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Seasonal variability of monosaccharide anhydrides, resin acids, methoxyphenols and saccharides in PM_{2.5} in Brno, the Czech Republic



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ABSTRACT

PM_{2.5} aerosols were collected over of 24-hrs on quartz fiber filters in the city of Brno (Czech Republic) in a week campaign in winter, spring, summer and autumn 2010 and winter 2011. Selected organic compounds including monosaccharide anhydrides, methoxyphenols, resin acids and saccharides were determined in collected samples using GC-MS. The analysis of the source specific molecular markers in collected aerosols identified the contributions of three main emission sources, i.e., wood combustion within residential heating, various biological sources and resuspended soil.

All analysed particulate organic compounds show seasonal trend. Wood burning products predominate in winter and autumn, while the compounds produced by biological sources or via soil resuspension have the highest concentrations during spring and summer. Softwood was found as a predominantly burnt kind of wood.

Levogluconan was dominant analysed organic compound in winter, autumn and summer, while sucrose prevailed in spring season. Levogluconan was the most concentrated representative of monosaccharide anhydrides, vanillic acid prevailed among methoxyphenols while dehydroabietic acid and sucrose were the most abundant compounds among resin acids and saccharides, respectively.

Within the study, we optimized the extraction procedure and derivatization process to be applicable at the same time for all the studied particulate organic compounds. As a result, the all compounds were extracted from collected aerosols with mixture dichloromethane:methanol (1:1, v/v), derivatized into trimethylsilyl derivatives with MSTFA + 1% TMCS and determined using GC-MS.

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1. Introduction

Comprehensive characterization of chemical composition of atmospheric aerosols is necessary for the understanding of their impact on the global climate, air quality and human health (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000; Brunekreef and Holgate, 2002). Organic compounds constitute a substantial fraction of atmospheric aerosols (Andreae and Crutzen, 1997; Zhang et al., 2011), however, hundreds of individual organic compounds in different concentrations make a detailed chemical characterization of aerosols difficult (Kubátková et al., 2002; Pietrogrande and Bacco, 2011).

Organic compounds in aerosols originate from various emission sources. They are mixed in various proportions depending on environmental conditions and sources (Medeiros et al., 2006). Several organic compounds, so called molecular markers, were proposed to identify specific emission sources such as biomass burning, coal combustion, traffic emissions etc. (Oros and Simoneit, 2001; Schauer et al., 2002; Simoneit, 2002; Simoneit et al., 2004). Emissions from the biomass burning, in contrast to emissions from most other sources of air pollution, are increasing and, especially in winter, biomass burning makes an important contribution to ambient PM_{2.5} (Sigsgaard et al., 2015). Presently, PM_{2.5} emissions from residential biomass combustion contribute by about 20% to the total emissions in the EU (Jokiniemi et al., 2008). Although combustion of biomass is known to produce a lot of different air pollutants, attention is largely paid to only the determination of PM, PAHs or monosaccharide anhydrides. Other organic compounds identified in the emissions from biomass burning, such as methoxyphenols, resin acids, terpenoids, sterols etc. (Simoneit,

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2002), are probably due to low concentrations mostly outside of interest. However, these compounds, in contrast to PAHs or monosaccharide anhydrides, may give a more detailed view of the origin and kind of wood emissions, so attention must be focused on the wide group of the molecular markers of wood combustion.

In the Czech Republic, only a few studies have dealt with the chemical composition of aerosols in urban environments (Pokorná et al., 2015; Hovorka et al., 2015; Vossler et al., 2016). Moreover, characterization of particulate organic compounds in the Czech Republic concentrates mostly only to PAHs (Dvorská et al., 2012; Topinka et al., 2013; Krůmal et al., 2013) while information about the concentrations of other organic components of aerosols are less frequent (Krůmal et al., 2010, 2013, 2015; Mikuška et al., 2015). Biomass (especially wood) combustion is also in the Czech Republic important source of air pollution, particularly in winter in small villages. Despite this fact, the measurement of aerosol composition focused on detailed characterization of the products of biomass/wood combustion is still rare in the Czech Republic (Krůmal et al., 2010, 2015; Mikuška et al., 2015).

This study reports an evaluation of seasonal variations of selected organic compounds in the PM_{2.5} aerosols collected in the city Brno, the Czech Republic, in five consecutive seasons. It is focused on molecular markers of biomass and wood combustion and saccharides as representatives of organic compounds emitted from both biogenic sources and biomass/wood combustion. Among the markers of biomass/wood combustion, besides frequently analysed monosaccharide anhydrides we also concentrated on the determination of methoxyphenols and in particular the resin acids, which are usually outside the center of attention. In the frame of the study, we also optimized a method for the simultaneous determination of all studied organic compounds in atmospheric aerosols. An extraction of studied compounds in different organic solvents and the application of two reagents for the silylation derivatization process were compared.

2. Materials and methods

2.1. Aerosol sampling

Aerosol particles in the size fraction of PM_{2.5} were collected in a city Brno (Czech Republic) at the balcony on the first floor of the Institute of Analytical Chemistry faced to Veverí Street. The aerosols were collected daily for 24-h during one week in winter (24 February–2 March), spring (10–16 May), summer (24–30 June) and autumn (8–14 October) of 2010 and in winter of 2011 (6–12 January). 7 samples in each season were collected. The aerosols were sampled on quartz fibre filters (150 mm diameter, Whatman QM-A) using a high-volume sampler (DHA-80, Digitel, 30 m³ h⁻¹). To remove possible organic contamination, the quartz filters were burned at 500 °C for 24 h before sampling.

2.2. Sample preparation and extraction

Mass concentrations of PM_{2.5} aerosols were determined by weighing filters, using a microbalance M5P (± 1 µg, Sartorius, Germany). Before weighing, the filters were equilibrated for 48-h in air-conditioned room under constant conditions (temperature 20 ± 1 °C and humidity $50 \pm 3\%$). After weighing, the filters were cut into four parts and each quarter was weighed again.

One quarter of each filter was analysed for the content of selected organic compounds. Before extraction, a recovery standard methyl- β -L-arabinopyranoside was added to filters. The spiked filters were extracted for 30 min with 20 mL of mixture dichloromethane:methanol 1:1 (v/v) under ultrasonic agitation in 40 mL vials. After that, the extraction was two times repeated with new

portion of solvents. Final volume of combined extracts (60 mL) was then reduced by vacuum evaporator to 2 mL. This 2 mL of extract was filtered through the Teflon syringe filters (diameter 13 mm, porosity 0.45 µm) and gently evaporated to dryness under a stream of nitrogen.

2.3. Derivatization

The dried extract was derivatized with 40 µL of derivatization mixture containing MSTFA + 1% TMCS and pyridine (2:1, v/v). To ensure perfect dissolution of organic compounds in filter extracts, another portion of pyridine (100 µL) was added to silylation mixture. Derivatization process was performed under temperature 70 °C for 3 h. After derivatization, the whole mixture was evaporated to dryness under a stream of nitrogen; then 1 mL of hexane was added to redissolve the sample. The prepared sample in hexane was finally analysed by GC-MS.

2.4. GC-MS analysis

Quantification of chosen organic compounds in collected atmospheric aerosols was carried out by GC-MS (Agilent, 7890A, 5975C) with a capillary column (HP5-MS, 320 µm i.d., 30 m length, 1 µm film thickness). 1 µL of sample was injected into a splitless injector (temperature 260 °C). The flow rate of helium was 4 mL min⁻¹. The temperature program started at 120 °C for 2 min, a gradient of 5 °C min⁻¹ was used up to 300 °C and held for 6 min.

The mass spectrometer was operated in the electron ionization (70 eV) with quadrupole as a mass analyzer. First, standards of measured compounds were analysed in full scan mode and then specific masses m/z (191, 194, 196, 204, 217, 239, 256, 297, 305, 319, 327, 361 and 437) were chosen for SIM mode for analysis and quantification of organic compounds in real samples.

