Atmospheric Pollution Research 8 (2017) 930–939

Contents lists available at ScienceDirect

Atmospheric Pollution Research

journal homepage: http://www.journals.elsevier.com/locate/apr

Characterization of organic compounds in winter PM1 aerosols in a small industrial town

K. Křůmal*, P. Mikuška, Z. Večeřa

Institute of Analytical Chemistry of the Czech Academy of Sciences, v. v. i., Veveří 97, 602 00, Brno, Czech Republic

ARTICLE INFO

Article history:
Received 9 January 2017
Accepted 16 March 2017
Available online 27 March 2017

Keywords:
Monosaccharide anhydrides
Sugars
Resin acids
Polycyclic aromatic hydrocarbons
Toxic equivalent factor
Carcinogenic risk

ABSTRACT

PM1 aerosol, collected during winter campaign in urban area situated close to a large automobile factory, was analysed on content of selected organic compounds, namely monosaccharide anhydrides, diterpenoids (including retene and resin acids), *n*-alkanes (including pristane and phytane), polycyclic aromatic hydrocarbons (including picene), monosaccharides, disaccharides, polyols, hopanes and steranes.

Monosaccharide anhydrides (MAs, markers for biomass burning) were the most abundant organic compounds (the mean sum of concentration of 513 ng m^{-3}). The sum of MAs constituted in average 70.0% of the mass of all analysed organic compounds and 1.91% of the PM1 mass. Diterpenoids, markers for softwood combustion, were the second most abundant analysed organic compounds (the mean concentration of 119 ng m^{-3}). The mean concentrations of other studied organic compounds were smaller, namely saccharides 31.6 ng m^{-3}, *n*-alkanes, including isoprenoids 35.3 ng m^{-3}, PAHs 15.6 ng m^{-3} and hopanes, including one sterane 1.54 ng m^{-3}.

Combustion of solid fuels (coal and wood) for household heating was the dominant emission source of carbonaceous aerosols sampled during the campaign. The composition of aerosols collected in the studied locality was affected by local emissions and also by regional transport of polluted air from small villages nearby Mladá Boleslav.

Two unit risks (WHO and CalEPA) were applied for the estimation of carcinogenic risk of PAHs exposure. The computed lifetime cancer risk at the studied locality during the campaign period was 1.93×10^{-4} (WHO unit risk) and 2.43×10^{-6} (CalEPA unit risk) on average. However, the real cancer risk for the lifetime exposure (70 years) is lower at the studied locality because our measurement lasted only 2 weeks in winter when the concentrations of PAHs were higher than in other seasons of the year.

© 2017 Turkish National Committee for Air Pollution Research and Control. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

Many large cities around the world have problems with smog formation and worse air quality, which is a result of high concentrations of atmospheric aerosols. The effects of aerosols on the atmosphere, public health and climate are among the main topics in current environmental research. Aerosols are involved in the formation of clouds and they also affect the abundance and distribution of atmospheric trace gases by chemical reactions and other multiphase processes. Aerosol particles absorb and also scatter terrestrial and solar radiation (Poschl, 2005; and references therein). Moreover, airborne particles play an important role in spreading of biological organisms, pathogens and reproductive materials (viruses, bacteria, spores, pollen etc.), and they can cause or enhance cardiovascular, respiratory, infectious and allergic diseases (Poschl, 2005; and references therein).

The effects of atmospheric aerosols depend on their chemical composition and particle size. Numbers of epidemiological studies demonstrate that fine air particulate matter (i.e., PM2.5, particles smaller than 2.5 μm in diameter) is correlated with severe health effects (Poschl, 2005). The WHO 24-h mean limit for PM2.5 and PM10 is 25 μg m^{-3} and 50 μg m^{-3}, respectively (Kuklinska et al., 2015; WHO, 2005), however, the limit value for PM2.5 should be decreased in the EU to the 20 μg m^{-3} by 2020 (Directive 2008/50/EC, ANNEX XIV). No limit for PM1 particles has been established in the Czech Republic or in the EU.

* Corresponding author.
E-mail address: krumal@iach.cz (K. Křůmal).

Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

http://dx.doi.org/10.1016/j.apr.2017.03.003

1309-1042/© 2017 Turkish National Committee for Air Pollution Research and Control. Production and hosting by Elsevier B.V. All rights reserved.

Aerosols contain enormous amount of both organic and inorganic compounds emitted from various sources (Alves, 2008). A detailed characterization of chemical composition of aerosol particles is required to reveal major aerosol emission sources. Detailed characterization of particulate organic compounds in urban areas has been a subject of a number of studies in Europe, e.g., Barcelona (Spain; van Drooge et al., 2012), Madrid (Spain; Mirante et al., 2013), Ostrava (Czech Republic; Mikuška et al., 2015), Oporto and Coimbra (Portugal; Alves et al., 2014), Augsburg (Germany; Pietrogrande et al., 2011), Bologna (Italy; Pietrogrande et al., 2015), Munich (Germany; Qadir et al., 2013).

The aim of the presented article is to study organic compounds in PM1 aerosols collected in an urban area situated close to a large automobile factory in Central Europe in winter campaign 2013. The studied organic compounds include monosaccharide anhydrides (MAs), diterpenoids, saccharides, hopanes, steranes, aliphatic hydrocarbons, acyclic isoprenoids and polycyclic aromatic hydrocarbons (PAHs). The identification of emission sources of PM1 carbonaceous aerosols in the studied area was performed on the basis of calculated diagnostic ratios of the selected organic markers (i.e., MAs and hopanes), PAHs and *n*-alkanes.

2. Experimental

2.1. Collection of aerosol and details of the sampling site

PM1 aerosols were sampled daily for 24-h over two weeks in winter 2013 (15–28 February) in a football stadium in Mladá Boleslav. The sampling site was located inside a residential district at a distance of about 500 m from a large automobile factory (Fig. 1). The town Mladá Boleslav (over 44 thousand inhabitants and about 64 km northeast of Prague) has been a center of the Czech automobile industry for more than 110 years. The collection of aerosols was carried out by means of a high-volume sampler (DHA-80, Digitel, 30 m^3 h^{-1}) equipped with a PM1 size selective inlet on quartz fibre filters (150 mm diameter, Whatman QM-A). Before sampling, the quartz filters were baked at 500 °C for 24 h. Filters with collected aerosols were then analysed to detect present organic compounds: 3 monosaccharide anhydrides, 3 diterpenoids (including 2 resin acids), 7 monosaccharides, 3 disaccharides, 4 polyols, 4 hopanes, 1 sterane, 27 *n*-alkanes, 2 acyclic isoprenoids, and 16 polycyclic aromatic hydrocarbons.

2.2. Sample preparation

Determination of mass concentration of the collected aerosols and detailed description of the sample preparation (including fractionation and derivatization) can be found in our previous papers (Křůmal et al., 2010, 2013; Mikuška et al., 2015; Mikuška et al., 2017).

In short, exposed filters were cut into pieces and each of them was analysed for the presence of organic compounds. PAHs (including retene and picene), *n*-alkanes, hopanes and cholestane were extracted with mixture of dichloromethane and hexane (v/v 1:1) under ultrasonic agitation, and then the extracts were fractionated by flash chromatography on a column filled with silicagel. Monosaccharide anhydrides, resin acids, monosaccharides, disaccharides and polyols were extracted using a mixture of dichloromethane and methanol (v/v 1:1) under ultrasonic agitation, and then the extracts were derivatized with a silylation mixture containing MSTFA + 1% TMCS and pyridine. Prior to the extraction, recovery standards (deuterated PAHs, ααα(20R)-cholestane-D2 and methyl-β-L-arabinopyranoside) were added to the filters.

The extraction recoveries were determined by evaluating recovery standards spiked to the exposed filters. The mean extraction recovery was 86% for ααα(20R)-cholestane-D2, 89% for methyl-β-L-arabinopyranoside, 78% for phenanthrene-D10, 72% for chrysene-D12, and 76% for perylene-D12.

2.3. GC-MS analysis

Organic compounds were quantified by GC-MS (Agilent, 7890-A, 5975C). The separation was carried out with a capillary column HP5-MS, 1 μm film thickness, 0.32 mm i.d., 30 m length. More details can be found in our previous papers (Křůmal et al., 2010, 2013; Mikuška et al., 2015; Mikuška et al., 2017). Concentrations of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene, and galactose and mannose, are given as a sum because of their poor separation. The limits of detection (LODs, three times the standard deviation of a blank signal) of each analysed organic compound are shown in Table 1.

The identification of all organic compounds and recovery standards was based on the comparison with retention times and mass spectra of analytical standards. All organic compounds were quantified according to calibration curves with 5 concentrations of each standard. Field blank filters were also analysed with the exposed samples, however, the concentrations of all organic compounds in the blank filters were under the LODs (Table 1) due to baking all filters at 500 °C for 24 h.

