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

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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.

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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.

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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 m³ 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 (Krůmal 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, $\alpha\alpha\alpha$ (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 $\alpha\alpha\alpha$ (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 μ m film thickness, 0.32 mm i.d., 30 m length. More details can be found in our previous papers (Krůmal 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 μ g 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 μ g 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

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