Chemical Characterization of PM<sub>1-2.5</sub> and its Associations with PM<sub>1</sub>, PM<sub>2.5-10</sub> and Meteorology in Urban and Suburban Environments

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ABSTRACT

This study investigated the PM<sub>1-2.5</sub> (the intermodal fraction of particulate matter) representing the transition area between the fine and coarse size ranges. Due to this characteristic, PM<sub>1-2.5</sub> may contain particles from both modes. The aim of this work was to examine the associations between PM<sub>1-2.5</sub> and the coarse (PM<sub>2.5-10</sub>) and fine (PM<sub>1</sub>) fraction under different meteorological conditions at various sites in the Czech Republic during winter and summer.

Size-resolved PM mass concentrations were determined and meteorological parameters recorded at an urban industrial and a suburban site in Ostrava during winter 2014 and at an urban traffic site and a suburban site in Prague during summer 2014 and winter 2015. The influence of sources producing the coarse/fine fraction on PM<sub>1-2.5</sub> was investigated with an elemental composition analysis and an ion analysis (Ca<sup>2+</sup>-representing PM<sub>2.5-10</sub> and SO<sub>4</sub><sup>2-</sup>-representing PM<sub>1</sub>).

During all campaigns, PM<sub>1-2.5</sub> accounted for 1–26% of PM<sub>10</sub>. In winter, crustal elements (Si, Fe, and Ca) significantly influenced the coarse fraction and even PM<sub>1-2.5</sub> at all sites, while sulfur was significant in PM<sub>1-2.5</sub> and the fine fraction at suburban sites. The median SO<sub>4</sub><sup>2-</sup> concentration was higher than the Ca<sup>2+</sup> concentration in PM<sub>1-2.5</sub> at all sites, except the industrial site, due to a specific source. The increased SO<sub>4</sub><sup>2-</sup> amount in PM<sub>1-2.5</sub> was also observed in summer during rainy days (Prague urban site). In summer, crustal elements were important in both PM<sub>1-2.5</sub> and the coarse fraction, while S still dominated in PM<sub>1</sub>. Median SO<sub>4</sub><sup>2-</sup> concentrations in PM<sub>1-2.5</sub> and the coarse fraction were significantly lower than in winter. The enrichment factors and wind speed-direction analysis helped to reveal potential air pollution sources.

To conclude, according to the performed analyses, PM<sub>1-2.5</sub> was influenced by the sources of the coarse fraction during all campaigns. The additional significant influence of sources producing the fine fraction was evident under increased relative humidity conditions.

Keywords: Aerosol intermodal fraction; Personal cascade impactor sampler; Enrichment factor; Elemental composition; Scanning electron microscope; Multisite measurement.

INTRODUCTION

Atmospheric aerosols comprise two fundamental size categories: fine and coarse (Whitby et al., 1972; Lundgren and Burton, 1995). These categories are considered separate classes of pollutants (Wilson and Suh, 1997; US EPA, 2004) due to their different health effects (Pope III and Dockery, 2006; Zanobetti and Schwartz, 2009; WHO, 2013). The national ambient air quality standards (NAAQS), established by the US EPA, define particles with aerodynamic diameters (d<sub>a</sub>) less than 2.5 µm (PM<sub>2.5</sub>) and particles with d<sub>a</sub> less than 10 µm as PM<sub>10</sub>, which includes the coarse fraction (PM<sub>2.5-10</sub>). PM<sub>10</sub> and PM<sub>2.5</sub> are emitted by a variety of natural and anthropogenic sources. The physical and chemical properties of fine and coarse PM are temporally and spatially highly variable (Anlauf et al., 2006; Herner et al., 2006; Pérez et al., 2008; Schwarz et al., 2012). Coarse PM, generally formed by mechanical processes, contains the earth’s crustal metals (e.g., Ca, Fe Si, Al, Ti), sea salt, abrasion products from road traffic, and bioaerosols (Colbeck et al., 2008; Viana et al., 2008). Fine PM is usually formed via combustion or
from gas-to-particle conversions and is generally characterized by a high content of carbonaceous material, sulfates, and nitrate and ammonium ions. In addition, minor elements occurring in PM can be excellent tracers for specific sources of aerosols (Colbeck et al., 2008).

A sharp delineation between fine and coarse fractions cannot be clearly defined because these two fractions overlap in the size range 1 < d < 2.5 (up to 3) µm. This size range is called the intermodal fraction, or intermediate range, PM_{1-2.5} (Whitby et al., 1972; Lundgren and Burton, 1995; Wilson and Suh, 1997; Colbeck et al., 2008). PM_{1-2.5} can constitute a significant part of the respirable fraction measured by NAAQS, on average, 6–22% of PM_{10} and even 11–34% of PM_{2.5} (Lundgren et al., 1996; Geller et al., 2004; Pérez et al., 2008; Kozáková et al., 2017).

Depending on the meteorological conditions, PM_{1-2.5} can consist predominantly of aerosols originating from sources of either the coarse or fine fraction. For example, in arid/semiarid environments, the particles from sources releasing primary coarse particles (coarse PM sources) can occur in the size range below 2.5 µm (Lundgren et al., 1984; Lundgren and Burton, 1995; Claiborn et al., 2000; Husar et al., 2001; Pérez et al., 2008). In environments with high relative humidity (RH), the accumulation mode of fine particles can grow into the intermodal size range (Berner and Lürzer, 1980; Geller et al., 2004; Wang et al., 2012; Tian et al., 2014; Tan et al., 2016).

