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Air quality in the German–Czech border region: A focus on harmful fractions of PM and ultrafine particles



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HIGHLIGHTS

- Harmful contributions of ultrafine particles and PM concentration were determined.
- Vehicular PAH emissions were allocated to the Aitken mode.
- Traffic-related nucleation particles and soot particles dominate the ultrafines.
- Heavy metals and PAH in the accumulation mode are related to solid fuel combustion.
- Major sources of solid fuel combustion are soft wood and domestic coal combustion.

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ABSTRACT

A comprehensive air quality study has been carried out at two urban background sites in Annaberg-Buchholz (Germany) and Ústí nad Labem (Czech Republic) in the German–Czech border region between January 2012 and June 2014. Special attention was paid to quantify harmful fractions of particulate matter (PM) and ultrafine particle number concentration (UFP) from solid fuel combustion and vehicular traffic. Source type contributions of UFP were quantified by using the daily concentration courses of UFP and nitrogen oxide. Two different source apportionment techniques were used to quantify relative and absolute mass contributions: positive matrix factorization for total PM_{2.5} and elemental carbon in PM_{2.5} and chemical mass balance for total PM₁ and organic carbon in PM₁. Contributions from solid fuel combustion strongly differed between the non-heating period (April–September) and the heating period (October–March). Major sources of solid fuel combustion in this study were wood and domestic coal combustion, while the proportion of industrial coal combustion was low (<3%). In Ústí nad Labem combustion of domestic brown coal was the most important source of organic carbon ranging from 34% to 43%. Wood combustion was an important source of organic carbon in Annaberg-Buchholz throughout the year. Heavy metals and less volatile polycyclic aromatic hydrocarbons (PAH) in the accumulation mode were related to solid fuel combustion with enhanced concentrations during the heating period. In contrast, vehicular PAH emissions were allocated to the Aitken mode. Only in Ústí nad Labem a significant contribution of photochemical new particle formation (e.g. from sulfur dioxide) to UFP of almost 50% was observed during noontime. UFPs from traffic emissions (nucleation particles) and primary emitted soot particles dominated at both sites during the rest of the day. The methodology of a combined source apportionment of UFP and PM can be adapted to other regions of the world with similar problems of atmospheric pollution to calculate the relative risk in epidemiological health studies for different sub-fractions of PM and UFP. This will enhance the meaningfulness of published relative risks in health studies based on total PM and UFP number concentrations.

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1. Introduction

Most epidemiological evidence on health effects due to environmental aerosol particles has been derived from particulate matter (PM) mass concentrations as a metric (Krewski et al., 2003; R uckerl et al., 2011). Due to their nature as an integral parameter, total mass-based metrics are rather unspecific in their ability to identify the biological pathways of particle-related disease. Instead of PM₁₀ and PM_{2.5} (PM with aerodynamic diameter $\leq 10 \mu\text{m}$ and $\leq 2.5 \mu\text{m}$, respectively), specific sub-fractions of the environmental aerosol have been suspected to actually be responsible for the majority of the observed health effects. Epidemiological studies conducted in Europe (Ostro et al., 2011; de Hartog et al., 2009) and USA (Sarnat et al., 2008) found significant positive associations between PM_{2.5} concentrations attributed to traffic sources and cardiovascular health. Also positive associations between biomass combustion sources and cardiovascular disease-related emergency department visits (Sarnat et al., 2008) and cardiovascular health (Allen et al., 2011) were found. Usually, source apportionments techniques, e.g. chemical mass balance (CMB) and positive matrix factorization (PMF), were carried out for source identification in the past (Chow et al., 2007; Gu et al., 2011; Jaekels et al., 2007). However, most chemical compounds can be emitted from multiply types of sources, and thus a large variety of suitable chemical components is needed to identify specific sources.

Ultrafine particles (UFPs, particle diameter $< 100 \text{ nm}$) in urban air have gained attention due to a number of suspected health effects. Although contributing only little to particulate mass concentration, UFPs have considerable relevance for total particle number concentration. At present, only few epidemiological studies indicated that human morbidity and mortality are affected by ambient UFP number concentrations (Franck et al., 2011; Peters et al., 1997). As for PM, it is expected that some sources of UFP are more health relevant than other.

The overwhelming part of UFP in urban areas in continental Europe derives from human activities such as combustion processes and vehicular exhaust (Kumar et al., 2014; Morawska et al., 2008). There exist two accepted mechanisms for the development of UFP (HEI, 2013). First, UFP are emitted as primary particles during incomplete high-temperature combustion (e.g. through gasoline-powered and diesel-powered vehicles). These short-lived primary particles agglomerate to typical chain-like soot particles with a high surface area. During this process, organic, carcinogenic, and surface reactive substances are deposited on its surface. Second, UFP can originate from secondary gas-to-particle conversion (Kulmala et al., 2004). This means the homogeneous nucleation of sulfur dioxide (SO₂) oxidation products such as sulfuric acid and semi-volatile organic substances present in a polluted atmosphere (Riccobono et al., 2014; Sipil a et al., 2010). Typically, gas-to-particle conversion can be subdivided into photochemical-driven and high-temperature-combustion processes. Due to the molecular size of the precursor gases, the resulting UFP are only few nanometers in size. They can grow up in size up to 100 nm mainly due to condensation. During photochemical-driven processes, oxidation of precursor gases (e.g. SO₂) and conversion to particles take place at least if shortwave solar radiation is present (Boy and Kulmala, 2002; O'Dowd et al., 1999). During, high-temperature combustion processes, gas-to-particle conversion took place at any time and during dilution of hot gases with the colder environment (Giechaskiel et al., 2005).

The aim of this study is to quantify harmful sources with special attention to vehicular traffic and solid fuel combustion (wood combustion, domestic brown coal combustion, and industrial brown coal combustion) by combined measurements of UFPs and the chemical composition of PM. Sampling and chemical analysis of

various organic substances of PM is expensive and time consuming. Therefore, a combination of continuous (UFP) and quasi-continuous (PM_{2.5}) measurements as well as intensive field campaigns (PM₁) were carried out at two urban background sites Annaberg-Buchholz (Germany) and  st ı nad Labem (Czech Republic) between January 2012 and June 2014. The sites were chosen from a historically perspective. Before the end of the socialism era in 1990, the German–Czech border region was characterized by very poor air quality due to intensive industrial and domestic brown coal combustion. After the end of the socialism era, air quality has been steadily improving by the replacement of old heat stoves to individual gas and oil heating systems and renewal of brown-coal power plants. In recent time, a revival to combust cheap renewable resources, e.g. soft wood, appeared in this region due to rising oil and gas prices. Furthermore, the vehicular traffic has risen sharply in the last two decades and the fleet mix shifts from gasoline dominated passenger cars to a mix of gasoline and diesel passenger cars.

2. Experimental

2.1. Sampling site Annaberg-Buchholz (EU-code DESN001)

The sampling site Annaberg-Buchholz hereafter referred to as Annaberg (50° 34' 15" N, 12° 59' 50" E, and 559 m a.s.l) is situated in a small city of about 20.000 inhabitants on the foothills of the Ore Mountains. The website of the European Environment Agency (EEA, 2015) provides an interactive geographical map to explore the surrounding area by inserting the station name and corresponding EU-code. The sampling site is situated in a north-to-south directed valley and thus, accompanying meteorological parameters, e.g. prevailing wind direction and solar radiation, are influenced. Solar radiation, which triggers photo-chemically induced new particle formation, shows orographic-induced shadowing effects in the morning hours. The sampling site is also influenced by road traffic from a main road (B101), which passes the site in a distance of about 10 m. The annual average is about 17.000 vehicles per day, which is calculated from hourly traffic counting data. Additional particulate emission sources in the surroundings are domestic heating, a paper mill, two metalworking industries, and a stone quarry in a distance of 5.5 km. A 800 MW brown coal-fired power station Tušimice (Czech Republic) is located 32 km south-east of Annaberg and can affect air quality.

2.2. Sampling site  st ı nad Labem-m esto (EU-code CZOUJLM)

The city  st ı nad Labem hereafter referred to as  st ı (Labe is Czech language name for Elbe River, 39° 40' N, 14° 2' 35" E, and 147 m a.s.l) has a population of about 94.000 and is located in the  st ı region, which joins the border to Saxony State (Germany). Air quality in  st ı is influenced by chemical industry and a number of brown coal power plants for energy production in a large area west of the city. In contrast to Annaberg, large industrial plants have settled within the city long time ago, e.g. traditional chemical company for production of synthetic resins, an oilseed processing company, and a thermal power plant. Additionally, small metalworking industries are settled on the outskirts of  st ı. Due to the location at the Elbe River, the city is an important traffic junction in direction to Germany. A main road (1st category road No. 30) is an important entry/exit road with an annual mean of 16.500 vehicles per day. The sampling site for UFP is located in the residential area of the city center. Due to small residential roads in the vicinity of the measurement container, the influence by traffic emissions is lower than in Annaberg. Although most of the instrumentation was sitting inside the sampling container, measurements of size-

segregated PM were carried out with field devices on the enclosed area of Public Health Institute, which is 1 km away from the UFP sampling site.

