



Wood combustion, a dominant source of winter aerosol in residential district in proximity to a large automobile factory in Central Europe



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HIGHLIGHTS

- PMF revealed wood combustion for home heating to outclass industrial source.
- Mannosan and levoglucosan in PM₁ supported PMF receptor model results.
- Lignite combustion was indicated by the homohopane index of 0.05.
- Plumes from home chimneys caused PM₁₀ up to 500 µg m⁻³ at street level.

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ABSTRACT

Industries in close proximity to residential districts are a historical phenomenon of urban development frequently causing air quality problem in European cities. Mladá Boleslav, the long-time centre of the automobile industry in the Czech Republic, is typical example of urban development. However, this air pollution source reconnaissance study found a source of currently increasing importance for the European cities, wood burning. Receptor modelling, time series of organic tracers for wood and coal burning, small-scale multiple-site PM₁₀ monitoring and mobile PM₁₀ measurement were combined to identify sources of fine (PM_{0.15-1.15}) and coarse (PM_{1.15-10}) particles in a residential district of Mladá Boleslav in winter 2013. The receptor model was applied to hourly concentrations of organic and elemental carbon in fine and 27 elements in fine and coarse aerosol particles at a receptor site. Multiple-site measurements with PM₁₀ monitors showed no statistically significant differences among the monitors. Thus, the source apportionment derived from the central site data should apply to the entire residential district. Campaign average PM₁₀ (33.9 µg m⁻³) consisted of 88% fine particles. Wood burning (49%), coal combustion (34%), traffic (16%), and industry (1%) were identified as the fine particle sources while combined wood burning and coal dust (80%), road dust with salt (14%), and abrasion of car brakes (6%) were identified the coarse particle sources. The large contributions of wood and coal combustion were surprising for this residential district that is a block of flats with district heating. High correlations were observed between the wood combustion contributions and the levoglucosan and mannosan concentrations. The homohopane index of 0.05 indicated lignite combustion. Peak concentrations in excess of 500 µg m⁻³ of PM₁₀ recorded during mobile measurements along with visible plumes from home heating, support the source apportionment of the fine particle mass.

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1. Introduction

The deterioration of air quality in residential areas close to industrial facilities is a worldwide phenomenon. Problem areas have

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been observed in Jamshedpur (Sivacoumar et al., 2001), Kolkata (Karar and Gupta, 2006) in India, Ife–Ibadan, Nigeria (Owoade et al., 2015) and Beijing, China (Sun et al., 2004; Fang et al., 2009). In Europe, there were recent studies on air quality degradation from industry in Huelva, Spain (Querol et al., 2007), in Milan and Genoa, Italy (Vecchi et al., 2008), in Katowice, Poland (Juda-Rezler et al., 2011), and in Port Talbot, United Kingdom (Taiwo et al., 2014). In the Czech Republic, Central Europe, coal

combustion and landfill technology in a village Březno (Pokorná et al., 2013) and coal combustion and the steel industry in Ostrava (Pokorná et al., 2015) were found to be the main causes of local air pollution.

The city of Mladá Boleslav is situated about 64 km northeast of Prague in the Czech Republic (Fig. 1) and has been a center of the Czech automobile industry for more than 110 years. The factory was founded and has grown continuously within the urbanised area of the city. Currently, the factory occupies about one third (3.23 km²) of the urban area of Mladá Boleslav (Fig. 1). Across the street to the northwest of the factory, is the most populated district (population 19,000 of 45,000) of the city including a block-of-flats (Fig. 1). There were 55, 33, and 26 exceedances of the 24 h limit values for PM₁₀ in the district recorded in 2011, 2012 and 2013, respectively (CHMI, 2013). All of the exceedances were recorded in January or February. The city administration is planning to take measures to lower the air pollution. However, the development of cost-effective strategies depends critically upon a quantitative knowledge of the contribution of different sources to PM concentrations (Taiwo et al., 2014) and thus, this study will help guide their future actions.

Receptor models have proven to be useful tool to apportion PM sources in an ambient air (Viana et al., 2008; Belis et al., 2013). To obtain most accurate results in source apportionment studies, highly time resolved, size-segregated particle composition data is required (Zhou et al., 2004; Ogulei et al., 2005; Han et al., 2006; Peré-Trepart et al., 2007; Vecchi et al., 2009; Richard et al., 2011). Also, the measurement of levoglucosan, mannosan, and homohopane provides organic tracers for biomass or coal combustion within the cold, low photochemical activity time of year. This additional data helps to ensure an accurate aerosol source apportionment (Wang et al., 2012; Crilley et al., 2014; Qadir et al., 2014).

Positive Matrix Factorization (PMF) (Paatero, 1997) was applied to the hourly-resolved elemental composition and organic/elemental carbon concentrations of size-segregated particles

measured during the second half of February 2013 to identify sources of coarse and fine aerosol in the residential district of Mladá Boleslav. Multiple-site measurements using PM₁₀ monitors complemented the source apportionment measurements conducted at the central site. The time series of the resolved sources and the concentrations of the organic tracers for wood and brown coal burning were correlated. Also, the mobile PM₁₀ measurements conducted during perambulations in the urbanized areas helped to identify the causes of the observed elevated PM concentrations.

2. Material and methods

2.1. PM measurements

2.1.1. Monitoring station and PM sampling

The campaign was conducted between 14 and 28 February 2013. A mobile monitoring station was placed at a central site in a sports field in a residential district of Mladá Boleslav (50°25′32.50″N – 14°54′54.42″E) (Fig. 1). The site is very close to a large industrial complex spanning from the North-East to the South of the sampling site. A Davis Rotating-drum Uniform-size-cut Monitor - 3DRUM (Delta Group UC Davis) (Raabe et al., 1988) was used to collect particles in three size ranges. This sampler was the same as previously used in Ostrava study (Pokorná et al., 2015). Particles of aerodynamic diameter of 1.15–10 μm (PM_{1.15–10}) were considered to be the coarse aerosol, while other two size ranges, 0.34–1.15 μm (denoted as B fraction), and 0.15–0.34 μm (denoted as C fraction), were summed to provide a 0.15–1.15 μm fraction designated as the fine aerosol (PM_{0.15–1.15}). Particles were collected at a flow rate of 21.5 Lmin⁻¹ on Mylar substrates lightly greased with Apiezon-LTM. The strips were analyzed for 27 elements with synchrotron XRF (Perry et al., 2007) with a PM sample integration time of 1 h. PM sampling and analysis followed the DRUM Quality Assurance Protocols (Cahill et al., 2008). Hourly PM mass concentrations were

