

volatile organic compounds (VOCs), emitted from the biogenic sources such as forests or produced by primary sea spray over the Baltic Sea. In the Southern European air masses the size distribution of sulfate-containing particles and organic-containing particles was similar; the modal peaks of the sulfate and organic compounds became equal and were about 410 nm, which showed a great impact of long-range transport and regional emission sources.

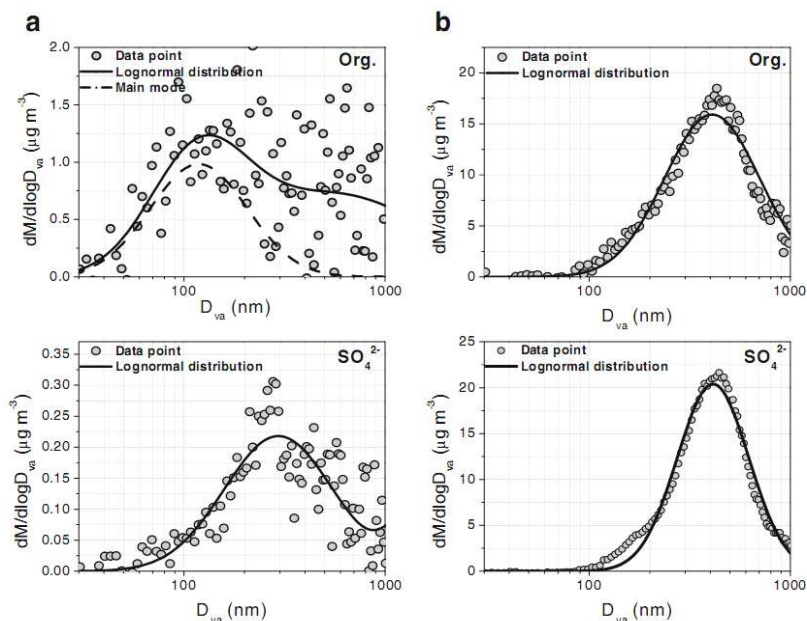


Fig. 4. The mass size distributions of sulfate and organic matter fractions in (a) air masses from the North Atlantic Ocean and (b) air masses from Southern Europe.

The PMF analysis revealed three factors of organic aerosol (OA): aged oxygenated low-volatility organic aerosol (LV-OOA), less oxygenated semi-volatile organic aerosol (SV-OOA), and biogenic organic aerosol (BGOA). The average relative contribution of the LV-OOA, SV-OOA and BGOA factors was 22 %, 63 % and 15 %, respectively. Fig. 5 shows the mass spectral profiles of the three components identified during the campaign and the time series of the three organic aerosol components were compared with corresponding tracers. The dominant feature of LV-OOA is a strong signal at m/z 44 (Fig. 5a) indicating strongly oxidized organic matter. In the SV-OOA spectrum m/z 44 and m/z 43 with smaller contribution at m/z 29, 41, 55 were the dominant features. The SV-OOA spectrum showed

less oxygenated organic aerosol than that of LV-OOA with a smaller contribution of m/z 44 (10 % for the SV-OOA, 28 % for the LV-OOA), consistent with less photochemically aged OA. The LV-OOA and SV-OOA time series strongly correlated with particulate sulfate ($r(\text{LV-OOA}) = 0.78$, $r(\text{SV-OOA}) = 0.79$, $N=3265$, $P<0.0001$), while SV-OOA also correlated with nitrate ($r(\text{SV-OOA}) = 0.69$), indicating that both factors were largely influenced by regional or long-range transport.