2.3. Measurement and analysis of ultrafine particle number concentration

At both sites, UFP number concentrations were measured continuously with a mobility particle size spectrometer designed by the Leibniz Institute for Tropospheric Research (TROPOS), Leipzig, Germany, following the recommendations of ACTRIS (Wiedensohler et al., 2012). The time resolution of the raw data is 5 min and the nominal particle size range is from 10 to 800 nm. The time stamp of the measurement was Central European Time (CET = UTC + 1). A calculation routine transferred the raw data into a true particle number size distribution (Pfeifer et al., 2014). Finally, the data were averaged to a time interval of 1 h and the particle number size distribution was integrated in the size range from 10 to 100 nm yielding the UFP number concentration. Maintenance work was done twice a month following the recommendations (Wiedensohler et al., 2012). To maintain stable instrument operation, on-site comparisons with reference mobility particle size spectrometer were performed six times a year. Additionally, data quality at the Annaberg site was checked quasi-continuously to the rather sporadic on-site comparisons (Schladitz et al., 2014). From these instrument checks, we derived an average measurement uncertainty for three different size ranges as follows: $\pm 50\%$ (10–20 nm), $\pm 10\%$ (20–200 nm), and $\pm 20\%$ (200–800 nm).

2.4. Measurement and chemical composition of size-segregated particulate matter

Mass concentrations of PM_{2.5} was measured at both sites every 6th day. PM_{2.5} was collected on 150 mm quartz filters using a high-volume sampler DHA-80 (Digital Elektronik AG, AlteGasse 18, Hegnau, Switzerland) for a 24 h period (from midnight to midnight). Before and after being sampled, all filters were equilibrated for 48 h at 50% relative humidity before weighing by a micro balance according to the European standard EN 12341. For quality assurance reasons of determining particle mass, blank filters were handled in a same way as probed filters. After weighing, filter probes were transported for analysis of water soluble ions, carbon fraction, polycyclic aromatic hydrocarbons (PAHs), and heavy metals (in total 25 chemical compounds) to the environmental laboratory TÜV Süd, Dresden, Germany.

Due to different used filter materials, collection of PM₁ filter probes at one site was always done by a set of two instruments: A high-volume sampler DHA-80 and an URG 3000 sampler (URG Corporation, Chapel Hill, NC, USA) both equipped with PM₁ pre-separators. The DHA-80 collected particles for analysis of organic compounds on preheated Munktell quartz filters followed by polyurethane foam (PUF), while the URG 3000 collected particles for gravimetric determination on Millipore Nuclepore filters. Sampling was performed during four measurement campaigns, two during the heating period (October–March) and two during the non-heating period (April–September) for both sites. Each campaign lasted 13 days, starting in Ústí followed by Annaberg. The sampling duration was 24 h beginning at 8:00 a.m. In total, 105 chemical compounds were analyzed including water soluble ions, carbon fraction, n-alkanes, alkenes, hopanes, PAHs, alcohols, sterols, acids, and 10 other tracer compounds.

Almost concomitantly with the collection of the PM₁ filter probes, particles were deposited on filters using a ten-stage micro-orifice uniform deposit impactor MOUDI (MSP Corporation, Shoreview, MN, USA). The size intervals in aerodynamic diameter

(D_{p,aero}) are: 0.056–0.1 μm, 0.1–0.18 μm, 0.18–0.32 μm, 0.32–0.56 μm, 0.56–1 μm, 1–1.8 μm, 1.8–3.2 μm, 3.2–5.6 μm, 5.6–10 μm, and 10–18 μm. Particles were analyzed for 12 PAHs as well as for 17 trace elements, which required again two types of filter media. Therefore, each campaign was split into two parts, collecting first PAHs with PALL Teflon[®]-coated glass microfiber filters and second trace elements with Whatman Nuclepore filters. Probed and blank Nuclepore filters were transported to Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering for analysis. Details about the analyzed chemical compounds of PM_{2.5}, PM₁, and MOUDI as well as used measurement techniques, protocol or reference, detection limit, and measurement uncertainty can be found in the supplement.

Measured values below the detection for each chemical compound of PM₁ and PM_{2.5} were replaced by the half of the detection limit. Mean values and standard deviations for the heating and non-heating periods are summarized in the supplement.

3. Receptor modeling

Receptor models are statistical procedures for identifying and quantifying the sources of air pollutants at a receptor site. They use the chemical and physical characteristics of particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations. For the quantification of different sources of UFP, PM₁ and PM_{2.5} two state-of-the-art receptor models, Chemical Mass Balance (CMB) and Positive Matrix Factorization (PMF) were used.

For several reasons, we investigate the sources of PM₁ and PM_{2.5} with two different methods: PMF for PM_{2.5} and CMB for PM₁. The main difference between CMB and PMF is that the CMB-model is fully constrained, which means a priori information in the form of known source profiles (factor profiles) is a must. Due to the large number of analyzed organic chemical compounds in PM₁, it is possible to use source profile information from literature, which allowed a clear identification of sources (e.g. split vehicular traffic sources into gasoline and diesel exhaust). In contrast, PMF requires no additional information about factor profiles and the number of factor profiles. Due to rather unspecific (related to the sources) and comparatively small number of analyzed chemical compounds, we used the PMF model for source identification of PM_{2.5}. This study used the ME-2 solver (Paatero, 1999), controlled by an IGOR Pro based graphical user interface called SoFi (Canonaco et al., 2013) for source apportionment of PM_{2.5}. EPA's chemical mass balance model CMB 8.2 was applied to quantify the sources of the organic aerosol composition in PM₁ using 10 predefined factor profiles. In summary, both models the CMB on the one hand and the PMF on the other hand are important for this study. PMF results are more representative for the average chemical composition of both sites, while results for CMB are based on environmental conditions for the time period when the intensive field campaign was carried out in favor for an in-depth identification of sources.

3.1. Source apportionment of ultrafine particles

This section presents a simple deterministic method to separate the contributions of UFPs originating from photochemical and traffic-induced gas-to-particle formation processes and primary emitted particles. The four steps to separate the contribution of UFPs are illustrated in Fig. 1. In step one, PMF (ME-2 solver) was applied to particle number size distributions (21 size bins, 1 h time resolution) in the UFP size range. The error matrix was calculated by multiplying bin-wise the uncertainties with the particle concentration. Obtained factor profiles represent nucleation, Aitken, and accumulation mode particles. In step two, a mean daily course

was calculated for the three particle modes from the factor time series.

In step three, a synthetic daily course of the traffic-induced number concentration of nucleation particles ($PN_{\text{nucl.traffic}}$) was calculated based on the mean diurnal nitrogen oxide (NO_x) concentration. Here, NO_x is used as a tracer for a variety of semi-volatile compounds emitted from local traffic, which were not measured so far. To calculate $PN_{\text{nucl.traffic}}$, a calibration factor was determined. This calibration factor was derived from the nighttime concentration of nucleation particles (local minimum typically between 1 and 4 CET), by dividing the nucleation particle number concentration ($PN_{\text{nucl.}}$) through the NO_x concentration. The nighttime concentration was selected because no other sources contributing to particle nucleation are expected. Finally, the site-specific calibration factor was multiplied with the daily course of the NO_x concentration to receive $PN_{\text{nucl.traffic}}$. In step four, $PN_{\text{nucl.traffic}}$ was subtracted from $PN_{\text{nucl.}}$ to receive a number concentration of nucleation particles from photochemical gas-to-particle conversion processes ($PN_{\text{nucl.SO}_2}$).

3.2. Source apportionment of $PM_{2.5}$ and elemental carbon

Sources of elemental carbon are related to the particle fraction $<2.5 \mu\text{m}$. The data and error matrix for the PMF analysis consists of daily concentration (rows) and chemical compounds of $PM_{2.5}$ (columns). New Year's Eve and Walpurgis Night (30 April) were excluded from the data matrix due to strong fireworks activities. The number of chemical compounds was reduced from formerly 25 to 16, by summarizing (sum) all less volatile PAHs to a single compound. The error matrix was calculated by multiplying each concentration value with the compound specific uncertainty specified in the supplement. To find out the most reasonable sources of $PM_{2.5}$ at both receptor sites, PMF analysis was carried out by varying the number of factors from 3 to 6. The 4-factors solution was not capable to split sulfate-rich and nitrate-rich particles, because the SO_4^{2-} and NO_3^- anions share the same NH_4^+ cation. The

5-factors solution did not separate the trace elements for solid fuel combustion and re-suspended (road) dust correctly. The solution failed since potassium revealed as a trace element for both sources and the concentration predominates in winter during wood combustion. The 6-factors solution was chosen and 50 seed runs were investigated to search for the minimum Q/Q_{exp} value. The lowest Q/Q_{exp} for Annaberg and Ústí was found to 4.94 and 3.43, respectively. Source apportionment of $PM_{2.5}$ revealed the following six sources:

- vehicular traffic (local)
- solid fuel combustion (local)
- secondary nitrate-rich particles (long-range transport)
- secondary sulfate-rich particles (long-range transport)
- re-suspended dust (local)
- de-icing salt (local)

Detailed information about the chemical composition for each source and the residual matrix (difference between measured and modeled values) is given in the supplement.

