Supplementary material

Chemical characterization of $PM_{1\text{-}2.5}$ and its associations with PM_1, $PM_{2.5\text{-}10}$ and meteorology in urban and suburban environments

Sampling sites

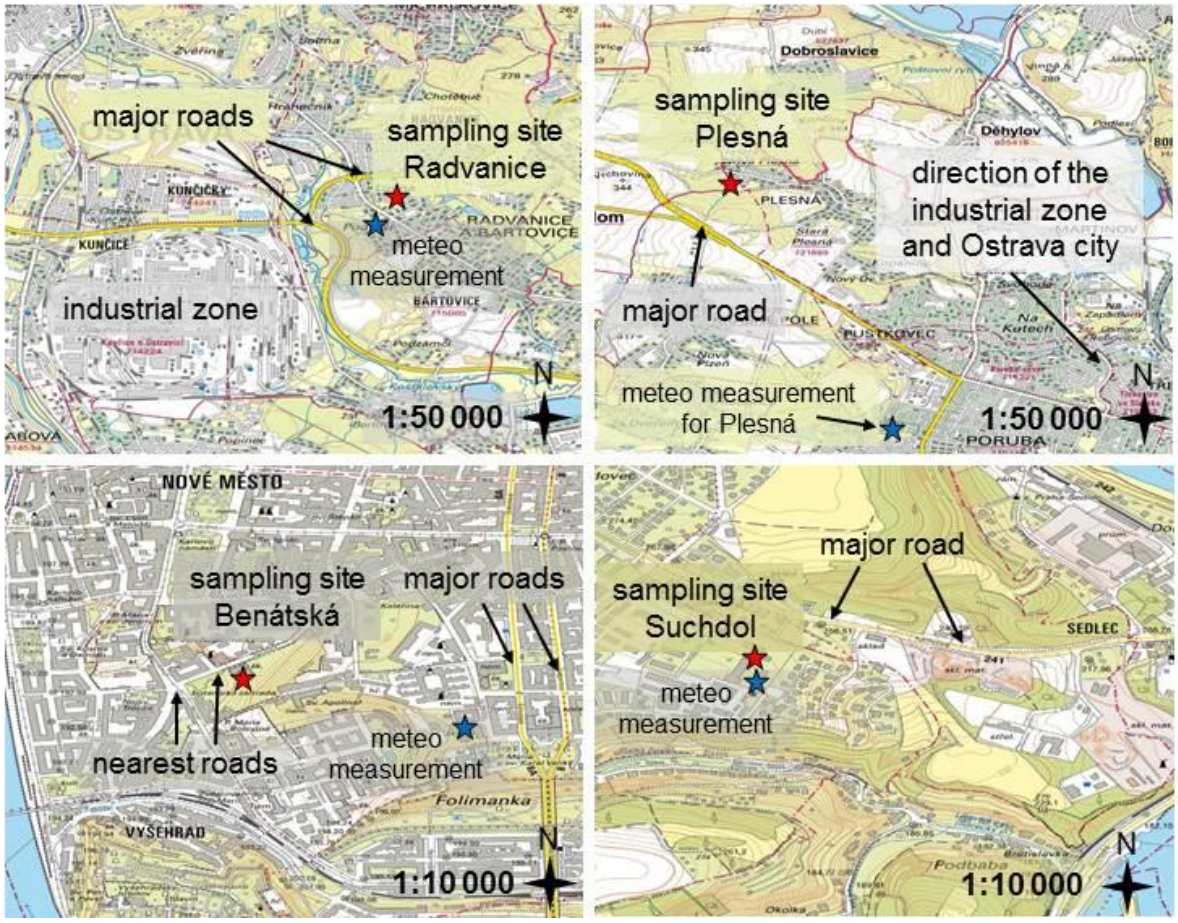


Figure S1. Sampling sites with main pollution sources (maps provided by State Administration of Land Surveying and Cadaster).