The limit of detection (LOD) is defined as three times the standard deviation of blank signal. The LODs of studied compounds measured under optimized conditions were determined from calibration curves. The LODs for saccharides ranged from 0.01 to 0.17 ng m⁻³, for monosaccharide anhydrides ranged from 0.01 to 0.03 ng m⁻³, for methoxyphenols ranged from 0.13 to 1.39 ng m⁻³ and for resin acids ranged from 0.26 to 0.44 ng m⁻³.

2.5. Chemicals

All analytical standards were obtained from Sigma Aldrich (Prague, Czech Republic) in the highest purity available. Silylation mixture containing silylation agents *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide + 1% trimethylchlorosilane (MSTFA + 1% TMCS) and *N*,*O*-bis(trimethylsilyl)trifluoroacetamide + 1% trimethylchlorosilane (BSTFA + 1% TMCS) were purchased from Pierce (Rockford, USA). Silylation reagents were stored in a fridge at 4 °C. Methanol, *n*-hexane and dichloromethane were obtained from Merck (Prague, Czech Republic) and pyridine from Penta (Chrudim, Czech Republic).

3. Results and discussion

3.1. Optimization of analysis of aerosol components

Collected aerosols were analysed for the content of selected organic compounds, namely monosaccharide anhydrides (MAs), resin acids, methoxyphenols and saccharides. There is a lot of papers in literature dealing with the determination of these particulate organic compounds, however, to our knowledge, no paper describes the determination of all above mentioned organic compounds together. Therefore, first we optimized conditions for the

derivatization and extraction of these organic compounds from aerosols collected on filters.

3.1.1. Optimization of derivatization

Derivatization process of studied organic compounds was investigated using standards of analysed compounds (the concentration of $10 \mu\text{g mL}^{-1}$) for two predominantly used derivatization reagents for the silylation of studied organic compounds into trimethylsilyl derivatives, *N,O*-bis-trimethylsilyl)trifluoroacetamide (BSTFA + 1% TMCS) and *N*-methyl-trimethylsilyl)trifluoroacetamide (MSTFA + 1% TMCS), both mixed in ratio 2:1 with pyridine (Zdráhal et al., 2002; Pashynska et al., 2002; Medeiros et al., 2006; Bauer et al., 2008; Jia et al., 2010; Pietrogrande et al., 2014).

First we tested effect of reaction time (1, 2 and 3 h) and temperature (60, 70, 80 and 90°C) for both derivatization reagents. The best results during derivatization of all studied compounds were obtained for reaction time of 180 min and reaction temperature of 70°C for both MSTFA + 1% TMCS and BSTFA + 1% TMCS reagent. Results of the derivatization process of studied compounds using of MSTFA + 1% TMCS and BSTFA + 1% TMCS under optimized conditions are compared in Fig. 1. GC-MS responses of BSTFA are normalized towards the response of MSTFA. It is evident that responses of MSTFA + 1% TMCS derivatives for most studied compounds were higher than corresponding responses of BSTFA + 1% TMCS derivatives with exception of syringic, abietic and dehydroabietic acids that provided higher responses with BSTFA reagent. As a result, MSTFA + 1% TMCS was chosen as a common reagent for the derivatization of all studied particulate organic compounds.

Within these optimization experiments we used $40 \mu\text{L}$ of mixture of silylation reagent (i.e., MSTFA + 1% TMCS) and pyridine (ratio 2:1) for the derivatization, however, during preliminary analyses of real samples we observed wrong reproducibility of derivatization process when RSDs obtained for 6 parts of the same real filter reached up to 30%. We supposed that these problems were caused by bad dissolution of extracted organic compounds in the mixture. To verify this hypothesis, we examined the derivatization for increased volume of the silylation mixture formed by addition of different amounts of another pyridine (i.e., 40 – $1000 \mu\text{L}$) to the mixture with constant amount ($40 \mu\text{L}$) of silylation reagent. We found out that enhanced amount of pyridine provided better

reproducibility of obtained concentrations of studied organic compounds. The best results (RSD smaller than 5%) were found for the addition of $100 \mu\text{L}$ of pyridine. GC-MS response of derivatization process for addition of higher amount of pyridine slightly decreased. The amount $100 \mu\text{L}$ of pyridine was then chosen to mix with $40 \mu\text{L}$ of silylation reagent during the derivatization of analysed compounds in the real samples.

3.1.2. Selection of extraction solvent

In next step we compared the extraction of analysed compounds from collected aerosols employing methanol, dichloromethane and their mixtures 1:1, 1:2 and 2:1 (v/v). These solvents have been mostly used for the extraction of organic compounds from aerosol particles (Pashynska et al., 2002; Medeiros et al., 2006; Wan and Yu, 2007; Jia et al., 2010; Pietrogrande et al., 2015), however, we did not find a solvent that had been used for the simultaneous extraction of all compounds of interest, i.e., monosaccharide anhydrides, resin acids, methoxyphenols and saccharides. For comparison we used 10 filters containing PM_{2.5} aerosols collected in Brno in January 2010. Each filter was cut to ten parts and each part of filter was weighed. The recovery standard methyl- β -L-arabinopyranoside was added on each part of filter. Two opposite parts of filter were then pooled to obtain 5 samples for each filter that were then extracted with methanol, DCM or their mixtures. The extraction process was performed three times with 20 mL of selected solvent for 30 min.

The extraction results (presented as a mean value of 10 filters for each solvent) are compared in Figs. 2 and 3. Extraction efficiency was calculated using the concentration of recovery standard. The concentration of studied organic compounds obtained with the mixture DCM:MeOH 1:1 (v/v) was assigned as 100%. Maltose and syringol are missing in Fig. 2 and in Fig. 3, respectively, because the concentrations of syringol in all samples and the concentrations of maltose in winter samples were below the LOD values. Dichloromethane was found as effective solvent for the extraction of MAS and vanillin, however, for dehydroabietic acid, abietic acid, syringic acid and vanillic acid the extraction efficiency of dichloromethane decreased (Fig. 2) while saccharides were not extracted from the filters using dichloromethane at all (Fig. 3). By contrast, the high polarity of methanol resulted in the extraction of huge amount of different particulate organic compounds, which probably reduced the efficiency of derivatization process of methanol extracts. The extraction efficiencies of tested mixtures of dichloromethane and

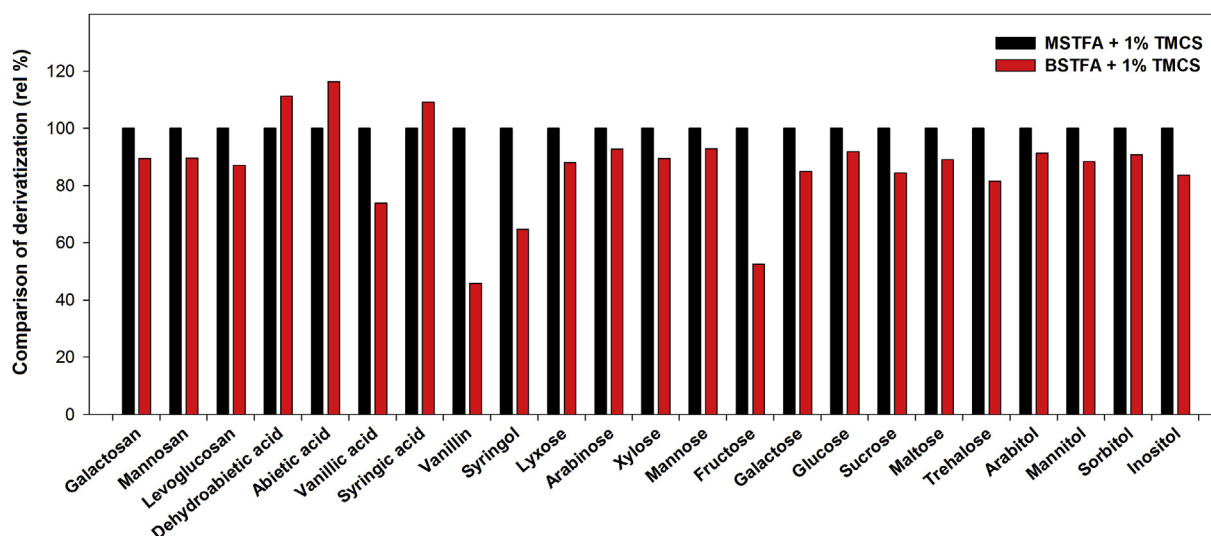


Fig. 1. The comparison of derivatization of studied compounds using of MSTFA and BSTFA in mixture with 1% TMCS.

