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Characterization and Source Identification of Elements and Water-Soluble Ions in Submicrometre Aerosols in Brno and Šlapanice (Czech Republic)

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Abstract: Submicrometre aerosol particles (particulate matter, PM_1) were collected in two Czech cities (Brno and Šlapanice) during week campaigns in winter and summer of 2009 and 2010. The aerosols were analysed for 14 elements and 12 water-soluble ions using inductively coupled plasma–mass spectrometry and ion chromatography techniques. The average PM_1 mass concentration was 14.4 and 20.4 $\mu g\,m^{-3}$ in Brno and Šlapanice, respectively. Most of the analysed elements and ions exhibit distinct seasonal variability with higher concentrations in winter in comparison to summer. The determined elements and ions together accounted for about 29% of total PM_1 mass, ranging between 16% and 44%. Ion species were the most abundant components in collected aerosols, accounting for 27.2% of mass of PM_1 aerosols, and elements accounted for 1.8% of mass of PM_1 aerosols. One-day backward trajectories were calculated using the Hysplit model to analyse air masses transported towards the sampling sites. The Pearson correlation coefficients between individual PM_1 components and PM_1 mass and air temperature were calculated. To identify the main aerosol sources, factor analysis was applied. Six factors were identified for each locality. The following sources of PM_1 particles were identified in Brno: a municipal incinerator, vehicle exhausts, secondary sulphate, a cement factory, industry and biomass burning. The identified sources in Šlapanice were as follows: a combustion source, coal combustion, a cement factory, a municipal incinerator, vehicle exhausts and industry.

Keywords: PM_1 aerosol; elements; water-soluble ions; factor analysis; source apportionment

1. Introduction

Atmospheric aerosol (particulate matter, PM) is an important airborne component with various environmental and health effects. Aerosols can deteriorate air quality, affect global climate, reduce visibility, and are involved in smog production [1]. Epidemiological studies showed an association between the concentration of aerosol particles in ambient air and adverse health effects [2–4]. The environmental and health effects of atmospheric aerosols depend on the particle size, shape and the chemical composition of particles. The atmospheric aerosol consists of a complex mixture of components including carbonaceous species (elemental and organic carbons), inorganic ions and elements in variable amounts, depending on their location and emission sources.

In the last decade, air pollution by atmospheric aerosols has also been a subject to increased interest in the Czech Republic. Numerous studies have reported the chemical composition of PM in the Czech

Republic, focusing on PM_{10} [5–10], $PM_{2.5}$ particles [6,7,11–17] and also on PM_1 particles [6,8,10,11,18–24] that have greater toxicity compared to $PM_{2.5}$ and PM_{10}. Due to their small sizes, PM_1 particles can penetrate deep into the alveolar part of the lungs and cause respiratory and cardiovascular diseases [4]. Moreover, ultrafine particles (i.e., particles smaller than 100 nm) are even able to translocate from the lungs into secondary organs [25,26].

A number of individual studies have reported the aerosol chemical speciation and PM levels at specific locations in the Czech Republic, such as Prague [6,7,20], Mladá Boleslav [5,23], Brno [11,15–19,21], background site in Košetice [9,14,27] or the heavily polluted Ostrava region [8,10,12,13,22,24]. However, unlike other sites in the Czech Republic, where all components of PM (i.e., organic compounds, elements or ions) are studied, the studies dealing with aerosol composition in Brno focus almost exclusively on organic compounds [11,15,17–19], whereas particulate ions [16] and elements [21,28] have been measured in PM in Brno only marginally and information on the content of ions and elements in aerosols in this area is still incomplete.

Receptor models based on the statistical evaluation of PM chemical data acquired at receptor sites are used to identify emission sources of aerosols [29]. The chemical mass balance model assumes knowledge of the composition of the emissions for all relevant sources, however, fulfilling this requirement is often problematic [29]. More widespread are two multivariate models, principal component analysis [30–33] and positive matrix factorisation [5,8,22,24,34–36], which apportion the sources on the basis of the ambient data from the receptor site alone.