Ion chromatography analysis

All samples from Prague campaigns and 18 days from each Ostrava campaign were analyzed using ion chromatography. One-half of each 25-mm filter and a circular slice (13 mm diameter)

of each 37-mm backup filter were extracted separately in a solution of 0.3 ml methanol and 2.7 ml deionized ultrapure water with conductivity below 0.08 μS m^{-1} (Ultrapure, Watrex Ltd., Prague, the Czech Republic). After 30 min inside an ultrasonic bath and 1 h of automatic shaking, the solution was filtered using a Millipore syringe filter with a porosity of 0.22 μm. An IC analysis was performed with a Watrex Ltd. instrument with a SHODEX CD-5 conductivity detector, an Alltech universal cation 7 μm 100 x 4.6 mm column and a Transgenomic ICSep AN300 150 x 5.5 mm column. A solution of methane sulfonic acid (1.15 mmol l^{-1}) and oxalic acid (2.0 mmol l^{-1}) was used as an eluent for the cation column, and a solution of sodium bicarbonate (1.8 mmol l^{-1}) and sodium carbonate (1.7 mmol l^{-1}) in water was used for the anion column. Ca^{2+}/SO_4^{2-} ratios were calculated for a comparison of individual PM fractions.

SEM+EDX analysis

A similar approach to the one we employed in our study has already been used by several authors (Broussolle *et al.*, 2015; Jiang *et al.*, 2015; Peřestý *et al.*, 2017) in order to get reliable estimates of the whole rock chemical composition using an EDX analysis of a representative area of rock sample in the form of a thin-section. While these authors analyzed polished samples, in our case, the surface of the samples is uneven, which may have some effect on the quality of the analysis. To estimate if and how much the uneven surface can influence the ratios of analyzed elements, the method was tested on powders of samples with known compositions (rock pulps analyzed by inductively coupled plasma mass spectrometry (ICP MS) at Bureau Veritas Laboratories, Vancouver, Canada). The results showed that there is good agreement in the ratios of the main elements obtained by the EDX analysis of the rock pulp spread on a horizontal surface with the data coming from precise ICP MS analyses of the rocks. Therefore, this approach can be used at least as a semi-quantitative method allowing the comparison of relative concentrations of elements (Figure S2).

An XRF matrix correction procedure (Pouchou and Pichoir, 1984) was applied to mitigate the effect of absorption of electron radiation and X-rays in the sample. However, for elemental heterogeneous stratification in the sample, e.g., heavier elements predominantly occurring in the surface layer in contrast with lower layers, the applied correction is ineffective, and the results

can be influenced by absorption effect. It can occur when a significant air pollution source(s) occurred at a certain time just before the end of the sampling period (in our case, a 24-h period). On the other hand, the correction procedure is effective for samples with homogenous stratification (the examined material is randomly mixed).

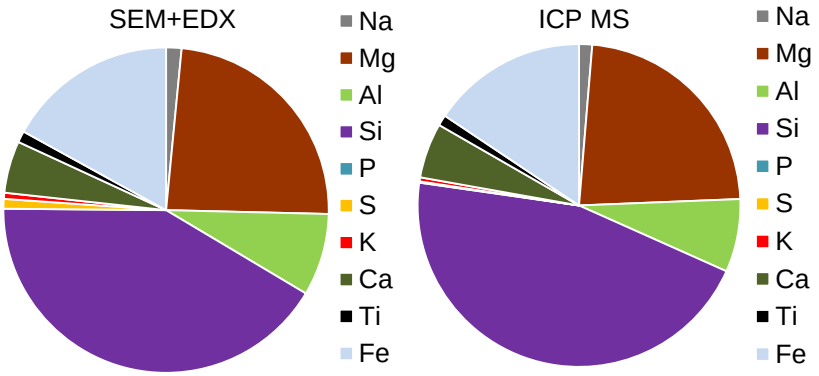


Figure S2. Comparison of the powder samples (rock pulps) analyzed by SEM+EDX and ICP MS.

SMPS and APS data processing

All the datasets were thoroughly observed, and the outliers that originated from malfunctioning instruments were removed (Table S1). The data were directly exported with the Aerosol Instrument Manager Software (TSI Inc.) as mass concentrations (dM). A Stokes correction was applied to the APS data. For the SMPS data, a multiple charges correction and a diffusion correction were applied.

Table S1. Missing data.