Several studies have characterized in detail the size-resolved PM, including the transition area between the accumulation and coarse mode, with statistical and chemical analyses (e.g., Klejnowski et al., 2012; Contini et al., 2014; Tian et al., 2016). Studies focused on the intermodal fraction have involved statistical analyses such as correlation coefficients (Lundgren et al., 1996; Haller et al., 1999; Claiborn et al., 2000; Vallius et al., 2000; Galindo et al., 2011; Perez et al., 2012) or regression analyses (Kozáková et al., 2017), have been based on the chemical composition of size-resolved aerosol particles (Hughes et al., 2000; Vecchi et al., 2004; Pérez et al., 2008; Perez et al., 2009, Pérez et al., 2010; Pasha a Alharbi, 2015; Rogula-Kozłowska, 2015), or have used a combination of both statistical and chemical composition methods (Kegler et al., 2001; Geller et al., 2004; Pérez et al., 2009). Nevertheless, further investigation of PM_{1-2.5} and its chemical composition is necessary for several reasons. The existing studies that have focused on the chemical composition of PM_{1-2.5} were performed mostly in dry environments (Hughes et al., 2000; Kegler et al., 2001; Geller et al., 2004; Pérez et al., 2008; Perez et al., 2009; Pérez et al., 2010; Pasha a Alharbi, 2015). To our knowledge, a single study that included the chemical composition of the intermodal fraction was performed in Katowice, Poland (Rogula-Kozłowska, 2015), at a crossroad site in summer and at a highway site in spring. Our study contains results of the chemical composition of PM_{1-2.5} during both seasons, winter and summer, from several urban and suburban sites of Central Europe where ambient conditions change significantly according to the season. The influence of the intermodal fraction on PM_{2.5} has not been well determined or quantified in most European regions. The contribution of the earth’s crustal components to PM_{2.5}, as well as fine particles growing into PM > 1 µm (d) during periods of higher RH, can cause inaccuracies in source apportionment and in epidemiological and exposure studies. Therefore, it is necessary to analyze the chemical composition of PM_{1-2.5} in different types of locations and to attempt to describe the conditions under which it is appropriate to consider PM_{1} as the independent fraction. Additionally, our results may contribute to the discussion between air quality experts and legislators about the possible establishment of an additional air quality standard for PM_{1}.

For the purposes of this study, PM_{1} is considered the fine fraction and PM_{2.5-10} the coarse fraction.

In our project on PM_{1-2.5} characterization, the first part was focused on statistical methods using mass concentrations of PM (Kozáková et al., 2017). Subsequently, in the present study, part of an extensive sample collection was analyzed using chemical methods. The aim of this work was to elucidate the associations between PM_{1-2.5} and the fine PM (PM_{1})/coarse PM (PM_{2.5-10}) under different meteorological conditions. The investigation was performed on the basis of a statistical analysis and chemical composition at various urban sites (industrial, urban traffic, suburban) in the Czech Republic during both winter and summer.

**METHODS**

**Sampling Sites**

Size-resolved PM measurements were performed at two urban and two suburban sites in the Czech Republic, Central Europe, during winter and summer (Table 1 and Supplemental Fig. S1).

**Ostrava Radvance and Bartovice** (campaign Radvanice) is a residential district in southeast Ostrava (Fig. S1) composed of family houses and greatly influenced by industrial sources (metallurgy complex) located approximately 2 kilometers to the southwest (Pokorná et al., 2015; Leoni et al., 2016; Pokorná et al., 2016). The nearest road is 80 m away, with a traffic flow of approximately 10,000–15,000 vehicles per day (MoT, 2010; RŠD, 2010). An air-conditioned (isothermal, 20°C) monitoring station containing all instruments was located in a garden approximately 50 m from the nearest family house.

**Ostrava Plesná** (campaign Plesná) is a suburban residential area in northwest Ostrava with family houses and low traffic (only residents and approximately 2 regular bus services per hour). The instruments were placed in a garden approximately 20 m from the nearest family house. The cascade impactors were protected against rain and snow, and the spectrometers were placed inside a wooden box.

**Prague Benátská** (summer campaign “Benátská_s,” winter campaign “Benátská_w”) is located in Prague in the city center in the Charles University botanical garden. The nearest intersection has a traffic flow of 15,000–20,000 vehicles per day, and the busiest city road, with a traffic flow of 30,000–50,000 vehicles per day, is located at a distance of 600 m (MoT, 2010). An air-conditioned (winter: 20°C; summer: 20–25°C) rooftop station of the Institute for Environmental Studies with all instruments was located on
the fourth floor; for additional details, see Thimmaiah et al. (2009).

**Prague Suchdol** (summer campaign “Suchdol_s,” winter campaign “Suchdol_w”) is a suburban background site in northwest Prague with residential houses and the Czech University of Life Sciences campus. The traffic flow along one major two-lane road is 20,000–30,000 vehicles per day (MoT, 2010), with very frequent bus service. The measurement site was located on the research campus of the Institute of Chemical Process Fundamentals, to the north and northeast of the major road at a distance of approximately 250 m. The impactors were placed outside and protected against rain and snow, and the other instruments (online monitoring) were placed inside a building (10 m from the impactors; for more details, see Talbot et al. (2016)).

### Instrumentation

Twenty-four-hour mass concentrations of size-resolved PM were measured with a US EPA-approved personal cascade impactor sampler (PCIS) at 9 L min⁻¹ (Misra et al., 2002). Using a cyclone to cut PM₁₀ upstream of the inlet to the impactor, the PCIS separated particles by aerodynamic diameter (d_a) in the following five size stages: A: 10 > d_a > 2.5 µm; B: 2.5 > d_a > 1 µm; C: 1 > d_a > 0.5 µm; D: 0.5 > d_a > 0.25 µm; E: d_a < 0.25 µm. Particles on stages A through D were collected on 25-mm PTFE filters (porosity of 0.5 µm; Pall Corporation, Ann Arbor, Michigan, USA) used as impaction substrates, and particles < 0.25 µm (stage P) were collected on 37-mm PTFE backup filters with a PMP ring with a porosity of 2.0 µm (Pall Corporation, Michigan, USA, and SKC Limited, Dorset, United Kingdom).