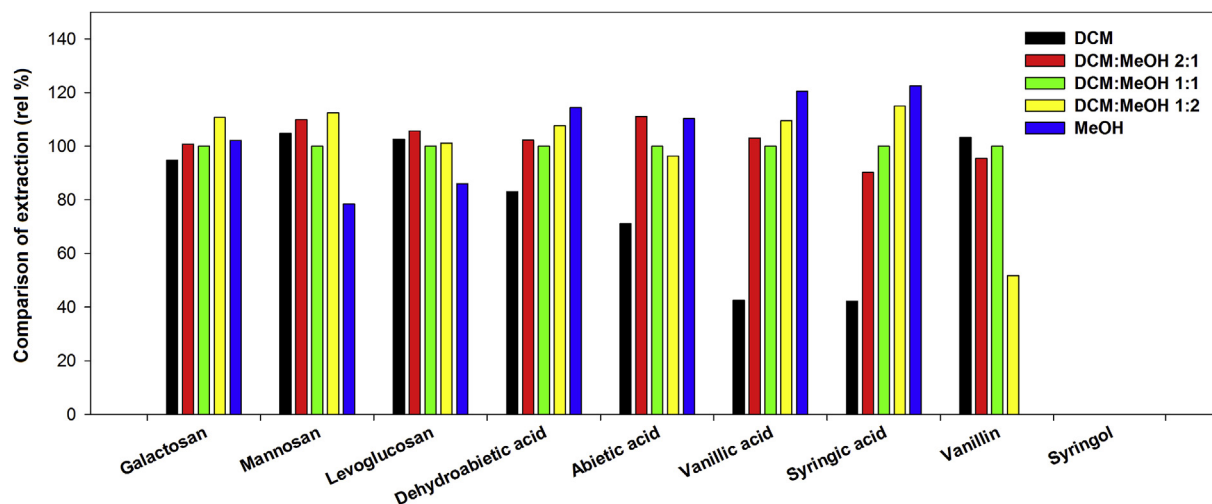


Fig. 2. The comparison of extractions of monosaccharide anhydrides, resin acids and methoxyphenols for methanol (MeOH), dichloromethane (DCM) and their mixtures.

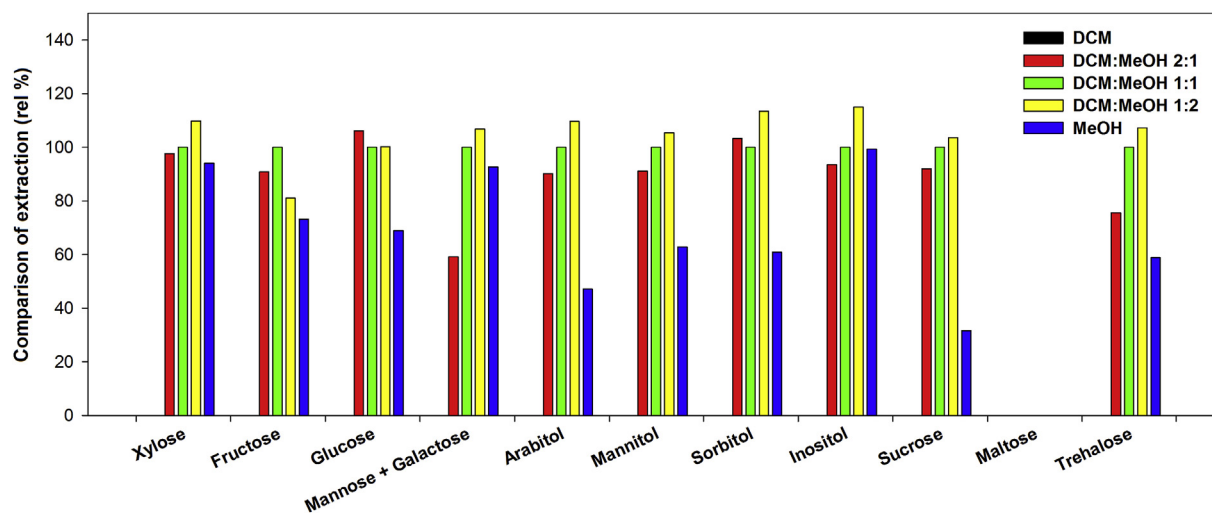


Fig. 3. The comparison of extractions of saccharides for methanol (MeOH), dichloromethane (DCM) and their mixtures.

methanol were mostly similar for all analysed compounds. The only exception is vanillin when we suppose that its high volatility caused its increasing losses from extracts with increasing content of methanol in extraction mixture. During evaporation of solvents under stream of nitrogen, the concentration of vanillin decreased in solvent mixture DCM:MeOH 1:2 while the evaporation of methanol extract led to complete loss of vanillin because of longer time necessary to evaporation of samples to dryness.

As a result of these comparison experiments we excluded DCM (disability of extraction of saccharides) and methanol (deteriorated derivatization process). The concentrations of analysed compounds during the extraction with the mixtures of DCM and methanol were roughly comparable for most compounds, however, the mixture DCM:MeOH 1:2 had problem with evaporation losses of more volatile compounds like vanillin. The reproducibility of the extraction process of studied compounds with the mixture DCM:MeOH 1:1 (v/v) was better than with the mixture DCM:MeOH 2:1 (v/v), therefore, as a compromise, the mixture DCM:MeOH 1:1 (v/v) was chosen as the optimum solvent mixture for the simultaneous extractions of MAS, resin acids, methoxyphenols and saccharides from filters. Recoveries for this mixture varied from 87 to 104%.

3.2. Mass concentrations of aerosols and meteorological conditions

Summary of mean mass concentrations of PM_{2.5} aerosols and their ranges in each season is shown in Table 1. The week mean mass concentration of PM_{2.5} was in the range from 13.9 (spring 2010) to 39.3 $\mu\text{g m}^{-3}$ (autumn 2010). The highest concentrations of PM_{2.5} were found during heating seasons, i.e., in autumn 2010 and in winter 2010 and 2011. By contrast, the concentrations of PM_{2.5} in spring and summer 2010 were much lower. Higher PM_{2.5} concentrations during winter and autumn than in summer and spring were most likely caused both by a combination of high local/regional emissions (increased combustion of biomass in the frame of residential heating) and unfavourable meteorological conditions (low mixing heights).

Temperature showed strong seasonal variation (Table 1) from the colder winter (mean value of 4.2 °C at 2010) through intermediate spring (13.0 °C) to the warmer summer (22.3 °C) and then back to a mild fall (6.9 °C in 2010) and the colder winter in 2011 (1.9 °C). The ambient temperature well correlated with PM_{2.5} concentrations. This dependence is supported by the high correlation between temperature and PM_{2.5} ($R = -0.79$). Rainfall (Table 1) during the campaigns unlike temperature had probably

Table 1Temperature (°C), rainfall (mm), concentrations of PM_{2.5} (μg m⁻³) and analysed organic compounds (ng m⁻³) in PM_{2.5} in each season.