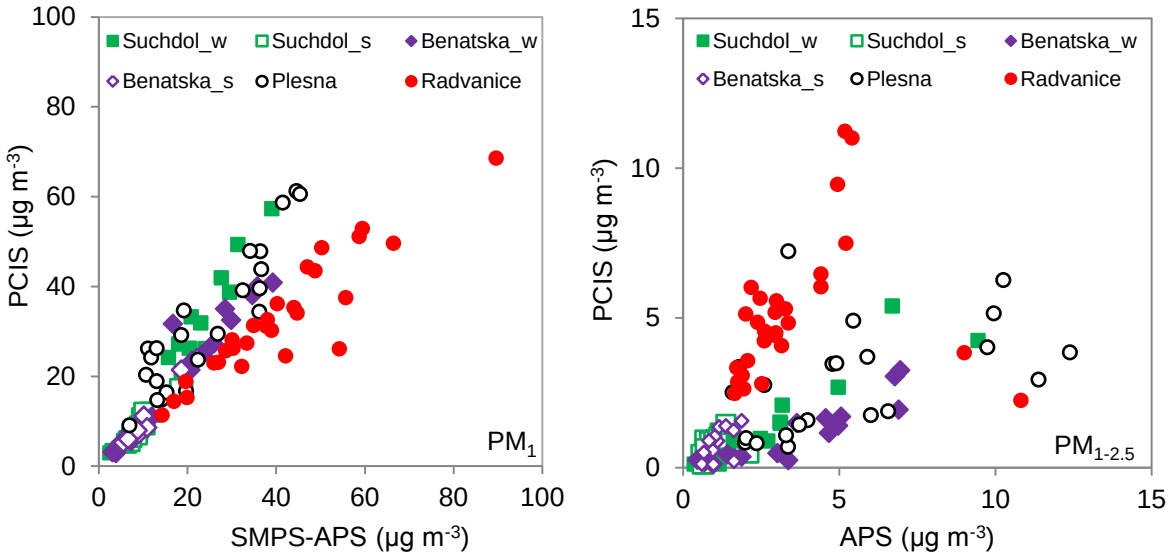
missing data	Radvanice	Plesná	Benátská_s	Benátská_w	Suchdol_s	Suchdol_w
SMPS	1.2%	3.2%	0%	5.2%	0%	0%
APS	1.2%	3.8%	0.1%	11.6%	0%	0%

The size distributions for SMPS and APS were combined without considering merging approaches. This choice is allowed by the compatibility between SMPS and APS measurements in

the overlapping region. Data from SMPS and APS size distribution were selected according to these three fractions:

- PM_1 (APS size range 0.542 – 0.965 µm + SMPS size range 14-532 nm)
- $PM_{1-2.5}$ (APS size range 1.037-2.458 µm)
- $PM_{2.5-10}$ (APS size range 2.642-10.37 µm)

To calculate the total PM_1 mass concentration, semi-continuous APS + SMPS mass concentration was obtained summing the fractions 0.542-0.965 µm and <0.532 µm. The SMPS mobility diameter (d_{eq}) was converted to the aerodynamic diameter (d_a) according to Hinds (1998), with an assumption that particles are spherical and the particle density is 1.5 g cm^{-3} (Shen *et al.*, 2002): $d_a = d_{eq}\sqrt{\rho_p}$. Mass concentrations for the SMPS and APS data were computed by averaging the 5-minute (Radvanice, Plesná, Benátská sites) and 10-minute (Suchdol site) concentrations over the sampling duration of the gravimetric method (24-h average; from 9 AM to 9 AM of the next day according to the PCIS sampling protocol) and compared (Figure S3). Differences in concentrations are due to the different measurement principles of instrumentations and the unknown real particle density in contrast to the single value of the density used for the calculation of mass concentrations from SMPS and APS. It is apparent, that particles at the industrial site (Radvanice) are different from particles from other sites.



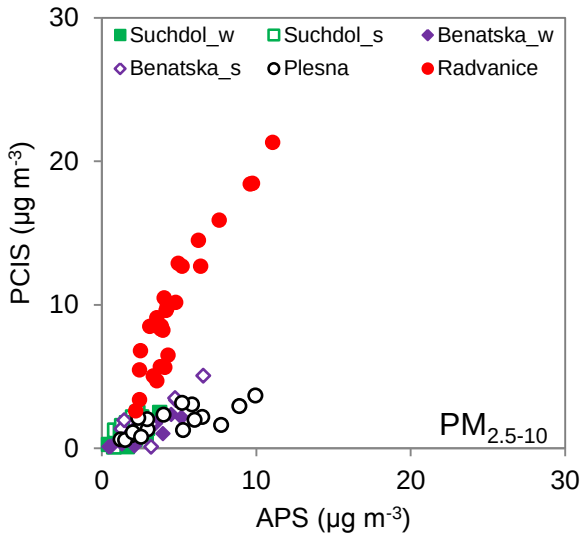


Figure S3. Comparison of PM_1, $PM_{1\text{-}2.5}$, and $PM_{2.5\text{-}10}$ measured with impactors and SMPS-APS.