3.3. Source apportionment of PM_1 and organic carbon

Sources of organic carbon (OC) are related to the particle fraction $<1 \mu\text{m}$. The selection of chemical compounds is crucial in a way that all major sources should be included in the model and the species should be conserved during transport from the sources to the receptor sites. In total 61 chemical compounds were used for the CMB (highlighted in bold in the supplement).

An uncertainty of $\pm 25\%$ for each organic compound was used to simplify the CMB modeling. Ten sources were identified in this study contributing to organic carbon (references for source profiles in brackets):

- diesel exhaust (Schauer et al., 1999)
- gasoline exhaust (Schauer et al., 2002b)
- domestic brown coal combustion (see the Supplement)

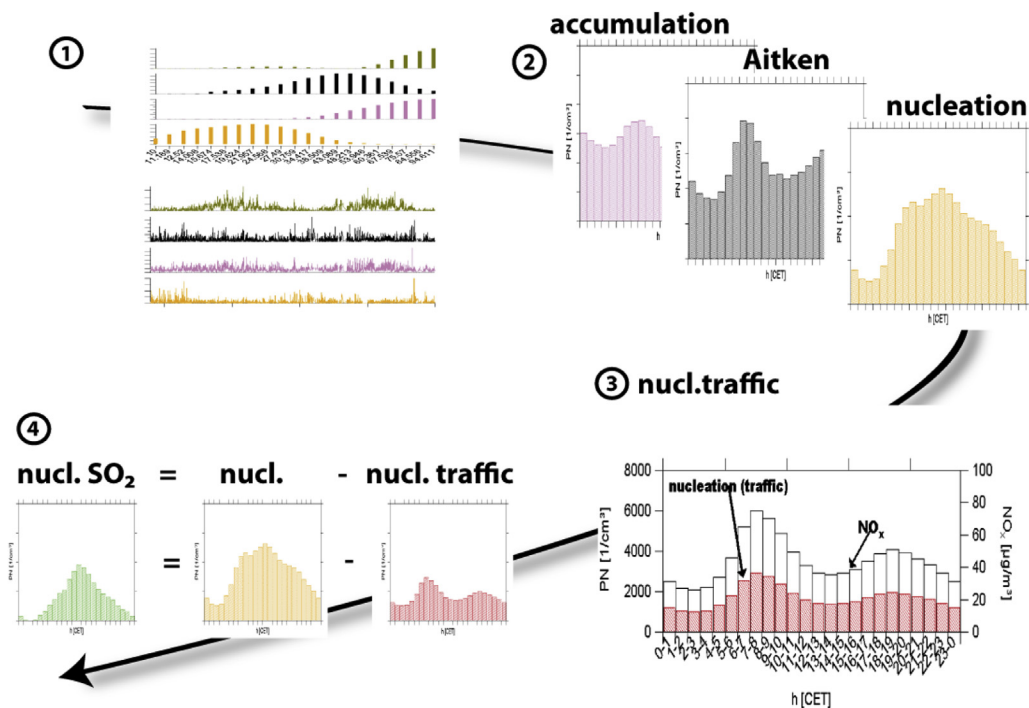


Fig. 1. Flow chart of source apportionment of ultrafine particles.

- industrial brown coal combustion (Zhang et al., 2008)
- wood combustion (Schauer et al., 2001)
- cooking (Zhao et al., 2007)
- gas combustion (Rogge et al., 1993c)
- garbage combustion (Simoneit et al., 2005)
- plant abrasion (Rogge et al., 1993b)
- re-suspended dust (Rogge et al., 1993a)

Based on recommendations from EPA's CMB user manual, performance measures for the least square calculation are in the range of the target values, which are enclosed in brackets: % mass explained by the model = 82.5% ($100 \pm 20\%$), $R^2 = 0.79$ (0.8–1.0), $\chi^2 = 3.3$ (0–4.0), and degree of freedom = 40 (>5). Contributions of organic carbon in PM₁ were averaged for heating and non-heating periods and divided through the OC/PM_{fine} ratio yielding average PM₁ source contributions. OC/PM_{fine} ratios were inferred from the literature and mean values are given for references with more than one OC/PM_{fine} ratio per source. They are as follows: diesel exhaust = 0.294 (Hildemann et al., 1991; Rogge et al., 1993a; Schauer et al., 1999), gasoline exhaust = 0.479 (Hildemann et al., 1991; Rogge et al., 1993a; Schauer et al., 2002b), domestic brown coal combustion = 0.409 and industrial brown coal combustion = 0.171 (Zhang et al., 2008), wood combustion = 0.530 (Hildemann et al., 1991; Schauer et al., 2001), cooking = 0.481 (He et al., 2004; Schauer et al., 2002a; See and Balasubramanian, 2008), garbage combustion = 0.209 (Simoneit et al., 2005), gas combustion = 0.849, plant abrasion = 0.324, and re-suspended dust = 0.135 (Hildemann et al., 1991). Other organic mass (other OM) was calculated by multiplying the unexplained OC (difference between calculated and measured OC) by a factor of 1.4 (Harrison et al., 2003).

4. Results and discussion

4.1. Sources of ultrafine particles

In Figs. 2 and 3, the mean diurnal contributions of $PN_{\text{nucl.SO}_2}$, $PN_{\text{nucl.traffic}}$, and the Aitken mode particle concentration ($PN_{\text{Aitken.traffic}}$) are presented. $PN_{\text{Aitken.traffic}}$ correlates significantly with the daily course of black carbon concentration with $R^2 = 0.81$ for Annaberg and $R^2 = 0.72$ for Ústí, representing primary emitted soot particles from local traffic and slightly from domestic activities. In Ústí the contribution of $PN_{\text{nucl.SO}_2}$ is much more pronounced than in Annaberg. The mean diurnal cycle looks like a triangle with highest concentration of about 4000 particles/cm³ around noon, accompanying with the highest shortwave global radiation of the day. During noon, almost half of UFP in Ústí are produced by photochemical processes. We suggest that the reason for this is the higher annual SO₂ concentration of 6.9 µg/m³ compared to 3.7 µg/m³ for Annaberg. Comparing the local traffic-induced contributions to UFP on both sites, we can conclude higher concentration of primary emitted Aitken particles ($PN_{\text{Aitken.traffic}} = 1703\text{--}3936$ particles/cm³) but lesser particles from the exhaust gases ($PN_{\text{nucl.traffic}} = 1041\text{--}2964$ particles/cm³) in Ústí. The corresponding minimum and maximum values for Annaberg are: $PN_{\text{Aitken.traffic}} = 1031\text{--}2678$ particles/cm³ and $PN_{\text{nucl.traffic}} = 829\text{--}4287$ particles/cm³. The Annaberg site has lower concentration of primary emitted Aitken particles compared to the Ústí site. In contrast, the traffic-induced nucleation particles behave inversely, with lower concentration during the day in Ústí compared to Annaberg. This is explained by the fact that semi-volatile material condenses preferably on the large surface area of the pre-existing soot particles (Imhof et al., 2006). If there is only a small surface area available, which is the case for Annaberg, new particles are formed by homogeneous nucleation. Our results were

compared with an approach based on regression analysis between UFP and particle concentration of equivalent black carbon (mass-specific absorption cross section of 6.6 m²/g) to determine the contributions of primary emitted particles and new formed particles to UFP (Rodríguez and Cuevas, 2007). Absolute UFP number concentrations are not appropriate for comparison due to different lower particle detection limits of the instruments. Nevertheless, the maximum contribution of primary emitted particles to total UFP of about 55% appears in the morning rush hours between 07:00–08:00 and agreed with our results. The contribution of newly formed particles in the study of Rodríguez and Cuevas is comparable to the sum of photochemical and traffic-induced gas-to-particle conversion in our study. Both studies revealed a daily evolution with a maximum during daytime contributing at least to 50% of total UFP. The results are consistent that this value is highly controlled by the concentration of SO₂ and the amount of solar radiation.