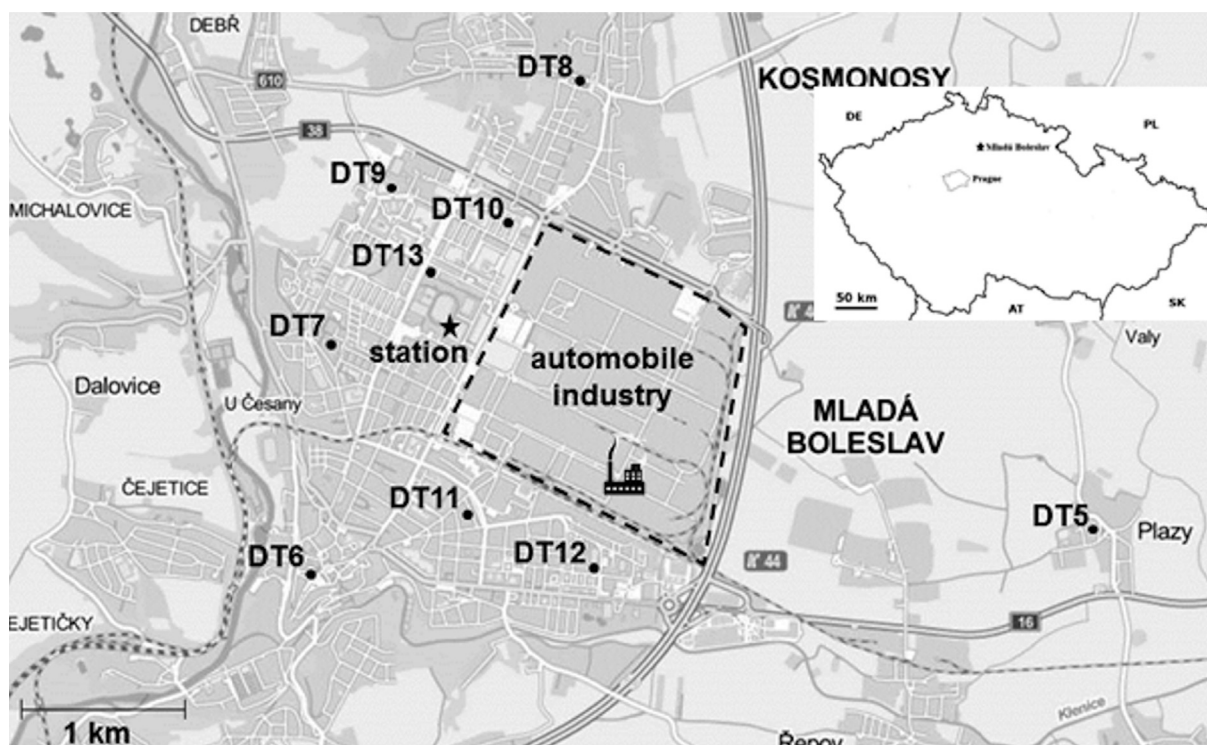


Fig. 1. Outline map of Czech Republic showing city Mladá Boleslav and detailed map of the sampling site with location of the monitoring station, network of PM₁₀ DustTrak monitors – DT5–13.

calculated from five minute integrations of the number size distributions for 0.542–10 μm size range recorded by an Aerodynamic Particle Sizer (APS-3321, TSI) and within the 0.018–0.545 μm aerodynamic particle diameter range measured using a Scanning Mobility Particle Sizer (SMPS 3963L25, TSI) assuming a particle density of 1.5 g cm^{-3} (Shen et al., 2002). Five minute integrated PM_{10} mass concentrations were measured with a beta attenuation monitor (FH 62 I-R, Thermo ESM Andersen). A strong linear regression between SMPS-APS and hourly beta PM_{10} concentrations was found (slope = 1.04 ± 0.02 , $r^2 = 0.87$, Fig. S1) that supported the assignment of the particle density used for number-to-mass size distribution conversion.

Hourly concentrations of organic and elemental carbon (OC/EC) in $\text{PM}_{2.5}$ (Sunset Laboratories) were measured semi-continuously (45 min collection and 15 min analysis) using the NIOSH protocol (Birch and Cary, 1996). Size-integrated samples of 24 h PM_1 were collected on quartz fiber filters (150 mm diameter, Whatman QMA) using a high-volume ($30 \text{ m}^3 \text{ h}^{-1}$) sampler (DHA-80, Digital) equipped with a PM_1 size selective inlet. Complete meteorological data including wind speed (WS) and wind direction (WD) (Wind-Sonic M, Gill), temperature – T (Comet 200-80/E), and precipitation by disdrometer (Laser Precipitation Monitor, Thies) were recorded concurrently.

2.1.2. PM_{10} monitoring network and mobile measurements

Along with the measurements at the central station, a small-scale network of 9 laser photometers, DustTrak – DT (8520, TSI), was deployed to measure 5-min PM_{10} concentrations. This PM_{10} measurement network was operated for the period of 17 February to 18 March 2013. Initially, these units were collocated at the central site to permit intercomparison of their performance and calibration of the individual monitors. Eight instruments (DT6–13) were distributed in the urbanized district of Mladá Boleslav and DT5 was placed in the steeple of a church in the village of Plazy located east of the automobile factory (Fig. 1). The DTs were positioned on roofs at an average height of 16 m, to avoid recording of intermittent sources, with exceptions of the DT13 and DT8, which were placed on the roof of monitoring station of the Czech Hydrometeorological Institute (CHMI) and the firehouse, respectively. Inter-DT distances ranged from 600 to 2780 m, and the network covers approximately 4.4 km^2 of the urban area of Mladá Boleslav (Fig. 1).

Besides PM_{10} monitoring at fixed sites, a series of nine approximately hour-long mobile PM_{10} measurements were conducted in the Plazy and Mladá Boleslav urbanised areas. During the perambulations, a DT monitor recorded 10 s integrates of PM_{10} and was carried in a backpack with an omnidirectional inlet at a height of 1.5 m. A vertical inlet protruded about 20 cm from the backpack. Concurrently with PM_{10} measurements, geographical coordinates were recorded using a hand-held GPS receiver (GPSMAP 60CSx, Garmin).

To calibrate the photometric PM_{10} detection, DT values were linearly regressed against the 5 min PM_{10} values recorded by the beta attenuation monitor. The regression with the intercept forced to zero yielding a slope 0.320 ± 0.001 ($r^2 = 0.96$). Therefore, the DT values were multiplied by 0.32 to correct the DT PM_{10} values for the whole campaign.

2.2. Gravimetric and chemical analyses

The quartz filters for the high-volume sampler were heated in a muffle furnace at 500 $^{\circ}\text{C}$ for 24 h prior to sampling. The PM_1 mass was determined by weighing filters on a microbalance (M5P, Sartorius) equipped with a large plate to allow weighing the 150 mm quartz filters. The particle samples were analyzed for

polycyclic aromatic hydrocarbons (PAHs), hopanes, $\alpha\alpha\alpha(20R)$ -cholestanes, alkanes, acyclic isoprenoids, monosaccharide anhydrides, saccharides, and resin acids. Details of the GC–MS analysis procedures are provided by Krůmal et al. (2010, 2013). In this study, the results for levoglucosan, mannosan, and 22R + S-17 α (H), 21 β (H)-homohopane are presented and discussed.

The DRUM samples were analyzed for 27 elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo and Pb) using synchrotron X-ray fluorescence (S-XRF) at Lawrence Berkeley National Laboratory (DELTA Group, 2008; Cahill, 2011).

2.3. Data analysis

2.3.1. PM_{10} spatial variability

Spatial variability of the PM_{10} values was evaluated using the pairwise coefficient of divergence (COD) (Kim et al., 2005). The COD approaches zero or unity if there is substantial similarity or difference between the sites, respectively. The critical value of the COD was set at 0.2 above which the samples are deemed to be dissimilar. (Pinto et al., 2004)

2.3.2. Positive Matrix Factorization

Positive Matrix Factorization (EPA PMF 4.2.0.0.) was applied to the data to obtain source profiles and their contributions. The data matrix was prepared in compliance with the procedure described in Polissar et al. (1998) based on analytical errors provided by Lawrence Berkeley National Laboratory. The below detection limit (BDL) values were replaced with the $\text{DL}/2$ and $(5/6) \cdot \text{DL}$ was used as corresponding uncertainty values. The fraction of BDL values ranged up to 29% according to species and the size fraction. Missing data were replaced by geometric mean species values and uncertainty values by triple of the arithmetic mean. The fraction of missing values ranged up to 14% according to species and size fraction. Eliminated elements were Ga (in all fractions) and As (in fraction A and C) because of the large percentage of missing data (>40%). The analytical uncertainties of OC/EC were multiplied by a factor of 4, similar to the approach used in the earlier Ostrava study (Pokorná et al., 2015).

In the PMF model, the species were classified according to the signal to noise ratio as strong, weak and bad variable (Paatero and Hopke, 2003). Mg, P, Se, Br, Rb, Sr, Y, Zr, Mo, Pb were bad in all of the size fractions and excluded from the fit. Al, S, Cl, K, Mn, Co were classified as weak in the A fraction and Al, Si, Cl, OC, EC in B + C fraction. The appropriate PM values were set to be the total variable and therefore as weak.

The data matrices for the model consisted of hourly PM masses and the elemental concentrations for $\text{PM}_{0.15-0.34}$, $\text{PM}_{0.34-1.15}$, $\text{PM}_{0.15-1.15}$ and $\text{PM}_{1.15-10}$. For $\text{PM}_{2.5}$, the OC/EC data were included in the matrix. The final matrices had 320 rows (samples) and 28/26 columns (species/elements) for fine and coarse matrices, respectively.

Initially, all the three aerosol size fractions were modelled separately and then B and C fractions were combined into a fine fraction data set and analyzed. The PMF results for the separate B and C fractions are presented in the Supplemental Material (Figs. S1–S6). Only the PMF results for the fine and coarse fractions are presented here, but PMF results for each of the three separate size fractions will be discussed.