Campaign overview

Table S2. Median values and the 25th and the 75th percentiles of meteorological parameters.

campaign	T, °C	RH, %	WS, m s^{-1}
Radvanice	4.9 (1.8-7.2)	79.0 (66.0-89.0)	1.0 (0.5-1.8)
Plesná	4.6 (2.2-6.8)	74.5 (62.0-86.0)	1.6 (0.9-2.4)
Benátská_s	14.5 (12.3-17.2)	78.5 (63.7-85.8)	0.5 (0.2-0.9)
Suchdol_s	15.6 (13.3-18.4)	84.1 (66.8-93.1)	0.9 (0.6-1.4)
Benátská_w	2.8 (0.9-5.3)	76.0 (61.0-84.0)	2.0 (1.2-3.4)
Suchdol_w	0.7 (-0.9-2.6)	80.0 (74.2-84.1)	1.3 (0.9-2.1)

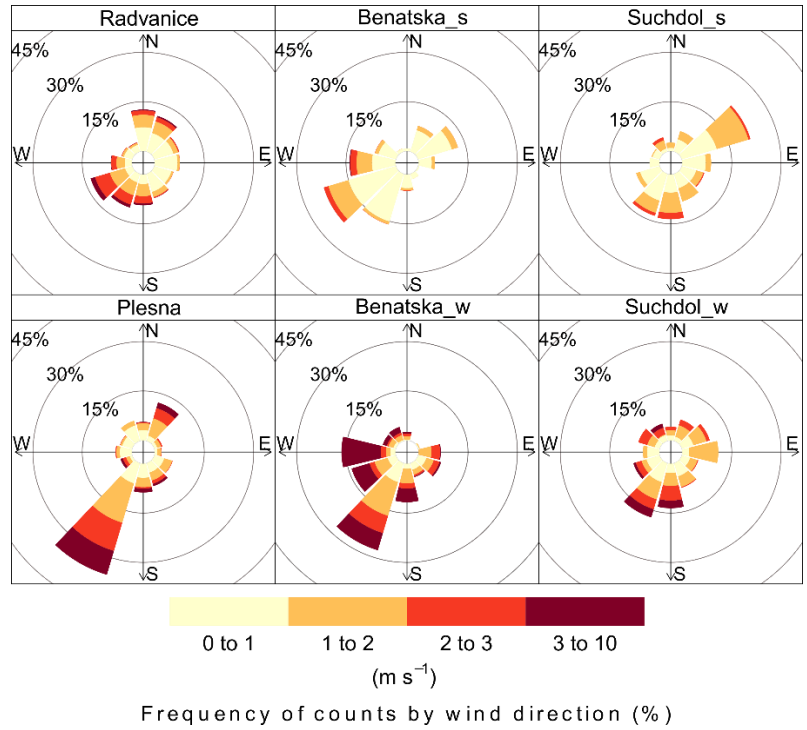


Figure S4. WS according to WD during individual campaigns.