	Winter 2010		Spring 2010		Summer 2010		Autumn 2010		Winter 2011	
	Mean	(Range)	Mean	(Range)	Mean	(Range)	Mean	(Range)	Mean	(Range)
Temperature	4.2	(2.6–5.8)	13.0	(9.2–17.3)	22.3	(19.7–25.9)	6.9	(4.5–8.0)	1.9	(-1.6–3.4)
Rainfall	1.8	(nr–8.7)	1.4	(nr–3.8)	0.0	(nr–nr)	0.0	(nr–nr)	0.7	(nr–2.2)
PM_{2.5}	30.9	(12.1–62.6)	13.9	(9.20–17.3)	16.8	(8.80–24.4)	39.3	(21.8–57.9)	39.2	(21.9–61.0)
Monosaccharide anhydrides										
Galactosan	37.8	(10.3–87.5)	4.18	(2.29–5.68)	3.58	(0.44–6.52)	47.4	(30.8–76.1)	44.4	(23.3–65.7)
Mannosan	99.2	(31.7–297)	12.4	(6.16–17.4)	13.0	(1.70–22.3)	133	(99.3–187)	113	(49.6–208)
Levogluconan	578	(246–1340)	82.7	(39.8–105)	79.3	(22.5–135)	713	(573–920)	806	(290–1118)
Sum	715	(290–1725)	99.3	(48.2–128)	95.9	(24.7–163)	893	(712–1167)	963	(363–1392)
Resin acids										
Dehydroabietic acid	150	(53.3–284)	24.7	(15.2–29.5)	27.7	(13.3–50.5)	154	(107–194)	119	(63.2–213)
Abietic acid	6.47	(4.26–8.23)	3.55	(3.29–3.86)	3.28	(3.12–3.70)	7.41	(5.94–8.97)	5.54	(4.08–7.71)
Sum	156	(57.8–291)	28.3	(18.8–32.9)	31.0	(16.4–54.2)	161	(113–203)	125	(67.3–221)
Methoxyphenols										
Vanillic acid	10.2	(5.08–25.1)	2.71	(nd–3.28)	4.35	(3.17–5.86)	15.2	(10.2–23.0)	12.6	(4.07–18.2)
Syringic acid	5.21	(nd–13.2)	nd	(nd–nd)	nd	(nd–nd)	9.24	(6.67–13.1)	6.38	(nd–9.57)
Vanillin	2.49	(nd–6.67)	nd	(nd–nd)	1.11	(nd–2.82)	9.57	(2.71–18.3)	5.42	(nd–12.5)
Syringol	nd	(nd–nd)	nd	(nd–nd)	nd	(nd–nd)	nd	(nd–nd)	nd	(nd–nd)
Sum	17.9	(7.79–38.3)	2.71	(nd–3.28)	5.46	(3.17–8.68)	34.0	(25.4–47.6)	24.4	(7.40–40.2)
Monosaccharides										
Arabinose	nd	(nd–nd)	nd	(nd–nd)	nd	(nd–nd)	nd	(nd–nd)	nd	(nd–nd)
Lyxose	nd	(nd–nd)	nd	(nd–nd)	nd	(nd–nd)	nd	(nd–nd)	nd	(nd–nd)
Xylose	5.64	(2.44–11.3)	2.28	(1.94–2.66)	2.52	(1.67–3.17)	7.73	(5.11–11.9)	11.4	(4.95–18.5)
Fructose	2.48	(1.72–3.59)	3.92	(1.41–6.73)	10.5	(5.18–17.2)	7.18	(4.58–12.1)	3.06	(1.96–4.08)
Glucose	5.34	(3.55–9.32)	6.31	(2.70–11.4)	11.4	(7.09–16.2)	10.5	(7.66–14.4)	6.54	(4.78–7.91)
Mannose + galactose	2.96	(2.74–3.48)	4.69	(3.11–5.16)	3.02	(2.68–3.18)	6.64	(5.68–7.43)	3.33	(3.02–3.68)
Sum	16.4	(10.6–27.7)	17.2	(13.1–22.9)	27.4	(18.1–39.5)	32.3	(24.4–40.8)	24.3	(14.7–30.4)
Disaccharides										
Sucrose	7.68	(5.38–15.6)	85.4	(5.17–161)	25.0	(6.30–57.5)	10.7	(8.19–13.3)	8.18	(4.03–18.6)
Maltose	nd	(nd–nd)	2.77	(2.57–2.88)	3.16	(2.57–4.95)	3.64	(3.13–5.67)	nd	(nd–nd)
Trehalose	2.47	(1.95–2.72)	3.75	(3.10–4.00)	3.92	(3.23–5.31)	5.20	(4.11–5.94)	2.27	(2.04–2.65)
Sum	10.2	(7.33–18.3)	91.9	(11.0–167)	32.1	(12.5–65.9)	19.5	(15.8–22.6)	10.5	(6.07–20.9)
Sugar alcohols										
Arabitol	2.70	(2.05–4.39)	4.45	(2.28–6.15)	7.71	(3.85–12.3)	7.23	(4.69–13.5)	3.15	(2.38–3.57)
Mannitol	1.66	(1.18–1.99)	4.68	(2.34–5.85)	7.35	(4.63–11.3)	7.09	(4.93–11.7)	1.60	(1.20–2.18)
Sorbitol	1.03	(0.67–1.49)	1.26	(0.88–1.69)	1.40	(0.61–1.76)	4.15	(1.75–9.06)	0.97	(0.67–1.32)
Inositol	2.22	(1.16–3.72)	1.76	(0.94–2.20)	3.87	(2.56–4.85)	4.25	(2.17–8.37)	2.53	(2.08–3.33)
Sum	7.61	(5.04–11.7)	12.2	(6.43–15.7)	20.3	(11.9–30.3)	22.7	(13.4–42.7)	8.25	(6.30–10.5)

nd - not detected, nr - no rain.

only a negligible effect on the PM_{2.5} concentrations. Nevertheless, the lower mean concentration of PM_{2.5} in winter 2010 than that in winter 2011 might be caused next to slightly higher temperature (resulting in lower emissions from residential heating) also by slightly higher rainfall in winter 2010 (Table 1).

3.3. Concentrations of analysed compounds in aerosols

The optimized procedure including extraction and derivatization process was subsequently used for the analysis of monosaccharide anhydrides, resin acids, methoxyphenols and saccharides in urban PM_{2.5} aerosols collected in five seasons (winter, spring, summer and autumn 2010 and winter 2011) in Brno.

3.3.1. Monosaccharide anhydrides

Monosaccharide anhydrides (MAs) such as levoglucosan, mannosan and galactosan have been considered as the candidate tracers for residential wood combustion (Simoneit et al., 1999). Levoglucosan as well as mannosan and galactosan were detected in all aerosol samples. The atmospheric concentrations MAs in collected PM_{2.5} aerosol samples were in the range of 0.44–1340 ng m⁻³, details are shown in Table 1. The concentrations of MAs in autumn and winter were in average 7–13 times higher than those in summer and spring (all for 2010 seasons). The seasonal variations of MAs concentrations (i.e., high concentration in

autumn and winter and small in spring and summer) can be attributed to difference in biomass (mainly wood) burning within residential heating (i.e., increased wood combustion in autumn and winter) and partly to different meteorological conditions in colder and warmer part of year that influence significantly pollutant dispersion (better dispersion in summer due to higher wind speeds, higher temperature and deeper mixing heights). A similar seasonal trend for MAs like in Brno has been observed also in other studies (Pashynska et al., 2002; Poore, 2002; Jia et al., 2010) as well as for levoglucosan at many European background stations (Puxbaum et al., 2007).

Recently, summer degradation of levoglucosan by its reaction with OH radicals was reported (Hoffmann et al., 2010). Therefore, one can suppose that summer decrease in levoglucosan concentration can also be partly caused via this way. However, the comparison of winter and summer concentrations of levoglucosan and retene in PM₁ aerosol sampled in Brno in the same seasons (Krúmal et al., 2015) indicates a negligible decrease in the concentrations of levoglucosan due to its reaction with OH radicals in summer in the Brno area.