2.4. Calculation of air trajectories

The analysis of air mass transported towards the sampling site (Mladá Boleslav) was performed using the Hysplit model (Stein et al., 2015; Rolph, 2017), by calculation of 1-day backward trajectories at 300, 750 and 1500 m a.g.l. (see Supplementary file).

3. Results and discussion

All filters with PM1 aerosol collected in Mladá Boleslav in winter season were analysed for the presence of 3 monosaccharide anhydrides, 3 diterpenoids (including 2 resin acids), 7 monosaccharides, 3 disaccharides, 4 polyols, 16 polycyclic aromatic hydrocarbons, 4 hopanes, 1 sterane, 27 *n*-alkanes and 2 acyclic isoprenoids.

For identification and quantification of the aerosol sources, we tried to use various statistical methods (Tauler et al., 2009). However, statistical methods require a large number of samples, therefore, the application of receptor models in this study was not successful. That is why, the identification of emission sources of PM1 carbonaceous aerosols was performed on the basis of diagnostic ratios of the selected organic markers (i.e., MAs and hopanes), PAHs and *n*-alkanes (Mikuška et al., 2015).

3.1. PM1 concentrations

Mass concentrations of the PM1 aerosols were in the range of 11.2–45.2 μg m^{-3} (Table 1) during the whole campaign. Currently, there are no prescribed standard limits for PM1 particles ambient concentrations in the Czech Republic or EU. However, the concentrations of PM1 in Mladá Boleslav exceeded the WHO 24-h mean limit for PM2.5 (25 μg m^{-3}; Kuklinska et al., 2015; WHO, 2005) in half of the days of the winter campaign.

The temporal variation of concentrations of PM1 aerosols during the campaign is shown in Fig. 2. The temperature ranged from −4.5 °C to +4.9 °C, and eastern or northern wind predominated during the campaign. The western wind was observed only during a single day (19 February) when a local minimum in the concentrations of PM1 and a local maximum in the concentrations

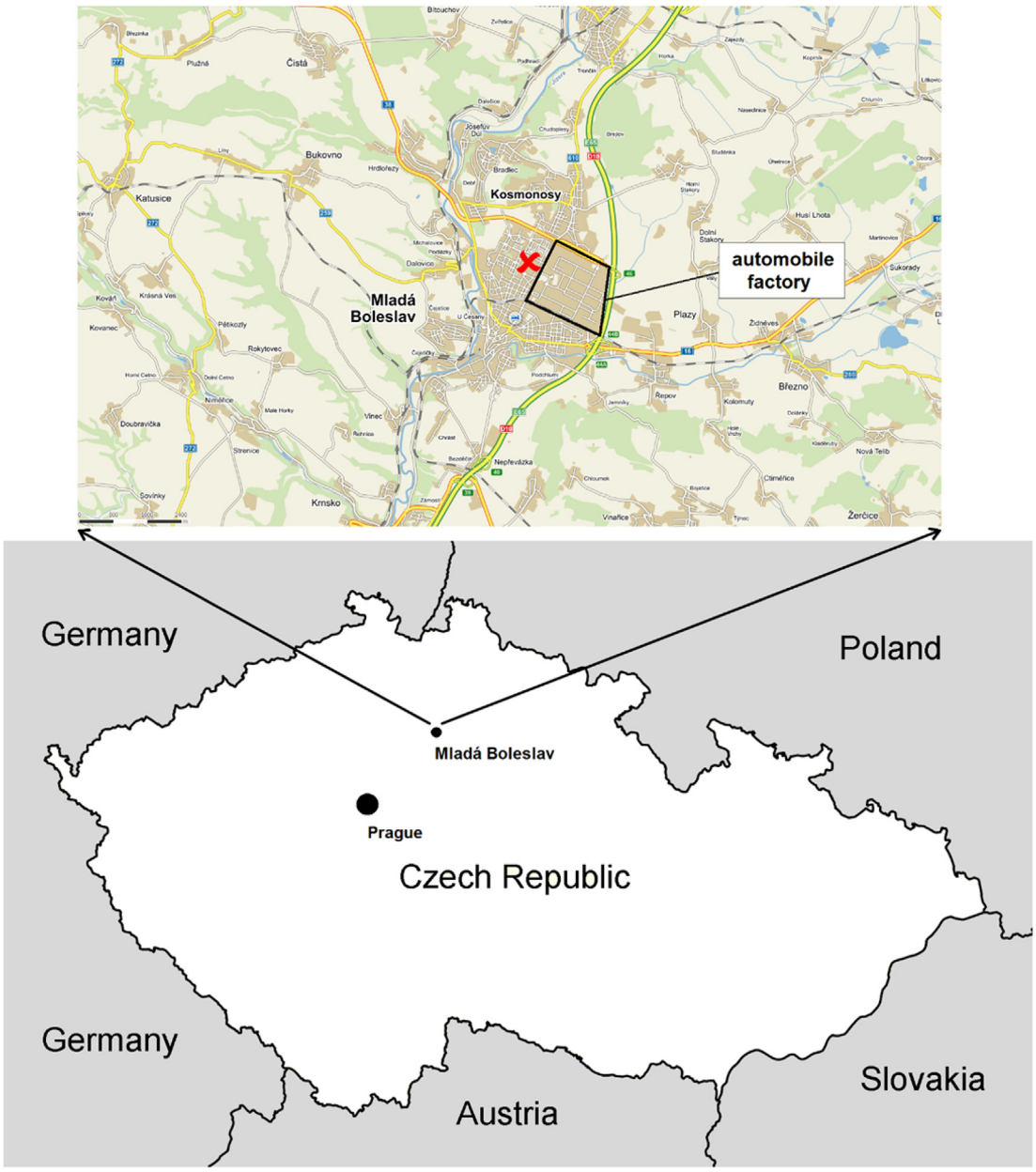


Fig. 1. Location of the sampling site on the map of the Czech Republic.

of sum of analysed organic compounds was identified. 1-Day backward trajectories ending at sampling site during the whole campaign are shown in Supplementary file.

The mean concentrations of PM1 aerosol (26.0 μg m^{-3}) found during the campaign in Mladá Boleslav correspond to winter concentrations of PM1 in other urban areas in Europe, e.g. Zagreb in Croatia (27.3 μg m^{-3}; Godec et al., 2012), Brno in the Czech Republic (19.9–33.4 μg m^{-3}; Křůmal et al., 2013, 2015), urban background in Zurich in Switzerland (17 μg m^{-3}; Minguillón et al., 2012), urban background in Barcelona in Spain under temperature inversion (41–42 μg m^{-3} for night and daytime; van Drooge et al., 2012), urban background in Zabrze in Poland (25.6–33.7 μg m^{-3}; Rogula-Kozłowska et al., 2013).

3.2. Monosaccharide anhydrides

Monosaccharide anhydrides (MAs) are emitted into the atmosphere during biomass burning, thus they are considered to be organic markers for biomass combustion (Simoneit, 2002). Levoglucosan, the most known representative of MAs, is a product of cellulose combustion and is accompanied with other stereoisomeric monosaccharide anhydrides, i.e. mannosan and galactosan, resulting from the pyrolysis of hemicellulose (Křůmal et al., 2015).

The average concentrations and ranges of monosaccharide anhydrides in PM1 aerosol, the most abundant class of analysed organic compounds in all samples, are summarized in Table 1. Levoglucosan was the most abundant MA with the concentrations ranging between 106 and 988 ng m^{-3} in winter season in Mladá Boleslav. The average contribution of levoglucosan was 83% to the total amount of MAs. The concentrations of mannosan and galactosan were considerably lower in all samples and the average contributions to the total concentrations of MAs were 13% (mannosan) and 4% (galactosan). The levoglucosan was highly correlated with mannosan and galactosan with correlation coefficients (R) of 0.98–0.99. The correlation coefficients of other MAs were in the same range, i.e. 0.98–0.99.

Table 1
Concentrations of PM1 (μg m^{-3}) and organic compounds (ng m^{-3}) and limits of detection (LOD) of organic compounds (pg m^{-3}) in Mladá Boleslav in winter 2013.