The aims of the study were to fill the gap in the missing information about the content of elements and water-soluble ions in aerosols in the Brno agglomeration; to obtain comprehensive information on the composition of PM_1 aerosols in Brno and Šlapanice in a combination with other studies in the same area focused on the characterization of organic compounds in PM_1 aerosols in Brno and Šlapanice [11,18,19]; to identify their sources. The paper presents the results of determination of elements and water-soluble ions in submicrometre aerosols (PM_1, particles with aerodynamic diameter smaller than 1 μm) collected in two cities in the Czech Republic (Brno and Šlapanice) in Central Europe. The seasonal differences (winter vs. summer) were evaluated and the sources of studied aerosol components were analysed.

2. Experiments

2.1. Sampling Sites

The PM_1 aerosols were sampled in Brno and Šlapanice that represent a large city and a small town in the Czech Republic. Brno, the second largest city in the Czech Republic (370,000 inhabitants), is an industrial and administration centre of Moravia, the eastern part of the Czech Republic. There are various local sources of aerosols in Brno, such as traffic (cars and trams on Veveří street), residential heating and large emission sources, such as heating plant, a municipal waste incinerator (on the eastern outskirts of Brno) and industry, including a foundry plant. Regional sources comprise mainly residential heating in the surrounding villages and a cement factory east of Brno. Šlapanice, a small town (6000 inhabitants), is located 3 km southeast from Brno. Overall, the sources of aerosols in Šlapanice are similar to those in Brno, but there is a difference between the composition of local and regional sources in both locations. Local sources of aerosols in Šlapanice include traffic, residential heating, small industrial factories and brickworks. Aerosols can be transported to Šlapanice from various regional sources, such as the nearby motorway between Brno and Šlapanice, Brno airport southwest of Šlapanice, a municipal waste incinerator northwest of Šlapanice, residential heating in the surrounding villages, a cement factory northeast of Šlapanice, etc. In addition, a large power plant in Hodonín that burns coal and biomass is located about 50 km southeast from Brno and Šlapanice. Moreover, a long-range transport of pollutants from distant areas or neighbouring countries to Brno and Šlapanice cannot be ignored.

2.2. Aerosol Sampling

Atmospheric aerosols in the size fraction of PM_1 were sampled for 24 h every day over one week in winter and one week in summer of 2009 and 2010 in Brno and Šlapanice (Figure 1) to compare the PM_1 composition in the large city and a nearby small town. The sampling of aerosols began every day at 9:00 a.m. Aerosol samples in Brno were collected in an urban locality on the balcony on the first floor (at the height of 8.9 m above ground level and at the distance of 15.6 m from the street Veveří) of the Institute of Analytical Chemistry facing northeast toward the street Veveří (49°12'28.27''N and 16°35'28.00''E). In Šlapanice the aerosols were collected in small urban locality in the garden of a family house (49°09'55.92''N and 16°43'26.18''E). Sampling locations are located relatively in the centre of both Brno and Šlapanice, and therefore, the influence of different PM sources is expected, although the sampling site in Brno is situated near the street with traffic.

Figure 1. Location of sampling sites (Brno and Šlapanice) on a map of the Czech Republic.

Submicrometre aerosols were collected at each site in parallel using a high-volume (HV) and a low-volume (LV) sampler. The HV sampler (DHA-80, Digitel, 30 m^3 h^{-1}) equipped with a PM_1 size selective impaction inlet (model DPM01/30/00, Digitel) collected PM_1 aerosols on cellulose nitrate filters (150 mm diameter, porosity 3 μm, Sartorius). A total number of 52 samples (24 samples from Brno and 28 samples from Šlapanice) were collected with HV sampler during all campaigns. The LV sampler (1 m^3 h^{-1}), consisting of a Teflon coated aluminium cyclone inlet (cut point diameter of 1 μm, model URG-2000-30EHB), and a NILU filter unit (type 9633) collected PM_1 aerosols on 47mm Teflon filters (Zefluor, porosity 1 μm, PALL). To eliminate interference of gaseous pollutants, such as SO_2, HNO_3, NH_3 and others, an annular diffusion denuder [37] was placed between the cyclone and Teflon filter. A total number of 56 samples (28 samples from Brno and 28 samples from Šlapanice) were collected with the LV sampler during all campaigns.