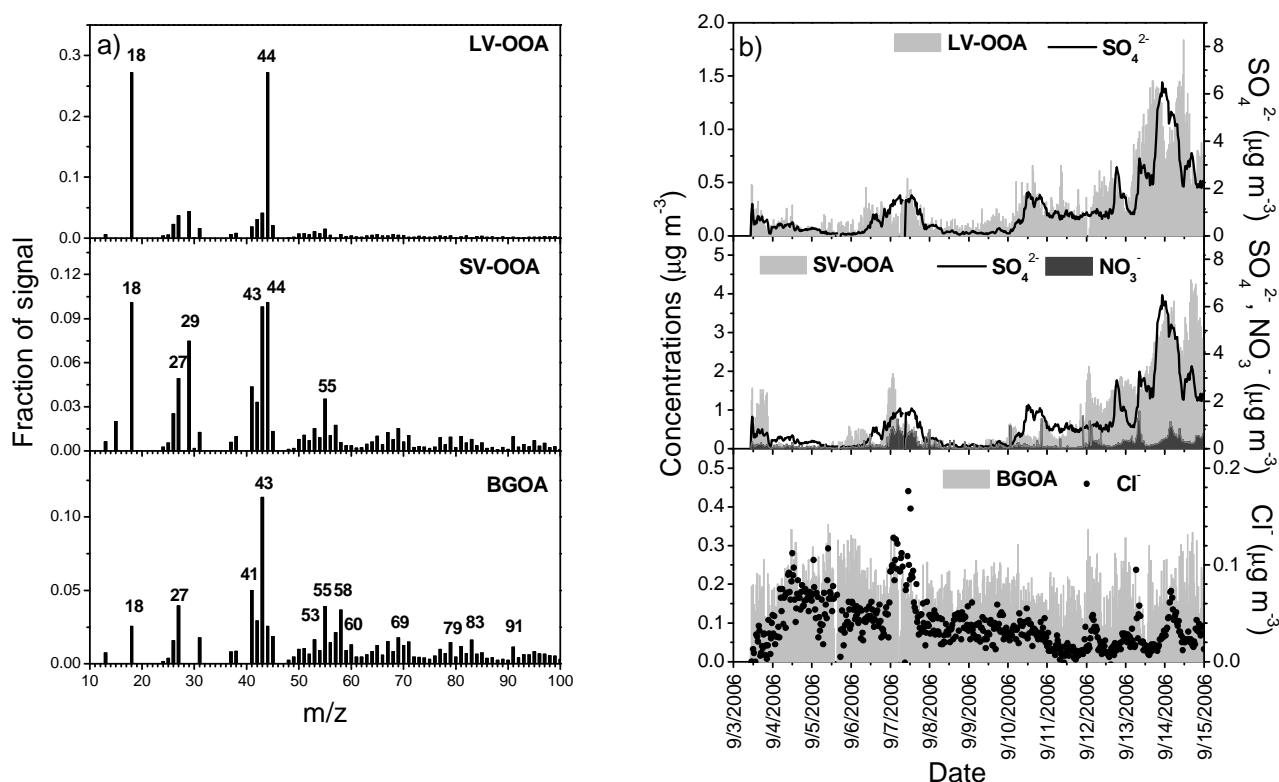


Fig. 5. The mass spectra (a) and time series (b) of three PMF factors. The time series of PMF factors are presented together with selected tracer species.

The BGOA factor did not contribute significantly during polluted periods, but in the North Atlantic air masses (5–6 September) this factor was up to 50 % (Fig. 5b). The dominant fragments at m/z 27, 43, 53, 55, 65, 67, 79, 91 were very similar to the primary marine organic aerosol [6] as well as during the particle growth event in Hyytiälä [7]. The mass spectrum of this factor also consisted of high loadings of m/z 58, 60 (Fig. 6a) that could be attributed to sodium chloride (NaCl^+) [8]. The BGOA factor slightly correlated

with chloride ($r = 0.15$, $N = 3265$, $P < 0.0001$) suggesting that the primary sea-spray significantly contributed to BGOA. This finding supports the existence of biogenic sources at the Preila site, possibly contributing through the secondary aerosol formation from the VOCs emitted over forests, but could be well representing the primary marine organic aerosol [6], which unfortunately is impossible to verify by the unit mass resolution.

2.3. Characterization of aerosol sources at urban and background sites of Lithuania

The background site was located at the Rūgšteliškis integrated monitoring station in North-East Lithuania, a strict reserve zone of Aukštaitija National Park with mature forest ($55^{\circ}27'48''N$, $26^{\circ}00'16''E$). 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. The first PM_{10} sampling site (Žirmūnų str.) 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 PM_{10} sampling site (A. Goštauto str.) was located close to the Vilnius city old town, in a relatively quiet location with a traffic throughput of about 25,000 vehicles per day. The measurement period was May 22 – June 10, 2008.

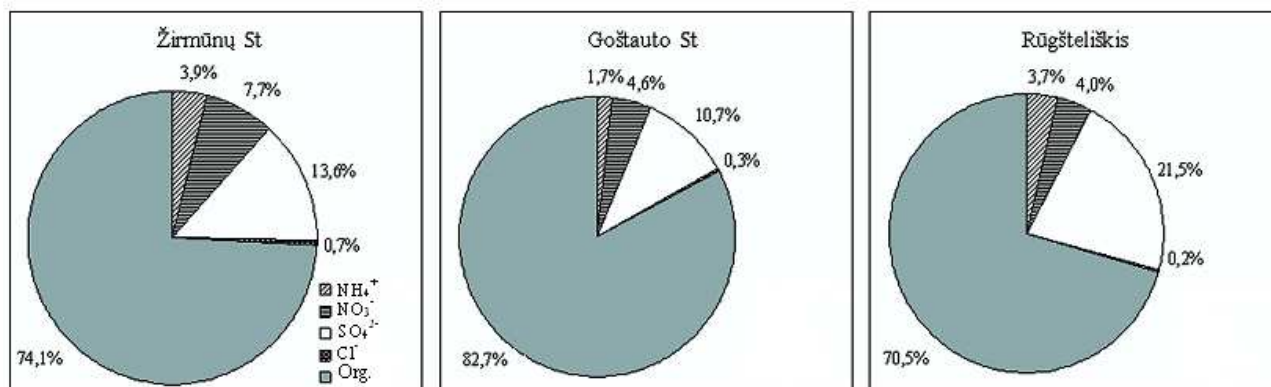


Fig. 6. Average chemical composition of PM_{10} at all three sampling sites.

The chemical composition of PM_{10} particles from all three sampling sites is presented in Fig. 6. Organic compounds dominated at all three sampling sites and made up 70–83%,

while sulfate concentration varied from 11 to 21% of the PM₁ mass. Nitrate and ammonium made small contributions to the total mass at all sites, but slightly larger contributions at the urban ones. The concentrations of organic matter 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. A very clear diurnal concentration variation of nitrates and organic matter in both locations of Vilnius city can be seen in Fig. 7. The concentration variation of nitrates and organic components was determined by the atmosphere mixing height and by emissions from traffic (see graphs at the bottom of Fig. 7). The nitrates and organic components were emitted by combustion sources and their diurnal cycles had a peak early in the morning during the rush hours. At midday, the concentration of nitrates and organic matter decreases because the atmosphere mixing layer height increases causing dispersion of this accumulated species that is much faster than the rate of emission at that time. However, the main source of sulfates was long-range transport with air masses from neighboring 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 were transferred into the atmosphere surface layer.

Three organic aerosol components were determined 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 determined at an urban (Vilnius) site. The major sources at the background (Rūgšteliškis) site were LV-OOA, SV-OOA, biomass burning organic aerosol (BBOA).