Five (Radvance, Plesná, Benátská_s/w) or ten (Suchdol_s/w) minutes of integration time for the particle number concentration and size distribution were measured with a scanning mobility particle sizer (SMPS model 3936L25 in Radvance and Benátská, and SMPS model 3936L75 in Plesná and Suchdol, TSI Inc., MN, USA; size range 14–532 nm) and an aerodynamic particle sizer (APS model 3321 at all sites, TSI Inc., MN, USA; size range 0.5–10 µm) using a PM₁₀ sampling head on the top of the sampling tubing. The two aerosol size spectrometers covered the size range from 14 nm to 10 µm.

Meteorological data, including wind speed (WS), wind direction (WD), temperature (T) and RH for the Benátská_s campaign, were measured using a Young vane-type monitor (Model 05103v, Fondriest Environmental Inc., USA). For the other measurement campaigns (Radvance, Plesná, Suchdol_s/w, Benátská_w), meteorological data were available from the nearest representative automated monitoring stations (at the distance of approximately 477 m from Radvance site, 4815 m from Plesná site, 25 m from Suchdol site, and 470 m from Benátská site) managed by the Czech Hydrometeorological Institute.

### Gravimetric Analysis

The PM concentrations were assessed by gravimetric analysis. Before weighing, the PTFE filters were preconditioned for at least 24 hours at 50 ± 5% RH and 20 ± 2°C in a weighing room. To dissipate any electrostatic charge, every filter was passed over a Haug U-electrode ionizer (PRXU 27 × 18 × 27 200 radiation; Haugh, GmbH&Co. KG, 120 Germany) immediately before being weighed with a microbalance (Mettler Toledo MX5; Mettler-Toledo GmbH, Greifensee, Switzerland; weighing range: 5100 mg–1 µg; sensitivity: ± 1 µg; and Sartorius M5P-000V001; Goettingen, Germany; range mode: 1500 mg–1 µg; sensitivity: ± 1 µg). The gravimetric analysis of PM samples was fully described in Kozáková et al. (2017).

PM concentrations were calculated as follows: PM₁ (fine fraction) as the sum of the aerosol masses on stages C to P (< 1 µm), PM₂,₅ as the sum of the aerosol masses on stages B to P (< 2.5 µm), and PM₁₀ as the sum of the aerosol masses of all stages (A–P); PM₁,₂,₅ was represented by stage B, and PM₂,₅,₁₀ (coarse fraction) was represented by stage A.

For every measurement campaign, at least 10% of the field blank filters were used to determine the limit of detection (LOD) of the weighing procedure. Field blank filters were exposed to the same conditions as the samples except for the sampling period. The LOD was calculated as three times the standard deviation of the mass changes of all field blank filters. The lowest level of the 24-h

<table>
<thead>
<tr>
<th>measurement site</th>
<th>type of locality</th>
<th>GPS</th>
<th>measuring periods</th>
<th>place of instruments</th>
<th>sampling height</th>
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<tbody>
<tr>
<td>Ostrava Radvance</td>
<td>urban industrial</td>
<td>49.811161 N, 18.337922 E</td>
<td>2/11–3/5/2014 (winter)</td>
<td>inside the monitoring station</td>
<td>5 m AGL</td>
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<td>and Bartovice</td>
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<tr>
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<td>suburban</td>
<td>49.865920 N, 18.132090 E</td>
<td>2/11–3/5/2014 (winter)</td>
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<td>2 m AGL</td>
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<tr>
<td>Prague Benátská</td>
<td>urban traffic</td>
<td>50.071318 N, 14.420950 E</td>
<td>8/21–9/4/2014 (summer)</td>
<td>inside the monitoring station</td>
<td>15 m AGL</td>
</tr>
<tr>
<td>Prague Suchdol</td>
<td>suburban</td>
<td>50.127523 N, 14.385224 E</td>
<td>8/21–9/4/2014 (summer)</td>
<td>outside (impactor), inside (other devices)</td>
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</table>

*AGL = above ground level.

### Table 1. Details of measurement sites.

<table>
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concentration (lowest concentration level) that could be measured was determined as the ratio of LOD to the nominal volume of the air flowing through the impactor (12.96 m$^3$). The measured concentrations below the lowest concentration level were replaced by half of this level (5% of the concentrations in the dataset).

The atmospheric aerosol collected on the filters was subsequently used for chemical analyses (ion and elemental composition).

**Chemical Analyses**

Ion chromatography (IC) was used for the determination of Ca$^{2+}$ and SO$_4^{2-}$ mass concentration in every aerosol size fraction (all days for Prague campaigns and 18 days for Ostrava campaigns). The ion chromatography analysis procedure is described in detail in the supplementary material. Ca$^{2+}$ was selected as a marker for PM$_{2.5-10}$ due to its abundant presence in the mineral coarse fraction (Kertész et al., 2002; Salma et al., 2002; Colbeck et al., 2008; Ondráček et al., 2011; Spindler et al., 2013). SO$_4^{2-}$ was chosen as a marker of PM$_{1}$ since it is one of the major constituents of fine particles in outdoor environments (Matta et al., 2002; Perry et al., 2004) in Central Europe (Kertész et al., 2002; Salma et al., 2002; Ondráček et al., 2011; Schwarz et al., 2012; Spindler et al., 2013; Talbot et al., 2016). Other ions, such as NO$_3^-$ and Cl$^-$, occur in the fine as well as in the coarse mode in urban and rural environments. For example, the distribution of NO$_3^-$ was bimodal in urban and suburban atmospheric aerosols (Colbeck et al., 2008), even in the Prague region during winter and summer (Ondráček et al., 2011; Schwarz et al., 2012). The presence of Cl$^-$ was also observed in both fine and coarse modes of Prague atmospheric aerosols reported in our previous study (Schwarz et al., 2012). The Ca$^{2+}$/SO$_4^{2-}$ ratios were calculated for a comparison of individual PM fractions.