Meteorological parameters (i.e., temperature and relative humidity) measured by means of a commercial sensor (type T3113, Comet Systems) are given in Table 1. We also present predominant wind directions obtained from one-day backward trajectories calculated using the Hysplit v5.0.0 model. All trajectories are shown in the Supplementary Material (Figures S1–S8) separately for each location and campaign.

Table 1. Meteorological parameters in Brno and Šlapanice during campaigns.

Locality—Season	Temperature (°C)		Relative Humidity (%)		Modelled Wind Direction (Predominant)
	Average	**(Range)**	**Average**	**(Range)**	
Brno—winter 2009	−1.9	(−3.0–0.1)	77.6	(67.7–89.5)	north, northwest
Šlapanice—winter 2009	0.6	(−2.4–1.6)	81.7	(69.6–92.2)	northeast
Brno—summer 2009	21.0	(18.5–21.8)	67.1	(54.3–80.7)	all directions
Šlapanice—summer 2009	20.0	(14.3–24.9)	71.9	(67.7–86.7)	northwest
Brno—winter 2010	−3.0	(−6.0–1.0)	75.2	(69.4–85.0)	all directions
Šlapanice—winter 2010	0.8	(−1.9–2.5)	88.1	(82.0–97.2)	south
Brno—summer 2010	18.0	(17.2–21.2)	71.3	(65.3–84.8)	west
Šlapanice—summer 2010	18.2	(15.1–20.1)	79.2	(65.9–93.4)	north

2.3. Processing and Filter Analysis

Mass concentrations of collected aerosols were determined by weighing filters, using a microbalance M5P (±1 μg; Sartorius). Filters were equilibrated before weighing in an air-conditioned room under constant conditions for 48 hrs (temperature 20 ± 1 °C, relative humidity 50 ± 3%). Static electricity was eliminated with an ionizer prior to weighing (PRX-U, Haug). After weighing, exposed filters were cut, using ceramic scissors, into two equal pieces; each of them was weighted again.

One half of the cellulose-nitrate filters was digested in 4 mL of sub-boiling nitric acid in the UniClever microwave device (Plazmatronika). The decomposed samples were transferred quantitatively along with 4 mL of deionized water into polyethylene scintillation vials (Kartel). The extracts were analysed for the content of 14 selected elements (Al, K, Ca, Fe, Mn, Zn, Cu, Cd, Ba, As, Pb, V, Ni, Sb), employing an inductively coupled plasma–mass spectrometry (model 7500 CE, Agilent). Relative uncertainty of element analysis was in the range of 1 to 3%.

Both halves of the Teflon filters were extracted in 8 mL of deionized water under ultrasonic agitation. The extract of the first half was analysed for the content of seven anions (fluoride, chloride, nitrite, nitrate, sulphate, oxalate, phosphate), while the second half of the filter was analysed for five cations (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) by means of ion chromatography (ICS-2100, Dionex). Relative uncertainty of water-soluble ion analysis was in the range of 4 to 7%.

2.4. Calculation of Air Trajectories

The analysis of air mass transported towards the sampling sites was performed using the Hysplit model v5.0.0 [38,39], by calculation of one-day backward trajectories at 300, 750 and 1500 m above ground level.

2.5. Factor Analysis Model

Measured aerosol components can be grouped by their correlations. The components within a particular group are highly correlated among themselves but have relatively small correlations with aerosol components in a different group. In the factor analysis presented in this paper, it is assumed the observed correlations in a given group of aerosol components are influenced by a factor, which for given group corresponds to a source of pollution (such a pollution source can be, for example, vehicle exhausts, coal combustion and others). Factors are unmeasurable and the number of factors is much smaller than the number of aerosol components. The correlation relationship among aerosol components can be described in terms of a few underlying factors.