	Mean	Range	LOD
PM1	26.0	(11.2–45.2)	
Galactosan	20.1	(5.76–47.9)	10.0
Mannosan	69.4	(16.9–177)	26.3
Levoglucosan	423	(106–988)	24.6
Sum of MAs	*513*	*(131–1212)*	
Dehydroabietic acid	114	(27.2–307)	71.3
Abietic acid	2.69	(0.326–8.54)	188
Retene	2.19	(0.864–4.17)	16.2
Sum of diterpenoids	*119*	*(28.4–320)*	
Lyxose	nd	(nd–nd)	142
Arabinose	4.04	(1.30–9.72)	22.2
Xylose	10.8	(3.20–24.7)	31.4
Mannose + Galactose	0.632	(0.150–1.76)	11.5
Fructose	2.10	(0.780–9.11)	39.6
Glucose	5.82	(1.30–13.4)	8.68
Sum of monosaccharides	*23.4*	*(6.99–50.9)*	
Saccharose (Sucrose)	3.66	(1.04–7.17)	32.3
Maltose	1.99	(0.642–5.07)	71.3
Trehalose	0.704	(0.183–1.90)	23.6
Sum of disaccharides	*6.35*	*(2.03–13.9)*	
Arabitol	0.807	(0.155–1.72)	44.6
Mannitol	0.340	(0.031–1.66)	18.6
Sorbitol	0.140	(0.019–0.340)	13.1
Inositol	0.512	(0.184–1.03)	25.5
Sum of polyols	*1.80*	*(0.45–4.42)*	
17α(H),21β(H)-norhopane	0.390	(0.095–0.888)	4.86
17α(H),21β(H)-hopane	0.122	(0.015–0.226)	4.11
22*S*-17α(H),21β(H)-homohopane	0.051	(nd–0.107)	8.59
22*R*-17α(H),21β(H)-homohopane	0.960	(0.153–2.53)	16.3
ααα (20R)-cholestane	0.019	(0.008–0.032)	5.85
Sum of hopanes + cholestane	*1.54*	*(0.271–3.78)*	
$C_{14}H_{30}$	0.282	(0.013–0.515)	6.96
$C_{15}H_{32}$	0.102	(0.028–0.188)	7.44
$C_{16}H_{34}$	0.234	(0.091–0.359)	7.79
$C_{17}H_{36}$	0.120	(0.072–0.205)	8.26
$C_{18}H_{38}$	0.206	(0.159–0.283)	9.17
$C_{19}H_{40}$	0.229	(0.125–0.337)	10.2
$C_{20}H_{42}$	0.614	(0.380–1.06)	10.7
$C_{21}H_{44}$	1.53	(0.624–2.74)	11.5
$C_{22}H_{46}$	3.17	(1.42–6.60)	12.3
$C_{23}H_{48}$	4.24	(1.56–8.96)	13.5
$C_{24}H_{50}$	4.51	(1.50–9.67)	14.9
$C_{25}H_{52}$	4.49	(1.27–9.66)	16.9
$C_{26}H_{54}$	3.68	(0.922–8.27)	19.2
$C_{27}H_{56}$	3.20	(0.793–7.24)	23.8
$C_{28}H_{58}$	2.09	(0.422–5.32)	28.9
$C_{29}H_{60}$	2.11	(0.420–5.27)	34.6
$C_{30}H_{62}$	1.11	(0.290–2.45)	45.1
$C_{31}H_{64}$	1.52	(0.390–3.39)	58.5
$C_{32}H_{66}$	0.583	(0.120–1.26)	73.1
$C_{33}H_{68}$	0.622	(0.172–1.23)	83.9
$C_{34}H_{70}$	0.332	(nd–0.838)	95
$C_{35}H_{72}$	0.222	(nd–0.726)	102
$C_{36}H_{74}$	0.157	(nd–0.411)	115
$C_{37}H_{76}$	nd	(nd–nd)	137
$C_{38}H_{78}$	nd	(nd–nd)	152
$C_{39}H_{80}$	nd	(nd–nd)	173
$C_{40}H_{82}$	nd	(nd–nd)	190
Sum of n-alkanes	*35.3*	*(12.4–74.2)*	
Pristane	0.193	(0.125–0.291)	10.3
Phytane	0.194	(0.144–0.265)	8.89
Fluorene	0.028	(nd–0.059)	2.38
Phenanthrene	0.831	(0.246–1.27)	1.59
Anthracene	0.094	(0.024–0.146)	2.03
Fluoranthene	2.01	(0.510–3.27)	1.85
Pyrene	1.83	(0.508–3.02)	1.72
Benz[*a*]anthracene	4.25	(0.563–12.3)	15.6
Chrysene	2.14	(0.543–4.10)	1.84
Benzo[*b*+*k*]fluoranthene	0.430	(0.056–0.904)	1.25
Benzo[*e*]pyrene	0.737	(0.120–1.31)	8.20
Benzo[*a*]pyrene	0.784	(0.103–1.73)	6.86
Perylene	0.401	(0.121–0.680)	4.06
Indeno[1,2,3-*cd*]pyrene	1.26	(0.206–2.86)	33.0
Dibenz[*a*,*h*]anthracene	0.159	(nd–0.310)	38.7
Picene	0.057	(nd–0.103)	25.7
Benzo[*g*,*h*,*i*]perylene	0.644	(0.117–1.33)	12.3
Sum of PAHs	*15.6*	*(3.30–30.6)*	

The average sum of concentrations of MAs in PM1 in Mladá Boleslav were 513 ng m^{-3} (Table 1), which corresponds to data from other Czech cities in winter (Křůmal et al., 2015), i.e. Brno (273 ng m^{-3} in 2009 and 646 ng m^{-3} in 2010) and Šlapanice (513 ng m^{-3} in 2009 and 547 ng m^{-3} in 2010). The average concentrations were in the same range as those found in European urban and rural areas in PM1 aerosol in winter (e.g. Fontal et al., 2015; Saarikoski et al., 2012; Sánchez-Soberón et al., 2016; van Drooge et al., 2014).

However, recently another source of MAs was reported, when levoglucosan (L), mannosan (M) and galactosan (G) were found among the products of lignite burning. To distinguish biomass and lignite burning as emission sources of MAs, two diagnostic ratios were advised (Fabbri et al., 2009). Values of ratios L/M and L/(M + G) calculated for all aerosol samples from Mladá Boleslav were in the ranges of 5.4–6.8 and 4.1–5.3, respectively, which corresponds to values stated for burning of wood, and were much smaller than those reported for lignite burning (i.e., 31–92 for both ratios; Fabbri et al., 2009). Therefore, we can eliminate lignite burning as a possible source of MAs and we can assume the biomass (especially wood) burning as a prevailing source of MAs in the PM1 samples collected at the sampling site.

The diagnostic ratio of levoglucosan to mannosan concentrations (L/M) was suggested to distinguish between the burning of hardwood and softwood (Schmidl et al., 2008). A range from 14.4 to 14.8 was observed during the combustion of oak and beech (i.e., hardwood) whereas the range of 3.6–3.9 was found during the burning of spruce and larch (i.e., softwood). Average ratio of L/M for PM1 aerosol sampled in the ambient air at Mladá Boleslav in winter season ranged from 5.4 to 6.8. These values indicate that MAs originate predominantly from softwood burning used for residential heating. The contribution of spruce smoke to ambient wood smoke level was estimated by an application of equation [% spruce = (14.8 − L/M)/0.112] (Schmidl et al., 2008). The obtained percent amounts (mean 77%, range of 72–84%) are close to data about supply of fuelwood in 2013 for domestic consumption in the whole of Czech Republic, comprising 58% of softwood and 42% of hardwood (Ministry of Agriculture (2014)).

3.3. Diterpenoids

Diterpenoid components (i.e., resin acids and retene) derive from the steroid skeletons of abietane and pimarane, which are the major constituents produced by conifers, and are used as a biogenic source indicator for conifer resin (Alves, 2008). High concentrations (Table 1) of dehydroabietic acid, the second most abundant compound from analysed organic compounds, suggest that softwood combustion was a big source of the PM1 aerosols during the study period.

Retene is a completely dehydrogenated resin diterpenoid and was proposed as a molecular tracer for coniferous wood combustion (Alves, 2008). Retene is sometimes classified as a polycyclic

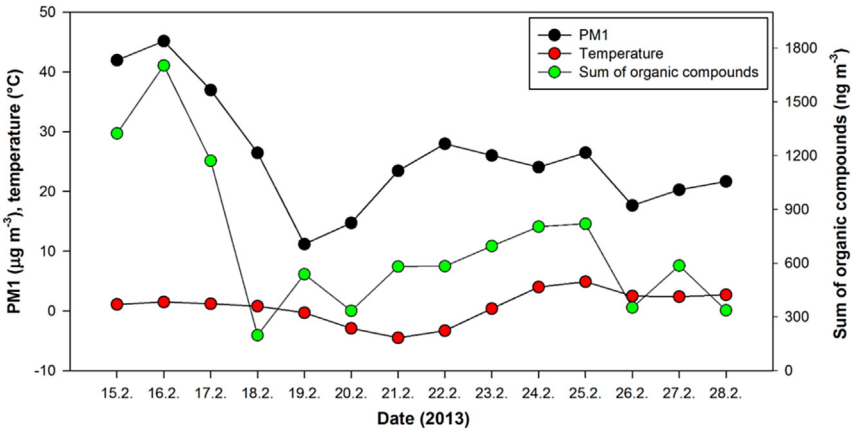


Fig. 2. Temporal variations of temperature (°C) and concentrations of PM1 (μg m^{-3}) and sum of analysed organic compounds (ng m^{-3}) during the campaign in Mladá Boleslav in winter 2013.

aromatic hydrocarbon (PAH) and its concentrations in the samples were higher than the corresponding concentrations of other PAHs (with exception of benz[*a*]anthracene). The mean ratio of concentrations of retene and ΣPAHs in Mladá Boleslav (0.123) was higher than those in other urban areas in the Czech Republic, namely in Brno (0.077 in 2009 and 0.084 in 2010; Křůmal et al., 2013), Šlapanice (0.113 in 2009 and 0.065 in 2010; Křůmal et al., 2013) and Ostrava (0.041 during smog period and 0.064 after smog; Mikuška et al., 2015). This fact demonstrates higher contribution of wood burning to PM composition in Mladá Boleslav than in those cities. Combustion of softwood as an important emission source in Mladá Boleslav is also confirmed by similar daily variations of dehydroabietic acid and retene during the campaign with a correlation coefficient of 0.71.