The HOA mass spectrum in Vilnius city showed characteristic ion groups of refined hydrocarbons, (m/z 41, 43, 55, 57, 69, 71, 83, 85) with little signal from m/z 44 (Fig. 8a). Diurnal variations of HOA showed strong morning emissions during rush hours (Fig. 9b). The HOA mass concentration showed a high correlation in time with NO_x ($R^2 = 0.67$) and CO ($R^2 = 0.68$), which is consistent with the determination of HOA as being dominated by combustion-related urban sources such as transport.

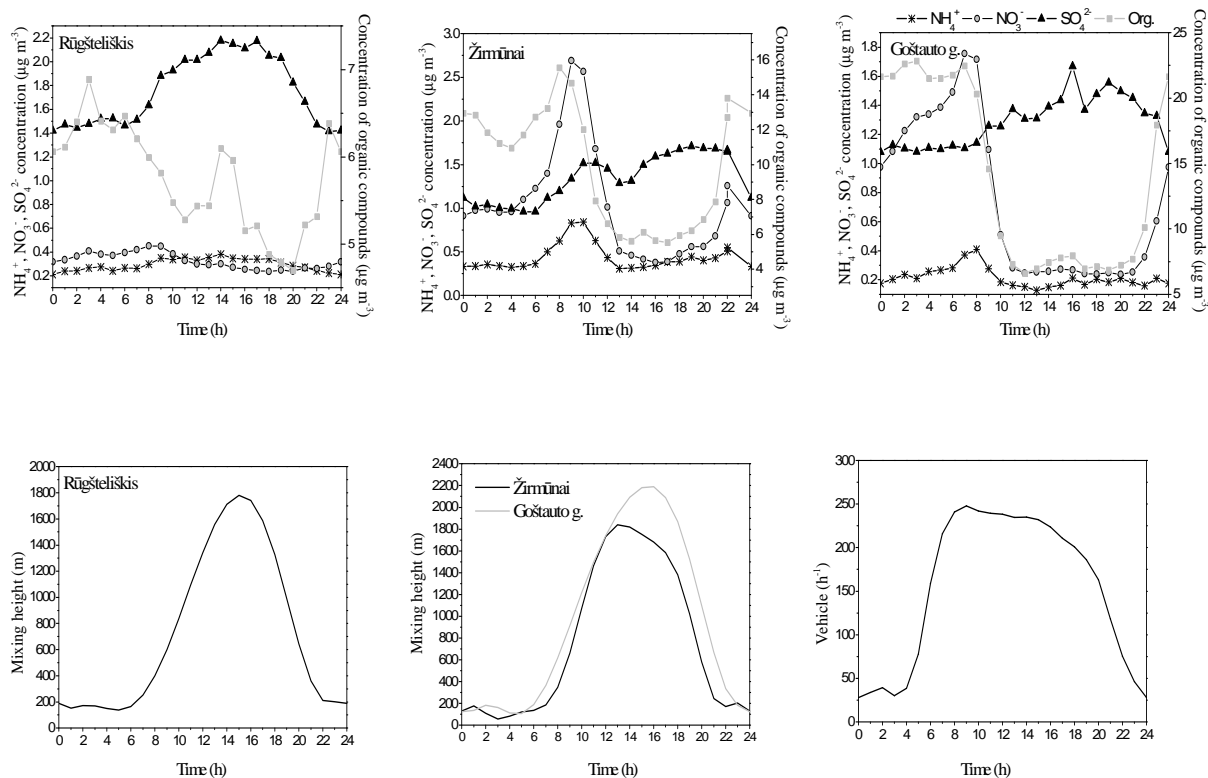


Fig. 7. Diurnal variation of PM_{10} components and atmosphere mixing heights at all three sampling sites. Averaged diurnal variation of the number of vehicles per hour is presented only for A. Goštauto street.

The primary emission mass spectrum at the Rūgštelėškis site (Fig. 8d) 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 m/z 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 feast on 6–7 July, due to an old tradition of making bonfires all over Lithuania. The peak in diurnal profiles tended to occur in the late evening, going into the night (Fig. 9 a), which could coincided with bonfire burning during the evening and night. The LV–OOA mass spectra recorded in Vilnius city and at Rūgštelėškis site were dominated by m/z 44, indicating strongly oxidized organic matter typical of the regional source (Fig. 8 b, e). The LV–OOA time series correlated with particulate sulfate ($R^2 = 0.5$) and with air mass

transport over industrial regions from the west/southwest of Europe. This factor did not show any strong diurnal cycle (Fig. 9 a, b), which is consistent with a regional source and domination by atmospheric transport.