Suppose the observed concentrations $X_1, \ldots, X_p$ of elements and ions in PM particles with means (expectations) $\mu_1, \ldots, \mu_p$. In our study $p = 16$. Let $F_1, \ldots, F_m$, $(m < p)$ be considered common factors corresponding to the sources of pollution. We then consider the linear model describing how the

concentrations of elements and ions $X_1, \ldots, X_p$ can be explained using linear combinations of these common factors $F_1, \ldots, F_m$. The model can be described by equation

$$X_i - \mu_1 = l_{1i}F_1 + \ldots + l_{1i}F_m + \varepsilon_i, \, i = 1, \ldots, p \tag{1}$$

where $l_{ij}, \, i = 1, \ldots, p, \, j = 1, \ldots, m$, are the coefficients of linear combinations. They represent the so-called factor loadings indicating how strong is the statistical association between the i-th aerosol component X_i and the j-th factor F_j. The higher the absolute value of l_{ij} is, the higher is the statistical association between the aerosol component X_i and the factor F_j. The term ε_i stands for random errors. Random errors are supposed to be independent with zero mean and variance $Var(\varepsilon_i) = \psi_i$, and common factors are assumed to have a zero mean and unit variance. The independence of common factors and random errors ($Cor(\varepsilon_{i, \, Fj}) = 0$ for $i = 1, \ldots, p, \, j = 1, \ldots, m$) is also considered. From the above assumptions follows $Var(X_i) = l_{i1}{}^2 + l_{i2}{}^2 + \ldots + l_{im}{}^2 + \psi_i = h_i{}^2 + \psi_i$, where $h_i{}^2 = l_{i1}{}^2 + l_{i2}{}^2 + \ldots + l_{im}{}^2$ is called the i-th communality, the proportion of the variance of the variable X_i contributed by the m common factors.

Various methods [40] that allow us to estimate the parameters of model (1) exist. Here, the principal component method [41], which does not impose restrictions on distribution of analysed variables, is preferred. A crucial task of the factor analysis is the selection of appropriate number of common factors m. Since the higher values of m lead to common factors that are difficult to interpret, the aim is to choose the smallest possible value m, such that a sufficient proportion of variability in the data is explained. For this problem, Kaiser´s criterion and scree plot [41] are considered.

The original factor loads obtained by the principal component method can be difficult to interpret. Thus, the factor rotation is performed for better interpretation of factor loads. A common goal of rotation in this paper is to ensure that each aerosol component loads highly on a single factor and has small-to-moderate loads on the remaining single factors. The factor model with such rotated loads is called the model with a simpler structure. Usually the criterion, which is used to obtain a simpler structure, is the varimax criterion [41].

3. Results

3.1. Characterization of Submicrometre Aerosols

Mass concentrations of PM$_1$ aerosols collected at both sites during all campaigns are given in Table 2. The average measured PM$_1$ mass concentration was 19.1 µg m^{-3} in winter and 9.65 µg m^{-3} in summer in Brno, and 30.8 and 10.0 µg m^{-3} in winter and in summer, respectively, in Šlapanice. PM$_1$ samples in both locations were collected at a different time; therefore, we tested if the mass concentrations of PM$_1$ aerosols in Brno and Šlapanice were similar in the same season. Agreement of mass concentration of PM$_1$ aerosols collected in Brno and Šlapanice was statistically tested by non-paired t-test for equal means. Probability of equality of mean concentrations (P) smaller than 0.05 indicates disagreement of tested mean values at both sampling sites. P value was 0.0081 for winter 2009; 0.1366 for summer 2009; 0.1339 for winter 2010 and 0.1399 for summer 2010, which indicates that the mean mass concentrations of aerosols in Brno and Šlapanice in the same season were similar in summer 2009, winter 2010 and summer 2010 but different in winter 2009. The difference in the PM$_1$ concentration in Brno and Šlapanice in winter 2009 was caused by heavy snow during days 2–5 of the campaign in Brno leading to lower concentration of PM$_1$ in Brno, while in Šlapanice (no snow during the campaign), the PM$_1$ concentration remained at a normal level for this time of a year. The concentrations of aerosols in winter were higher than in summer both in Brno and Šlapanice, which can be attributed to increased anthropogenic emissions in heating season due to household heating of local residents [11,18,19] and to lower mixing layer height due to the lower dispersive capacity of the lower atmospheric layers in winter, which favours the accumulation of pollutants and prevents air convention and the dispersion of pollutants [42,43]. The strong relationship of the PM$_1$ concentration with air temperature was confirmed by a significant negative correlation ($p < 0.01$) both