3.4. Sugars (monosaccharides, disaccharides, polyols)

Saccharides are basic structural units of plant tissues – cellulose (glucose) and hemicellulose (xylose, arabinose, mannose and galactose) and sources of energy for living organisms (Ek et al., 2009). Saccharides are present in biological aerosol particles (e.g. pollens, bacteria, spores, viruses, fungi, algae, protozoa, fragments of plants and animals) (Jia et al., 2010) and can be emitted during combustion of biomass, resuspension of soil particles and wind abrasion of leaf surfaces into the atmosphere (Wan and Yu, 2007). Plants, microorganisms and animals release primary saccharides into the atmosphere (i.e., monosaccharides glucose, fructose and xylose and disaccharides sucrose and trehalose), while saccharidic polyols (or sugar alcohols; arabitol, mannitol and sorbitol) are produced by bacteria, fungi and lichens (Caseiro et al., 2007; Mikuška et al., 2017).

The concentrations of saccharides in the samples were mostly low, only xylose, glucose, arabinose and sucrose were found at enhanced concentrations (Table 1). Xylose, glucose and arabinose can be emitted during biomass combustion (constituents of cellulose or hemicellulose). Significant correlations of levoglucosan (or mannosan) with xylose, R = 0.96 (or 0.97), with glucose, R = 0.84 (or 0.85) and with arabinose, R = 0.87 (or 0.87) indicate biomass (especially wood) burning as a source of saccharides during the campaign. Presence of other saccharides, such as trehalose, inositol, sorbitol or mannitol that are used as tracers for soil input into atmospheric particles (Simoneit et al., 2004) or are metabolic products of various microorganisms (Carvalho et al., 2003), could indicate soil resuspension or soil microorganisms as another source contributing to aerosol composition during the campaign. Nevertheless, the contribution of soil resuspension due to a low concentration of soil tracers and prevailing meteorological conditions during the campaign (low temperatures, higher humidity, thin snow layer) was probably negligible.

3.5. Hopanes and steranes

Hopanes with configuration 17α(H),21β(H) and steranes (only ααα(20R)-cholestane) were the least abundant class among organic compounds analysed in the samples. Their sum ranged between 0.271 and 3.78 ng m^{-3} (Table 1). Both hopanes and steranes are considered to be tracers for traffic emissions (they are present in lubricating oils), while only hopanes are also present in smoke from coal combustion (Alves, 2008).

22*R*-17α(H),21β(H)-Homohopane was the most abundant hopane with the mean concentration of 0.960 ng m^{-3}. The mean sum of concentrations of hopanes and steranes in PM1 during winter in the samples was 1.54 ng m^{-3} (Table 1), which is less than the corresponding concentrations reported from other Czech cities in winter (Křůmal et al., 2013), i.e. Brno (4.74 ng m^{-3} in 2009 and 2.93 ng m^{-3} in 2010) and Šlapanice (5.17 ng m^{-3} in 2009 and 3.10 ng m^{-3} in 2010).

Disproportion between the concentrations of *R*- and *S*- isomer of 17α(H),21β(H)-homohopane points to different emission sources. The similar concentrations of *R* and *S* isomers indicate traffic emissions, while much higher concentrations of *R* isomer than *S* isomer indicate coal combustion (Křůmal et al., 2013). The homohopane index (i.e., the ratio of *R*- and *S*-homohopane, $S/(S+R)$) ranged between 0.012 and 0.074, suggesting combustion of lignite or brown coal to be the main emission source of hopanes. We also identified but not quantified other hopanes in GC-MS chromatograms, i.e. 17β(H),21α(H)-norhopane and 17β(H),21α(H)-hopane, which are emitted mainly from the combustion of moderately mature coal (Oros and Simoneit, 2000).

3.6. n-Alkanes and acyclic isoprenoids

n-Alkanes can be emitted into the atmosphere from many sources; combustion of fossil fuel and biomass, vehicle emissions, and by resuspension of vegetative detritus. The higher molecular weight *n*-alkanes, especially the odd carbon numbered (C_{27}, C_{29} and C_{31}), are related to vegetation detritus, while the lower molecular weight *n*-alkanes ($C_{23}-C_{25}$) are more referred to traffic emissions (van Drooge et al., 2012). The homologous *n*-alkanes ($C_{14}-C_{33}$) were found in all samples (Table 1). Short chain *n*-alkanes ($\leq C_{13}$)

were not quantified because of their high volatility and loss both during sample collection on filters and volatilization during sample preparation (evaporation of samples under a stream of nitrogen). Higher *n*-alkanes ($C_{34} - C_{36}$) were found only in a few samples.

The carbon preference index (CPI) of *n*-alkanes, another diagnostic ratio, is useful for identification of emission sources. High values indicate higher plant contributions (vegetation detritus) and low values correspond to traffic emissions (van Drooge et al., 2012). The CPI value was calculated as the sum of concentrations of the odd carbon numbered *n*-alkanes divided by the sum of concentrations of the even carbon numbered *n*-alkanes: $CPI = \Sigma(C_{15}-C_{31})/\Sigma(C_{14}-C_{32})$. The CPI index of 1.05 on average (0.93–1.11) indicates vehicular exhaust as a specific emission source of *n*-alkanes in Mladá Boleslav.

The most abundant congeners were C_{23}, C_{24} and C_{25} with mean concentrations above 4 ng m^{-3}, suggesting gasoline to be a prevailing vehicle emission source (Mikuška et al., 2015; and references therein). However, the correlation between *n*-alkanes and ααα(20R)-cholestane (marker for traffic) was not strong (R = 0.56), which indicates that traffic was not the predominant source of n-alkanes. Much stronger correlations were found between alkanes and compounds originated from wood or biomass burning and coal combustion, i.e. MAs (R = 0.89), resin acids (R = 0.79), retene (R = 0.79), picene (R = 0.75) and hopanes (R = 0.96), which suggests combustion of wood and coal to be the dominant emission sources of *n*-alkanes in the samples.

Acyclic isoprenoids (i.e., pristane and phytane) were detected in all the samples at an average Pr/Ph ratio of 0.99 (ranging from 0.74 to 1.30). Most biological sources have a Pr/Ph ratio much higher than 1.0 because phytane is rarely found in biological material (except for some bacteria), while low ratios indicate petroleum origin of isoprenoids (Alves et al., 2014; Oliveira et al., 2007). Hence, the value of Pr/Ph ratio indicates traffic to be the main source of isoprenoids in Mladá Boleslav.

3.7. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) represent a class of organic compounds, which is more investigated than any other because some of them are considered to be carcinogenic and/or mutagenic (Alves, 2008). PAHs react with atmospheric oxidants, such as hydroxyl and nitrate radical, ozone, and nitrogen dioxide. The atmospheric reactions of PAHs with oxidants lead to the formation of nitro and oxy (mostly quinones) derivatives. Some PAH derivatives are strong mutagens and carcinogens (Keyte et al., 2013). PAHs are formed during all types of combustion, especially the incomplete combustion. The major anthropogenic emission sources of PAHs in the air include fossil fuel burning power plants, domestic burning (wood and coal), road transport, cooking and others (Keyte et al., 2013).

Sixteen PAHs present in the aerosol samples (including picene) were quantified, their concentrations are given in Table 1. The list of analysed PAHs does not contain low molecular weight PAHs because they are very volatile and their losses during sample preparation were significant. The concentrations of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene are summarized in Table 1 due to their poor separation on the GC column. The most abundant PAHs present in the samples were fluoranthene, pyrene, retene, benzo[*a*]anthracene, chrysene and indeno[1,2,3-*cd*]pyrene. The mean sum of total PAH concentrations in PM1 was 15.6 ng m^{-3} (Table 1), which is lower than the concentrations found in other Czech cities in winter (Křůmal et al., 2013), i.e. Brno (22.2 ng m^{-3} in 2009 and 39.8 ng m^{-3} in 2010) and Šlapanice (21.0 ng m^{-3} in 2009 and 38.7 ng m^{-3} in 2010).