2.3.3. Conditional probability function

To determine directionality of local sources, the conditional probability function (CPF) (Ashbaugh et al., 1985; Kim et al., 2003) was calculated using source contribution estimates resolved by the PMF analyses and the wind speed and direction values measured at the site. Here, the hourly factor mass contributions were combined

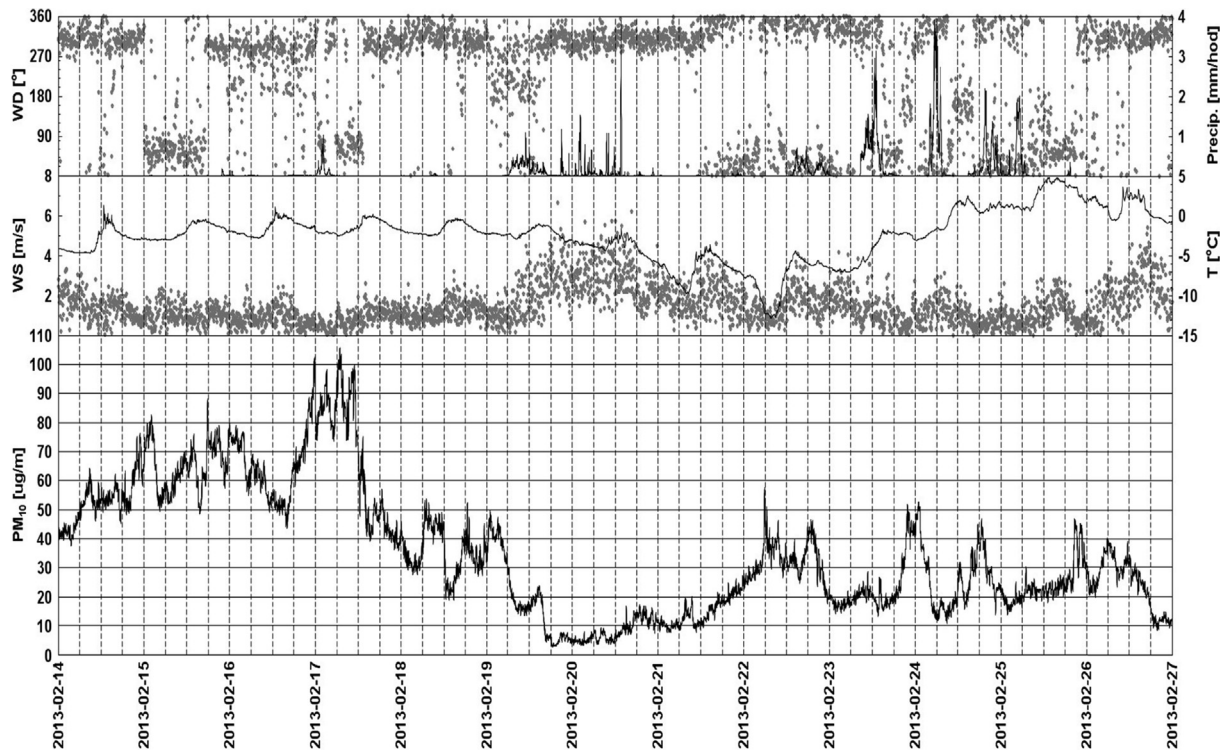


Fig. 2. Temporal variation of PM_{10} and meteorological data recorded during the measurement campaign (WD/WS – grey dots, T/Precipitation – black line).

with 5 min meteorological data. CPF is defined as:

$$CPF = m_{\Delta\theta} / n_{\Delta\theta}$$

where, $m_{\Delta\theta}$ is the number of occurrences from wind sector $\Delta\theta$ that are in the upper 10th percentile of the fractional contributions and $n_{\Delta\theta}$ is the total number of observations from the same wind sector. In this study, $\Delta\theta$ was set at 30° and about 38% of observations of wind speeds $< 1 \text{ m s}^{-1}$ were excluded from this analysis. The sources are likely to be located in the directions that have high conditional probability values.

3. Results and discussion

The campaign was characterized by mild winter temperatures (median = -2.2°C), low WS (median = 1.3 m s^{-1}), WD prevailing from NW (Fig. S7) and PM_{10} values below admissible EU daily limit for PM_{10} (median = $28.2 \mu\text{g m}^{-3}$) (Fig. 2). On average, fine and coarse PM constituted 87.6% and 12.4% of PM_{10} (Table 1).

Table 1

Basic statistics of mass concentration in $\mu\text{g m}^{-3}$ of the three aerosol size fractions.

Percentile	Size fraction		
	A 1.15–10 μm	B 0.34–1.15 μm	C 0.15–0.34 μm
5%	0.5	3.7	2.8
25%	1.2	10.5	5.9
50%	2.5	17.3	8.4
75%	5.4	29.9	10.5
95%	12.8	46.8	15.2
Mean	4.2	21.2	8.5

3.1. Spatial PM_{10} variability

There were no statistically significant differences among the DT values within the small-scale monitoring network for PM_{10} according to their COD values (Table 2). Nevertheless, the time series and basic statistics of PM_{10} data (Table 3) show substantially higher

Table 2

The COD of 5 min PM_{10} values determined by DustTrak – DT monitors for the period of the 17th–28th Feb 2013.

	DT6	DT7	DT8	DT9	DT10	DT11	DT12	DT13
DT5	0.157	0.137	0.134	0.144	0.128	0.141	0.127	0.176
DT6		0.141	0.125	0.161	0.121	0.089	0.117	0.168
DT7			0.094	0.077	0.085	0.114	0.098	0.080
DT8				0.107	0.077	0.109	0.104	0.106
DT9					0.081	0.129	0.117	0.072
DT10						0.087	0.087	0.097
DT11							0.089	0.128
DT12								0.115

Table 3

Descriptive statistics of 5 min PM_{10} recorded by DustTrak – DT monitors for the period of the 17th Feb–18th Mar 2013.

Monitor	$PM_{10}/\mu\text{g m}^{-3}$						Max
	5%	25%	50%	75%	95%	Mean	
DT5	4.7	13.4	23.3	32.1	56.6	25.9	539.4
DT6	6.7	16.0	24.9	32.7	45.7	25.2	76.4
DT7	4.5	12.0	20.9	27.1	40.1	20.9	69.9
DT8	4.8	13.1	23.0	29.6	43.6	22.7	92.1
DT9	5.1	11.8	20.0	26.7	40.3	20.6	92.9
DT10	4.9	12.5	22.4	31.0	44.5	23.1	83.3
DT11	5.1	14.3	24.8	34.0	46.7	25.2	62.0
DT12	3.7	13.2	22.5	31.4	41.9	22.8	62.2
DT13	4.7	12.5	20.0	26.7	38.3	20.4	66.8

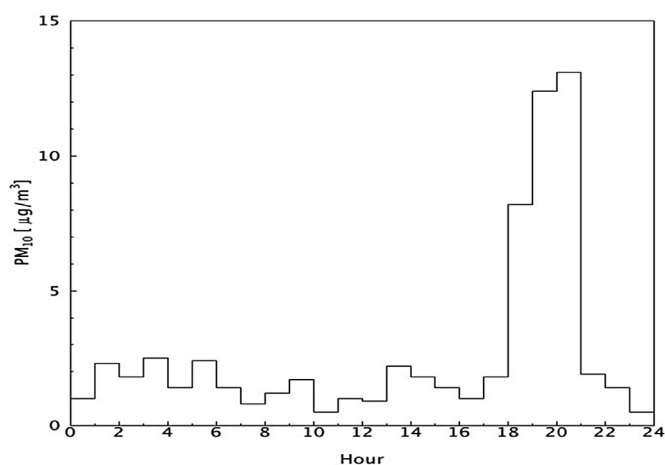


Fig. 3. Weekend average of diurnal variation of hourly the excesses PM_{10} in Plazy during the campaign.