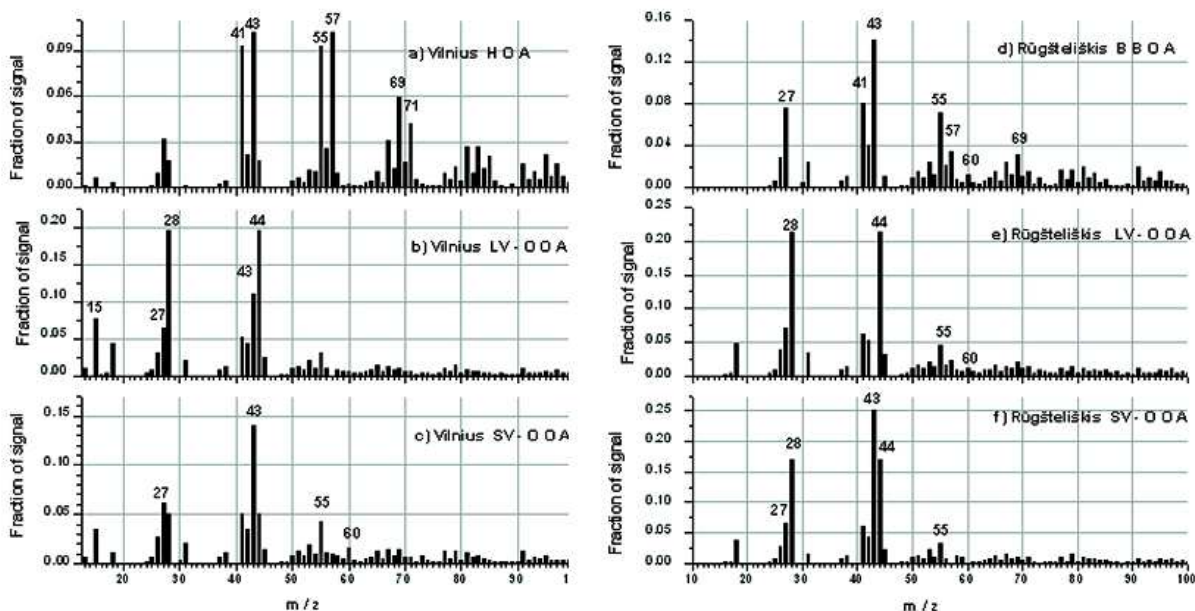


Fig. 8. Mass spectra of the PMF components from campaigns at Vilnius city and Rūgštelėškis sites.

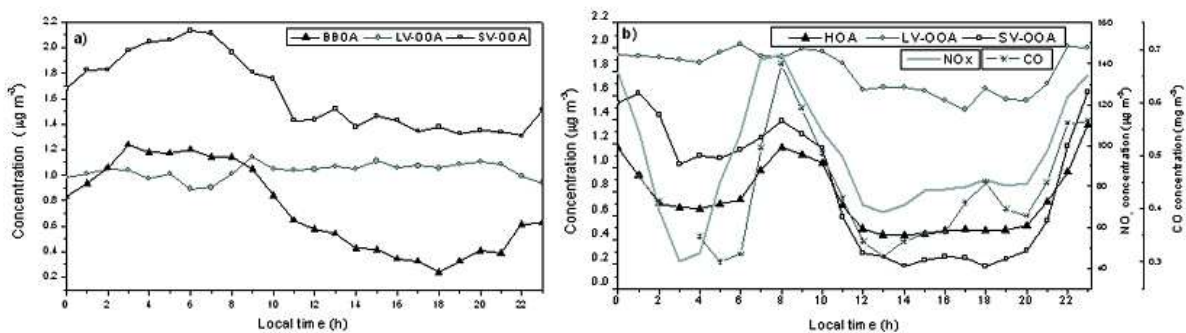


Fig. 9. Diurnal concentration course of aerosol components: (a) at Rūgštelėškis site, (b) in Vilnius city (Žirmūnų St). NO_x and CO concentration data are from monitoring station in Vilnius city (Žirmūnų St).

Moreover, LV-OOA factor at the Rūgštelėškis site contained a negligible contribution from m/z 60 (~1%) (Fig. 8e), 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 had a higher OOA concentration, probably due to secondary organic aerosol formed

from BB 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 m/z 41, 55, and 57 (Fig. 8c). This factor is widely reported as fresh oxygenated organic aerosol [9]. As shown in Fig. 9 b, the SV–OOA time series correlated 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. The mass spectrum of SV–OOA at the Rūgšteliškis site (Fig. 8 f) did not contained marker peaks for anthropogenic (m/z 57) and BB emission (m/z 60), but had similarities with spectra obtained from α -pinene oxidation products [10] and from the particle growth event at Hyytiälä [7]. 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.

The variation of carbon isotope values in size segregated aerosol particles was investigated at background Rūgšteliškis and urban Vilnius stations simultaneously.

Total carbon (TC) $\delta^{13}\text{C}$ values at Rūgšteliškis and Vilnius sites were similar in the PM_{10} aerosol particles and it was not possible to distinguish different carbonaceous aerosol sources at urban and background sites (Fig. 10). However, a clear difference between elemental and organic carbon $\delta^{13}\text{C}$ values at forested (Rūgšteliškis) and urban (Vilnius) stations was observed (Fig. 10). Traffic is the main source of elemental carbon in the city therefore $\delta^{13}\text{C}$ values of elemental carbon in Vilnius ($-27.2 \pm 0.24\text{‰}$) can be attributed to the traffic emissions. Meanwhile the $\delta^{13}\text{C}_{\text{EC}}$ values in Rūgšteliškis varied from -22.9‰ to -26.3‰ (mean value $-24.7 \pm 1\text{‰}$) and clearly indicate other sources of carbonaceous aerosol. PMF analysis revealed that the primary organic compound source in Rūgšteliškis was biomass burning. Carbon isotope values of organic carbon in Vilnius varied from -27.9‰ to -29.9‰ with the mean value of $-28.9 \pm 0.7\text{‰}$ and reflected dominant fraction of secondary anthropogenic (traffic) organic aerosol ($76.4 \pm 10.9\%$). $\delta^{13}\text{C}$ values of organic carbon in Rūgšteliškis were more negative ($-30.6 \pm 0.8\text{‰}$). PMF analysis revealed that OA in Rūgšteliškis was composed of biomass burning (20 %), secondary biogenic (50 %) and

regional origin (30 %) organic carbon. Smog chamber experiments [11] revealed that the stable carbon isotope value for the β -pinene was $-30,1\text{‰}$, while $\delta^{13}\text{C}$ values for the nopinone (main oxidative product of the β -pinene) and acetone were $-29.6\pm 0.2\text{‰}$ and -36.6‰ , respectively. In above mentioned studies it was revealed that $\delta^{13}\text{C}$ values were in the range of $-30 - -32 \text{‰}$ for the secondary organic aerosol, which originated from α -pinene and limonene.