Some individual PAHs or groups of PAHs are used as source markers, e.g. retene (correlation with resin acids, R = 0.70) as a tracer for combustion of conifers or picene (correlation with hopanes, R = 0.81) as a marker for coal combustion (Alves, 2008). Lighter PAHs, phenanthrene, fluoranthene and pyrene, are prevailing in emissions from combustion of conifers, angiosperm and graminenae (Simoneit, 2002).

Many researchers have used specific values of PAH diagnostic ratios for a source identification (e.g. Alves, 2008; Ravindra et al., 2008; Yadav et al., 2013). However, it is often difficult to distinguish emission sources with them (Ravindra et al., 2008) because many ratios often overlap for different sources (Dvorská et al., 2011). In addition, the diagnostic PAH ratios can be affected by PAHs degradation in atmosphere in the presence of air oxidants as well as by the PAHs decomposition due to reaction of air oxidants during the aerosol sampling on filters (Ravindra et al., 2008; Tsapakis and Stephanou, 2003). In this study, the diagnostic ratios of PAHs point to combustion as a dominant source of PAHs, but distinguishing the exact type of organic material, which was combusted, is very difficult. The values for ratio of indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene + benzo[*g,h,i*]perylene) show to wood burning (0.658) and ratio of benzo[*a*]pyrene/benzo[*g,h,i*]perylene to combustion of brown coal (1.243). The diagnostic ratios for identification of emissions from traffic are inconclusive.

Benzo[*a*]pyrene is often used as a marker for the carcinogenicity of PAHs in the environment (Ravindra et al., 2008), but it is strongly reactive in atmosphere (Alves, 2008). Concentrations of benzo[*a*]pyrene in this investigation exceeded the recommended concentration limit (1 ng m^{-3}) for the Czech Republic and EU in five samples. Fresh exhausts have usually similar contents of benzo[*a*]pyrene (B*a*P) and benzo[*e*]pyrene (B*e*P), however B*a*P is less stable in the air than B*e*P, so the increasing ratio of B*e*P/(B*e*P + B*a*P) can be considered as an index of the aging of particles (Alves, 2008). The values of the B*e*P/(B*e*P + B*a*P) ratio were a bit less than 0.5 during sampling (15–28 February) in the samples, which indicates fresh emissions of particles from local or nearby regional emission source.

To hypothesize the suspected sources of PAHs detected in PM1 samples and to determine relationships between the concentrations of PAHs and organic markers, relevant correlations were calculated. A strong correlation of the concentrations of PAHs with the concentrations of MAs (R = 0.86), monosaccharides (R = 0.81), resin acids (R = 0.75) and retene (R = 0.81) shows that emissions of PAHs arise from wood combustion. In addition, a strong correlation with hopanes (R = 0.95) and picene (R = 0.83) indicates that emissions also arise from coal combustion. Traffic is supposed to be a less important source of PAHs, as indicated by a lower correlation of concentrations of PAHs with the concentrations of ααα(20R)-cholestane (marker for traffic, R = 0.61). To summarize, PAHs were emitted mainly from combustion of wood and coal.

3.8. Toxicity and carcinogenic risk assessment of PAHs

Because of the potential carcinogenic and mutagenic properties of PAHs, health effects have been widely studied. The carcinogenic properties increase with the number of aromatic rings of PAHs. Benzo[*a*]pyrene has been the most extensively studied PAH (Ramírez et al., 2011). Benzo[*a*]pyrene is classified as the agent carcinogenic to humans (Group 1) according to IARC (International Agency for Research on Cancer). Dibenz[*a,h*]anthracene is classified as the agent probably carcinogenic to humans (Group 2A). Other 5 investigated PAHs, namely benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and indeno[1,2,3-*cd*]pyrene, are classified as agents possibly carcinogenic to humans (Group 2B) (IARC, 2015; Lerda, 2011; Ramírez et al., 2011). While the US Environmental Protection Agency (US EPA) considers all 7 PAHs as

probable human carcinogens (ATSDR, 2009). Moreover, chemical reactions in atmosphere between PAHs and nitrogen oxides can produce nitro-PAHs that are considered to be 100,000 times more mutagenic and 10 times more carcinogenic (Schneider et al., 2016).

The mean concentrations of 7 carcinogenic PAHs (cPAHs) in PM1 during the winter campaign in Mladá Boleslav was 9.02 ng m^{-3} (1.47–22.2), which suggests that 47.5% (34.6–63.8) of total analysed PAHs had carcinogenic potential. The day-to-day trend of concentrations of cPAHs and total PAHs during the campaign was very similar (Fig. 3) with a strong correlation (R = 0.98). Thus, the main emission sources of cPAHs were the same as for other analysed PAHs (i.e., combustion of wood and coal).

To evaluate health risk of PAHs to humans, the benzo[*a*]pyrene equivalent concentration (B*a*P-eq) was introduced instead of the sole benzo[*a*]pyrene. The B*a*P-eq is an index that expresses the health risk related to the exposure of ambient carcinogenic PAHs to humans. The index is calculated by multiplication of each individual PAH concentration by its corresponding toxic equivalent factor (TEF) for cancer potency relative to B*a*P (Alves et al., 2014; Bian et al., 2016). The inhalation cancer risk for the PAHs was calculated by multiplication of the sum of the individual B*a*P-eq concentrations by the unit risk (UR) of exposure to B*a*P (UR_{BaP}). The UR_{BaP} is the estimated theoretical upper limit of possibility of causing cancer when humans are exposed to B*a*P at a concentrations of 1 μg m^{-3} for a 70-year lifetime (Jia et al., 2011). The World Health Organization (WHO) calculated UR_{BaP} at 8.7 × 10^{-5} (ng m^{-3})$^{-1}$ based on an epidemiology study on coke-oven workers (WHO, 2000; Jia et al., 2011), whereas the California Environmental Protection Agency (CalEPA) estimated a UR_{BaP} at 1.1 × 10^{-6} (ng m^{-3})$^{-1}$ according to the data of inhalation exposure of hamsters (OEHHA, 2005; Jia et al., 2011). The WHO proposed UR_{BaP} for lifetime (70 years) means that 8.7 per 100,000 people with chronic inhalational exposure to 1 ng m^{-3} B*a*P may develop a lung cancer (Bian et al., 2016; Ramírez et al., 2011). In this study, both UR_{BaP} values were used to calculate excess PAH-induced inhalation cancer risk. The equation for lifetime lung cancer risk is as follows:

$$CancerRisk = UR_{BaP} \times BaP_{eq} = UR_{BaP} \times \sum_{i} (c_{PAH_i} \times TEF_i)$$

TEF estimates from the literature (Nisbet and LaGoy, 1992) were used in this study. The average of calculated B*a*P-eq was 2.21 ng m^{-3} (0.194–4.94). Applying the suggested unit risk of 8.7 × 10^{-5} (ng m^{-3})$^{-1}$ for lifetime (70 years) PAH exposure, the corresponding lifetime lung cancer risk is 1.93 × 10^{-4} on average (range of 1.69 × 10^{-5} – 4.30 × 10^{-4}). Thus, if 1,000,000 people are exposed to 2.21 ng m^{-3} of ambient (B*a*P-eq)Σ16PAH for 70 years, then lung cancer may develop in 193 people. However, if the CalEPA unit risk is used, the calculated lifetime lung cancer risk is much lower (2.43 × 10^{-6}). If other toxic equivalent factors found in literature (i.e., Bian et al., 2016; Jia et al., 2011; Ramírez et al., 2011; Sánchez-Soberón et al., 2016) were applied, the computed lifetime lung cancer risks for WHO unit risk were lower (i.e., 1.37 × 10^{-4}; Bian et al., 2016; Sánchez-Soberón et al., 2016), almost twice lower (i.e., 1.14 × 10^{-4}; Ramírez et al., 2011) or almost twice higher (i.e., 3.51 × 10^{-4}; Jia et al., 2011). The lower level was influenced by lower TEF values of some carcinogenic PAHs (especially for dibenz[*a,h*]anthracene, TEF = 1) and the higher level was affected by higher RPF (relative potency factor, instead of TEF) values for some carcinogenic PAHs, especially for dibenz[*a,h*]anthracene (RPF = 10). The real lifetime lung cancer risk values are probably a little higher because we analysed PAHs only in PM1 aerosol fraction. On the other hand, PM1 aerosol is more dangerous than PM10 aerosol, because it can penetrate more deeply into lung. The WHO unit risk and TEFs from Nisbet and LaGoy (1992) for calculation of lifetime lung cancer risk were also applied for data from our previous studies in the Czech Republic. The computed risks (winter/summer values) in the city of Brno (4.67–7.60 × 10^{-4}/0.39–2.76 × 10^{-4}) and a small town of Šlapanice (5.18–8.06 × 10^{-4}/0.31–2.68 × 10^{-4}) (Křůmal et al., 2013) were a little higher for winter period and a little lower or comparable for summer period than those in Mladá Boleslav. However, the computed risks in the industrial city of Ostrava in winter were more than 10 times higher; i.e. 8.92 × 10^{-3} on an average in smog episode and 2.34 × 10^{-3} after smog episode