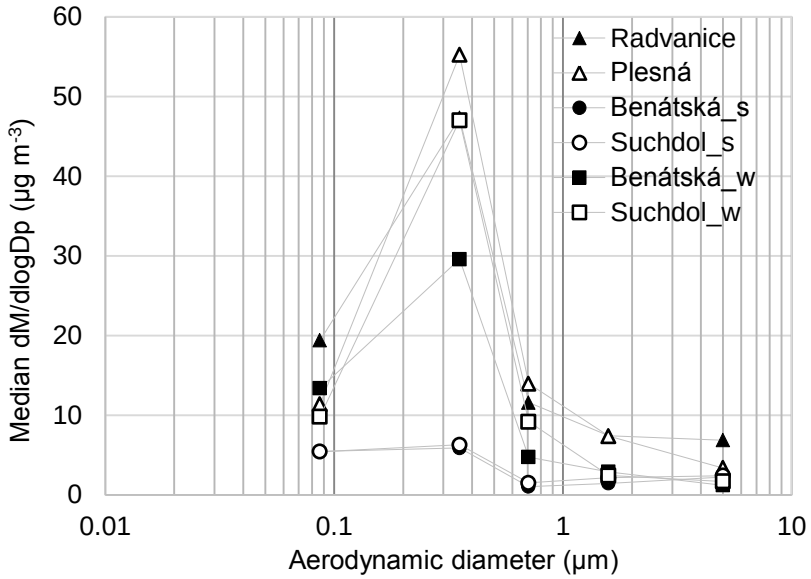


Figure S5. Median mass size distribution measured by PCIS (the lower limit of 0.03 µm used for backup filter to construct the mass size distribution).

$PM_{1\text{-}2.5}$ investigation at various sites

Table S3. Median mass concentrations of Ca^{2+} and SO_4^{2-} in size fractions of $PM_{2.5\text{-}10}$, $PM_{1\text{-}2.5}$, and PM_1.

campaign	Ca^{2+} (ng m^{-3})			SO_4^{2-} (ng m^{-3})		
	$PM_{2.5\text{-}10}$	$PM_{1\text{-}2.5}$	PM_1	$PM_{2.5\text{-}10}$	$PM_{1\text{-}2.5}$	PM_1
Radvanice	1 544.4	52.7	60.2	114.1	73.9	1 904.6
Plesná	20.5	9.2	22.9	54.1	103.9	1 796.4
Benátská_s	29.9	12.7	17. 9	11.9	15.7	644.2
Benátská_w	38.1	25.6	13.2	37.1	84.5	1 975.4
Suchdol_s	32.2	15.4	7.4	29.0	17.9	725.1
Suchdol_w	19.5	12.2	13.8	50.0	94.4	3 672.3

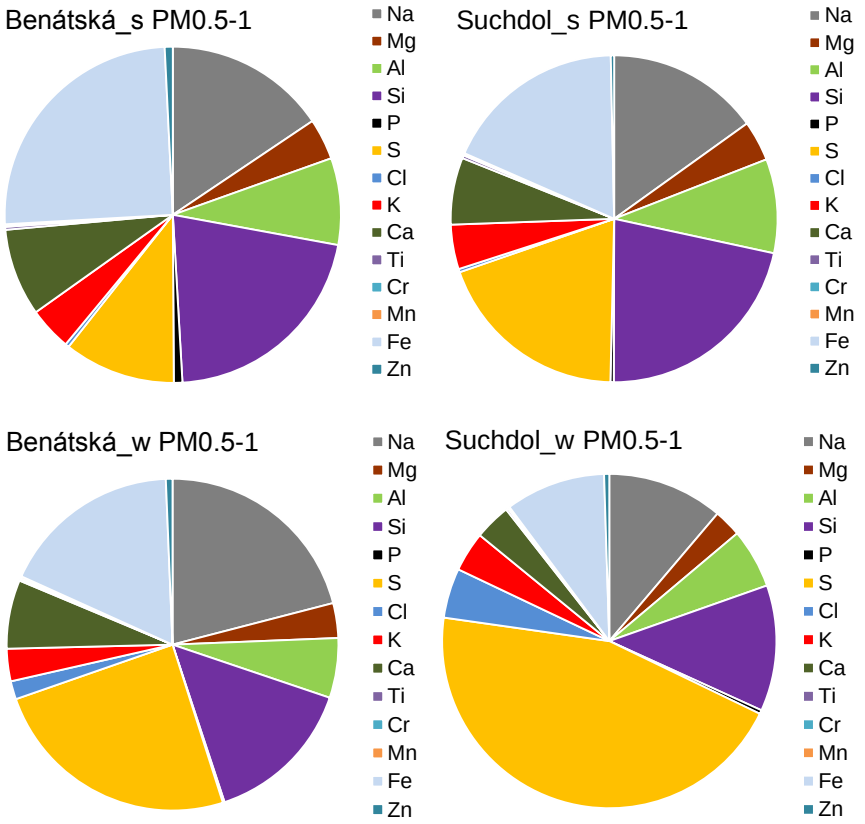


Figure S6. Seasonal comparison in the semi-quantitative elemental composition of $PM_{0.5\text{-}1}$.

References

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