4.2. Size-segregated composition of trace elements and PAHs during heating and non-heating periods

As previously mentioned PAHs and trace elements measurements using MOUDI were not operated continuously and are not synchronous at both receptor sites. Therefore, only a distinction between non-heating and heating periods was made. However, our measurements provide important information of typical markers (e.g. trace elements) for solid fuel combustion, re-suspended dust, and vehicular emissions that will be useful for the interpretation of source apportionment results. Figs. 4 and 5 shows the particle mass size distribution of the elemental composition for the heating and non-heating period. Comparable particle mass size distributions of different elements were combined in one panel. Finally, we obtain three different particle mass size distributions that are visualized in three panels a, b, and c for Annaberg as well as for Ústí. Panel a) reveals highest concentration of lead (Pb), arsenic (As), selenium (Se), bromine (Br), potassium (K), and sulfur (S) in the accumulation mode for both sites. Interestingly, the peak concentration shifts to lower sizes during the non-heating period. The similarity of the particle mass size distributions in Fig. 4a and from selected PAHs in Fig. 6 with $R^2 = 0.67$ for Annaberg and $R^2 = 0.62$ for Ústí, suggests that these are markers mainly from the same source. The main source of crustal metals (e.g. aluminum (Al), silicon (Si), K, calcium (Ca), iron (Fe), copper (Cu), and titanium (Ti)) can be attributed to the re-suspension of dust at both source and receptor sites (Singh et al., 2002). All these crustal materials are predominantly present in >1 µm particles (cf. Figs. 4b and 5b) with highest concentration during the non-heating period due to intensified re-suspension of road dust. The re-suspension of road dust is also traffic induced, due to enhanced concentration of about 80 ng/m³ of the brake abrasion marker Fe in the size range from 2.5 to 5.6 µm. K was also identified as an important trace element from fireplace combustion of wood (Schauer et al., 2001). Therefore, it is enhanced in the size range >1 µm during the non-heating period and enhanced in the accumulation mode during the heating period. Highest concentrations of chromium (Cr) and nickel (Ni) (panel c) were observed in the Aitken and coarse mode. Cr and Ni were implicated with exhaust emission and brake wear from local traffic (Johansson et al., 2009; Zechmeister et al., 2006). Sources of the additionally peak in the accumulation mode in Ústí could be oil combustion (Ni) and metalworking industries in the outskirts of the city.

Residential heating with wood fires, as well as vehicular emissions, are considered the main sources of PAHs in urban and near-city environments (Marchand et al., 2004). From the analyzed PAHs (see the supplement), pyrene, fluoranthene, phenanthrene, and

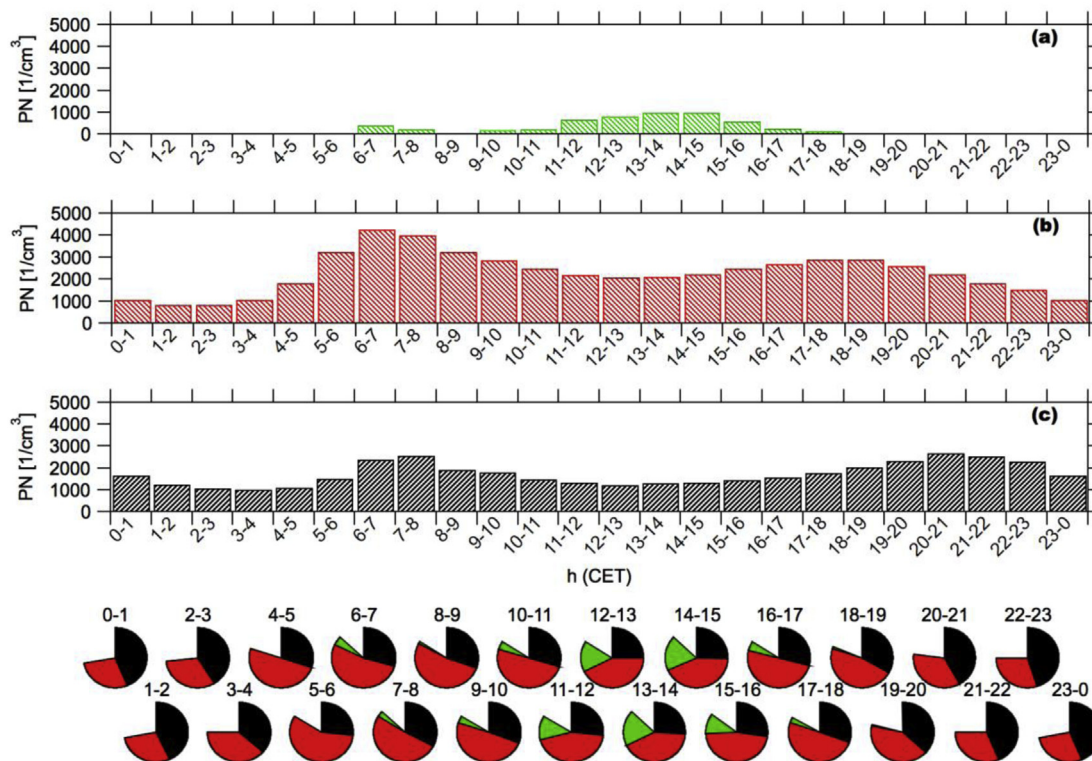


Fig. 2. Diurnal split of ultrafine particle number concentration in Annaberg into absolute (upper diagrams) and relative source type contributions (pie charts). Contributions were estimated from photochemical gas-to-particle conversion processes of sulfur dioxide (a, green color), traffic-induced gas-to-particle conversion processes (b, red color), and from primary emitted soot particles (c, black color). The unfilled transparent wedge represents the accumulation mode particles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

anthracene are the most volatile (Peters et al., 2000). In our case, the particle mass size distributions are similar for the less volatile PAHs ($\log [p_i] \leq -3.2$), but different for the more volatile PAHs ($\log [p_i] \geq -2.06$) caused by the difference of the mean temperature between non-heating and heating periods. Therefore, Fig. 6 presents only the less volatile PAHs for both periods such as benzo(b)fluoranthene (BbF), chrysene (Chr), benz(a)anthracene (BaA), benzo(g,h,i)perylene (BghiP), benzo(a)pyrene (BaP), benzo(k)fluoranthene (BkF), and indeno(1,2,3-cd)pyrene (InP). They show highest concentration in the accumulation mode during the heating period for both sites obviously caused by residential wood and coal burning. Especially during the colder heating period, particulate PAHs in the Aitken mode are enhanced in Annaberg due to the fact that this site is more affected by vehicular emissions (cf. section 2.1). This is in agreement with emission measurements of gasoline and diesel vehicles in the US, which revealed peak concentration of four-through six-ring PAHs in the MOUDI stages 0.1–0.18 μm , 0.18–0.32 μm , and 0.32–0.56 μm (Zielinska et al., 2004).

4.3. Organic carbon composition of PM_1

In this chapter we investigate the composition of organic carbon (OC) based on the PM_1 filter measurements. Different markers and indices are presented to characterize the aerosol in the German–Czech border region differentiated between non-heating and heating periods.

4.3.1. N-alkanes, carbon preference index, and unresolved complex mixtures of hydrocarbons

N-Alkanes (NA) are an important part of organic aerosol in urban and rural environments. They are emitted by natural sources

from plants as well during combustion of fossil fuels. Generally, n-alkanes were monitored in a range of C_{13} (n-tridecane) to C_{35} (n-pentatriacontane). The Carbon Preference Index ($\text{CPI} = \Sigma \text{C}_{2n+1} / \Sigma \text{C}_{2n}$) is a single value expressing the ratio of odd carbon (C_{2n+1}) to even carbon n-alkanes (C_{2n}) that was used to differentiate biogenic from anthropogenic n-alkanes in organic particulate matter (Didyk et al., 2000; Gogou et al., 1996; Simoneit and Mazurek, 1982).

N-alkanes from epicuticular waxes of terrestrial plants exhibit high values of $\text{CPI} \gg 1$, whereas CPI values for anthropogenic emissions are ~ 1 . The CPI values at both sampling sites were close to one (1.11–1.28) both for the non-heating and heating period, which clearly demonstrates the importance of anthropogenic sources of n-alkanes.

The unresolved complex mixture of branched and cyclic hydrocarbons (UCM) to resolved n-alkanes ratio UCM/NA can be used as a marker to indicate incompletely combusted hydrocarbons from vehicle traffic (Simoneit, 1985). Wood and coal combustion exhibit UCM/NA ratios from 2.3 to 3.9 whereas vehicular emissions result in ratios higher than 4.0 (Kavouras et al., 2001). Higher values found in summer periods (8.10–9.39) suggest the importance of traffic emissions. Much lower UCM/NA ratios in winter (2.73–4.36) indicate the impact of domestic heating sources in the aerosol composition at both sites.

4.3.2. Hopanes

For this study, the four most abundant hopanes: $17\alpha(\text{H})$ - $21\beta(\text{H})$ norhopane, $17\alpha(\text{H})$ - $21\beta(\text{H})$ hopane, 22S $17\alpha(\text{H})$ - $21\beta(\text{H})$ homohopane, 22R $17\alpha(\text{H})$ - $21\beta(\text{H})$ homohopane were quantified.