95th percentile values and very high maxima for PM_{10} measured in the steeples in Plazy mainly during weekends. To evaluate the statistical significance of such 5-min weekend PM_{10} peak values, hourly mean PM_{10} values were calculated; separately for Plazy along with combined mean values for the remaining sites. Then the corresponding weekend hourly PM_{10} values from the remaining sites were subtracted from those in Plazy and the differences, larger

than $3 \mu g m^{-3}$ PM_{10} , were considered as excess PM_{10} . Diurnal variation of the excess value in Plazy averaged over 4 weekends showed large maxima ($13 \mu g m^{-3}$ PM_{10}) between 18 and 21 h (Fig. 3) in accordance with known building heating patterns. The excess PM_{10} values always coincided with calm winds, and changing wind direction from NE to W (Fig. 2), pointing to local home heating emissions from low heights. Also, the effect of home heating on PM_{10} values was recorded with the mobile measurements. Concentrations higher than $500 \mu g m^{-3}$ of PM_{10} were recorded when the observer passed through an intermittent plume originating from a home chimney in Plazy (Fig. S2).

In Mladá Boleslav urbanized area, there were peak PM_{10} values usually in the $30\text{--}60 \mu g m^{-3}$ range (Figs. S3–S6, S8), but up to $260 \mu g m^{-3}$ (Fig. S7) of PM_{10} was recorded during perambulation in a district of family houses heated by local heating. In contrast to home heating peaks, transportation-associated peak PM_{10} values that were on average ranged from 10 to $30 \mu g m^{-3}$ were recorded near busy roads or crossroads similar to the values recorded during mobile measurements in Leipzig (Birmili et al., 2013). Similar to Leipzig measurements, a peak of $70 \mu g m^{-3}$ of PM_{10} was recorded (Fig. S3) when passing a cigarette smoker during the perambulation.

3.2. PMF results

To determine the optimal number of sources, 2 to 7 factors were tested. The resulting Q values, the resulting source profiles, and the scaled residuals were examined. The optimum number of factors

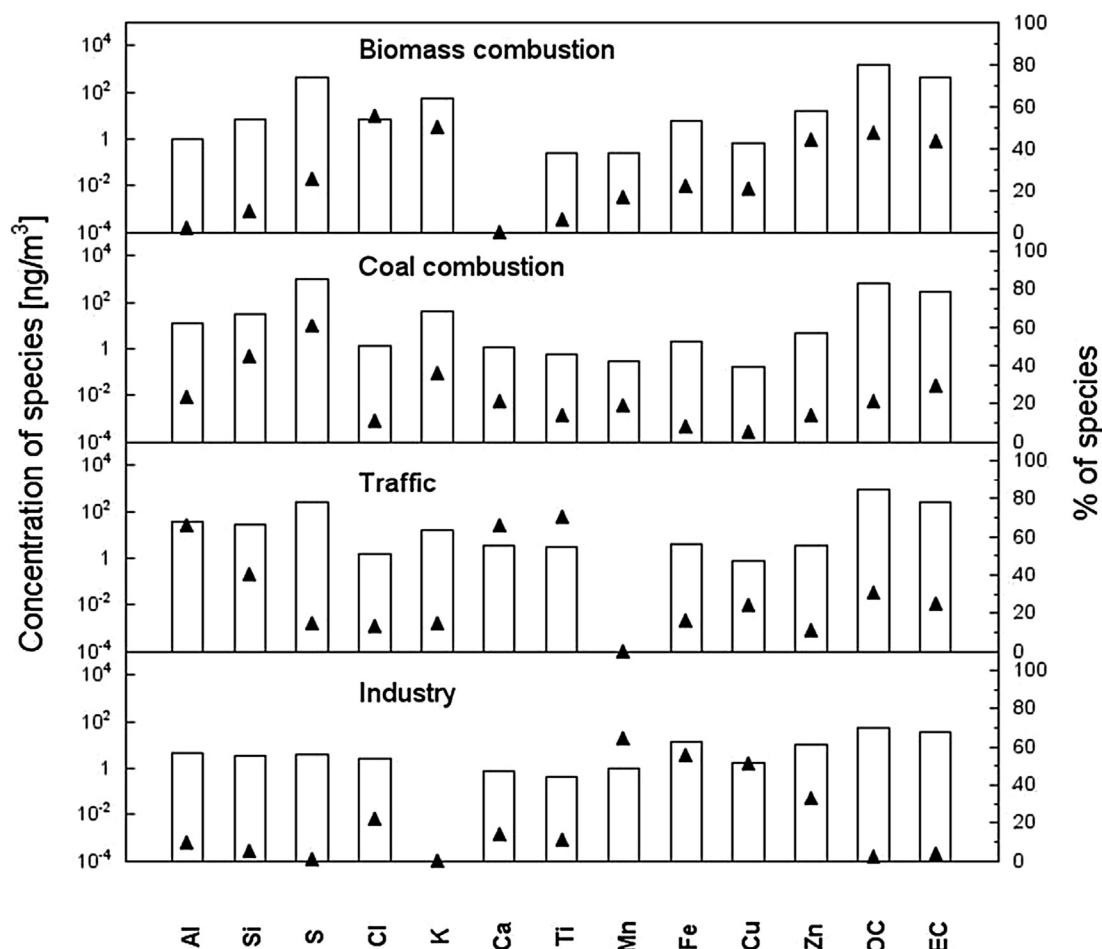


Fig. 4. Factor profiles for the PMF resolved factors from the fine fraction data.

was chosen based on the most physically reasonable results and an adequate fit of the model to the data. The optimal factor number was 4 for fine fraction (C fraction 3 and B fraction 5) and 3 for coarse fraction. The FPEAK parameter (−0.5, −0.4, −0.3, −0.2, −0.1, 0, 0.1, 0.2, 0.3, 0.4, 0.5) was used to refine the source profiles. The optimum solution was chosen to be no rotation (FPEAK = 0) for all of the fractions.

3.2.1. Sources of fine aerosol

The four resolved fine fraction factors were assigned as wood combustion, coal combustion, traffic, and industry. The factor profiles and the time-series plots of the estimated hourly $PM_{0.15-1.15}$ mass contributions are shown in Figs. 4 and 5.

The first factor, *wood combustion*, was associated with high concentrations of Cl, K, Zn, OC and EC (Kleeman et al., 1999; Watson et al., 2001; Kim et al., 2003). Factor contributions were significant primarily during the weekend of February 16th – 17th and on the 23rd and 24th of February. The contributions increased in the afternoon with midnight maxima, which suggests wood burning in the local heating boilers in the suburban area of the city. On average, wood combustion contributes by 49% to mass of fine aerosol particles. This factor correlates well with wood combustion factor derived for the B fraction ($r = 0.84$) and with wood and coal combustion assigned for C fraction ($r = 0.84$). Also, the wood combustion factor contributions correlated well (Fig. 6, $r^2 = 0.88$) with concentrations of levoglucosan and mannosan, specific tracers

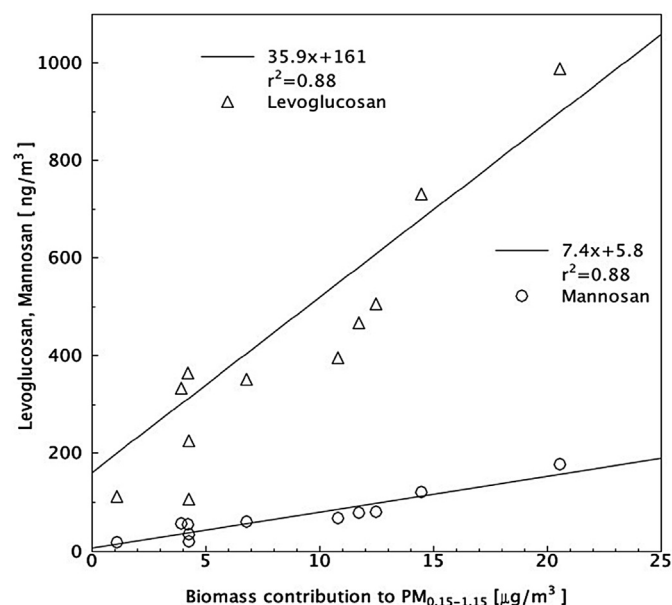


Fig. 6. Comparison of 24 h average concentrations between wood burning contributions for fine aerosol and levoglucosan and manosan in PM_1 .