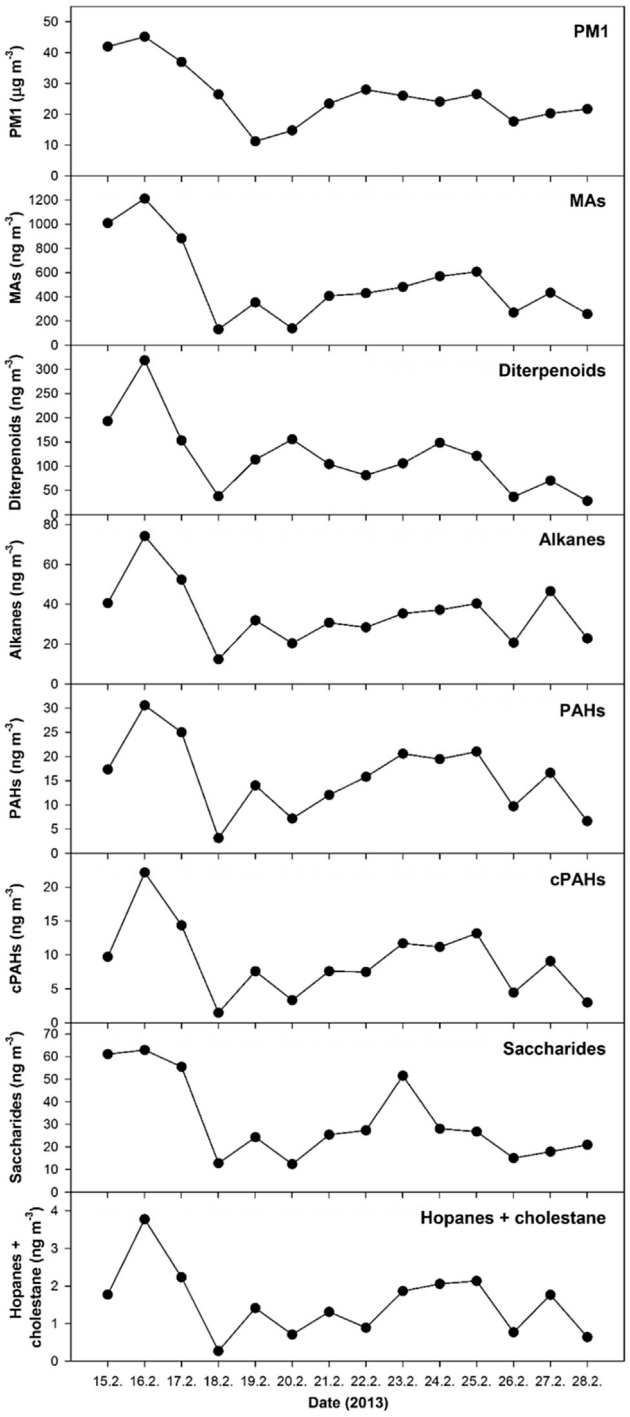


Fig. 3. Temporal variations of concentrations of PM1, saccharides, MAs, diterpenoids, *n*-alkanes, hopanes + steranes, PAHs and 7 carcinogenic PAHs during the campaign in Mladá Boleslav in winter 2013.

(Mikuška et al., 2015).

It is also important to note that the response among various subpopulations to the carcinogenic potential of PAHs is not uniform. The different response can be the result of genetic factors (susceptibility of individuals to tumor development) or other factors, such as smoking. Occupation can be another important factor for an individual cancer risk due to PAHs exposure (Jia et al., 2011). Finally, the inhalation cancer risk models assume a lifetime exposure, whereas our measurement was realized for a relatively short duration (only two weeks in winter) when the combustion of solid fuels for household heating is a dominant emission source of air pollution. The concentrations of PAHs and carcinogenic PAHs are mostly smaller in other seasons, therefore the overall cancer risk for the whole year will also be smaller. We estimated the inhalation cancer risk of PAHs in the studied locality for the entire year, using PM10 data of the Czech Hydrometeorological Institute (CHMI). The CHMI measures PM10 in Mladá Boleslav throughout the year. The average of PM10 concentrations related to the studied period (15–28 February) was 41.2 μg m^{-3}, while the annual mean (2013) of PM10 concentrations was 25.7 μg m^{-3} (CHMI, 2013). The ratio between the annual mean PM10 concentrations in the whole of 2013 and the concentrations of PM10 within the studied period was 0.624. If we suppose the similar ratios also for the concentrations of PM1 and PAHs, the recalculated lifetime lung cancer risk for PAHs in PM1 in Mladá Boleslav for the entire 2013 was estimated to be 1.21×10^{-4} (WHO unit risk) and 1.52×10^{-6} (CalEPA unit risk) on average.

3.9. Localization of emission sources

We applied the alternative way for the identification of emission sources (i.e., diagnostic ratios and content of selected organic markers in the collected samples) because the total amount of 14 samples collected during the winter campaign in Mladá Boleslav is too small for a successful application of multivariate receptor models (PCA, PMF) (Viana et al., 2008).

Temporal day-to-day variations of sum of analysed organic compounds given in Fig. 2 show a similar trend with PM1 aerosols for most days of the campaign (correlation coefficient $R = 0.85$). Majority of the analysed organic compounds highly correlated with the PM1 mass. Opposite trend was found only on 19 and 27 February. Similar temporal trend with the concentrations of PM1 over most days of the campaign can also be observed for all analysed classes of organic compounds (Fig. 3). However, on 19 and 27 February 2013, MAs, alkanes, hopanes (including cholestane) and PAHs provide different course when these organic compounds show a one-day increase, while PM1 decreases in comparison with the previous day. On 19 February, there was a local maximum for all organic compounds (with the exception of resin acids) and a local minimum for concentration of PM1. The concentrations of all organic compounds were, on that day, at least twice higher than the day before. 19 February was the only day when the western wind blew and brought the regional pollution from a few fossil fuel (brown coal) based power plants situated west of Mladá Boleslav (at a distance of 85 km approximately). On 23, 24 and 25 February, the wind blew from south-east direction and brought the air pollution from the automobile factory (see the backward trajectories in Supplementary file). The concentrations of PAHs, MAs, alkanes and hopanes slightly increased. A heating plant, located inside the automobile factory, is equipped with 5 boilers for the combustion of brown and black coal with an addition of biomass. The heating plant supplies heat also to about 12 thousand of flats in the neighbouring housing estate, which represents approximately two thirds of a total number of households in Mladá Boleslav. Within 27 February, there was the second local maximum for all organic compounds (without saccharides). However, the wind direction (north-east) on that day was the same as the day before (see the backward trajectories in Supplementary file). We assume that the increase of concentrations of organic compounds (especially *n*-alkanes, PAHs and hopanes) was caused by an accidental emission from unidentified local source (probably combustion of coal). The concentrations of all organic compounds (with the exception of saccharides) decreased on 28 February, while the concentrations of PM1 and saccharides slightly increased. The wind direction changed to south-east and east on that day and brought the air pollution from both automobile factory and the older part of Mladá Boleslav, where a big portion of houses still use combustion of wood or coal for household heating. It was impossible to distinguish emissions from factory and residential heating.

According to data of the Czech Statistical Office (CSO) from the last census in 2011, only 1.44% of households with own boiler in the town of Mladá Boleslav used solid fuels (coal or wood) for household heating (CSO, 2011). Houses in Mladá Boleslav, that utilize combustion of wood or coal, are located mainly in the older part of the town, representing thus local emission sources. However, plenty of small villages around Mladá Boleslav (the district of Mladá Boleslav) increase the portion of houses (own boiler) with wood/coal combustion to 22.2% (CSO, 2011). Thus, the composition of PM1 aerosols sampled in Mladá Boleslav was probably affected by local emission sources and also by regional transport of polluted air from villages both nearby Mladá Boleslav and at larger distances from Mladá Boleslav (see the backward trajectories in Supplementary file).