The homohopane index ($i_{\text{hh}} = \text{S}/(\text{S} + \text{R})$) is defined as the ratio of $17\alpha(\text{H})$ - $21\beta(\text{H})$ homohopane R and S epimers and enables to distinguish between different coal types and traffic emissions (Oros

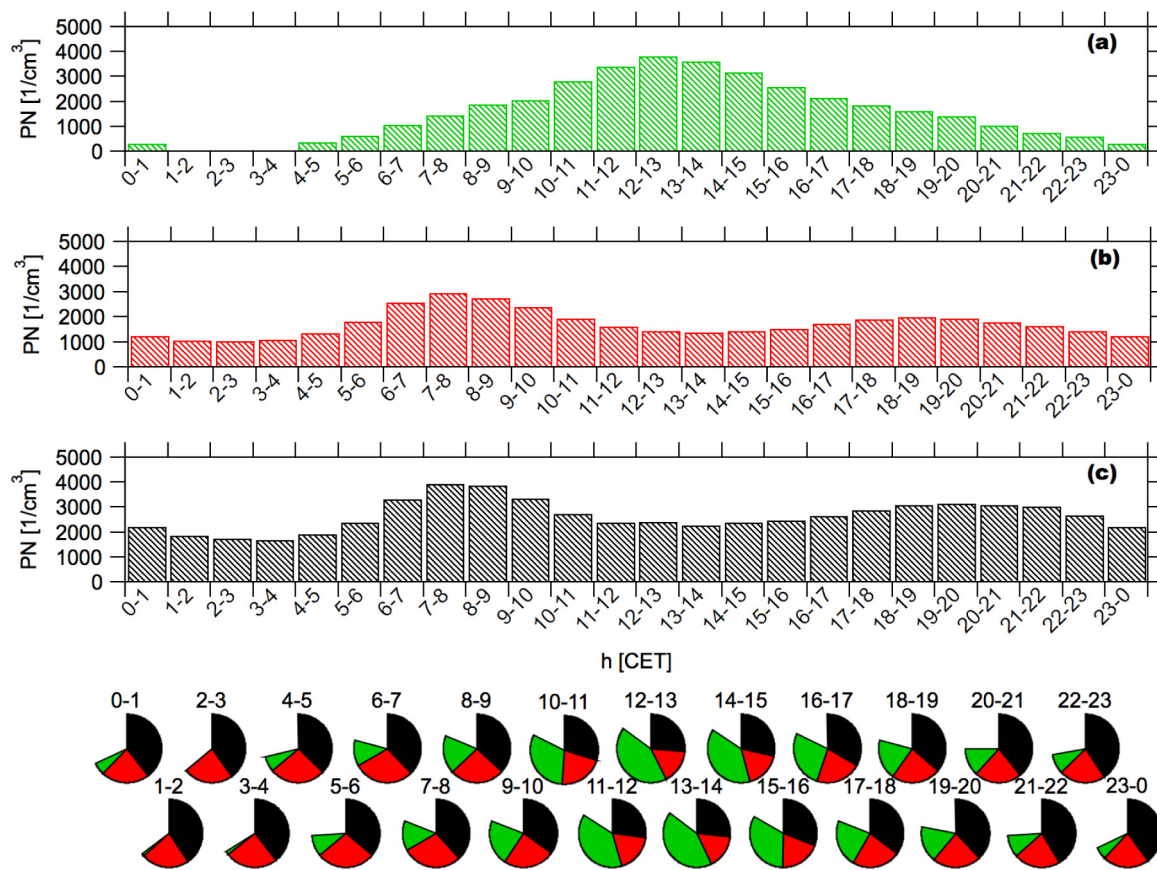


Fig. 3. Same as Fig. 2 but for Ústí.

and Simoneit, 2000).

Generally, higher hopanoid ratios are measured from vehicular emissions than from brown coal combustion. Table 1 displays hopanoid ratios for the different periods. By comparing literature data from traffic and brown coal mines in the region of study, we exhibit a mixed character with prevailing coal combustion during the heating period and traffic emissions in the non-heating period at both sampling sites. Tetracyclic diterpenes are other organic constituents which were isolated from various German coals (Schulze and Michaelis, 1990), lignite from Slovakia – Handlová (Zubrik et al., 2009), and fossil wood from North Bohemia – Bílina. Bouska et al. (1998) described very pure material found in Bílina coal corresponding to hartite (16 α (H)-phylocladane). This compound was identified and quantified in brown coal combustion emissions and in ambient air in this project. High concentrations of phyllocladane were measured in urban air samples in Ústí and close correlation ($R^2 = 0.897$) of 16 α (H)-phylocladane to 22R 17 α (H)-21 β (H) homohopane was found in winter 2012. Thus, phyllocladane can be proposed as a specific marker of brown coal combustion in this region.

4.3.3. PAHs

The concentration ratios of PAHs have been used to reconcile their presence with potential emission sources (Takada et al., 1990). The ratio of the sum of concentration of major non-alkylated compounds (italics in the supplement), expressed as combustion-related PAHs (CPAHs), to the total concentration of PAHs (TPAHs) has often been used as a characteristic value for PAHs produced by combustion (Gogou et al., 1996). CPAHs/TPAHs values between 0.30 and 0.51 are related to gasoline and diesel combustion (Rogge et al.,

1993d), while values around 0.7 is attributable to solid fuel combustion. In our study, CPAHs/TPAHs ratios ranged from 0.45 to 0.48 (heating period) to 0.36–0.37 (non-heating period). These values confirm the findings and conclusions from the previous sections.

4.3.4. Anhydrous sugars

Cellulose decomposes at temperatures >300 °C yielding source specific molecular tracers mainly levoglucosan, mannosan, and galactosan (Orasche et al., 2012; Schauer et al., 2001). Levoglucosan has been described as a tracer for biomass combustion from any cellulosic material (Simoneit et al., 1999). The different ratio of levoglucosan to mannosan in hardwood (14–15) and soft wood (3.6–3.9) can be used to estimate the proportion of soft- and hardwood combustion with the following equation (Schmidl et al., 2008): % soft wood = $(14.8 - R_{\text{levo/man}})/0.112$. In the 2 sampling sites, wood combustion appears to be dominated by soft wood at both sites ranging from 58% to 98%. These results are in a good agreement with measurements made during the European EUCAARI project (Alves et al., 2012).

4.3.5. Cholesterol and monoglycerides

The emissions of organic compounds in smoke from meat cooking include e.g. n-alkanes, n-alkanoic acids, n-alkenoic acids, n-alkanals, n-alkanols, furans, lactones, amides, and cholesterol (He et al., 2004; McDonald et al., 2003). The above mentioned emitted compounds have many other sources (Mohr et al., 2009), therefore cholesterol and monoglycerides (glycerol monopalmitate and monostearate) were proposed as tracers for atmospheric particles generated by meat cooking (Nolte et al., 1999). N-alkanoic acids (C₁₄, C₁₆, C₁₈), glycerol monopalmitate, glycerol monostearate,

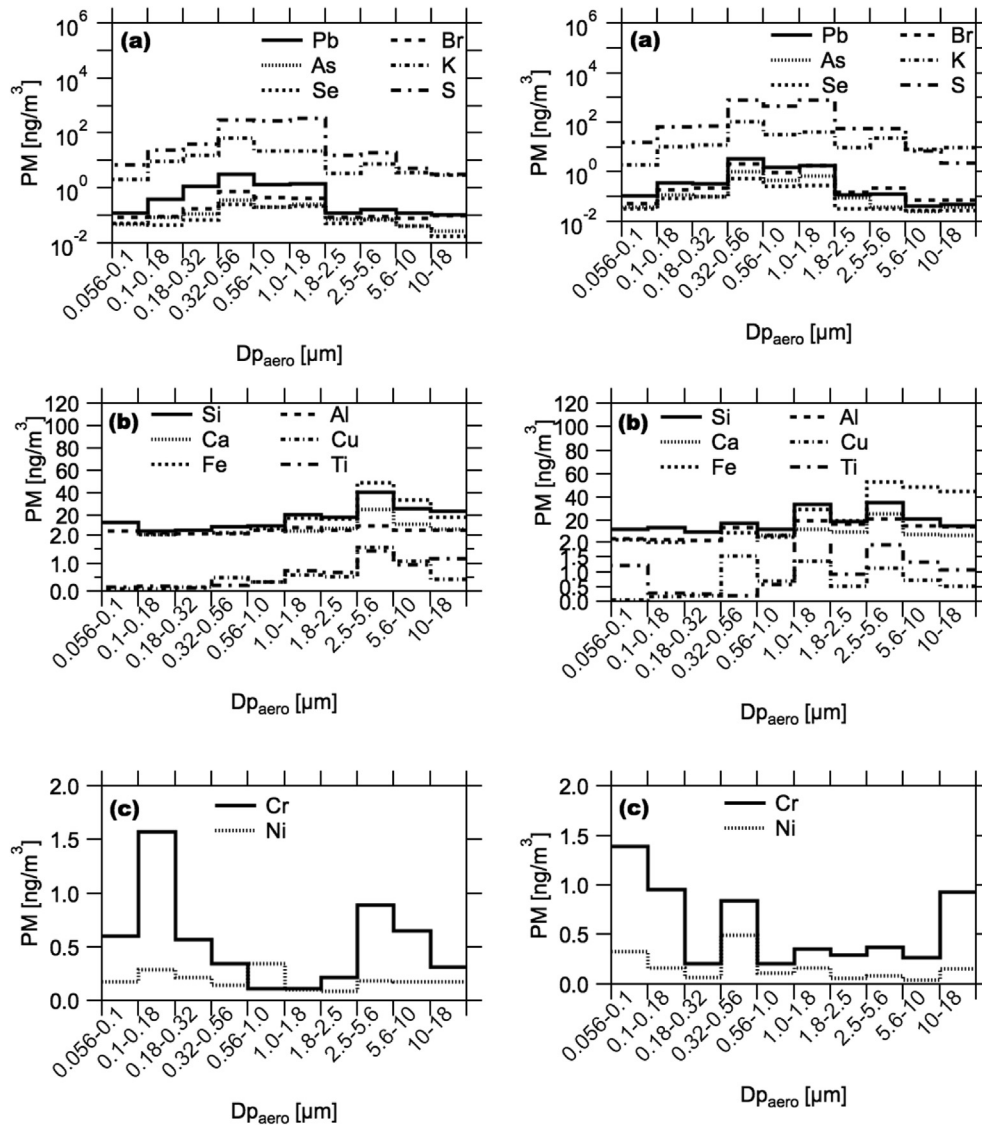


Fig. 4. Particle mass size distribution of elemental chemical composition for Annaberg (left) and Ústí (right) during the heating period (October–March).

cholesterol, and sitosterol were used in this study as markers of cooking and grilling.