A scanning electron microscope (TESCAN Vega, TESCAN ORSAY HOLDING a.s., Czech Republic) equipped with an energy dispersive spectroscopy (EDS-detector X-Max 50, Oxford Instruments plc, United Kingdom; SEM+EDX) was used for the elemental semi-quantitative microanalyses (C, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, and Zn) of all days/impactors from the Prague campaigns, 17 days for Radvanice, and 12 days for the Plesná campaigns. The samples were coated with a thin electroconductive layer of amorphous carbon (ca. 15 nm thick). On each filter, seven square areas containing a PM sample with an edge length of 200 µm were scanned for 200 seconds of lifetime in order to cover a representative area and minimize the effects of possible heterogeneities. The elements C and F were excluded from the subsequent analysis because they are present in the PTFE filters and C is also in the coating layer, as well as in the samples. Individual elements (without C and F) were expressed as percentages of their sum normalized to 100% (not percentages from the total aerosol mass). The normalization to 100% is necessary in order to avoid the effect of variations in the amount of material covering the surface of the filters. The analyses were conducted with an accelerating voltage of 15 kV and beam current of 1.5 nA. The percentages of elements in PM$_1$ were calculated as a mass of weighted averages of impactor stages C, D, and P. For more details, see the supplementary material.

**Quality Assurance and Control**

The flowrate passing through every impactor was measured three times with the mass flowmeter (4040, TSI Inc., MN, USA) before and after the sampling period. The values were recalculated according to the actual temperature and atmospheric pressure and subsequently averaged to obtain the final flowrate. The PM concentrations from the impactors were corrected against field blank measurements (see chapter Gravimetric analysis). The ion composition data were field blank corrected as well (at least 10% of blank filters from all samples). The Ca$^{2+}$ and SO$_4^{2-}$ field blank concentrations were below the LOD for both size types of PTFE filters.

**Data Analysis**

The enrichment factor, EF, was calculated to characterize the origin of airborne PM. EF relates the concentration of an element (X) to the concentration of an airborne crustal element normalized to the ratio of these elements in the average continental crust (Saliba et al., 2007):

$$EF_x = \frac{(X/Si)_{air}}{(X/Si)_{crust}}$$

where X indicates the element concentration in the sample of atmospheric aerosol (air) or upper continental crust (crust) and Si is the concentration of Si in the sample of atmospheric aerosol (air) or upper continental crust (crust). Si was chosen as a normalizing crustal element (Saliba et al., 2007), and element concentrations in the upper continental crust were given by Wedepohl (1995). An EF value greater than 10 indicates high enrichment due to contributions from non-crustal sources (Torfs and van Grieken, 1997; Chester et al., 1999).

The SMPS-APS dataset was used for an analysis of PM$_1$, PM$_{1-2.5}$, and PM$_{2.5-10}$ concentrations versus WD and WS (polar plots) in order to find the potential sources. The mass concentrations of individual PM fractions were calculated from SMPS and APS number concentrations with a particle density of 1.5 g cm$^{-3}$ (Shen et al., 2002), as described in the supplementary material. To fit meteorological and SMPS-APS datasets, PM concentrations were averaged as follows: 1-hour average concentrations for Plesná and Benátská w and 10-minute average concentrations for Radvanice and Suchdol s/w. For the Benátská s campaign, meteorological and SMPS-APS measurements were performed with the same integration time of 5 minutes. In addition, the comparison between SMPS-APS (24-h average dataset) and PCIS measurements was performed for three PM fractions (Supplemental Fig. S3).

The impactor PM mass concentration data were not normally distributed (Shapiro-Wilk test of normality). Therefore, nonparametric Spearman’s rank correlation coefficients ($r_s$) were calculated. The correlation test was calculated to detect statistically significant correlations between two variables ($p$-value < 0.05). The nonparametric
Kruskal-Wallis test and the two-sample Wilcoxon test (p-value < 0.05) were used to determine statistically significant differences among individual campaigns and between seasons, respectively.

The meteorological and statistical analyses were performed with the R software and the package Openair (Carslaw and Ropkins, 2012; Carslaw, 2015).

RESULTS AND DISCUSSION

Campaign Overview

Median values of the monitored meteorological variables (T, RH, and WS) for each campaign are presented in Table S2, and the WS and WD are shown in Fig. S4 (Supplementary Material). Seasonal differences at the Prague sites Benátská and Suchdol were evident for T but not as apparent for RH. During summer days at the Suchdol site, the RH varied more significantly, resulting in a wide interquartile range (25th and 75th percentiles). Generally, the prevailing WDs were from the SW during the campaign in Plesná, from the SW and NE in Radvanice, and from the SW/W during the summer and winter campaigns in Benátská. Clear prevailing WDs for the Suchdol campaigns were not possible to determine (Supplemental Fig. S4).

Median mass concentrations of PM$_{10}$, PM$_{2.5}$ and the investigated PM fractions–PM$_{2.5-10}$, PM$_{1-2.5}$, and PM$_{1}$ are displayed in Table 2 for each campaign. The differences in mass concentrations of PM$_{2.5-10}$, PM$_{1-2.5}$, and PM$_{1}$ among campaigns were statistically significant (p-values < 0.001).