3.10. Relative contribution of compounds to PM1

The mean total concentrations of monosaccharide anhydrides, diterpenoids (including retene and resin acids), *n*-alkanes (including pristane and phytane), PAHs (including picene), monosaccharides, disaccharides, polyols, hopanes and ααα(20R)-cholestane, as well as the mean contribution of individual groups to the total amount of analysed organic compounds and to PM1 mass during the campaign in Mladá Boleslav, are shown in Table 2. The analysed organic compounds formed in average 2.76% of PM1 mass. It is evident that monosaccharide anhydrides (MAs, markers for biomass burning) formed the biggest portion of all analysed organic compounds in the aerosol samples. The sum of MAs constituted 70.0% of the mass of all analysed organic compounds and 1.91% of the PM1 mass. Diterpenoids, markers for softwood combustion, were the second most abundant analysed organic compounds (0.48% in PM1). The contribution of MAs and diterpenoids to PM in Mladá Boleslav was, thus, about twice higher than corresponding contributions in another Czech city, Ostrava, i.e. 1.18% and 0.18%; Mikuška et al., 2015). Conversely, the contribution of PAHs, the group of analysed organic compounds with probably the most toxic properties, was only 0.07% in Mladá Boleslav, which is less than in other Czech cities, i.e., 0.69% in Ostrava (Mikuška et al., 2015) and 0.11–0.12% in Brno and Šlapanice (Křůmal et al., 2013, 2015). The contribution of hopanes (markers for coal combustion) to PM in Mladá Boleslav was also smaller than in those Czech cities. Thus, the contribution of biomass burning (especially wood burning) seems to be a more dominant emission source in Mladá Boleslav than in other monitored Czech cities. Moreover, the combustion of solid fuels (coal and wood) for household heating was the dominant emission source of aerosols sampled during the campaign in Mladá Boleslav in winter 2013. The same result was obtained in other paper dealing with the identification of emission sources of fine aerosols in Mladá Boleslav during the same campaign in winter 2013, namely wood burning and coal combustion (Hovorka et al., 2015).

Table 2
The mean total concentrations of analysed organic compounds (ng m^{-3}) and the mean contribution of individual groups to the total amount of analysed organic compounds and PM1 during the campaign in Mladá Boleslav.

Compounds	Mean sum of concentrations (ng m^{-3})	Contribution to the sum of analysed organic compounds (%)	Contribution to PM1 mass (%)
Monosaccharide anhydrides	513	70.0	1.91
Diterpenoids (resin acids and retene)	119	17.4	0.478
n-Alkanes (+pristane and phytane)	35.3	5.48	0.145
Polycyclic aromatic hydrocarbons (+picene)	15.6	2.28	0.063
7 carcinogenic polycyclic aromatic hydrocarbons	9.02	1.24	0.035
Monosaccharides	23.4	3.30	0.089
Disaccharides	6.35	1.05	0.024
Polyols	1.80	0.25	0.007
Hopanes + cholestane	1.54	0.22	0.006

4. Conclusion

Atmospheric aerosols in the size fraction PM1 were sampled in winter 2013 in Mladá Boleslav at a site located in an urban district situated approximately 500 m from a large automobile factory.

Mass concentrations of the PM1 aerosols were in the range of 11.2–45.2 μg m^{-3} during the campaign and exceeded the WHO 24-h limit for PM2.5 in half of the days of the winter campaign. The mass concentration of PM1 highly correlated with the sum of analysed organic compounds, especially with the compounds originating from combustion of wood/biomass and coal. Monosaccharide anhydrides were the most abundant group of analysed organic compounds in all samples, followed by diterpenoids, *n*-alkanes, monosaccharides, PAHs and disaccharides. The concentrations of polyols and hopanes with cholestane were the smallest. The analysed organic compounds formed in average 2.76% of PM1 mass. A significant portion (34.6–63.8%) of analysed PAHs had a carcinogenic potential.

We applied the combination of diagnostic ratios and amount of selected organic markers in the collected aerosol samples for the identification of emission sources because we collected only 14 aerosol samples in the winter campaign in Mladá Boleslav, which is too little for the successful application of statistical methods.

The air pollution in the studied locality was mainly influenced by combustion of solid fuels (coal and wood) from household heating in residential houses in the older part of Mladá Boleslav, and especially from small villages nearby Mladá Boleslav, and also by combustion of solid fuels originating from the heating plant located inside the automobile factory.

Acknowledgement

The work was supported by the Grant Agency of the Czech Republic (grant No. P503/12/G147) and by the Institute of Analytical Chemistry of the Czech Academy of Sciences (RVO:68081715). The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apr.2017.03.003.

References

ATSDR (Agency for Toxic Substances and Disease Registry), 2009. Case Studies in Environmental Medicine, Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs), 68 pp. Available at: http://www.atsdr.cdc.gov/csem/pah/docs/pah.pdf.

Alves, C.A., 2008. Characterisation of solvent extractable organic constituents in atmospheric particulate matter: an overview. An. Acad. Bras. Cienc 80, 21–82.

Alves, C., Nunes, T., Vicente, A., Gonçalves, C., Evtyugina, M., Marques, T., Pio, C., Bate-Epey, F., 2014. Speciation of organic compounds in aerosols from urban background sites in the winter season. Atmos. Res. 150, 57–68.

Bian, Q., Alharbi, B., Collett Jr., J., Kreidenweis, S., Pasha, M.J., 2016. Measurements and source apportionment of particle-associated polycyclic aromatic hydrocarbons in ambient air in Riyadh, Saudi Arabia. Atmos. Environ. 137, 186–198.

Carvalho, A., Pio, C., Santos, C., 2003. Water-soluble hydroxylated organic compounds in German and Finnish aerosols. Atmos. Environ. 37, 1775–1783.

Caseiro, A., Marr, I.L., Claeys, M., Kasper-Giebl, A., Puxbaum, H., Pio, C.A., 2007. Determination of saccharides in atmospheric aerosol using anion-exchange high-performance liquid chromatography and pulsed-amperometric detection. J. Chromatogr. A 1171, 37–45.

CHMI (Czech Hydrometeorological Institute, 2013. Air Pollution and Atmospheric Deposition in Data, the Czech Republic, Annual Tabular Overview, 2013. Available at:http://portal.chmi.cz/files/portal/docs/uoco/isko/tab_roc/tab_roc_EN.html.

CSO (Czech Statistical Office), 2011. Population and Housing Census, Table 119: Occupied Dwellings by Type of Heating. Available at: https://www.czso.cz/csu/czso/zakladni-informace-o-vybranych-uzemnich-celcich-podle-sldb-2011-cr-kraje-okresy-spravni-obvody-orp-a-obce-vcetne-mestskych-casti-uzemne-clenenych-statutarnich-mest-2011-dml5agynjw. accessed in 2016.

Dvorská, A., Lammel, G., Klánová, J., 2011. Use of diagnostic ratios for studying source apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central Europe. Atmos. Environ. 45, 420–427.

Ek, M., Gellerstedt, G., Henriksson, G. (Eds.), 2009. Pulp and Paper Chemistry and Technology. Wood Chemistry and Biotechnolgy, vol. 1. Walter De Gruyter, Berlin.

Fabbri, D., Torri, C., Simoneit, B.R.T., Marynowski, L., Rushdi, A.I., Fabiańska, M.J., 2009. Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites. Atmos. Environ. 43, 2286–2295.

Fontal, M., van Drooge, B.L., López, J.F., Fernández, P., Grimalt, J.O., 2015. Broad spectrum analysis of polar and apolar organic compounds insubmicron atmospheric particles. J. Chromatogr. A 1404, 28–38.

Godec, R., Čačković, M., Šega, K., Bešlić, I., 2012. Winter mass concentrations of carbon species in PM10, PM2.5 and PM1 in Zagreb air, Croatia. Bull. Environ. Contam. Toxicol. 89, 1087–1090.

Hovorka, J., Pokorná, P., Hopke, P.K., Křůmal, K., Mikuška, P., Píšová, M., 2015. Wood combustion, a dominant source of winter aerosol in residential district in proximity to a large automobile factory in Central Europe. Atmos. Environ. 113, 98–107.

IARC (International Agency for Research on Cancer), 2015. Agents Classified by the IARC Monographs, vols. 1–116. Available at:http://monographs.iarc.fr/ENG/Classification/List_of_Classifications.pdf.

Jia, Y., Clements, A.L., Fraser, M.P., 2010. Saccharide composition in atmospheric particulate matter in the southwest US and estimates of source contributions. J. Aerosol. Sci. 41, 62–73.

Jia, Y., Stone, D., Wang, W., Schrlau, J., Tao, S., Simonich, S.L.M., 2011. Estimated reduction in cancer risk due to PAH exposures if source measures during the 2008 Beijing olympics were sustained. Environ. Health Perspect. 119, 815–820.

Keyte, I.J., Harrison, R.M., Lammel, G., 2013. Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons – a review. Chem. Soc. Rev. 42, 9333–9391. http://dx.doi.org/10.1039/c3cs60147a.

Křůmal, K., Mikuška, P., Večeřa, Z., 2013. Polycyclic aromatic hydrocarbons and hopanes in PM1 aerosols in urban areas. Atmos. Environ. 67, 27–37.