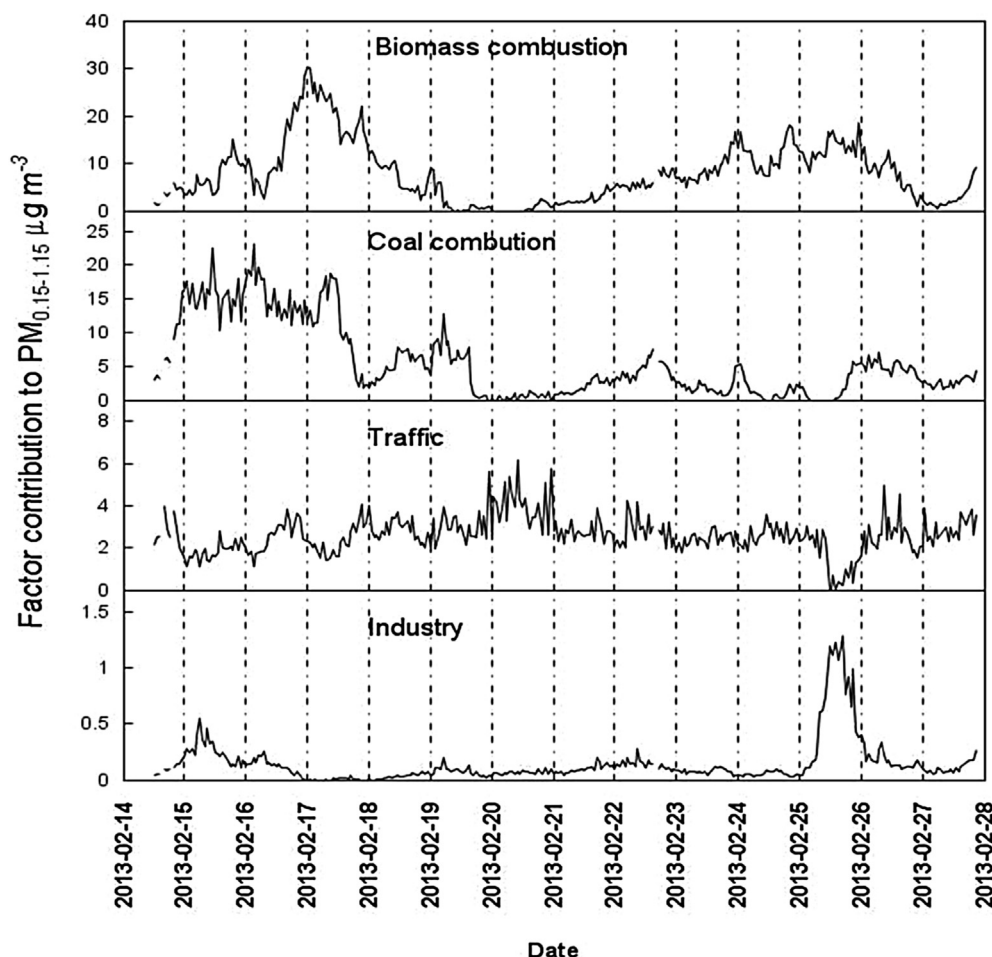


Fig. 5. Temporal variations of hourly source contributions to the mass of fine aerosol particles resolved by PMF.

for wood burning (Simoneit et al., 1999; Wang et al., 2012; Qadir et al., 2014). Levoglucosan was the most abundant organic compound determined in PM₁ samples collected during the campaign. The CPF plots point to the northeast-east (Fig. 7).

The second factor was associated with S, K, EC, and OC (Almeida et al., 2005; Han et al., 2005; Rogula-Kozłowska et al., 2012), and was ascribed to *coal combustion*. The factor contributed significantly at the beginning of the campaign when the meteorology was characterized by calm winds and mild temperatures averaging -2°C . The campaign's average factor contribution was 34%. The contributions correlated well with coal combustion factor for the only B fraction ($r = 0.91$) and moderately with the wood and coal combustion solely for the C fraction ($r = 0.54$). Coal combustion can be indicated by homohopane index, the ratio of the concentration of R- and S- isomer of the 17 α (H), 21 β (H)-homohopane, $[S/(S + R)]$ (Oros and Simoneit, 2000; Qadir et al., 2013). The higher the R/S ratio indicates coal combustion with the contributions of traffic emissions being small. The homohopane index ranged 0.012–0.074 (mean 0.05) pointing to lignite combustion (Křůmal et al., 2013). The coal factor CPF plot was similar to the wood combustion factor, indicating co-combustion of wood and coal for

home heating. Nevertheless, additional CPF branch from the south (Fig. 7) indicates the contribution from coal heating plant (icon in Fig. 1), which combusts lignite and wood pellets and contributes to the coal factor by 24%.

The third factor assigned as *traffic* contained road dust elements, OC and EC and Cu, indicating metal brake wear particles (Vecchi et al., 2008; Richard et al., 2011). This factor includes tailpipe and non-tailpipe vehicular emissions. Factor contributions to PM_{0.15–1.15} were constant with minor diurnal variation over the whole campaign. It contributes 16% to the mean PM_{0.15–1.15} mass concentration. The time series plots of the traffic factor with the comparable factors of the B and C fractions having identical factor time series showing good to moderate correlations with $r = 0.75$ and $r = 0.54$ for the B and C fractions, respectively (Figs. S9–S13). The CPF plots show weak directionality and points to the west to the nearby streets (Fig. 7).

The fourth factor was ascribed to *industry I*. Its profile shows high concentrations of Mn, Fe, Cu and Zn (Querol et al., 2007; Zhou et al., 2004; Cohen et al., 2010). The significant contribution peaks on 15th and 25th February were related to a wind-direction shift with wind coming from the east. The mean PM_{0.15–1.15} mass

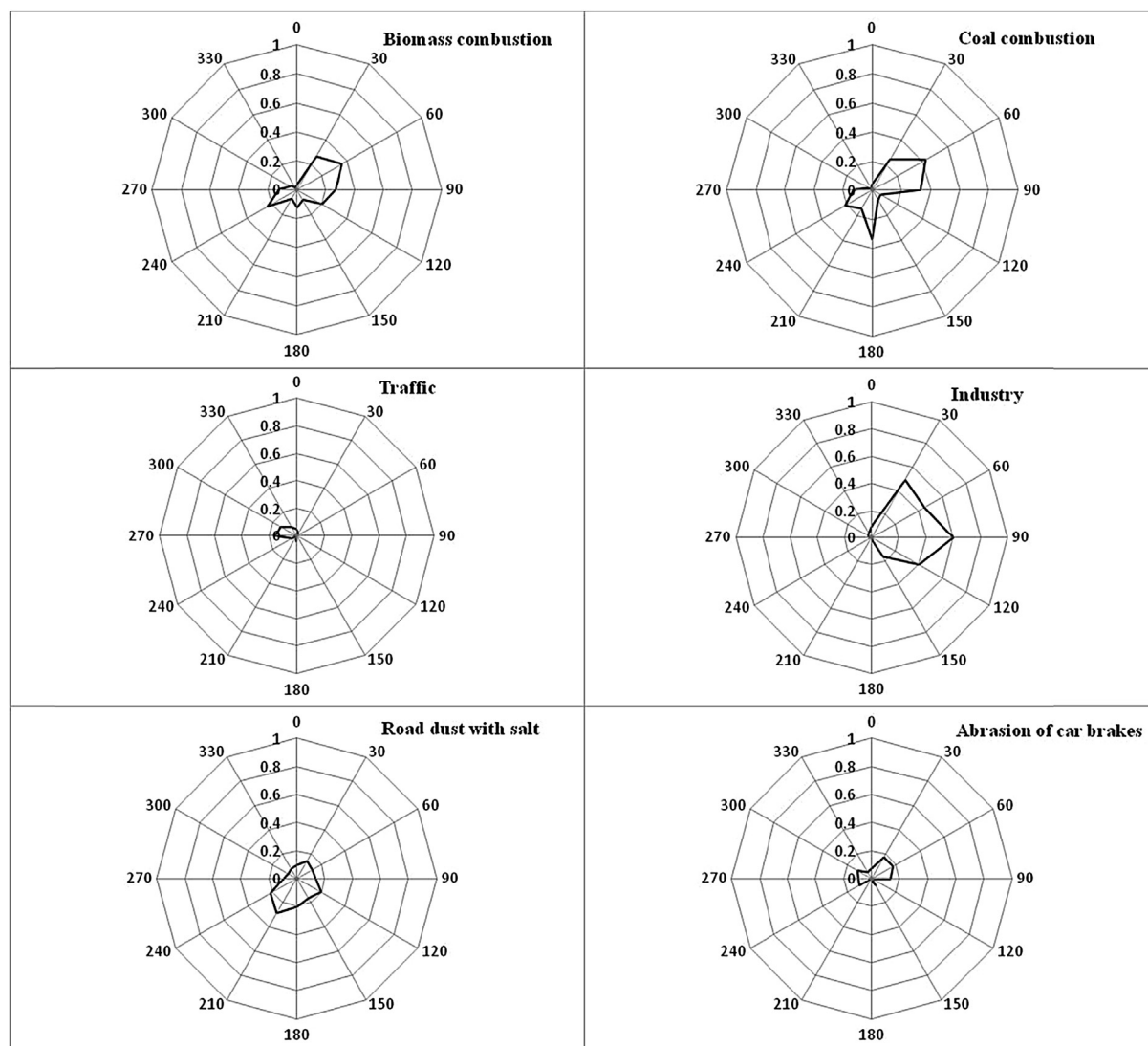


Fig. 7. CPF plots for wood and coal combustion, traffic and industry contributing to fine aerosol and road dust and abrasion contributing to coarse aerosol particles in Mladá Boleslav.