4.3.6. 1,3,5-Triphenylbenzene

Plastics are an important part of domestic waste, because they are readily combustible and generate black smoke and toxic decomposition as well as volatilization products. Major compounds in smoke from burning plastics include no specific compounds such as aliphatic hydrocarbons, 1,4-dibenzoic acid, phthalates, bisphenol A, and 4-hydroxybenzoic acid with minor concentration of PAHs and oxy-PAHs (Christian et al., 2010; Sidhu et al., 2005). Significant concentrations of 1,3,5-triphenylbenzene was found in regions where refuse is burned in open fires (e.g. 17–44 ng/m³ in Santiago de Chile). Thus, this compound was proposed as a specific tracer for plastic combustion (Simoneit et al., 2005). In our study mean concentrations of 1,3,5-triphenylbenzene ranged from 0.06 to 0.28 ng/m³. Despite of a peak concentration of 2.07 ng/m³ on one day in Annaberg in summer 2012, no significant differences between the sites and during the periods were observed.

4.4. Sources of PM_{2.5} and elemental carbon

The scope of this section is to present relative and absolute contributions of PM_{2.5} and elemental carbon sources for the heating and non-heating period at both receptor sites. Pie charts illustrate the relative source contributions for PM_{2.5} and elemental carbon for the heating and non-heating period for Annaberg (Fig. 7) and Ústí (Fig. 8). Absolute source contributions calculated by the model are given in μg/m³. The mean ratio of total modeled source contributions of PM_{2.5} to measured PM_{2.5} mass concentration is 62% for Annaberg and 51% for Ústí. The absolute source contributions for PM_{2.5} for the heating and non-heating period were calculated as a mean from the factor time series split. Nearly the same procedure was applied to calculate the source contribution of elemental carbon, but previously the factor time series were weighted with the corresponding factor profile for EC. Vehicular traffic, solid fuel combustion, re-suspended road dust, and de-icing salt, which we suppose that they are mainly locally produced are outlined by a thick black line in the pie charts. More than one third of PM_{2.5} is locally produced during the heating period (around 20% during the non-heating period). The main pollutants are solid fuel

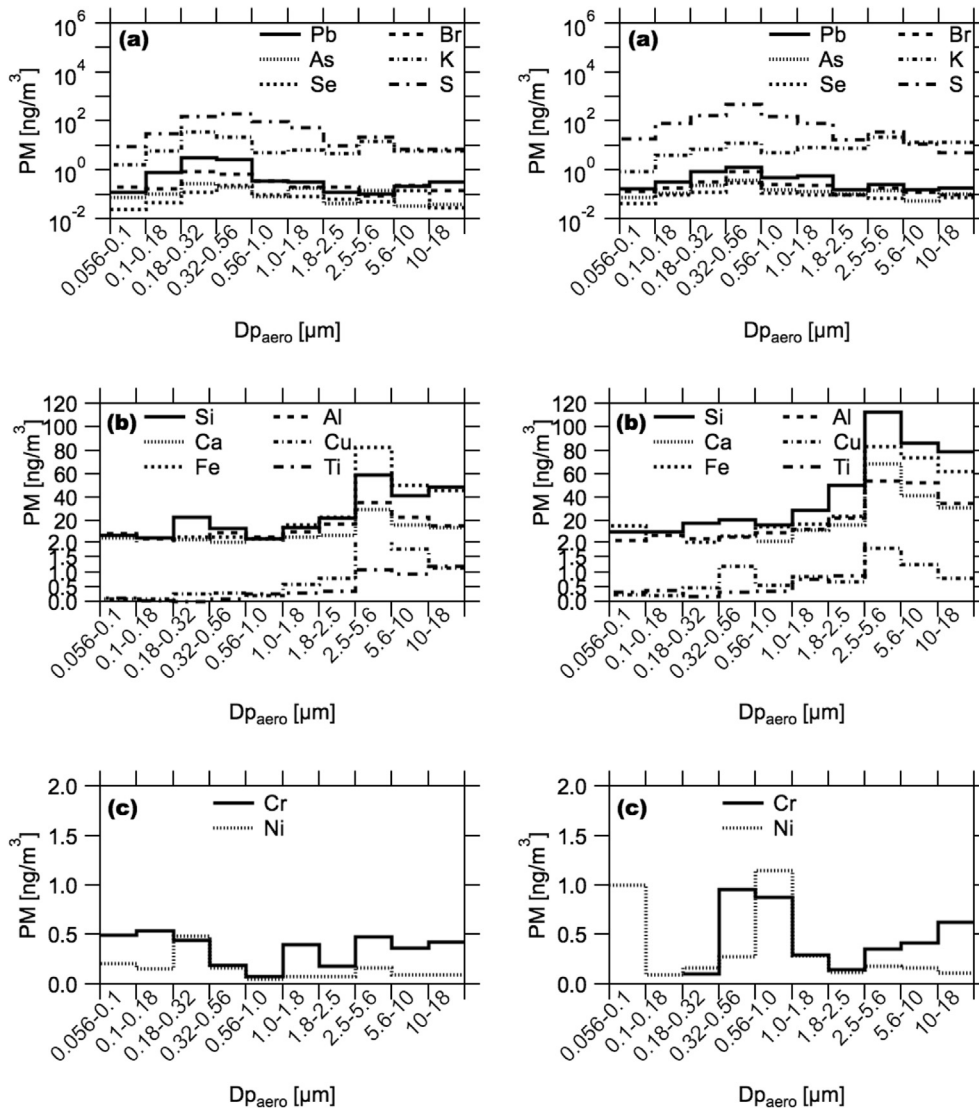


Fig. 5. Same as Fig. 4 but for the non-heating period (April–September).

combustion and vehicular traffic. More than the half of PM_{2.5} is of secondary origin from remote sources and is classified as so called “long range transported aerosol”. Looking at the results for the source contributions of elemental carbon (lower pie charts) the proportions in relation to PM_{2.5} are completely changed.

During the heating period, mainly local sources are responsible for the elemental carbon contribution at both sites. In Annaberg 1.03 μg/m³ of EC (55% of total EC) is related to solid fuel combustion. The value for Ústí is twice as high with 1.93 μg/m³ EC (57% of total EC). In contrast to the number-based analysis, a relative small contribution of only 0.27 μg/m³ EC (0.11 μg/m³ in Ústí) is related to vehicular traffic. Local traffic counts and therefore emissions of primary (soot) particles didn't change a lot over the year and the production process is not dependent of the ambient temperature. Therefore, the absolute contributions of EC do not change much between non-heating and heating periods. Surprisingly, a large proportion of the “long range transported aerosol”, especially sulfate-rich particles is related to EC. This phenomenon can be explained by chemical conversion processes, where particle material is coagulated and vapors are condensed on a pre-existing primary soot particle.