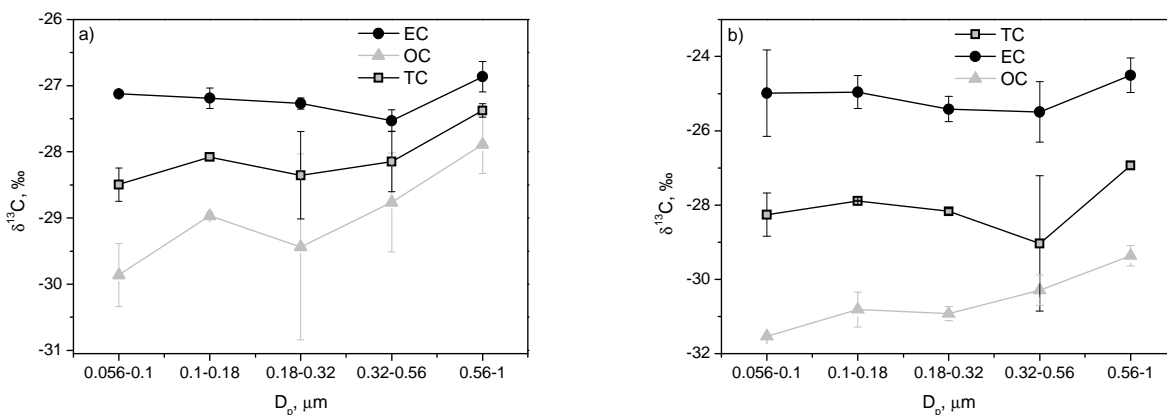


Fig. 10. $\delta^{13}\text{C}$ variation in carbonaceous aerosols particles of accumulation mode a) in Vilnius, b) in Rūgštelėškis.

The stable carbon isotope ratio was in the range of $-29.1 - -32.5 \text{‰}$ for the fatty acids of the biomass burning origin [12]. Organic carbon $\delta^{13}\text{C}$ values obtained at the Rūgštelėškis station can be explained by above mentioned processes and allow concluding that these values indicate local biogenic secondary organic aerosol.

2.4. Influence of the volcanic eruption on the physical and chemical properties of the submicron aerosol particles of urban and background environment

A four-week field campaign was conducted at Mace Head Research Station, Ireland (53°19'N, 9°54'W) in June 2007. The station is located on a peninsula and the wind direction sector between 190° and 300° was from the open North Atlantic Ocean providing excellent conditions for carrying out marine aerosol measurements.

We observed a continuous increase in sulfate concentrations in advected air masses with trajectories crossing over Iceland. Over the period of 26th of June 2007 (from 11:00 UTC) the non-sea salt (nss)-sulfate concentration increased from 1.2 to 4.6 (± 0.9) $\mu\text{g m}^{-3}$ (Fig. 11). Concurrent nitrate levels remained low and largely unchanged indicating no major contribution from anthropogenic pollution.

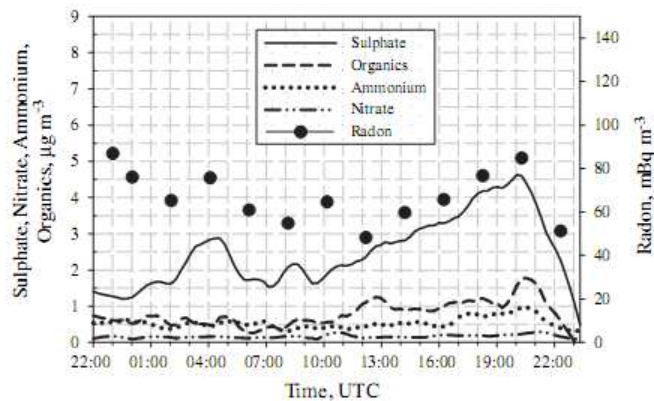


Fig. 11. Temporal trends of chemical composition of PM₁ aerosol, measured with Q-AMS and concurrent radon concentrations on June 26, 2007.

In addition, the concurrent increase in radon concentrations (Fig. 11) confirmed a predominantly land origin of sulfate in this air mass. Radon concentrations were initially elevated due to regional contributions from Ireland but then decreased when trajectories shifted from north to north-west. It started to increase again later (from 12:00 UTC) in conjunction with air mass passage over Iceland. The radon temporal trend followed the sulfate trend. Generally, the radon concentration on June 26 was lower than 400 mBq m⁻³

indicating an oceanic air mass [13] and little to no contact with land over the past 2–3 days. From these results we assume that the observed increase in sulfate concentration ($3.4 \mu\text{g m}^{-3}$ above background level) was entirely caused by advection of volcanic sulfur emissions from Iceland.

The sulfate particles were only partly neutralized by ammonium based on the results obtained by the Q-AMS. Q-AMS measured at least 35 % of the total sulfate mass being a pure sulfuric acid (Fig. 12). The modified marine air flow touching the west coast of Ireland in conjunction with the northerly wind direction brought nearly neutralized sulfate particles in the form of ammonium sulfate and bisulfate (00:00 UTC–01:00 UTC, Fig. 12). However, the degree of neutralization decreased and sulfuric acid constituted about 50 % of the total sulfate mass (10:00 UTC–23:00 UTC, Fig. 12) after trajectories shifting to the west and air masses coming from the marine sector.