Median mass size distributions determined with PCIS varied for every campaign (Supplemental Fig. S5). In winter, they were unimodal, with the modes at approximately d$_{a}$ = 350 nm. Similar distributions were observed between the Prague summer campaigns, with the modes at approximately d$_{a}$ = 350 nm.

A measurement at an urban site in Como (northern Italy) showed a similar median mass size distribution with the dominant peak in an accumulation mode (around d$_{a}$ = 400 nm) during the heating season (Rovelli et al., 2017), as was observed in the winter Prague (Benátská and Suchdol) and Plesná campaigns. Mass size distributions were different for the summer and winter campaigns in Prague (Fig. S5) and at the urban site in Como as well (Rovelli et al., 2017). The unimodal mass size distribution, as measured at the Radvanice site, was observed during winter in Zabrze, an industrial town in southern Poland (Zwozdziak et al., 2017), with the dominant peak in the accumulation range (impactor stage d$_{a}$ = 0.65–1 µm).

Mass Portions of PM Fractions

The median masses of PM fractions for different types of localities were presented and discussed in our previous work (Kozáková et al., 2017) and included data from campaigns that were also investigated in the present study. Fig. 1 shows median masses only for the campaigns of interest. During these campaigns, PM$_{1}$ was the predominant component of the PM$_{10}$, while PM$_{1-2.5}$ accounted for 3–8% of PM$_{10}$. PM$_{2.5-10}$ accounted for 4–15% of PM$_{10}$. In the Benátská and Suchdol campaigns, the seasonality of the PM$_{1-2.5}$ mass portions was compared. In summer, the mass portions of PM$_{1-2.5}$ (5%, 8%) were higher than in winter (PM$_{1-2.5}$: 4% and 3%, respectively), probably due to the

<table>
<thead>
<tr>
<th>campaign</th>
<th>PM$_{10}$ µg m$^{-3}$</th>
<th>PM$_{2.5-10}$ µg m$^{-3}$</th>
<th>PM$_{2.5}$ µg m$^{-3}$</th>
<th>PM$_{1-2.5}$ µg m$^{-3}$</th>
<th>PM$_{1}$ µg m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radvanice</td>
<td>48.0 (39.3–56.5)</td>
<td>4.1 (3.6–5.5)</td>
<td>41.6 (32.8–52.4)</td>
<td>3.0 (2.2–4.4)</td>
<td>38.5 (29.7–49.2)</td>
</tr>
<tr>
<td>Plesná</td>
<td>34.2 (25.2–48.2)</td>
<td>2.0 (1.2–2.7)</td>
<td>30.6 (23.4–46.3)</td>
<td>2.8 (1.5–3.9)</td>
<td>29.2 (19.6–41.7)</td>
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<td>Benátská, s</td>
<td>9.4 (8.2–12.5)</td>
<td>1.3 (1.0–1.7)</td>
<td>8.5 (6.9–11.1)</td>
<td>0.6 (0.2–1.1)</td>
<td>7.9 (6.8–9.8)</td>
</tr>
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<td>Benátská, w</td>
<td>28.4 (10.3–35.3)</td>
<td>0.7 (0.1–1.6)</td>
<td>27.7 (9.7–34.6)</td>
<td>1.1 (0.3–1.7)</td>
<td>24.8 (8.9–33.7)</td>
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<td>Suchdol, s</td>
<td>11.3 (8.4–13.5)</td>
<td>1.6 (1.2–2.0)</td>
<td>9.6 (6.8–12.0)</td>
<td>0.9 (0.5–0.9)</td>
<td>8.5 (6.3–11.3)</td>
</tr>
<tr>
<td>Suchdol, w</td>
<td>27.9 (17.8–40.2)</td>
<td>1.0 (0.7–1.3)</td>
<td>27.6 (16.9–39.2)</td>
<td>1.0 (0.5–1.8)</td>
<td>26.2 (16.5–35.9)</td>
</tr>
</tbody>
</table>

Fig. 1. Median mass portions of PM$_{1}$, PM$_{1-2.5}$, and PM$_{2.5-10}$ in PM$_{10}$; error bars represent the 25th and the 75th percentiles.
increased contribution of soil dust, as shown by Kegler et al. (2001) and Vecchi et al. (2004) in summer, while the high RH reduced the occurrence of dust resuspension in winter (Vallius et al., 2000).

**PM$_{1-2.5}$ Investigation at Various Sites**

The investigation of the intermodal fraction in terms of its association with the coarse or fine fractions at various sites was performed using different analyses: statistical, chemical, and meteorological. The Spearman correlation coefficients for the relationship of PM$_{1-2.5}$ with PM$_{2.5-10}$, PM$_1$, and meteorological parameters are displayed in Table 3. The EFs (Fig. 2) and Ca$^{2+}$/SO$_4^{2–}$ ratios (Fig. 3) were calculated for individual PM fractions. Ca$^{2+}$ and SO$_4^{2–}$ mass concentrations are presented in the supplementary material (Table S3). The analysis of the polar plots (Fig. 4) obtained with online measurements helps with the investigation of the PM sources according to WS and WD. The sources can have the same directionality and be related to either low or high speeds (local versus distant sources).

Fig. 5 shows the percentages of elements related to their sum (not related to the total aerosol mass). Because some major chemical species, for example, carbon and nitrate, were omitted from the analyses, this approach is limited in determining the size distributions of individual species, the mass reconstruction, and source apportionment analysis, such as Positive Matrix Factorization, as performed in other studies (e.g., Contini et al., 2014; Tian et al., 2016). However, for the determination of the similarity between the individual PM fractions, these methods based on ratios of species can be used to identify possible indicators for the relative importance of various sources in the atmosphere (Prospero et al., 2001; Anlauf et al., 2006; Alharbi et al., 2015; Cesari et al., 2016). Some elements mentioned in the legend (Fig. 5) are not sufficiently visible in the pie charts due to their very low percentage proportions.