Levoglucosan, used as a marker of biomass combustion, was the most abundant monosaccharide anhydride during all seasons while galactosan occurred in the lowest concentrations from the group of MAs in all seasons. Moreover, levoglucosan with exception of spring in all other seasons was dominant organic compound between all organic compounds analysed in this study.

Relative average contribution of levoglucosan, mannosan and galactosan to the total amount of MAs in sampled PM_{2.5} aerosols was relatively constant within all seasons ranging from 79.8 to 83.7% for levoglucosan, from 11.7 to 14.9% for mannosan and from 3.7 to 5.3% for galactosan. The small seasonal differences in the ratios of levoglucosan, mannosan and galactosan indicate a stable ratio in amount of hardwood and softwood burned during individual seasons.

Levoglucosan together with mannosan and galactosan comprised an important part of PM_{2.5} aerosol mass (Table 2). In winter 2010, autumn 2010 and winter 2011, the sum of levoglucosan, mannosan and galactosan formed in average 2.32%, 2.27% and 2.46% of PM_{2.5} mass, respectively, indicating wood burning as the important contributor to composition of urban PM_{2.5} aerosols in Brno during winter and autumn seasons. In spring 2010 and summer 2010, the average contribution of the sum of MAs to the total mass of PM_{2.5} decreased to 0.71% and 0.57%, respectively. The difference in MAs contribution to PM_{2.5} mass points larger effect of wood combustion on chemical composition of atmospheric aerosols in winter and autumn than in spring and summer. The obtained values are similar to values found for PM_{2.5} aerosol in our previous study from Brno (Krůmal et al., 2010).

The concentrations of levoglucosan and other MAs found in this study in winter periods are comparable to the reported values at many other sites in Europe (Table 3) for PM_{2.5} or PM₁₀ such as Augsburg in Germany (Pietrogrande et al., 2011), Bologna and San Pietro in Italy (Pietrogrande et al., 2014), Oporto in Portugal (Alves et al., 2014), Gent in Belgium (Zdráhal et al., 2002), Salzburg in Austria (Caseiro et al., 2009), K-Puszt, Hungary (Puxbaum et al., 2007), Elverum in Norway (Yttri et al., 2005), Ostrava in the Czech Republic (Mikuška et al., 2015) or in Tuscany in Italy (Giannoni et al., 2012) but lower than in Dettenhausen in Germany (Bari et al., 2010), Lycksele in Sweden (Hedberg et al., 2006), Aveiro in Portugal (Puxbaum et al., 2007) or in Graz in Austria (Caseiro et al., 2009), but higher than in Coimbra in Portugal (Alves et al., 2014) or in Oslo in Norway (Yttri et al., 2005). The summer concentrations of MAs in Brno were comparable to the summer values observed at other European sites.

3.3.2. Resin acids and methoxyphenols

Both resin acids and methoxyphenols originate from wood combustion serving thus as wood combustion markers (Hawthorne et al., 1989; Oros and Simoneit, 2001; Simoneit, 2002). Methoxyphenols are emitted to the atmosphere by pyrolysis of wood lignine (Hawthorne et al., 1989) while resin acids are emitted to the atmosphere specially from combustion of softwood (Simoneit, 2002). The concentrations of methoxyphenols and resin acids in collected PM_{2.5} aerosol samples are shown in Table 1 except of syringol, which concentration in all samples was below limit of detection. The highest concentrations of both resin acids and methoxyphenols were found in autumn and winter seasons and the smallest in spring and summer. Enhanced concentrations of

these compounds in autumn and winter seasons likewise in the case of MAs correspond to periods with the increased biomass (especially wood) burning within residential heating. Dehydroabietic acid, abietic acid and vanillic acid were found in all aerosol samples whereas syringic acid was absent in all samples from spring and summer 2010 and also in two samples from winter 2010.

Vanillin and vanillic acid, guaiacol derivatives of methoxyphenols, are present in smoke of both soft and hard wood and are used as general markers of wood combustion (Hawthorne et al., 1989; Mikuška et al., 2015) while syringol derivatives of methoxyphenols (i.e., syringic acid and syringol) are present predominantly in smoke of hard wood serving thus as tracers of hardwood combustion (Simoneit, 2002). Resin acids (i.e., abietic and dehydroabietic acids) are used as tracers of softwood combustion (Oros and Simoneit, 2001; Mikuška et al., 2015) because they are emitted only within the combustion of the softwoods.

Dehydroabietic acid is a dominant resin acid occurring in all samples at the highest concentration (Table 1) of all wood combustion markers. The highest concentrations of dehydroabietic acid were observed in winter (the mean concentration of 150 ng m⁻³) and autumn 2010 (154 ng m⁻³), respectively. The mean concentrations of abietic acid were relatively stable during all seasons ranging from 3.3 ng m⁻³ (summer 2010) to 7.4 ng m⁻³ (winter 2011). The highest mean concentration of vanillic acid (15.2 ng m⁻³), vanillin (9.57 ng m⁻³) and syringic acid (9.24 ng m⁻³) were found in autumn 2010. Dehydroabietic acid as a dominant compound of analysed markers of wood combustion contributed the most significantly to the total amount of markers of wood combustion within all seasons (the range between 76.0 and 86.0%) while the contribution of other markers was much smaller: the average contribution of abietic acid was in the range from 3.72 to 11.5%, vanillic acid from 5.88 to 11.9%, syringic acid from 0.00 to 4.73% and vanillin ranged from 0.00 to 4.90%. Seasonal differences in the ratios of individual markers are caused likewise in the case of monosaccharide anhydrides by difference in amount of hardwood and softwood amounts burned during individual seasons (Krůmal et al., 2010) and by different content of their precursors (i.e., lignin and hemicellulose) in burned wood.

The concentrations of individual marker compounds in PM_{2.5} aerosols depend on amount and type of burned wood. Low concentrations of syringic acid (as well as syringol) resulting probably from low amount of burned hard wood indicates thus low influence of hardwood combustion emissions. On the other hand, high concentrations of dehydroabietic acid could be attributed to its two major sources, direct emission from softwood combustion and secondary production by atmospheric oxidation of other resin acids (i.e., abietic acid and its derivatives; Yan et al., 2008). Besides, the contribution from tire wear should also be considered (Rogge et al., 1993), however, the contribution of this source is probably negligible in Brno area. Moreover, high concentrations of dehydroabietic acid as the marker of softwood combustion prove the dominant share of softwood on total content of wood combusted in the frame of residential heating.

Contrary to levoglucosan and monosaccharide anhydrides, wood burning markers such as resin acids and methoxyphenols are subject of interest of a much smaller number of studies. The concentrations of dehydroabietic acid found in this study are in winter and autumn periods much higher than those in other locations such as Ghent in Belgium (i.e., 20 ng m⁻³; Kubátová et al., 2002), Dettenhausen (3.8 ng m⁻³; Bari et al., 2010) or Augsburg (30 ng m⁻³; Pietrogrande et al., 2011) in Germany, Oporto or Coimbra in Portugal (72 and 84 ng m⁻³, respectively; Alves et al., 2014) or in Fresno, California (99 ng m⁻³; Schauer and Cass, 2000), however, they are lower than in Libby, Montana, USA

Table 2

Relative average contributions (%) to PM_{2.5} mass concentrations. Monosaccharide anhydrides (MAs), resin acids (RAs), methoxyphenols (MPs), saccharides (SAs = moSAs + diSAs + POs), monosaccharides (moSAs), disaccharides (diSAs), polyols (POs) and sum (= MAs + RAs + MPs + SAs).