4.5. Sources of PM₁ and organic carbon

This section presents relative and absolute contributions of PM₁ and organic carbon sources for the heating and non-heating period based on source apportionment with CMB. Pie charts illustrate the relative source contributions for PM₁ and organic carbon for the heating and non-heating period for Annaberg (Fig. 9) and Ústí (Fig. 10). Looking at pie charts for OC, most of the vehicular traffic OC is caused by the exhaust of gasoline-powered engines. For OC from solid fuel combustion, local sources of wood and domestic brown coal combustion play a major role, while the proportion of industrial brown coal combustion is low (<3%). In Ústí combustion of domestic brown coal is the most important source of OC during the non-heating (34%) and heating period (43%). In contrast, the proportion of OC in Annaberg due to wood combustion is higher than in Ústí. During the non-heating period, wood combustion probably caused by fireplace combustion is the second largest source (19%) for OC. Surprisingly, cooking organic aerosol is the most important source in Annaberg (35%) and second largest source in Ústí (26%). We suppose increased grilling activities in the summer months, which is a very common outdoor activity in both

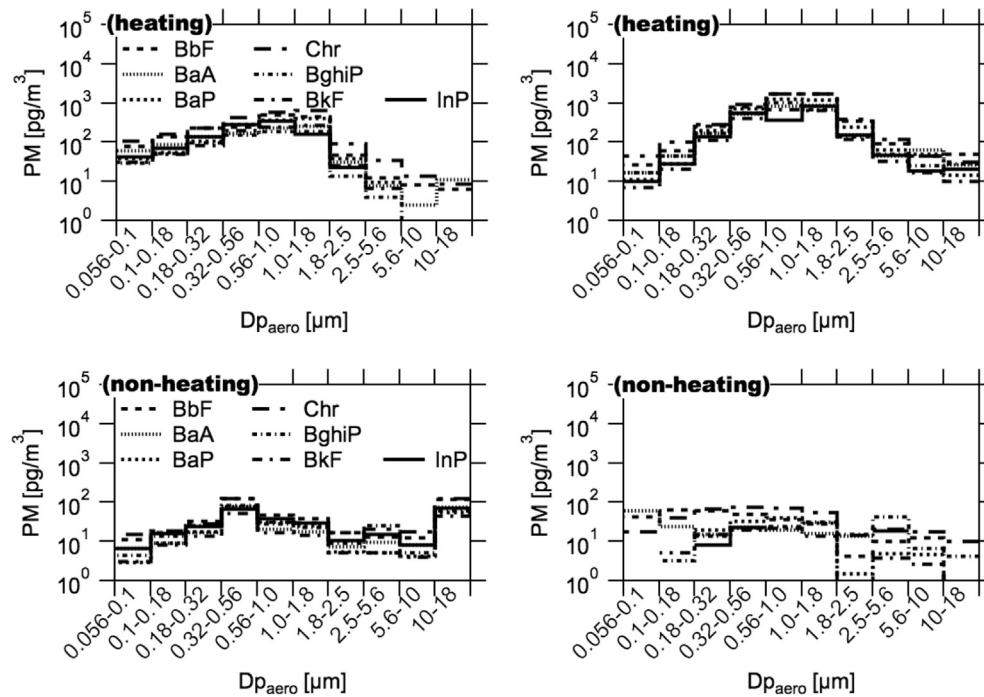


Fig. 6. Particle mass size distribution of selected PAHs for Annaberg (left) and Ústí (right).

Table 1

Hopanoïd ratios for non-heating and heating periods in Annaberg and Ústí compared with literature data.

	17 α -norhopane/22R-homohopane	17 α -hopane/22R-homohopane	17 α -hopane/17 α -norhopane	i_{hh}
Ústí (heating)	0.92	0.35	0.38	0.20
Annaberg (heating)	0.65	0.36	0.55	0.24
Ústí (non-heating)	1.23	0.83	0.67	0.36
Annaberg (non-heating)	0.98	0.79	0.80	0.37
Brown coal				
Bilina ^a	0.7	0.20	0.29	0.11
Leuna ^b	1.6	0.80	0.53	0.08
Vehicular traffic				
Diesel ^c	1.0	2.5	2.4	0.59
Gasoline ^c	2.0–3.1	3.3–4.7	1.5–1.7	0.58

^a Coal mine in the North Bohemian basin.

^b Data from Oros and Simoneit (2000).

^c Data from Rogge et al. (1993d).

countries to explain the large contribution of cooking aerosol. For reasons of comparability of PM₁ sources (upper pie charts of Figs. 9 and 10) with the PM_{2.5} sources, we summarize diesel and gasoline exhaust to one source “vehicular traffic” as well as domestic, industrial, and wood combustion to one source “solid fuel combustion”. For comparison purposes we used the same wedge colors. A comparison of PM_{2.5} and PM₁ is tough, due to different source apportionment approaches, sample periods, and size fractions. Therefore, in the following only differences without any detailed explanations are described.

Especially during the non-heating period, the proportion of the secondary aerosol including nitrate-rich and sulfate-rich particles is higher for PM_{2.5} than for PM₁. Vice versa, the proportion of re-suspended dust is higher for PM₁ than for PM_{2.5} for the same period. The cooking aerosol source was not quantified in the source apportionment of PM_{2.5} due to the lack of suitable markers for this source.

5. Summary and conclusion

A study of chemical composition of PM_{2.5}, PM₁ and UFP number

concentration measurements has been carried out at two urban background sites in Annaberg-Buchholz (Germany) and Ústí nad Labem (Czech Republic) between January 2012 and June 2014. Special importance has been given to quantify harmful sources such as vehicular traffic and solid fuel combustion in terms of UFP number concentration and particle mass concentration. A source apportionment method was developed to split the diurnal UFP number concentration into source contributions from Aitken particles (representing primary emitted soot particles), nucleation particles from photochemical-driven gas-to-particle conversion, and traffic induced nucleation particles. From the comparison of two measurement sites we concluded a higher number concentration of traffic induced nucleation particles when the number concentration of primary emitted soot particles is comparatively low. Thus, we confirmed the findings from other studies that semi-volatile exhaust gases preferably condenses on the large surface area of the pre-existing soot particles and thus decreasing the traffic-induced nucleation particles.

It is known that sulfuric acid in the atmosphere is the main cause of acid rain. For air quality studies, SO₂ plays an important role in the production of gaseous sulfuric acid and triggers new

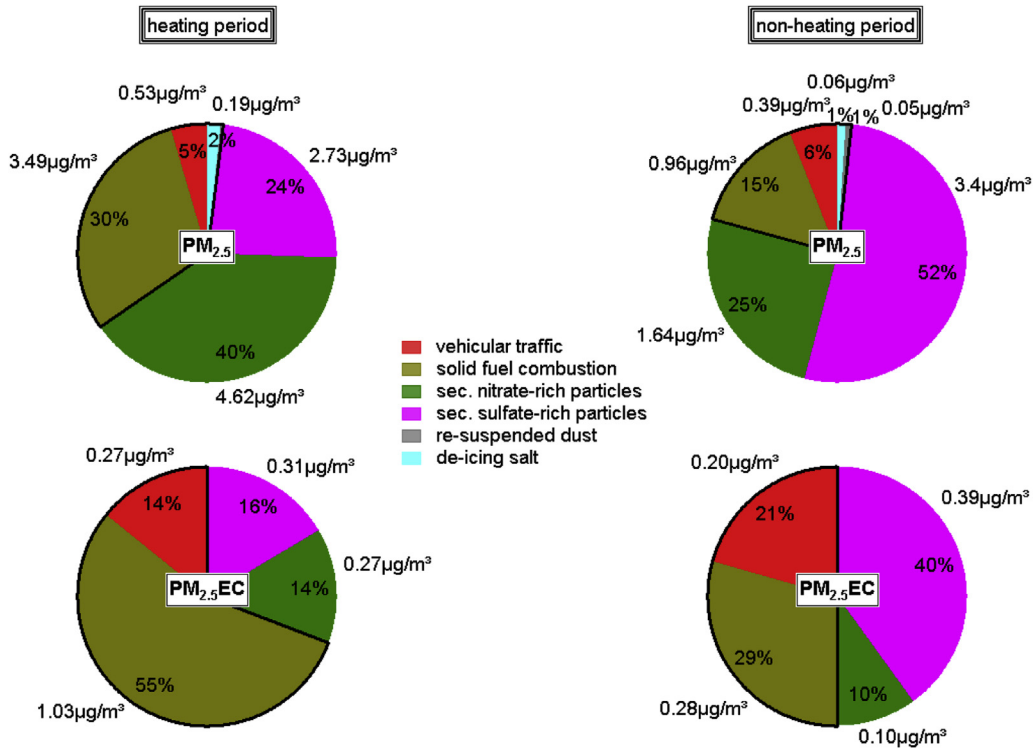


Fig. 7. Relative and absolute source contributions of PM_{2.5} and elemental carbon for the heating period (left) and non-heating period (right) for Annaberg.