**Radvanice**

In Radvanice, all analyses, including the correlation coefficients (Table 3), Ca$^{2+}$/SO$_4^{2–}$ ratios (Fig. 3), WD analysis (Fig. 4), and elemental proportion (Fig. 5), suggested an association between PM$_{1-2.5}$ and the coarse fraction. PM$_{1-2.5}$ and the coarse fraction have the same source location, likely the industrial zone. In contrast, the highest mass concentrations of PM$_1$ originated from local sources or from sources located to the north and northeast (Fig. 4). The most abundant elements in PM$_{1-2.5}$ and the coarse fraction were Fe, Si, Ca, and Na, whereas Fe, S, and Cl were the most abundant elements in PM$_1$ (Fig. 5).

The EFs in PM$_{1-2.5}$ and PM$_{2.5-10}$ had similar values for the elements Cl, K, Mn, Fe (EF lower than for PM$_1$), and Ca (EF higher than for PM$_1$; Fig. 2). The elements with increased EF (Fig. 2) point to the air pollution sources, which were documented in previous source apportionment studies conducted in this region (Rogula-Kozlowska et al., 2012; Pokorná et al., 2015; Pokorná et al., 2016). They represent industry (the processing of iron ore and production of raw iron and steel), coal combustion, biomass burning, and traffic related emissions.

**Plesná**

In Plesná, PM$_{1-2.5}$ was correlated with the fine and coarse fraction and RH ($r_\text{S} = 0.53, 0.35, 0.49$, respectively). In all three fractions, the SO$_4^{2–}$ concentrations were higher than the Ca$^{2+}$ concentrations (Fig. 3), and the variability, expressed as the 25th and 75th percentiles, was low. SO$_4^{2–}$ or S in atmospheric aerosols is primarily raised as a secondary component from the atmospheric oxidation of SO$_2$ (Colbeck et al., 2008). Sulfur, although it is also part of the minerals (sulfid-S$^{2–}$ and sulfate-SO$_4^{2–}$ minerals), represented mainly the secondary component in Plesná due to the atmospheric pollution transport from Polish regions (Fig. 4), which was also documented in several studies (Swietlicki and Krejci, 1996; Pokorná et al., 2015; Hovorka et al., 2016). In addition, elemental sulfur was apparently increased in PM$_{1-2.5}$ (9% points more) in comparison with the coarse fraction, even if the percentages of main elements (Si, Na, Fe, and Al) were similar for these fractions (Fig. 5). On the other hand, S was the predominant element in PM$_1$. The analyses clearly suggested that both fractions, the fine and coarse, may be associated with PM$_{10}$.

The EFs in PM$_{2.5}$ and PM$_{2.5-10}$ showed similar values for the crustal element Mg (EF slightly higher than for PM$_1$), as well as for Fe, Mn, Cl, and K (EF lower than for PM$_1$). The origin of Fe and Mn could be the industrial sources likely affecting the whole region (Pokorná et al., 2015). Cl and K being highly enriched in the fine fraction are probably the result of coal combustion and biomass

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**Table 3.** Spearman correlation coefficients between PM$_{1-2.5}$ and other monitored variables (statistically significant correlations in bold, p-value < 0.05).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ostrava Radvanice winter</th>
<th>Ostrava Plesná winter</th>
<th>Prague Benátská summer</th>
<th>Prague Benátská winter</th>
<th>Prague Suchdol summer</th>
<th>Prague Suchdol winter</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_1$</td>
<td>-0.03</td>
<td><strong>0.53</strong></td>
<td>0.71</td>
<td>0.36</td>
<td>-0.03</td>
<td><strong>0.75</strong></td>
</tr>
<tr>
<td>PM$_{2.5-10}$</td>
<td><strong>0.39</strong></td>
<td><strong>0.35</strong></td>
<td>0.45</td>
<td><strong>0.79</strong></td>
<td><strong>0.59</strong></td>
<td><strong>0.59</strong></td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>0.06</td>
<td><strong>0.62</strong></td>
<td><strong>0.79</strong></td>
<td>0.42</td>
<td>0.02</td>
<td><strong>0.79</strong></td>
</tr>
<tr>
<td>RH</td>
<td>0.17</td>
<td><strong>0.49</strong></td>
<td>-0.08</td>
<td>-0.41</td>
<td>-0.38</td>
<td>0.40</td>
</tr>
<tr>
<td>T</td>
<td>0.08</td>
<td>0.06</td>
<td>0.31</td>
<td>-0.19</td>
<td>-0.07</td>
<td>-0.35</td>
</tr>
<tr>
<td>WS</td>
<td>-0.02</td>
<td>-0.10</td>
<td>-0.29</td>
<td><strong>-0.63</strong></td>
<td>-0.21</td>
<td><strong>-0.52</strong></td>
</tr>
<tr>
<td>count of obs.</td>
<td>23</td>
<td>22</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>
burning (Swietlicki and Krejci, 1996; Han et al., 2005; Rogula-Kozłowska et al., 2012). This conjecture was also confirmed by the high enrichments in S and Zn.