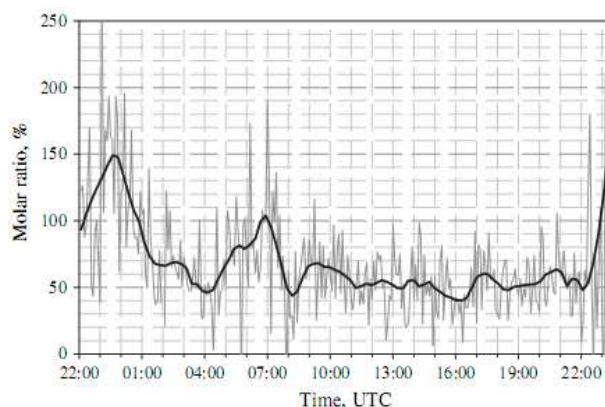


Fig. 12. Time trends of ammonium to sulfate molar ratios in PM_{10} aerosol, measured with Q-AMS on June 26, 2007.

Initially, a higher fraction of sulfate resulted in the growth of both accumulation and Aitken mode particles. However, this changed later due to the increasing fraction of dust particles (17:30 UTC). The Aitken mode diameter continued to increase while the accumulation mode diameter shifted towards smaller sizes (Table 2). In addition, dust particles increased the number concentration in both the Aitken and accumulation modes. From 20:30 UTC air masses were advected from the North Atlantic Ocean which had not passed over Iceland. In this context, a rapid decrease in sulfate concentrations and a

significant change in the aerosol size spectrum resulting in typical aerosol size distribution were observed for a very clean air mass at Mace Head.

Table 2. Summary of modal parameters obtained by fitting lognormal functions to aerosol number size distribution measured with a scanning mobility particle sizer in Mace Head on June 26.

Tame, UTC	11:30	14:00	15:50	17:30	19:00	20:00	21:30
Aitken mode median diameter, nm	34 ± 0,1	34 ± 0,1	35 ± 0,1	41 ± 0,2	46 ± 0,3	52 ± 0,3	36 ± 0,2
Number concentration, 1 cm ⁻³	613 ± 11	471 ± 9	439 ± 9	383 ± 7	473 ± 8	437 ± 9	218 ± 3
Accumulation mode median diameter, nm	162 ± 4	184 ± 3	191 ± 4	186 ± 2	163 ± 4	154 ± 2	209 ± 4
Number concentration, 1 cm ⁻³	130 ± 1	127 ± 2	129 ± 2	158 ± 2	209 ± 2	263 ± 4	108 ± 1

During the eruption of the volcano at Grimsvötn in Iceland (21 May 2011), an inflow of volcanic pollutants to the atmospheric surface layer of Vilnius, Lithuania from 07:00 UTC 24 May until the end of 29 May 2011 was observed. A cloud of volcanic plume rose up from Grimsvötn and reached an altitude of 19 km. The analysis of possible volcanic origin PM₁ aerosol sources was supplemented with forward and backward air mass trajectories, concentration and composition measurements and size distribution calculations of aerosol particles. According to the forward air mass trajectories from the volcano at Grimsvötn, the plume from the layer of 3000–4500 m was advected southeastward from Iceland towards the British Isles and the Baltic Sea. The plume reached Vilnius and descended from the troposphere to the surface after about 86 h. The sulfate concentrations increased by a factor of 3 (from 1.13 to 3.86 µg m⁻³) and reached 90 % of PM₁, over the period of the volcanic eruption (Episode 1, Episode 2), while the nitrate and organic levels remained low and unchanged (Fig.13). The volcanic sulfate contribution made up about 250 % of the average concentration of anthropogenic sulfate in Vilnius.

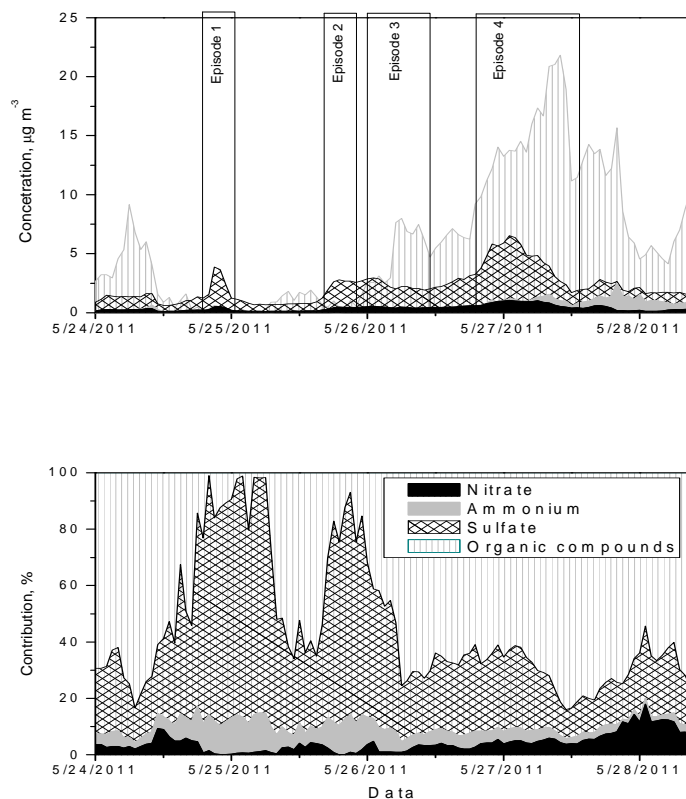


Fig.13. Time series of hourly averaged PM₁ concentrations and relative contribution of chemical components measured in Vilnius from 24–29 May 2011, after the volcano eruption (21 May 2011) at Grimsvötn in Iceland. The vertical lines in the figure indicate the selected Episodes (E1–E4).

The previous study [14] demonstrated that the main sulfate source in Vilnius was long-range transport. Moreover, the average sulfate concentrations in Vilnius were about $1.36 \mu\text{g m}^{-3}$ and made up 14% of submicron aerosol particles. These findings additionally support our assumption that PM₁ chemical composition on 25–26 May 2011 (sulfate fraction was about 90 %) was clearly unusual for Lithuania and Vilnius.