contribution was 1%. The time series plots for fine fraction show correlations ($r = 0.46$ and $r = 0.94$) with B and C fractions, respectively. The CPF plots indicated contributions from east-northeast, where the automobile factory is situated (Fig. 7).

Factor of B fraction assigned as the *industry II* contained Cu and metals. The factor correlates well with industry factor of fine fraction ($r = 0.93$). The mean $PM_{0.34-1.15}$ mass contribution was 2%. The CPF plots indicated easterly contributions from the automobile factory (Fig. 7).

3.2.2. Sources of coarse aerosol

The three resolved coarse fraction factors were assigned to combined wood and coal dust, road dust with salt, and metallic brake wear particles. Their profiles and time-series plots of contributions are shown in Figs. 8 and 9, respectively.

The first factor, *wood combustion and coal dust*, was associated with S, K, and metals (Almeida et al., 2005; Han et al., 2005; Hien et al., 2001), and its 80% contribution to the coarse fraction was dominant. The wood combustion can be explained as fly ash from local heating boilers and agrees with WD analysis for the fine particle wood combustion factor. The coal dust can be attributed to fugitive emissions from exposed coal piles near the heating plant in the industrial complex and significantly decreased with a snowfall (Fig. 2). The CPF plot points northeast-east and matches plots of the corresponding fine fraction factors (Fig. 7).

The second factor assigned as *road dust with salt* was represented by high contributions of soil components and Cl (Han et al., 2005; Cheung et al., 2012). It represents re-suspended road dust and salt used for road clearing after the snowfall episodes. The factor contributed by 14% to the $PM_{1.15-10}$ mass during the whole

campaign. The CPF plot primarily points to south-southeast (Fig. 7) to the car park of the sports field and shopping center (Fig. 1).

The third factor, *abrasion of car brakes* was characterized by Cu and Zn (Peré-Trepat et al., 2007; Thorpe and Harrison, 2008). The factor contributed to the $PM_{1.15-10}$ mass by 6%. The CPF plots points to the nearby streets (Fig. 7).

3.2.3. Sources of PM_{10}

Combining the results of the fine and coarse fraction analyses provided the apportionment of PM_{10} . Wood and coal combustion was the dominant source of PM_{10} (82%) followed by traffic (17%) and industry (1%).

4. Conclusions

Wood burning was found to be the dominant source of PM_{10} mass followed by coal combustion in the residential district of the city of Mladá Boleslav during the winter. The large industrial source had a minor influence. Dominance of wood combustion was supported by elevated mannosan and levoglucosan concentrations in PM_{10} , while lignite combustion was indicated by the homohopane index of 0.05. Also, peak values about $13 \mu\text{g m}^{-3}$ of PM_{10} in village of Plazy occurred regularly in late afternoon on weekends due to home heating, recorded by fixed PM_{10} monitor. Peak values of PM_{10} up to $500 \mu\text{g m}^{-3}$, attributable to plumes from chimneys of local home heating, were recorded by the mobile measurements providing additional support for the PM_{10} source attribution.

Dominance of wood burning contrasts to the expectation that local industrial sources would dominate the PM pollution based on the results of our source apportionment studies conducted in

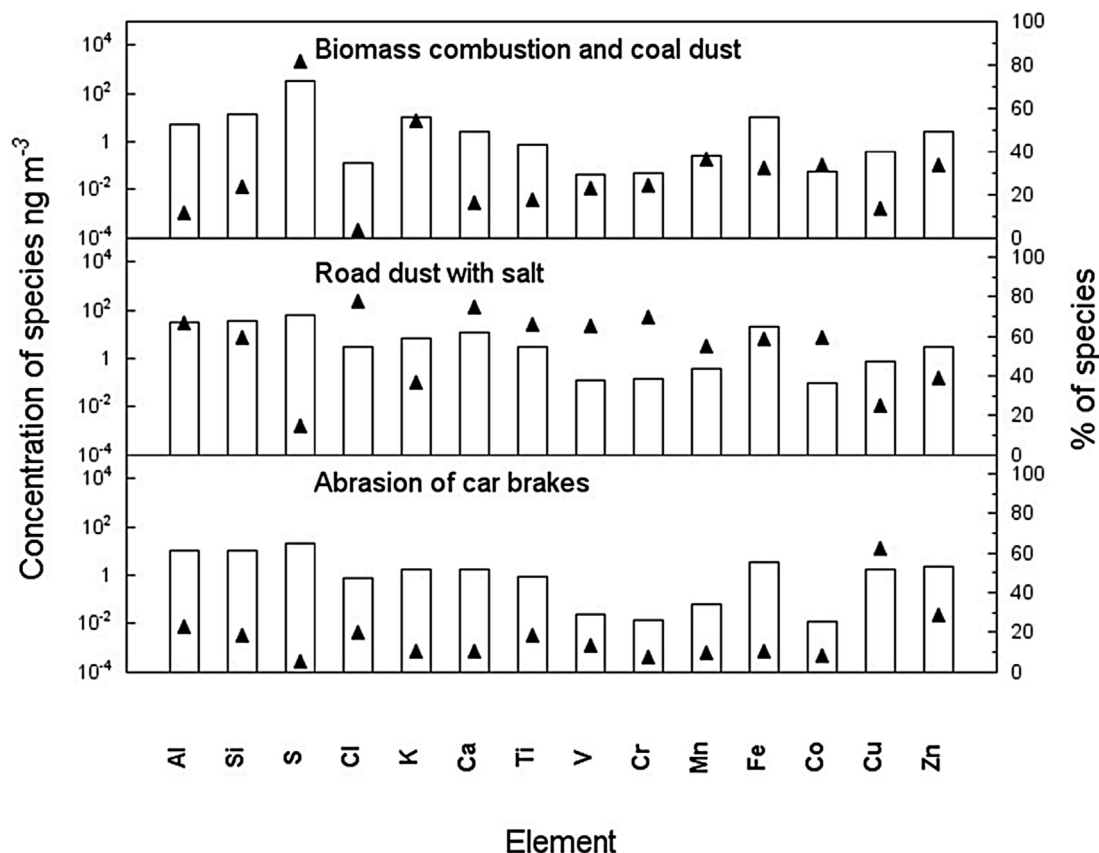


Fig. 8. Factor profiles for the resolved factors of coarse fraction by PMF.