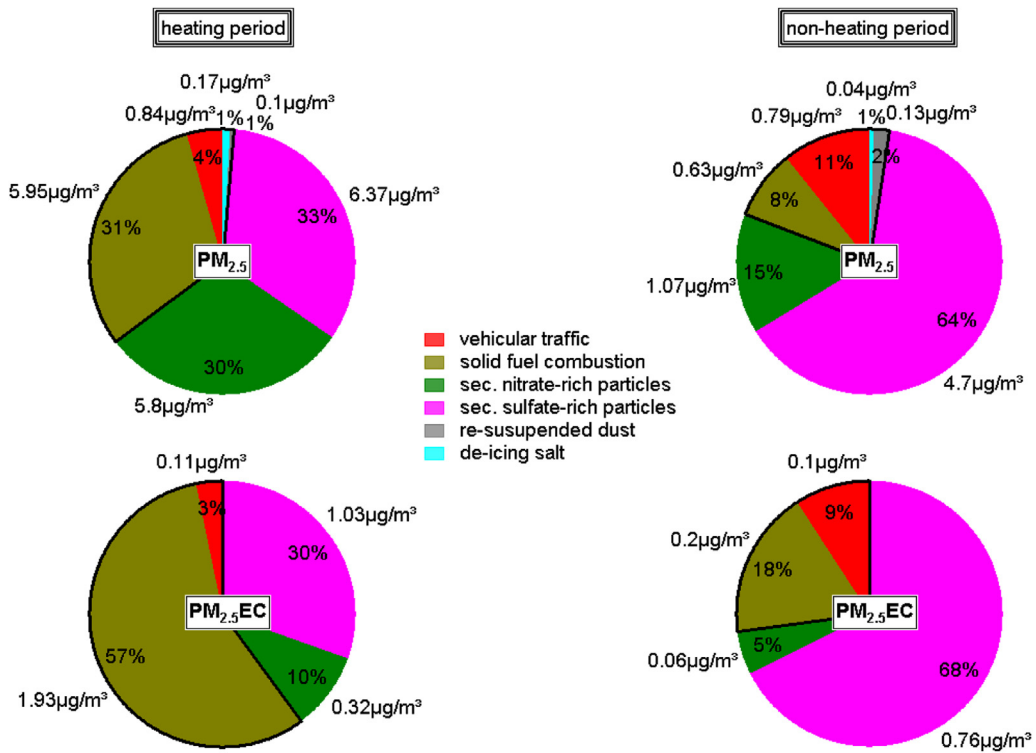


Fig. 8. Same as Fig. 7 but for Ústí.

particle formation. Our study revealed a significant source contribution of new particle formation from SO₂, which corresponds to almost 50% UFP around noon in Ústí. Size-segregated measurements of the carcinogenic PAHs in PM revealed that PAH emissions

from vehicular traffic occurs in the Aitken mode, whereas PAHs emitted from solid fuel combustion are present in the accumulation mode preferably during the heating period. Major sources of solid fuel combustion in this study are wood and domestic coal

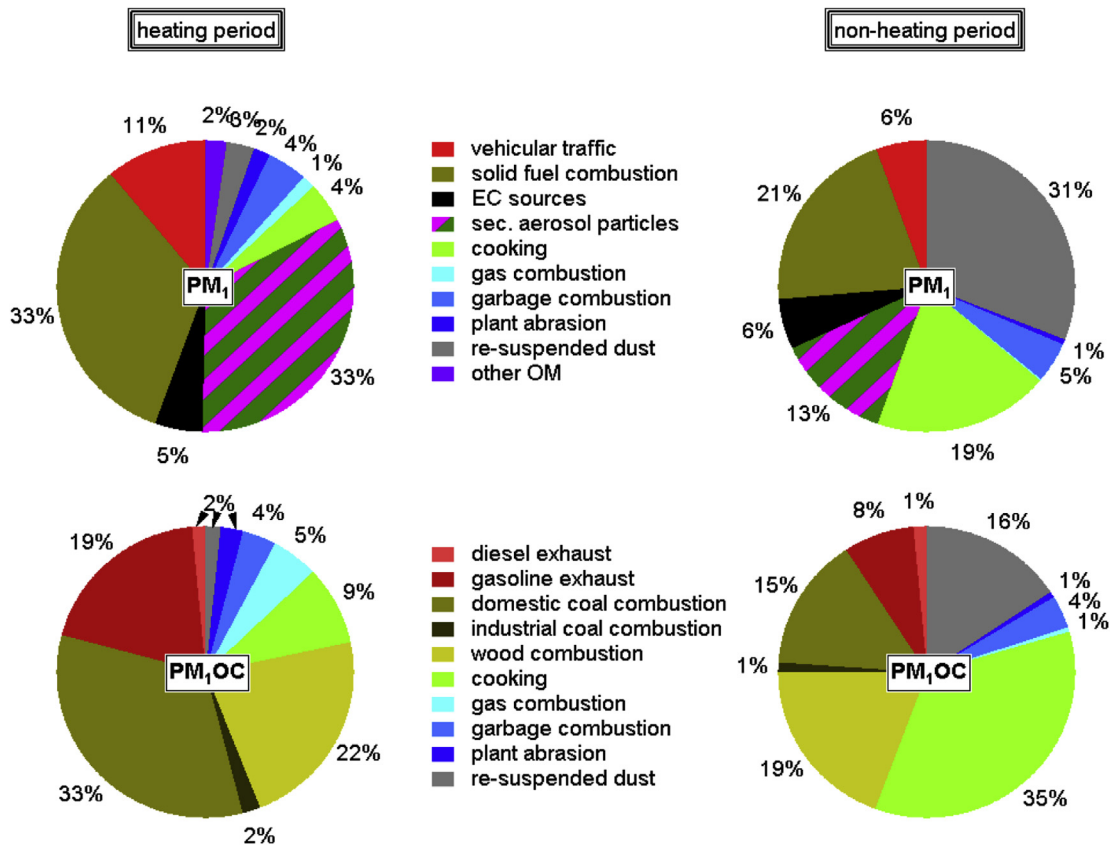


Fig. 9. Relative source contributions of PM₁ and organic carbon for the heating period (left) and non-heating period (right) for Annaberg.

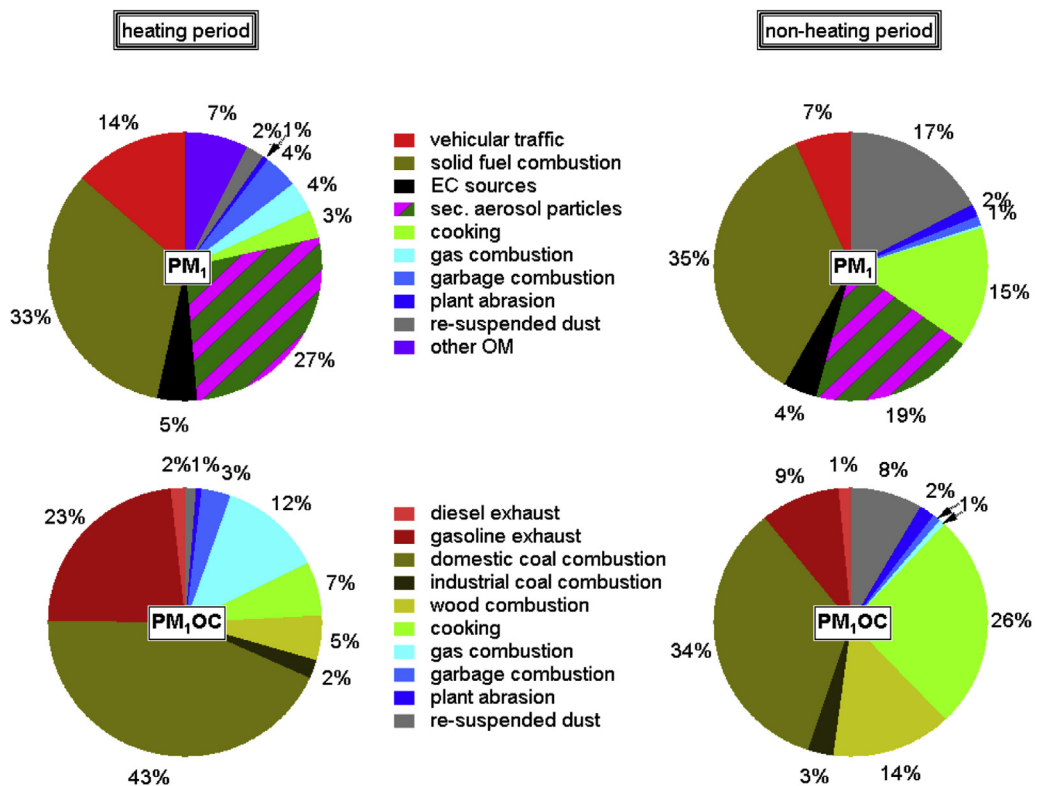


Fig. 10. Same as Fig. 9 but for Ústí.

combustion, while the proportion of industrial coal combustion is low (<3%). Another important message from the size-segregated measurements of trace elements is that crustal metals (e.g. Al; Si, K, and Ca) are enhanced in the PM₁₀ fraction during the non-heating period. Although no negative health effects of crustal material are known, PM₁₀ is a widely used air quality indicator for epidemiological health studies. Interestingly, we observed a shift of the peak concentration of chemical markers of solid fuel combustion such as Pb, As, Se, Br, and S to lower sizes during the non-heating period. Source apportionment analysis of PM₁ conducted for both sites revealed that cooking organic aerosol is a very important source of PM₁ and OC during the non-heating period. It can also be stated that most of the vehicular emitted OC originate from gasoline rather than diesel powered engines.

25 years after the end of the socialism era in both countries, our study revealed that combustion of fossil fuel products and soft wood are still the largest sources of harmful substances in particulate matter and UFP. To reduce health effects due to poor ambient air quality, we appeal to all experts and decision makers to force the shift to clean energy for cars and home heating.

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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.2015.09.044>.

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