According to PM₁ composition concentration measurements, along with the backward trajectories calculation, we can assume that the main source of sulfate during Episodes 1 and 2 was from the volcano at Grimsvötn in Iceland. The ammonium to sulfate molar ratio (ASR) during Episodes 1 and 2 was 0.81, suggesting that sulfate particles were partially neutralized by ammonium and determined by volcanic eruptions.

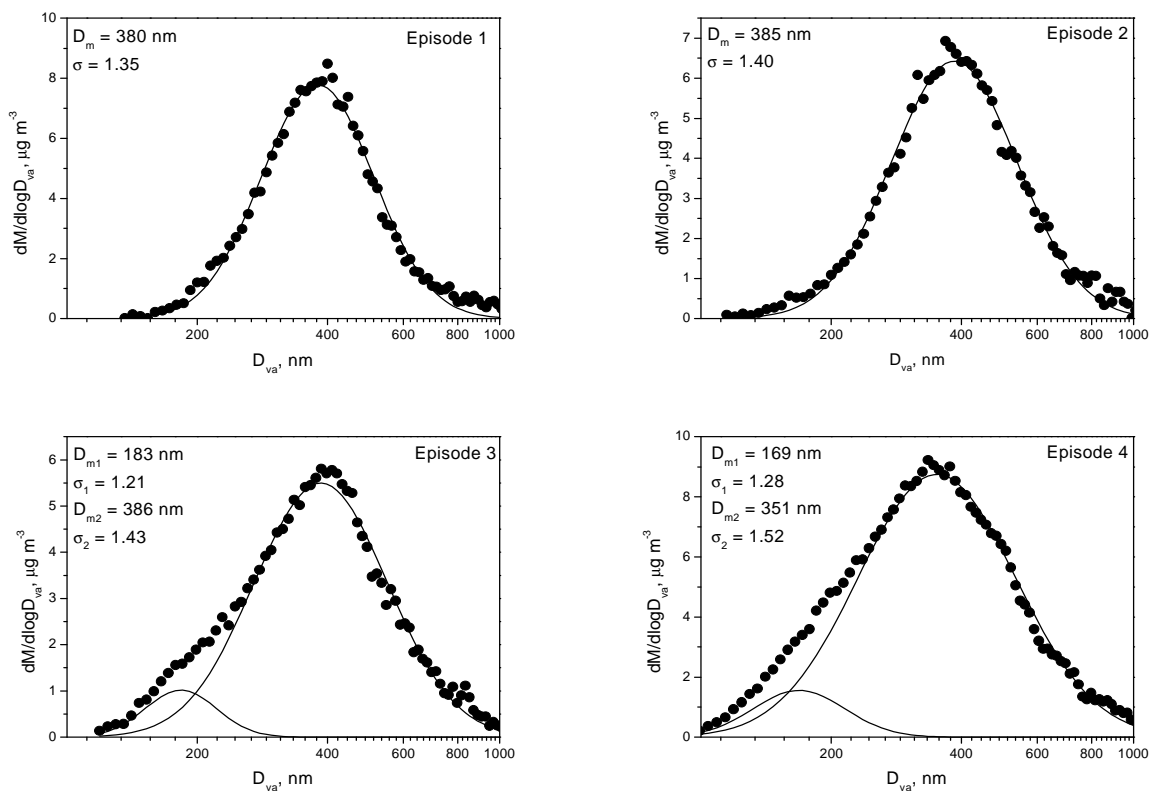


Fig. 14. Size-resolved distribution spectra of sulfate concentrations during Episodes 1–4, 24–29 May 2011.

The lognormal distributions of the sulfate consisted only of the accumulation mode (averaged values) $D_m(\text{SO}_4^{2-}) = 382 \text{ nm}$ (geometrical standard deviation $\sigma = 1.37$) (Fig. 14) for Episodes 1 and 2. Very negligible peaks were visible in smaller size range of the accumulation mode for sulfate during Episodes 3 and 4 (Fig. 14). In this case, we can assume that alongside with the volcanic particles, additional particles in smaller size were formed, possibly due to the impact of fresh (nearest) aerosol sources. The accumulation mode peaks for sulfate during Episodes 3 and 4 were wider than those during Episodes 1 and 2 (see Fig. 14), possibly due to the increased volcanic plume dispersion with time. The increased volcanic plume dispersion showed a variety of mixed aerosol particles from different origin sources, and different transformation processes.

CONCLUSIONS

1. The main mass of the carbonaceous aerosol particles is concentrated in the submicron size range. Over 80 % of the mass in the carbonaceous aerosol particles is attributed to the submicron range in the Vilnius city center, while in the background and suburban areas — 60–70 %. In the Vilnius city the highest aerosol mass concentrations were in the size range of 0.18–0.32 μm , while in background (Preila, Rūgšteliškis) and suburban areas — in the size range of 0.32–0.56 μm .
2. Aerosol and stable isotope ratio mass spectrometry revealed that traffic was the primary source of aerosol particles in the city with the $\delta^{13}\text{C}_{\text{EC}} = -27.2 \pm 0.24\text{‰}$ while biomass burning was the primary source at the forested background site (Rūgšteliškis) ($\delta^{13}\text{C}_{\text{EC}} = -24.7 \pm 1\text{‰}$).
3. Positive matrix factorization and organic carbon stable isotope ratio analysis revealed that in Vilnius secondary anthropogenic organic compounds (having $\delta^{13}\text{C} = -28.9 \pm 0.7\text{‰}$) are dominating (76%), while at the forested background site secondary biogenic organic compounds ($\delta^{13}\text{C} = -30.6 \pm 0.8\text{‰}$) made up 50 % of the total organic aerosol mass.
4. Biogenic organic aerosol made up 15 % of the organic aerosol mass at the coastal background site of the Baltic Sea (Preila) but in the North Atlantic air masses this factor was up to 50 %.
5. It was determined that aerosol particles of the volcanic origin were not fully neutralized and sulfuric acid made up over 35 % of the sulfate mass. The particle number concentration increased in the Aitken and accumulation modes due to the volcanic plume.
6. Sulfate concentration was increased up to 250 % in Vilnius due to the volcanic origin (Grimsvötn, Iceland) sulfate emission and it comprised up to 90 % of the total PM_{10} mass. A clear sulfate size distribution spectrum was characteristic of volcanic origin aerosol particles in the accumulation mode ($D_m = 382 \text{ nm}$).