Season	MAs	RAs	MPs	SAs	moSAs	diSAs	POs	Sum
Winter 2010	2.32	0.50	0.06	0.11	0.05	0.03	0.03	2.99
Spring 2010	0.71	0.20	0.02	0.87	0.12	0.66	0.09	1.81
Summer 2010	0.57	0.18	0.03	0.47	0.16	0.19	0.12	1.26
Autumn 2010	2.27	0.41	0.09	0.19	0.08	0.05	0.06	2.96
Winter 2011	2.46	0.32	0.06	0.11	0.06	0.03	0.02	2.95

Table 3Mean concentrations of MAs (ng m^{-3}) in aerosols in winter period in literature.

Location	Levogluconan	Mannosan	Galactosan	Source
Brno ^{a,c}	692	106	41	This study
Augsburg (Germany) ^a	337	—	—	Pietrogrande et al., 2011
Bologna (Italy) ^a	259	64	32	Pietrogrande et al., 2014
San Pietro (Italy) ^a	253	62	32	Pietrogrande et al., 2014
Oporto (Portugal) ^a	456	47	22	Alves et al., 2014
Ghent (Belgium) ^a	477	66	20	Zdráhal et al., 2002
Ostrava (Czech Republic) ^a	613	111	29	Mikuška et al., 2015
K-Pusztá (Hungary) ^a	653	—	—	Puxbaum et al., 2007
Tuscany (Italy) ^a	371	—	—	Giannoni et al., 2012
Salzburg (Austria) ^b	330	69	24	Caseiro et al., 2009
Elverum (Norway) ^b	407	116	2	Yttri et al., 2005
Dettenhausen (Germany) ^b	806	71	25	Bari et al., 2010
Lycksele (Sweden) ^b	897	—	—	Hedberg et al., 2006
Graz (Austria) ^b	860	212	63	Caseiro et al., 2009
Oslo (Norway) ^b	166	41	3	Yttri et al., 2005
Coimbra (Portugal) ^a	138	32	11	Alves et al., 2014

^a PM2.5.^b PM10.^c Average of concentrations in winter 2010 and winter 2011.

(364 ng m^{-3} ; Bergauff et al., 2008). The concentrations of syringic and vanillic acids found in winter in Brno are comparable with those in Portugal ($3.2/5.8$ and $5.1/6.7 \text{ ng m}^{-3}$ in Oporto and Coimbra, respectively; Alves et al., 2014).

3.3.3. Saccharides

Saccharides originate from different biological source types such as microorganisms, plants, fungi and animals (Graham et al., 2003; Simoneit et al., 2004; Medeiros et al., 2006), or from biomass burning (Simoneit, 2002).

The mean concentrations of saccharides as well as range of daily concentrations in collected PM2.5 aerosol samples are shown in Table 1 except of lyxose and arabinose, which concentrations in all samples were below the limit of detection (0.15 and 0.10 ng m^{-3} , respectively). The highest concentration of saccharides was found in spring 2010 (121 ng m^{-3} , expressed as a sum of mean concentrations of all analysed saccharides) while in winter 2010 and 2011 the total concentration of saccharides was about three times smaller than in spring 2010. The concentrations of individual groups of analysed saccharides (i.e., monosaccharides, disaccharides and polyols, also known as sugar-alcohols) varied significantly in different seasons. Disaccharides were the most abundant saccharides in spring and summer 2010 while monosaccharides were dominant group of saccharides in autumn and winter. The highest concentration of polyols (expressed as a sum of mean concentrations of all polyols) was found in autumn 2010 (Fig. 4).

Glucose was the most abundant monosaccharide with maximum concentration in summer and minimum in winter, which corresponds to glucose role in carbon cycling in plant growth (Medeiros et al., 2006) and in production of pollen (Pacini et al., 2006). Analogous seasonal trend was also observed for fructose indicating similar sources of fructose and glucose. Both saccharides are important component of plants and pollen pores (Fu et al., 2012). Glucose is also main structural component of cellobiose that forms repeating basic building unit of cellulose (Rowell, 2005) and glucose as well as other monomeric and dimeric saccharides observed in winter and also in other seasons may be therefore partly formed also during biomass burning (Nolte et al., 2001; Schmidl et al., 2008). Moreover, glucose was recently found in emissions from combustion of lignite (Fabbri et al., 2009), however, ratios of monosaccharide anhydride concentrations excluded lignite combustion as significant winter source of urban aerosols in

Brno. Enhanced concentrations of xylose, a component of hemicellulose (Simoneit, 2002), in autumn and especially in winter samples result from biomass burning in these periods. Mannose and galactose are presented as their sum in the results because they were not completely separated under used experimental conditions. Due to their presence in wood biopolymers (Simoneit, 2002), we suppose that both these monosaccharides are formed mainly during biomass burning. Alternatively, glucose, arabinose and galactose were also found in the atmosphere as uncombusted biomass materials during the burning process (Medeiros et al., 2006). Arabinose is a component of hemicellulose (Simoneit, 2002) while lyxose occurs only rarely in nature, for example, as a component of bacterial glycolipids (Khoo et al., 1996), however, both arabinose and lyxose were not detected in any PM2.5 sample collected within this study.

Sucrose was dominant disaccharide compound in PM2.5 aerosols with maximum concentration in spring reaching up to 161 ng m^{-3} (Table 1). Simultaneously, sucrose was the most abundant saccharide compound measured in this study (Table 1) with relative high concentration throughout all seasons. Except of winter 2011 when dominated xylose, sucrose was predominant saccharide in all other seasons. High concentrations of sucrose in spring can be explained by its important role in developing flower buds (Jia et al., 2010) and, moreover, sucrose is a known component of pollen grain (Pacini et al., 2006; Fu et al., 2012). In spring, the mean concentration of sucrose (i.e., 85.4 ng m^{-3}) was even slightly higher than those of levoglucosan (i.e., 82.7 ng m^{-3}). Chestnut alley along street Veverí in front of Institute and various fruit trees in near park are supposed to be the main sources of sucrose and other “pollen” saccharides found in urban PM2.5 aerosols in spring and summer. Spring dominance of sucrose was also found at Gosan in Korea (Fu et al., 2012) or, alternatively in Ghent in beginning of summer (Pashynska et al., 2002). Both mean and maximum concentration of sucrose observed in this study was about three times higher than those reported for suburban site in Norway (Yttri et al., 2007). Maltose, a microbial degradation product of starch (Medeiros et al., 2006), was observed only in spring, summer and autumn whereas, in winter, the concentrations of maltose were below the detection limit (0.13 ng m^{-3}), which corresponds with growth cycle of plants. Another analysed disaccharide, trehalose (also known as mycose), was found in all PM2.5 samples. Trehalose concentration showed a maximum in autumn 2010 and minimum in winter periods. Trehalose occurs in a large range of organisms,

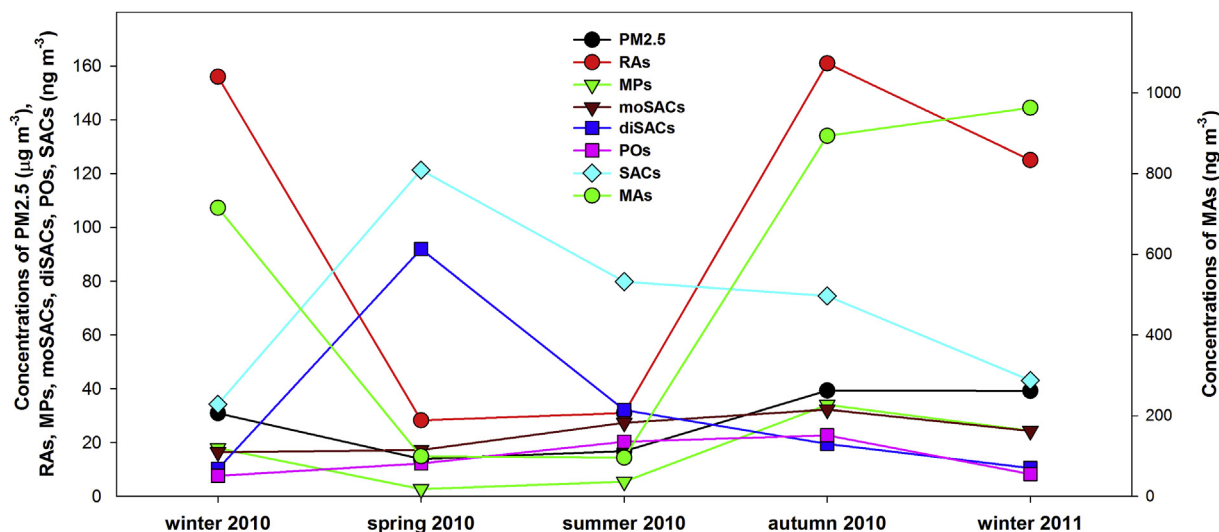


Fig. 4. Seasonal variations of PM_{2.5} ($\mu\text{g m}^{-3}$) and organic compounds (ng m^{-3}). Monosaccharide anhydrides (MAs), resin acids (RAs), methoxyphenols (MPs), saccharides (SAs = moSAs + diSAs + POs), monosaccharides (moSAs), disaccharides (diSAs) and polyols (POs).