in Šlapanice (a correlation coefficient R = −0.71, Table S1) and in Brno (−0.64, Table S2). Calculated one-day backward trajectories (Figures S1–S8) indicate possible transport of not only regional air pollution from surrounding villages but also long-range transport of polluted air from more distant localities, such as heavy polluted areas in the Silesian Voivodeship in southern Poland that has been recently identified as an important PM source in winter [12]. The differences in the concentration of PM_1 aerosols in corresponding seasons in 2009 and 2010 (Table 2) were probably caused mainly by different meteorological and dispersal conditions in those two years.

Table 2. Mass concentrations of PM_1 aerosols during the campaigns.

Locality—Season	PM_1 ($\mu g/m^3$)	
	Mean	**(Range)**
Brno—winter 2009 (10–16 February 2009)	12.3	(10.3–20.3)
Šlapanice—winter 2009 (25–31 January 2009)	28.5	(13.1–47.8)
Brno—summer 2009 (3–9 August 2009)	8.89	(7.72–10.7)
Šlapanice—summer 2009 (25–31 August 2009)	12.2	(5.99–18.6)
Brno—winter 2010 (1–7 February 2010)	25.9	(20.9–32.5)
Šlapanice—winter 2010 (16–22 February 2010)	33.1	(19.1–52.8)
Brno—summer 2010 (17–23 August 2010)	10.4	(5.77–17.6)
Šlapanice—summer 2010 (25–31 July 2010)	7.73	(5.88–11.3)

The mass of determined elements and ions together accounted for about 29% of total PM_1 mass, ranging between 16% and 44%. The rest of the mass probably consists of organic compounds, elemental carbon and water. Previous studies at the same locations showed that organic material and elemental carbon formed on average 37.6% and 7.80% of PM_1 mass [11,18,19].

The concentration of PM_1 aerosols found in Brno and Šlapanice in 2009 and 2010 are similar to those observed in other study from this site [11] as well as in PM_1 from other localities in the Czech Republic [6,23], or from other sites in Europe, such as Birmingham [44], Melpitz [45], Bologna [46], Granada [34], Katowice [47] and Racibórz, whereas the concentration of PM_1 in Zabrze [48] was higher than in Brno and Šlapanice.

Two recent studies [21,49] from the same location in Brno do not show any decrease in air pollution with PM_1 aerosol. The concentration of PM_1 aerosols collected in summer 2014 (i.e., the mean value of 10.8 $\mu g/m^3$) was similar to the concentration found in the presented study, while the concentration found in winter 2015 (i.e., the mean value of 16.5 $\mu g/m^3$) [21] was in the middle of the concentrations found in the present study in winter 2009 and 2010. The sampling of PM_1 aerosols in winter 2017 was accompanied by a few days of smog event, which resulted in an increased PM concentration in Brno and the concentrations of PM_1 aerosols measured in this study (i.e., the mean value of 34.2 $\mu g/m^3$) [49] was thus even higher than the concentrations found in the present study.