List of publications

1. **I. Rimšelytė**, J. Ovadnevaitė, D. Čeburnis, K. Kvietkus, E. Pesliakaitė, Chemical composition and size distribution of fine aerosol particles on the east coast of the Baltic Sea, *Lithuanian Journal of Physics*, Vol. 47, No. 4, pp. 523-529 (2007).
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2. J. Ovadnevaitė, D. Čeburnis, K. Kvietkus, **I. Rimšelytė**, E. Pesliakaitė, Chemical composition and size distribution of fine Aerosols particles measured with AMS on the east coast of the Baltic Sea. Nucleation and Atmospheric Aerosols 17th International conference, Galway, Ireland, 2007.
3. **I. Rimšelytė**, J. Ovadnevaitė, D. Čeburnis, K. Kvietkus, D. Šopauskienė and J. Šakalys, Online measurements of fine aerosol particles chemical composition and size distribution in Preila, Lithuania. European Aerosol Conference, Thessaloniki, Greece, 2008.
4. A. Milukaitė; **I. Rimšelytė**; K. Kvietkus; X. Chi; W. Maenhaut, Measurement of organic and elemental carbon in coastal atmospheric aerosol in Lithuania. ESF-COST High-Level Research Conference Systems Chemistry, Acquafredda di Maratea, Italy, 2008.
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SANTRAUKA

Pastaruoju metu padidėjęs dėmesys aerozolio dalelių tyrimams siejamas su įrodytu neigiamu jų poveikiu žmonių sveikatai, klimato kaitai, matomumui ir tiesioginiu jų dalyvavimu teršalų pernešime. Aerozolio dalelių poveikis klimato kaitai yra sunkiai įvertinamas, nes vis dar nėra tiksliai apibrėžti žmogaus veiklos sukelti atmosferos sudėties pokyčiai. Būtina žinoti veiksnius įtakančius aerozolio dalelių sudėtį, pasiskirstymą pagal dydį ir sklaidą. Taigi, šio darbo tikslas buvo įvertinti smulkiosios aerozolio dalelių frakcijos šaltinius, fizikines ir chemines savybes, kompleksiskai apjungiant įvairius tyrimo metodus.

Darbe eksperimentiškai įrodyta, kad pagrindinę anglies turinčio aerozolio dalelių masę sudaro submikroninio dydžio dalelės (80 % Vilniuje, apie 60–70 % foninėje vietovėje). Suminės anglies akumuliacinės modos didžiausios dalelių koncentracijos Vilniuje buvo 0,18–0,32 μm dydžių intervale, o foninėse Preilos ir Rūgšteliškio bei priemiesčio vietovėse - 0,32–0,56 μm dydžių intervale.

Atlikus kompleksinę aerozolio ir stabilijų anglies izotopų masių spektrometrinę analizę buvo nustatyta, kad pirminis anglies turinčio aerozolio dalelių šaltinis mieste yra autotransportas, kurio elementinės anglies $\delta^{13}\text{C} = -27,2 \pm 0,24\%$, o rytų Lietuvos miškingoje foninėje vietovėje (Rūgšteliškis) – biomasės deginimas ($\delta^{13}\text{C}_{\text{EC}} = -24,7 \pm 1\%$). Vilniuje organinių medžiagų $\delta^{13}\text{C} = -28,9 \pm 0,7\%$, o miškingoje aplinkoje $\delta^{13}\text{C} = -30,6 \pm 0,8\%$. Aerozolio dalelių ir organinės anglies stabilijų anglies izotopų santykio masių spektrometrijos matavimai parodė, kad Vilniuje dominavo antropogeninės antrinės organinės medžiagos (76 % nuo visų organinių junginių masės), o Rūgšteliškyje vyravo biogeninės antrinės organinės medžiagos (50 % nuo visų OA).

Parodyta, kad Baltijos jūros pakrantės aplinkoje (Preila) biogeninis organinių medžiagų šaltinis vidutiniškai sudaro 15 % nuo organinių medžiagų masės, tačiau Šiaurės Atlanto oro masėje biogeninių medžiagų indėlis siekia net 50 %.

Vertinant tolimosios oro masių pernašos įtaką vietinės kilmės aerozolio dalelių formavimuisi ir kaitai, buvo nustatyta, kad vulkaninės kilmės sulfatai atmosferoje nėra pilnai neutralizuoti, o sieros rūgštis sudaro virš 35 % nuo sulfatų masės. Vulkaninės kilmės

medžiagų koncentracijos padidėjimas didina skaitinę koncentraciją Aitkeno ir akumuliacinėje modoje.

Vulkaninės kilmės sulfatų emisija 250 % padidino vidutinę foninę sulfatų jonų koncentraciją Vilniuje ir šio periodo metu sulfatai sudarė iki 90 % submikroninės aerosolio dalelių masės. Vulkaninės kilmės oro masių epizodams būdingas aiškus sulfatų pasiskirstymo pagal dydį spektras akumuliacinėje modoje ($D_m = 382 \text{ nm}$).

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