Křůmal, K., Mikuška, P., Večeřa, Z., 2015. Monosaccharide anhydrides, monocarboxylic acids and OC/EC in PM1 aerosols in urban areas in the Czech Republic. Atmos. Pollut. Res. 6, 917–927.

Křůmal, K., Mikuška, P., Vojtěšek, M., Večeřa, Z., 2010. Seasonal variations of monosaccharide anhydrides in PM1 and PM2.5 aerosol in urban areas. Atmos. Environ. 44, 5148–5155.

Kuklinska, K., Wolska, L., Namiesnik, J., 2015. Air quality policy in the U.S. and the EU – a review. Atmos. Pollut. Res. 6, 129–137.

Lerda, D., 2011. Polycyclic Aromatic Hydrocarbons (PAHs) Factsheet, fourth ed. JRC 66955 – Joint Research Centre – Institute for Reference Materials and measurements. 27 pp. Available at: https://ec.europa.eu/jrc/sites/default/files/Factsheet%20PAH_0.pdf.

Mikuška, P., Křůmal, K., Večeřa, Z., 2015. Characterization of organic compounds in the PM2.5 aerosols in winter in an industrial urban area. Atmos. Environ. 105, 97–108.

Mikuška, P., Kubátková, N., Křůmal, K., Večeřa, Z., 2017. Seasonal variability of monosaccharide anhydrides, resin acids, methoxyphenols and saccharides in PM2.5 in Brno, the Czech Republic. Atmos. Pollut. Res. 8, 576–586.

Minguillón, M.C., Querol, X., Baltensperger, A., Prévôt, A.S.H., 2012. Fine and coarse PM composition and sources in rural and urban sites in Switzerland: local or regional pollution? Sci. Total Environ. 427–428, 191–202.

Ministry of Agriculture, 2014. Report on the State of Forests and Forest Management in the Czech Republic in 2013. Available at: http://eagri.cz/public/web/mze/lesy/lesnictvi/zprava-o-stavu-lesa-a-lesniho/zprava-o-stavu-lesa-2013.html. accessed in 2015.

Mirante, F., Alves, C., Pio, C., Pindado, O., Perez, R., Revuelta, A., Artiñano, B., 2013. Organic composition of size segregated atmospheric particulate matter, during summer and winter sampling campaigns at representative sites in Madrid. Spain. Atmos. Res. 132–133, 345–361.

Nisbet, I.C.T., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16, 290–300.

OEHHA (Office of Environmental Health Hazard Assessment), 2005. Air Toxics Hot Spots Program Risk Assessment Guidelines. Part II Technical Support Document for Describing Available Cancer Potency Factors. California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section, Oakland, CA. Available at:http://oehha.ca.gov/media/downloads/crnr/may2005hotspots.pdf.

Oliveira, T.S., Pio, C.A., Alves, C.A., Silvestre, A.J.D., Evtyugina, M., Afonso, J.V., Fialho, P., Legrand, M., Puxbaum, H., Gelencser, A., 2007. Seasonal variation of particulate lipophilic organic compounds at nonurban sites in Europe. J. Geophys. Res. 112, D23S09.

Oros, D.R., Simoneit, B.R.T., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. Fuel 79, 515–536.

Pietrogrande, M.C., Abbaszade, G., Schnelle-Kreis, J., Bacco, D., Mercuriali, M., Zimmermann, R., 2011. Seasonal variation and source estimation of organic compounds in urban aerosol of Augsburg, Germany. Environ. Pollut. 159, 1861–1868.

Pietrogrande, M.C., Bacco, D., Silvia Ferrari, S., Kaipainen, J., Ricciardelli, I., Riekkola, M.L., Trentini, A., Visentin, M., 2015. Characterization of atmospheric aerosols in the Po valley during the supersito campaigns d Part 3: contribution of wood combustion to wintertime atmospheric aerosols in Emilia Romagna region (Northern Italy). Atmos. Environ. 122, 291–305.

Poschl, U., 2005. Atmospheric aerosols: composition, transformation, climate and health effects. Angew. Chem. Int. Ed. 44, 7520–7540.

Qadir, R.M., Abbaszade, G., Schnelle-Kreis, J., Chow, J.C., Zimmermann, R., 2013. Concentrations and source contributions of particulate organic matter before and after implementation of a low emission zone in Munich, Germany. Environ. Pollut. 175, 158–167.

Ramírez, N., Cuadras, A., Rovira, E., Marcé, R.M., Borrull, F., 2011. Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites. Environ. Health Perspect. 119, 1110–1116.

Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmos. Environ. 42, 2895–2921. http://dx.doi.org/10.1016/j.atmosenv.2007.12.010.

Rogula-Kozłowska, W., Kozielska, B., Klejnowski, K., Szopa, S., 2013. Hazardous compounds in urban PM in the central part of Upper Silesia (Poland) in winter. Arch. Environ. Prot. 39, 53–65.

Rolph, G.D., 2017. Real-time Environmental Applications and Display System (READY). NOAA Air Resources Laboratory, College Park, MD. Available at: http://www.ready.noaa.gov.

Saarikoski, S., Carbone, S., Decesari, S., Giulianelli, L., Angelini, F., Canagaratna, M., Ng, N.L., Trimborn, A., Facchini, M.C., Fuzzi, S., Hillamo, R., Worsnop, D., 2012. Chemical characterization of springtime submicrometer aerosol in Po Valley, Italy. Atmos. Chem. Phys. 12, 8401–8421.

Sánchez-Soberón, F., van Drooge, B.L., Rovira, J., Grimalt, J.O., Nadal, M., Domingo, J.L., Schuhmacher, M., 2016. Size-distribution of airborne polycyclic aromatic hydrocarbons and other organic source markers in the surroundings of a cement plant powered with alternative fuels. Sci. Total Environ. 550, 1057–1064.

Schmidl, C., Marr, I.L., Caseiro, A., Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. Atmos. Environ. 42, 126–141.

Schneider, I.L., Teixeira, E.C., Agudelo-Castañeda, D.M., Silva, G.S., Balzaretti, N., Braga, M.F., Oliveira, L.F.S., 2016. FTIR analysis and evaluation of carcinogenic and mutagenic risks of nitro-polycyclic aromatic hydrocarbons in PM1.0. Sci. Total Environ. 541, 1151–1160.

Simoneit, B.R.T., 2002. Biomass burning – a review of organic tracers for smoke from incomplete combustion. Appl. Geochem 17, 129–162.

Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, K., Rushdi, A.I., Medeiros, P.M., Rogge, W.F., Didyk, B.M., 2004. Sugars – dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. Environ. Sci. Technol. 38, 5939–5949.

Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA's HYSPLIT atmospheric transport and dispersion modeling system. Bull. Am. Meteorol. Soc. 96, 2059–2077.

Tauler, R., Viana, M., Querol, X., Alastuey, A., Flight, R.M., Wentzell, P.D., Hopke, P.K., 2009. Comparison of the results obtained by four receptor modelling methods in aerosol source apportionment studies. Atmos. Environ. 43, 3989–3997.

Tsapakis, M., Stephanou, E.G., 2003. Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling. Atmos. Environ. 37, 4935–4944.

van Drooge, B.L., Crusack, M., Reche, C., Mohr, C., Alastuey, A., Querol, X., Prevot, A., Day, D.A., Jimenez, J.L., Grimalt, J.O., 2012. Molecular marker characterization of the organic composition of submicron aerosols from Mediterranean urban and rural environments under contrasting meteorological conditions. Atmos. Environ. 61, 482–489.

van Drooge, B.L., Fontal, M., Bravo, N., Fernández, P., Fernández, M.A., Muñoz-Arnanz, J., Jiménez, B., Grimalt, J.O., 2014. Seasonal and spatial variation of organic tracers for biomass burning in PM1 aerosols from highly insolated urban areas. Environ. Sci. Pollut. Res. 21, 11661–11670.

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A.S.H., Hueglin, C., Bloemen, H., Wåhlin, P., Vecchi, R., Miranda, A.I., Kasper-Giebl, A., Maenhaut, W., Hitzenberger, R., 2008. Source apportionment of particulate matter in Europe: a review of methods and results. J. Aerosol. Sci. 39, 827–849.

Wan, E.C.H., Yu, J.Z., 2007. Analysis of sugars and sugar polyols in atmospheric aerosols by chloride attachment in liquid chromatography/negative ion electrospray mass spectrometry. Environ. Sci. Technol. 41, 2459–2466.

WHO (World Health Organization), 2000. Air Quality Guidelines for Europe, second ed. WHO Regional Office for Europe, Copenhagen. Available at: http://www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf.

WHO (World Health Organization), 2005. Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide. Global Update 2005, Summary of Risk Assessment. WHO Press, Geneva.

Yadav, S., Tandon, A., Attri, A.K., 2013. Characterization of aerosol associated non-polar organic compounds using TD-GC-MS: a four year study from Delhi, India. J. Hazard. Mater. 29–44.