**Benátská**

In the summer campaign (Benátská_s), PM$_{1-2.5}$ was more significantly correlated with PM$_1$ ($r_s = 0.71$) than with the coarse fraction ($r_s = 0.45$). However, as observed in the other studies (Lundgren et al., 1984; Lundgren and Burton, 1995; Clai born et al., 2000; Husar et al., 2001; Pérez et al., 2008), a stronger association between PM$_{1-2.5}$ and the coarse fraction was supposed in summer due to a generally lower average RH than in winter. After closer examination of the weather situation, we recorded the rainy conditions during the second half of the campaign. The median mass concentration of PM$_{1-2.5}$ was higher on rainy days, with a higher average RH (2.0 µg m$^{-3}$) than on sunny days (0.6 µg m$^{-3}$), and SO$_4^{2-}$ in PM$_{1-2.5}$ was more abundant than Ca$^{2+}$ on rainy days (median of Ca$^{2+}$/SO$_4^{2-}$ for rainy days: 0.57; for sunny days: 1.45). In addition, the major sources of the atmospheric aerosols have a similar location (Fig. 4). The highest mass concentrations of all PM fractions occurred with east and southeast WDs (WS = 0.5–1 m s$^{-1}$), i.e., they corresponded to a strong traffic source (busy city road at a distance of 600 m), and this was confirmed by the enrichment in elements such as Cr, Mn (in PM$_1$), Fe, and
Zn (Veron et al., 1992; Manoli et al., 2002; Samara and Voutsas, 2005; Viana et al., 2008; Chang et al., 2009). These findings indicated the significant influence of the sources producing fine PM (fine PM sources) to PM1-2.5.

On the other hand, the elemental composition of PM fractions suggested the association between PM1-2.5 and the coarse fraction. The percentages of elements were similar between PM1-2.5 and the coarse fraction for the most abundant crustal elements (Si, Fe, further Ca, Na, and Al). In Katowice, Poland, organic matter and crustal material prevailed in PM1-2.5 at a crossroad site in summer (Rogula-Kozáková et al., 2018). S and Fe with Si and K were predominant in PM1 during the Benátská_s campaign. A closer examination of the upper part of the fine fraction, PM0.5-1 (particles dₐ = 0.5–1 µm), showed a significant influence of the crustal elements Si, Fe, and Na, as in PM1-2.5 and the coarse fraction (Supplemental Fig. S6), which was also observed by Schwarz et al. (2012) for sea salt-related ions (Na⁺ and Cl⁻) in Prague. This phenomenon may be an artifact created by a particle bounce-off effect inside the impactors that changes the size distribution (Cheng and Yeh, 1976). However, the laboratory evaluation of PCIS (Misra et al., 2002; Singh et al., 2018) indicated that the 50% collection efficiency cut-off points of 1.0 and 2.5 µm (dₐ) were very close to the theoretical cut-off points.

The EFs in PM1-2.5 and the coarse fraction had similarly low values for S, Cl, K, and Mn in comparison with the EFs in PM1, PM0.5-1, and the coarse fraction were more enriched in P than PM1 due to the greater abundance of bioaerosols, especially pollen and plant debris, in the coarse fraction (Mahowald et al., 2008).

During the Benátská_w campaign, the PM1-2.5 was significantly correlated with the coarse fraction (rₛ = 0.79) and negatively correlated with WS (rₛ = −0.63). These results correspond to dominant local sources (the nearest road and intersection) of PM1-2.5 and the coarse fraction, as shown in Fig. 4. In contrast, the highest concentrations of PM1 occurred with an east WD (busy city road). The significant influence of traffic on PM fractions is represented by the enrichment in the same elements (Cr, Fe, and Zn) as those in the summer. The EFs for S and K in PM1-2.5 and the coarse fraction achieved similar lower values in comparison with their EFs in PM1, confirming their origin in sources of the fine fraction.

The percentages of elements were very similar between PM1-2.5 and the coarse fraction with the most abundant share being Fe, Si, and Na. On the other hand, the predominant element in PM1 was S (Fig. 5). The influence of the coarse PM sources on the fine fraction (especially PM0.5-1) was much less significant, as it was observed in summer (Supplemental Fig. S6). At an urban site in Milan, a decreased portion of crustal elements in PM1-2.5 was observed during winter in contrast with summer (Vecchi et al., 2004).

At the Benátská site, SO₄²⁻ concentrations in PM1-2.5 and the coarse fraction were significantly higher (p-value = 0.0003 and 0.007, respectively) in winter than in summer (Supplemental Table S3). In contrast, seasonal differences of Ca²⁺ in all three fractions were not statistically significant (0.136 ≤ p-value ≤ 0.967). Therefore, in winter, the Ca²⁺/SO₄²⁻ ratio in PM1-2.5 was lower than that in summer (Fig. 3). To conclude, these findings suggested the effect of PM sources producing both fractions, the coarse and fine, on PM1-2.5 during the Benátská_w campaign.

During the Suchdol campaign in summer (Suchdol_s), PM1-2.5 was significantly correlated only with the coarse fraction (rₛ = 0.59), even if the location of the dominant sources of all PM fractions was similar (north WD; Fig. 4). A certain but statistically insignificant negative correlation between PM1-2.5 and RH (rₛ = −0.38) also indicated a similarity with the coarse fraction because the decrease in RH enhances the resuspension (Vallius et al., 2000; Hien et al., 2002; Galindo et al., 2011). In addition, the ion and elemental compositions (Figs. 3 and 5) clearly show an association between these two fractions. Crustal components (Si, Fe, Na, Ca, and Al) were predominant in PM1-2.5 and the coarse fraction. In PM1, S was predominant, and elements such as Fe and Si were significant. As we observed in the Benátská_s campaign, the coarser part of the fine fraction, PM0.5-1, was also highly influenced by the crustal elements (Fig. S6).
Fig. 4. Polar plots: PM$_{1.2.5}$, PM$_{2.5.10}$, and PM$_1$ concentrations (µg m$^{-3}$) by WD and WS.
Fig. 5. Semi-quantitative elemental composition of PM fractions for each campaign (expressed as percentages of individual elements normalized to 100%).
At an urban background site in Barcelona during long-term measurements, PM1-2.5 was made up of a mixture originating in fine and coarse PM sources consisting predominantly of mineral dust and secondary inorganic aerosols (SIA: \(\text{SO}_4^{2-}, \text{NO}_3^-, \text{NH}_4^+\)) and lesser parts of carbonaceous matter and sea spray (Pérez et al., 2008; Pérez et al., 2009; Pérez et al., 2010).