such as plants, mushrooms, bacteria, fungi, microorganisms (yeast), insects and invertebrate animals where plays an important role in stress protection and as a storage carbohydrate and transport saccharide (Carvalho et al., 2003; Medeiros et al., 2006; Jia et al., 2010). Several studies have reported trehalose as the most abundant saccharide in soil, which can be used as a tracer for the resuspension of surface soil (Simoneit et al., 2004; Jia et al., 2010; Fu et al., 2012). Seasonal trend of trehalose concentration observed in this study indicates thus soil resuspension as year-long source of saccharides in collected urban aerosols.

Inositol, a constituent of various phosphatidylinositols, originates from plants (Loewus and Murthy, 2000; Wu et al., 2010) and microorganisms (Chhetri et al., 2006), which corresponds to the highest concentrations of inositol found in summer and autumn 2010. Other polyols have different sources. Arabitol, mannitol and sorbitol are metabolic products of various microorganisms such as fungi, lichens and bacteria (Wong et al., 1993; Carvalho et al., 2003; Jia et al., 2010). Mannitol and arabitol, the dominant polyols, were observed throughout all year with the highest concentrations in summer and autumn (Table 1). They are frequently used as fungal biomarkers (Carvalho et al., 2003; Bauer et al., 2008), however, they were reported to have other important sources like biomass burning and sea spray (Wan and Yu, 2007). Moreover, they occur in plants as primary photosynthesis products in mature leaves (Pashynska et al., 2002; Graham et al., 2003; Burshtein et al., 2011). Seasonal trend and the concentrations of arabitol and mannitol were similar (a strong positive correlation, $R = 0.94$). We suppose that observed maximum of mannitol and arabitol in summer and autumn may be attributed not only to fungal spores but also to high levels of vegetation (Burshtein et al., 2011) while in winter and autumn they may originate from biomass burning too. Sorbitol and mannitol were proposed together with trehalose and other saccharides as tracers for soil input into atmospheric particles (Simoneit et al., 2004; Medeiros et al., 2006). These saccharides were present in all aerosol samples collected in Brno, which confirms soil as another source contributing to aerosol composition in all seasons. We suppose that soil originating from several city parklands and grasslands in short distance from sampling site at our institute gets into analysed PM_{2.5} aerosols via the resuspension process.

The concentration of saccharides in fine aerosol fraction is

subject of interest of various studies. The concentration of polyols found within this study in Brno were relatively similar with those from other sites for PM_{2.5} and also for PM₁₀ (arabitol $< 6.6 \text{ ng m}^{-3}$; mannitol $< 10.2 \text{ ng m}^{-3}$; inositol $< 2.5 \text{ ng m}^{-3}$; sorbitol $< 0.6 \text{ ng m}^{-3}$; Medeiros et al., 2006; Yttri et al., 2007; Wan and Yu, 2007; Jia et al., 2010). For Ghent, the concentration of arabitol (i.e., mean winter/summer concentration, 26/105 ng m^{-3}), mannitol (26/97 ng m^{-3}), glucose (73/270 ng m^{-3}) and fructose (37/193 ng m^{-3}) were many times higher than those in Brno while the concentrations of inositol (4.7/40 ng m^{-3}) and sucrose (48/100 ng m^{-3}) were comparable at both urban sites (Pashynska et al., 2002).

3.4. Diagnostic ratios

Levoglucosan is known as a product of cellulose combustion while mannosan and galactosan are produced during hemicellulose combustion (Simoneit, 2002; Schmidl et al., 2008). High concentrations of MAs and wood markers in aerosols collected in this study suggest wood combustion as the main source of these compounds. However, combustion of lignite was recently reported as another important source of levoglucosan and other monosaccharide anhydrides (Fabbri et al., 2009). To identify source of MAs, we used diagnostic ratios levoglucosan/mannosan and levoglucosan/(mannosan + galactosan). Mean results of the ratios, levoglucosan/mannosan of 6.70 (range 4.51–13.2) and levoglucosan/(mannosan + galactosan) of 4.96 (range 3.48–10.5), correspond in all seasons to biomass burning and exclude lignite as a source of MAs, which is in agreement with results of our recent study from Brno area (Krůmal et al., 2015). In addition, these diagnostic ratios may also be used to distinguish the emissions from hardwood and softwood combustion. The results of both ratios obtained within this study confirm predominant share of softwood combustion on a total amount of wood combusted in the frame of residential heating. Another diagnostic ratio was applied to quantify the difference between the burning of hardwood and softwood. The ratio of levoglucosan and mannosan calculated according to equation [% spruce = $(14.8 - \text{ratio}_{\text{lev/man}})/0.112$] (Schmidl et al., 2008) showed the average contribution of spruce combustion (as a representative of softwood) to total wood combustion was in the range of 66.9–83.3% during all seasons. The results of all

diagnostic ratios prove softwood as predominantly burnt kind of wood.

This outcome corresponds well with the results of other studies from the Czech Republic where softwood was found as a predominant type of wood used for residential heating in Brno region (Křmál et al., 2010, 2015) or in Ostrava (Mikuška et al., 2015), while hardwood was employed as fuel wood only to a lesser extent. Moreover, spruce was recently reported as the most commonly burnt wood in the Czech Republic (Dvorská et al., 2011). Softwood was found as prevailing combusted wood also in studies from other locations like Austria (Schmidl et al., 2008), Norway (Yttri et al., 2007), Ghent in Belgium (Pashynska et al., 2002; Zdráhal et al., 2002) or Fresno (Schauer and Cass, 2000) or Libby (Bergauff et al., 2008) in USA. Opposite results were found in Dettenhausen (Germany) where hardwood was identified as prevailing wood burned during residential heating (Bari et al., 2010).

3.5. Seasonal variations and sources of organic compounds

Difference in the concentrations of studied organic compounds in urban PM_{2.5} aerosols in Brno in individual seasons proves seasonal variations of all studied particulate organic compounds. The comparison of total concentrations of all analysed group of particulate organic compounds presented as sum of mean concentrations of their members in different seasons is shown in Fig. 4. It is evident that likewise the concentrations of PM_{2.5} aerosols, the concentrations of all groups of analysed organic compounds varied significantly in different seasons too. The observed concentration trends were similar both for PM_{2.5} aerosols and for MAs or markers of wood combustion (resin acids, methoxyphenols; Fig. 4) while the trend in saccharide concentration changes was different. Moreover, individual saccharide groups showed diverse course throughout the year. Disaccharides were the most abundant saccharides in spring and summer whereas monosaccharides prevailed among saccharides in autumn and winter.