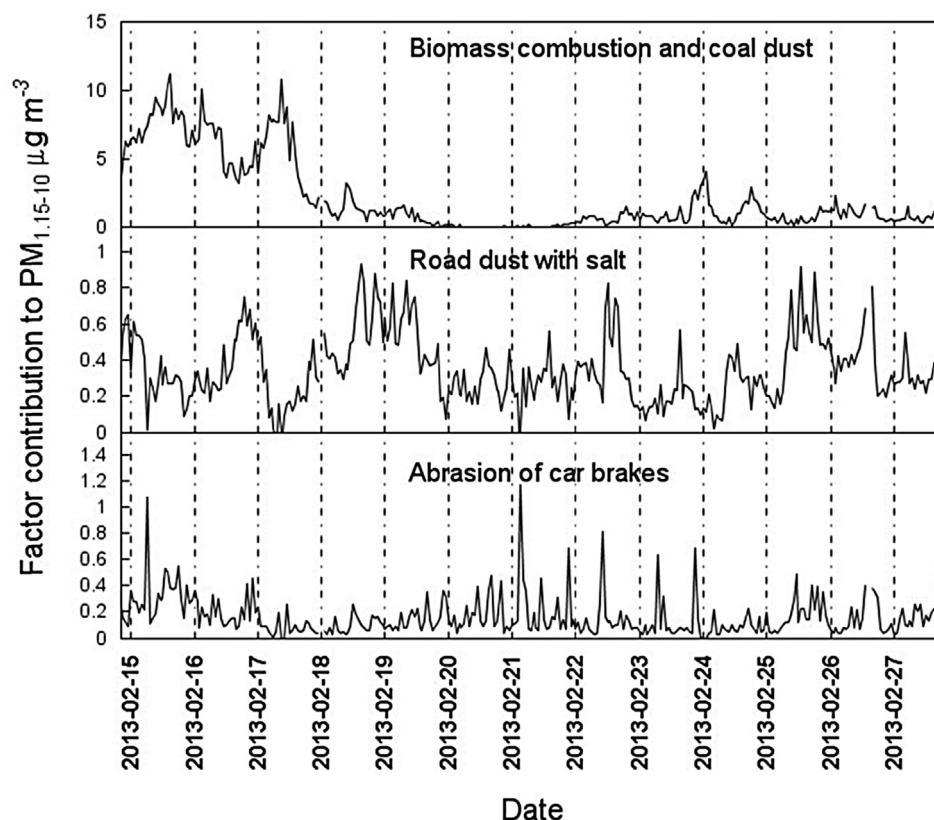


Fig. 9. Temporal variations of factor hourly contributions to the coarse particle mass resolved by PMF.

residential areas in proximity to an industry in Ostrava (Pokorná et al., 2015) or in Prague (Thimmaiah et al., 2009).

This study agrees with other recent studies indicating the increasing importance of wood burning on air quality in Europe. There was a wood burning contribution of 59% to PM_{10} mass found in Dettenhausen near Stuttgart (Bari et al., 2010), 20% in Augsburg (Gu et al., 2013), and 25% in Lens, Northern France (Waked et al., 2014).

To conclude, our study provides an affirmative answer to the question “Time to tackle urban wood burning?” raised by Fuller et al. (2013) in New directions as also being applicable to air quality in Central and Eastern Europe.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.04.068>

References

- Almeida, A.M., Pio, C.A., Freitas, M.C., Reis, M.A., Trancoso, M.A., 2005. Source apportionment of fine and coarse particulate matter in sub-urban area at the Western European Coast. *Atmos. Environ.* 39, 3127–3138.
- Ashbaugh, L.L., Malm, W.C., Sadeh, W.Z., 1985. A residence time probability analysis

- of sulphur concentrations at Grand Canyon National Park. *Atmos. Environ.* 19, 1263–1270.
- Bari, M.A., Baumbach, G., Kuch, B., Scheffknecht, G., 2010. Temporal variation and impact of wood smoke pollution on a residential area in southern Germany. *Atmos. Environ.* 44, 3823–3832.
- Belis, C.A., Karagulian, F., Larsen, B.R., Hopke, P.K., 2013. Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. *Atmos. Environ.* 69, 94–108.
- Birch, M.E., Cary, R.A., 1996. Elemental carbon based methods for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol.* 25, 221–241.
- Birmili, W., Rehn, J., Vogel, A., Boehlke, C., Weber, K., Rasch, F., 2013. Micro-scale variability of urban particle number and mass concentrations in Leipzig, Germany. *Meteorol. Z.* 22, 155–165.
- Cahill, T.A., Cliff, S.S., Perry, K.D., Barnes, E., D.E., Portnoff, L., 2008. DRUM Quality Assurance Protocols. <http://drumair.com/includes/DQAP1.pdf>.
- Cahill, T.A., Barnes, D.E., Spada, N.J., Lawton, J.A., Cahill, T.M., 2011. Very fine and ultrafine metals and ischemic heart disease in the California Central Valley 1: 2003–2007. *Aerosol Sci. Technol.* 45, 1123–1134.
- Cheung, K., Schafer, M., Schauer, J.J., Sioutas, C., 2012. Historical trends in the mass and chemical species concentrations of coarse particulate matter in the Los Angeles Basin and relation to sources and air quality regulations. *J. Air Waste Manag. Assoc.* 62, 541–556.
- CHMI, Czech Hydrometeorological Institute, 2013. Air Pollution and Atmospheric Deposition in Data. http://portal.chmi.cz/files/portal/docs/uoco/isko/tab_roc/tab_roc_EN.html.
- Cohen, D.D., Crawford, J., Stelcer, E., Bac, V.T., 2010. Characterisation and source apportionment of fine particulate matter at Hanoi 2001 to 2008. *Atmos. Environ.* 44, 230–328.
- Crilly, L.R., Qadir, R.M., Ayoko, G.A., Schnelle-Kreis, J., Abbaszade, G., Orasche, J., Zimmermann, R., Morawska, L., 2014. Identification of the sources of primary organic aerosols at urban schools: a molecular marker approach. *Environ. Pollut.* 191C, 158–165.
- DELTA Group, 2008. DRUM Quality Assurance Protocols (DQAP). <http://delta.ucdavis.edu>.
- Fang, M., Chan, Ch.K., Yao, X., 2009. Managing air quality in a rapidly developing nation: China. *Atmos. Environ.* 43, 79–86.
- Fuller, G.W., Sciare, J., Lutz, M., Moukhtar, S., Wagnier, S., 2013. New Directions: time to tackle urban wood burning? *Atmos. Environ.* 68, 295–296.
- Gu, J., Schnelle-Kreis, J., Pitz, M., Diemer, J., Reller, A., Zimmermann, R., Soentgen, J., Peters, A., Cyrys, J., 2013. Spatial and temporal variability of PM_{10} sources in