The EFs in PM1-2.5 and the coarse fraction revealed similar low values (EF < 10) for elements K and Mn and further increased values (EF > 10) for P, S, Cl, Cr, and Zn. However, EFs for S and Zn in both fractions were significantly lower than in PM1. The Mn, Cr, and Zn could be related to a traffic emission source (Veron et al., 1992; Manoli et al., 2002; Samara and Voutsas, 2005; Viana et al., 2008; Chang et al., 2009). Sources of P in non-desert environments are mostly biogenic or from fossil fuel and biomass burning (Mahowald et al., 2008).

Different results were found at the Suchdol site in winter (Suchdol w). PM1-2.5 was positively correlated with PM1 and PM2.5,10 and negatively correlated with WS (\(r_s = 0.75, 0.59, -0.52\), respectively). A correlation between PM1-2.5 and RH (\(r_s = 0.40\)) was also apparent but statistically insignificant (Table 3). The location of a possible fine PM source seems to match the source of PM1-2.5 (Fig. 4). In addition, the results from chemical analyses also suggested a more significant effect of the fine PM sources on PM1-2.5 than during the summer campaign (Figs. 3 and 5). The winter mass concentrations of \(\text{SO}_4^{2-}\) in all PM fractions were significantly elevated (p-value = 0.0004–0.001) in comparison with the summer mass concentrations (Supplemental Table S3). On the other hand, no seasonal differences in \(\text{Ca}^{2+}\) mass concentrations were found (p-value = 0.3399–0.9667). The elemental distribution showed that S was most abundant in PM1-2.5, accompanied by Si, Na, and Fe (Fig. 5). The EFs in PM1-2.5 and the coarse fraction showed similar values for Cl and K (slightly lower than in PM1; Fig. 2).

**Ambient Conditions Affecting PM1-2.5**

According to our observations, the behavior of the intermodal fraction differed with the measurement campaign and season. No consistent pattern was observed in terms of location or the winter/summer season. The individual sites are affected by different air pollution sources, while the seasons are characterized by different meteorological conditions, especially RH and T, in Central Europe. In winter, when the humidity is generally higher than in summer, particles of the accumulation mode can grow into PM with \(d_a > 1\) due to the hygroscopic properties of inorganic salts, such as sulfates and nitrates (Charlson et al., 1978; Tang, 1980; Geller et al., 2004), contributing the predominant portion of atmospheric aerosols, especially in industrial regions, for example, see Zhuang et al. (1999) and Alharbi et al. (2015), and significantly elevated mass concentrations of sulfates were observed in our study in winter. Additionally, the presence of a source primarily producing fine PM can influence not only the intermodal but also the coarse fraction, as was observed in winter at the Plesná, Suchdol, and Benátská sites, as well as in summer during rainy days at the Benátská site. Although the Radvanice campaign was performed in winter, this phenomenon was not observed, probably due to the effects of the important industrial source of coarse PM on the intermodal fraction.

A statistically significant association between PM1-2.5 and T was not observed at any site (Table 3). However, as is well known, the increase of T causes the decrease of RH, which helps generate higher dust resuspension. Nevertheless, for the detailed investigation of the association between PM1-2.5 and T, a long-lasting measurement campaign is necessary to cover all seasons.

**SUMMARY AND CONCLUSIONS**

The presented study investigated the association between the intermodal fraction of atmospheric aerosols (PM1,2.5) and the fine (PM1) and coarse (PM2.5,10) fractions under different meteorological conditions. The investigation was performed based on statistical and chemical analyses at an urban industrial and a suburban site in Ostrava (winter 2014; 23 measurement days for campaign) and further at an urban traffic site and a suburban site in Prague (summer 2014 and winter 2015; 15 measurement days for campaign).

PM1,2.5 was associated with the coarse fraction during all measurement campaigns, with a stronger influence at the urban industrial site in Ostrava due to the presence of the specific source and at both Prague sites in summer. In these cases, crustal elements were dominant in PM1,2.5 and the coarse fraction. A wind speed-direction analysis (polar plots) matched the sources of PM1,2.5 and the coarse fraction.

An additional effect of the sources producing the fine fraction on PM1,2.5 was found at the Ostrava suburban site, both Prague sites in winter, and the Prague urban traffic site in summer during a week with rainfall. For these cases, characterized by higher ambient relative humidity, a significantly elevated amount of sulfate was observed. According to the literature, during higher relative humidity conditions, fine particles containing inorganic salts, such as sulfate and nitrate, can grow into PM with \(d_a > 1\) due to their hygroscopic properties and chemical reactions in the liquid phase.

The short periods of the measurement campaigns and the employed chemical analysis partially limited this pilot study. The investigation of PM1,2.5 using additional approaches would be valuable, for example, the source apportionment analysis. Despite these limitations, according to the obtained results, we are able to present the following implications and suggestions.

Our investigation of PM1,2.5 found that PM2.5, often considered the fine fraction, included a significant portion of particles originating from sources of coarse PM, which was especially significant in summer at 2 sites (urban background and urban traffic site) in Central Europe.

Future studies focused on source apportionment and epidemiology/exposure should consider our findings and target the parallel measurements of both PM1 and PM2.5 fractions and their chemical analysis. This focus would...
enable the correction of results for the intrusion of crustal particles into PM$_{2.5}$ that depends on local weather and emission situations.

ACKNOWLEDGEMENTS

This work was supported by Charles University [project GA UK No 274213] and the Czech Grant Agency [project No P503/12/G147]. We thank American Journal Experts (AJE) for English language editing.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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