In summer and spring, day-to-day variations in the concentrations of monosaccharide anhydrides, methoxyphenols, resin acids and xylose were very small. On the contrary, in autumn and in both winter seasons we observed large changes in the concentrations of these compounds. We calculated the backward trajectories of air masses to localize potential emission sources during days with high

concentrations of studied compounds to verify hypothesis that the distinct concentrations of these compounds are caused by difference in locations of emission sources arising from different wind direction. Comparison of 1-day backward trajectories (Fig. 5a–c and the concentrations of levoglucosan as pollution indicator) demonstrates that high concentrations of MAs and organic compounds originating from wood combustion correspond especially to south wind bringing to Brno polluted air from region located south of Brno. A portion of houses with wood burning used for heating is very small in Brno (0.33%), but a lot of small villages in proximity or in larger distances from Brno constitute much higher portion of houses with wood burning (up to 5.66%) (CSO, 2011), which implies that high concentrations of MAs in winter aerosol samples in Brno originate predominantly from regional transport of polluted air from villages located south of Brno.

Ambient temperature has major effect on residential heating and, consequently, also affects significantly emissions of PM_{2.5} and particle bound organic compounds. In contrast, due to low rain intensity, effect of rainfall on the concentration of particulate organic compounds was probably negligible. Monosaccharide anhydrides, methoxyphenols and resin acids occurred at the highest concentrations in autumn and winter seasons, which corresponds to increased residential heating in periods when temperature decreases. The dependence between ambient temperature and the concentrations of MAs or markers of wood combustion in collected atmospheric aerosols demonstrates the high value of correlation coefficient between temperature and both MAs ($R = -0.70$) and markers of wood combustion ($R = -0.66$). A strong correlation relation between the concentrations of MAs and markers of wood combustion ($R = 0.88$) indicates wood burning as common emission source of these compounds. The contribution of sum of MAs, methoxyphenols and resin acids to PM_{2.5} mass ranges between 2.8 and 2.9% in autumn and winter seasons while in spring and summer their contribution is much smaller (0.8–0.9%). High contribution of products of wood combustion to PM_{2.5} mass in autumn and winter implies wood combustion as significant emission source in these parts of year, which is in agreement with the fact that wood is important fuel used for residential heating in the Czech Republic. In general, wood is used for heating in 7.6% of households in the Czech Republic but in rural locations, the share increases to 17.6% (CSO, 2013). Our finding corresponds to results of other studies from

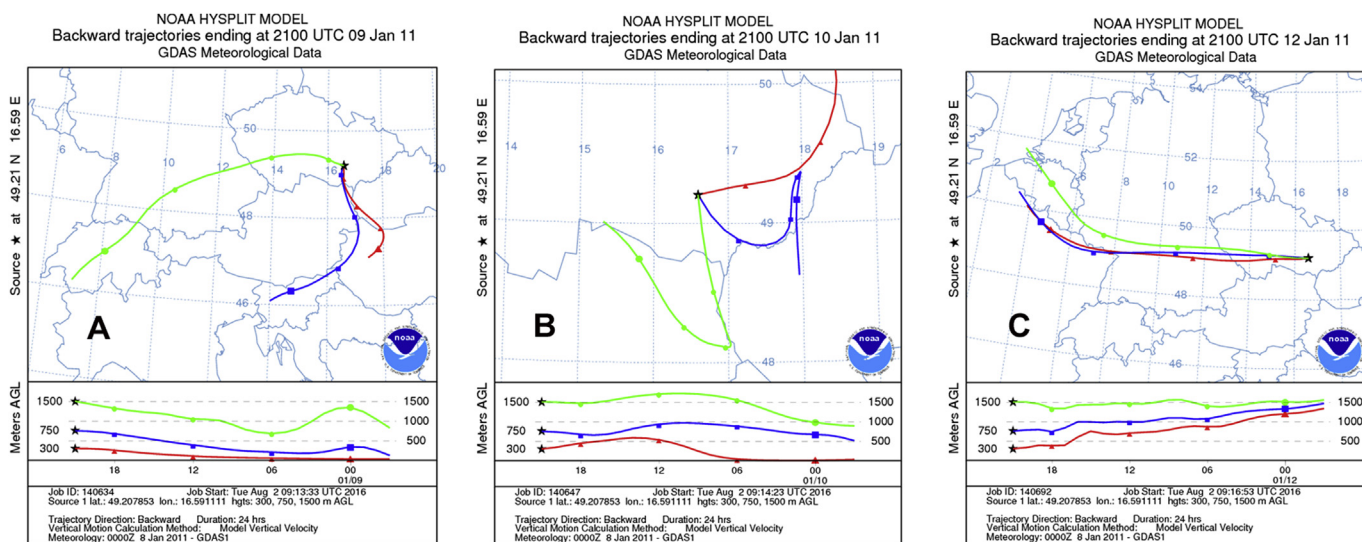


Fig. 5. Comparison of 1-day back-trajectories of regional air transport during winter 2011 and corresponding concentrations of levoglucosan. The concentrations of levoglucosan: A – 1118 ng/m³, B – 491 ng/m³, C – 289 ng/m³.

Central Europe that identified residential wood combustion as an important source of air pollution within winter and autumn (Puxbaum et al., 2007; Schmidl et al., 2008; Caseiro et al., 2009; Pietrogrande et al., 2015).

The methoxyphenol wood combustion markers (i.e., syringic acid and vanillic acid) were highly correlated with each other ($R = 0.96$). Levoglucosan also showed strong correlation with vanillic acid ($R = 0.94$) and with syringic acid ($R = 0.77$). The softwood marker compounds (i.e., dehydroabietic acid and abietic acid) were also highly correlated with each other ($R = 0.87$). Dehydroabietic acid showed also significant correlations with vanillic acid ($R = 0.80$) and levoglucosan ($R = 0.83$). The high values of correlations demonstrate wood burning as the identical emission source of these compounds.

Saccharides are group of compounds that prevail in spring season. Saccharides originate from various sources. Various biological sources such as inflorescence (source of sucrose, glucose, etc.) predominate in spring or summer while other sources such as burning of wood (source of xylose) prevail in autumn and winter. Park near of Institute is full of deciduous (limes, birches, acacias, etc.) and fruity (cherries, apricots, etc.) trees whereas street Veverí in front of Institute is bordered by chestnut alley that in spring during inflorescence is supposed to be source of sucrose and other saccharides. Grass area in the park and area adjacent to chestnut alley could be source of another saccharides (e.g., inositol, trehalose) produced by microorganisms living in grass soil. Soil resuspension hence probably also contributes to composition of PM_{2.5} aerosol. Metabolism of microorganisms is the highest in spring and summer, which corresponds to increased concentrations of saccharides. The contribution of sum of saccharides to PM_{2.5} mass (Table 2) was the highest in spring (0.87%) and summer (0.47%) while in other seasons their contribution decreased (0.11–0.19%).

The studied organic compounds formed especially in autumn and winter seasons considerable part of PM_{2.5} mass (Table 2). The mean contribution of sum of analysed organic compounds ranged from 2.95% to 2.99% in winter 2011 and 2010, respectively, while in summer and spring 2010 their contribution decreases to 1.26% and 1.81%, respectively.

4. Conclusions

The concentrations of urban PM_{2.5} aerosols and studied particulate organic compounds collected in Brno (Czech Republic) during week campaigns in five consecutive seasons in 2010 and 2011 demonstrate strong seasonal variations. The monosaccharide anhydrides, resin acids, methoxyphenols and xylose, that arise from wood combustion in the frame of residential heating, occur primarily in autumn and winter seasons while saccharides originating mainly from various biological sources and soil resuspension occur principally in spring and summer. The high concentrations of studied organic compounds such as monosaccharide anhydrides, resin acids and methoxyphenols in winter aerosol samples support the statement that the biomass burning aerosol was significantly impacted by the softwood burning. The high concentrations of MAS and organic compounds originating from wood combustion in winter aerosol arise largely from regional transport of pollution from villages located south of Brno.

The studied organic compounds contributed considerably to PM_{2.5} mass. The mean relative contribution of sum of analysed organic compounds ranged from 1.26% in summer 2010 to 2.99% in winter 2010, respectively.

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