- Augsburg, Germany. *Atmos. Environ.* 71, 131–139.
- Han, J.S., Moon, K.J., Ryu, S.Y., Kim, Y.J., Perry, K.D., 2005. Source estimation of anthropogenic aerosols collected by a DRUM sampler during spring 2002 at Gosan, Korea. *Atmos. Environ.* 39, 3113–3125.
- Han, J.S., Moon, K.K., Lee, S.J., Kim, Y.J., Cliff, S.S., Yi, S.M., 2006. Size-resolved source apportionment of ambient particles by positive matrix factorization at Gosan background site East Asia. *Atmos. Chem. Phys.* 6, 211–223.
- Hien, P.D., Binh, N.T., Truong, Y., Ngo, N.T., Sieu, L.N., 2001. Comparative receptor modelling study of TSP, PM₂ and PM_{2.5–10} in Ho Chi Minh City. *Atmos. Environ.* 35, 2669–2678.
- Juda-Rezler, K., Reizer, M., Oudinet, J.P., 2011. Determination and analysis of PM₁₀ source apportionment during episodes of air pollution in Central Eastern Europe urban areas: the case of wintertime 2006. *Atmos. Environ.* 45, 6557–6566.
- Karar, K., Gupta, A.K., 2006. Seasonal variations and chemical characterization of ambient PM₁₀ at residential and industrial sites of an urban region of Kolkata (Calcutta), India. *Atmos. Res.* 81, 36–53.
- Kim, E., Hopke, P.K., Edgerton, E.S., 2003. Source identification of Atlanta aerosol by positive matrix factorization. *J. Air Waste Manag. Assoc.* 53, 731–739.
- Kim, E., Hopke, P.K., Pinto, J., Wilson, W., 2005. Spatial variability of fine particle mass, components, and source contributions during the regional air pollution study in St. Louis. *Environ. Sci. Technol.* 39, 4172–4179.
- Kleeman, M.J., Schauer, J., Cass, G.R., 1999. Size and composition distribution of fine particulate matter emitted from wood burning, meat charbroiling and cigarettes. *Environ. Sci. Technol.* 33, 3516–3523.
- Křůmal, K., Mikuška, P., Vojtěšek, M., Večeřa, Z., 2010. Seasonal variations of monosaccharide anhydrides in PM₁ and PM_{2.5} aerosol in urban areas. *Atmos. Environ.* 44, 5148–5155.
- Křůmal, K., Mikuška, P., Večeřa, Z., 2013. Polycyclic aromatic hydrocarbons and hopanes in PM₁ aerosols in urban areas. *Atmos. Environ.* 67, 27–37.
- Ogulei, D., Hopke, P.K., Zhou, L., Paatero, P., Park, S.S., Ondov, J.M., 2005. Receptor modelling for multiple time resolved species: the Baltimore supersite. *Atmos. Environ.* 39, 3751–3762.
- Oros, D.R., Simoneit, B.R.T., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel* 79, 515–536.
- Owoade, K.O., Hopke, P.K., Olise, F.S., Ogundele, L.T., Fawole, O.G., Olaniyi, B.H., Jegede, O.O., Ayoola, M.A., Muniru, I., Bashiru, M.I., 2015. Chemical compositions and source identification of particulate matter (PM_{2.5} and PM_{2.5–10}) from a scrap iron and steel smelting industry along the Ife–Ibadan highway, Nigeria. *Atmos. Pollut. Res.* 6, 107–119.
- Paatero, P., 1997. Least squares formulation of robust nonnegative factor analysis. *Chemom. Intellig. Lab. Syst.* 37, 23–35.
- Paatero, P., Hopke, P.K., 2003. Discarding or downweighting high-noise variables in factor analytic models. *Anal. Chim. Acta* 490, 277–289.
- Peré-Trepat, E., Kim, E., Paatero, P., Hopke, P.K., 2007. Source apportionment of time and size resolved ambient particulate matter measured with a rotating DRUM impactor. *Atmos. Environ.* 41, 5921–5933.
- Perry, K.D., Cliff, S.S., Jimenez-Cruz, M.P., 2007. Evidence for hygroscopic mineral dust particles from the Intercontinental Transport and Chemical Transformation Experiment. *J. Geophys. Res.* 109, D23S28.
- Pinto, J.P., Lefohn, A.S., Shadwick, D.S., 2004. Spatial variability of PM_{2.5} in urban areas in the United States. *J. Air Waste Manag. Assoc.* 54, 440–449.
- Pokorná, P., Hovorka, J., Kroužek, J., Hopke, P.K., 2013. Particulate matter source apportionment in a village situated in industrial region of Central Europe. *J. Air Waste Manag. Assoc.* 63, 1412–1421.
- Pokorná, P., Hovorka, J., Klán, M., Hopke, P.K., 2015. Source apportionment of size resolved particulate matter at a European air pollution hot spot. *Sci. Total Environ.* 502, 172–183.
- Polissar, A.V., Hopke, P.K., Paatero, P., Malm, W.C., Sisler, J.F., 1998. Atmospheric aerosol over Alaska—2. Elemental composition and sources. *J. Geophys. Res.* 103, 19045–19057.
- Qadir, R.M., Abbaszade, G., Schnell-Kreis, J., Chow, J.C., Zimmermann, R., 2013. Concentrations and source contributions of particulate organic matter before and after implementation of low emission zone in Munich, Germany. *Environ. Pollut.* 175, 158–167.
- Qadir, R.M., Schnell-Kreis, J., Abbaszade, G., Arteaga Salas, J.M., Diemer, J., Zimmermann, R., 2014. Spatial and temporal variability of source contribution to ambient PM₁₀ during winter in Augsburg, Germany using organic and inorganic tracers. *Chemosphere* 103, 263–273.
- Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., Rosa, J., Sánchez de la Campa, A., Artinano, B., Salvador, P., García Dos Santos, S., Fernández-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, Gil, J.I., Inza, A., Ortega, L.A., Santamaría, J.M., Zabalza, J., 2007. Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. *Atmos. Environ.* 41, 7219–7231.
- Raabe, O.G., Braaten, D.A., Axelbaum, R.L., Teague, S.V., Cahill, T.A., 1988. Calibration studies of the DRUM impactor. *J. Aerosol Sci.* 19, 183–195.
- Richard, A., Gianini, M.F.D., Mohr, C., Furger, M., Bukowiecki, N., Minguillón, M.C., Lienemann, P., Flechsig, U., Appel, K., DeCarlo, P.F., Heringa, M.F., Chirico, R., Baltensperger, U., Prevot, A.S.H., 2011. Source apportionment of size and time resolved trace elements and organic aerosols from an urban courtyard site in Switzerland. *Atmos. Chem. Phys.* 17, 8945–8963.
- Rogula-Kozłowska, W., Klejnowski, K., Rogula-Kopiec, P., Mathews, B., Szopa, S., 2012. A study of the seasonal mass closure of ambient fine and coarse Dust in Zabrze, Poland. *Bull. Environ. Contam. Toxicol.* 88, 722–729.
- Shen, S., Jaques, P.A., Zhu, Y., Geller, M.D., Sioutas, C., 2002. Evaluation of the SMPS-APS system as a continuous monitor for measuring PM_{2.5}, PM₁₀ and coarse (PM_{2.5–10}) concentrations. *Atmos. Environ.* 36, 3939–3955.
- Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos. Environ.* 33, 173–182.
- Sivacoumar, R., Bhanarkar, A.D., Goyal, S.K., Gadkari, S.K., Aggarwal, A.L., 2001. Air pollution modeling for an industrial complex and model performance evaluation. *Environ. Pollut.* 111, 471–477.
- Sun, Y., Zhuang, G., Wang, H., Guo, J., Dan, M., Zhang, W., Wang, Z., Hao, Z., 2004. The air-borne particulate pollution in Beijing – concentration, composition, distribution and sources. *Atmos. Environ.* 38, 5991–6004.
- Taiwo, A.M., Daddows, D.C.S., Calzolari, G., Harrison, R.M., Lucarelli, F., Nava, S., Shi, Z., Valli, G., Vecchi, R., 2014. Receptor modelling of airborne particulate matter in the vicinity of a major steelworks site. *Sci. Total Environ.* 490, 488–500.
- Thimmaiah, D., Hovorka, J., Hopke, P.K., 2009. Source apportionment of winter submicron Prague aerosols from combined particle number size distribution and gaseous composition data. *Aerosol Air Qual. Res.* 9, 209–236.
- Thorpe, A., Harrison, R.M., 2008. Source and properties of non-exhaust particulate matter from road traffic: a review. *Sci. Total Environ.* 400, 270–282.
- Vecchi, R., Chiari, M., D'Alessandro, A., Fermo, P., Lucarelli, F., Mayey, F., Nava, S., Piayyalunga, A., Prati, P., Silvani, F., Valli, G., 2008. A mass closure and PMF source apportionment study on the submicron aerosol fraction at urban sites in Italy. *Atmos. Environ.* 42, 2240–2253.
- Vecchi, R., Bernardoni, V., Fermo, P., Lucarelli, F., Mazzei, F., Nava, S., Prati, P., Piazzalunga, A., Valli, G., 2009. 4-hours resolution data to study PM₁₀ in “hot spot” area in Europe. *Environ. Monit. Assess.* 154, 283–300.
- 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., Wählin, P., Vecchi, R., Miranda, A.I., Kasper-Giebl, A., Maenhaut, W., Hiltzberger, R., 2008. Source apportionment of particulate matter in Europe: a review of methods and results. *J. Aerosol Sci.* 39, 827–849.
- Waked, A., Favez, O., Alleman, L.Y., Piot, C., Petit, J.-E., Delaunay, T., Verlinden, E., Golly, B., Besombes, Jaffrezo, J.-L., Leoz-Garziandia, E., 2014. Source apportionment of PM₁₀ in a north-western Europe regional urban background site (Lens, France) using positive matrix factorization and including primary biogenic emissions. *Atmos. Chem. Phys.* 14, 3325–3346.
- Wang, Y., Hopke, P.K., Xia, X., Chalupa, D.C., Zhang, Y., Utell, M.J., 2012. Source apportionment using positive matrix factorization on daily measurements of organic and inorganic speciated PM_{2.5}. *Atmos. Environ.* 55, 525–532.
- Watson, J.G., Chow, J.C., Houck, J.E., 2001. PM_{2.5} chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in north-western Colorado during 1995. *Chemosphere* 43, 1141–1151.
- Zhou, L., Hopke, P.K., Paatero, P., Ondov, J.M., Pancras, J.P., Pekney, N.J., Davidson, C.I., 2004. Advanced factor analysis for multiple time resolution aerosol composition data. *Atmos. Environ.* 38, 4909–4920.