3.2. Characterization of Elements

We analysed 14 elements in all submicrometre aerosol samples collected in Brno and Šlapanice. The average element concentrations in PM_1 aerosols from both sampling sites are summarized in Table 3 (campaigns of 2009) and Table 4 (campaigns of 2010). In winter 2009, the concentrations of elements in Šlapanice were higher than those in Brno, whereas in all other seasons the concentrations of elements at both localities were comparable. The sum of concentrations of the analysed elements accounted for 1.77% of PM_1 mass. In winter, the contribution of elements to PM_1 mass was 2.17% (1.70–2.76%) and in summer decreased to 1.37% (0.92–1.97%). In winter, lead and potassium were the two most abundant elements accounting for 65–84% of the total element mass in PM_1, while in summer potassium prevailed (27–40% of the total element mass in PM_1). The daily changes in element concentrations in 2009 and 2010 are shown in Figures 2 and 3, respectively. As, Cd, Pb and Ni are elements known to be toxic to human health [50,51]. The annual average concentration of these

elements, calculated as the average of summer and winter concentrations, do not exceed the annual limit valid in the Czech Republic [52] in both Brno and in Šlapanice in 2009 and 2010.

Table 3. Summary of concentrations of elements and water-soluble ions (ng m^{-3}) in PM$_1$ aerosols collected during the winter and summer campaigns in Brno and Šlapanice in 2009.

PM Component	Brno		Šlapanice	
	Winter	**Summer**	**Winter**	**Summer**
	Mean (range)	Mean (range)	Mean (range)	Mean (range)
V	0.41 (0.29–0.66)	0.13 (nd–0.30)	0.51 (0.36–0.77)	0.07 (nd–0.27)
Cd	0.09 (0.05–0.14)	0.18 (nd–0.35)	0.48 (0.20–0.93)	0.20 (0.08–0.45)
As	0.32 (0.15–0.58)	0.55 (nd–1.51)	0.74 (0.19–1.47)	0.17 (nd–0.42)
Sb	0.24 (0.14–0.42)	0.67 (0.20–0.98)	1.08 (0.41–2.26)	0.78 (0.41–1.35)
Cu	0.46 (0.25–0.76)	1.08 (nd–1.56)	1.33 (0.38–3.16)	0.50 (0.23–0.98)
Ni	0.37 (0.09–0.66)	nd (nd–nd)	3.79 (0.77–20.7)	nd (nd–nd)
Mn	1.18 (0.54–2.23)	1.38 (0.42–2.11)	3.10 (0.69–6.36)	1.94 (0.39–5.50)
Al	9.44 (1.82–18.8)	7.07 (nd–18.9	9.32 (3.64–14.0)	9.35 (nd–27.8)
Ba	22.1 (2.39–63.9)	11.42 (3.15–20.0)	31.9 (0.48–107)	10.2 (1.99–17.7)
Fe	28.8 (14.7–45.9)	5.45 (nd–10.9)	37.9 (10.2–123)	4.01 (nd–12.6)
Zn	8.49 (5.48–15.6)	8.52 (2.60–12.8)	35.8 (13.6–72.6)	17.2 (5.61–66.1)
Ca	30.0 (4.12–47.3)	54.7 (19.3–119)	31.7 (14.8–48.1)	40.9 (29.9–51.2)
K	63.3 (32.9–127)	68.1 (34.3–124)	201 (95.2–326)	76.7 (24.7–145)
Pb	133 (90.5–265)	27.3 (5.93–44.9)	211 (83.4–465)	42.9 (15.5–96.0)
F$^-$	5.87 (nd–16.9)	5.51 (0.99–14.6)	29.1 (4.46–67.1)	4.90 (1.20–10.2)
Cl$^-$	10.4 (nd–36.5)	6.59 (1.05–17.1)	515 (47.3–1461)	13.1 (1.93–26.4)
NO$_2^-$	3.20 (2.11–4.29)	5.14 (0.99–22.5)	8.35 (5.83–13.7)	5.97 (0.74–12.1)
NO$_3^-$	2462 (969–5224)	79.9 (8.39–294)	3460 (1128–6090)	215 (82.9–530)
SO$_4^{2-}$	1386 (846–1775)	1012 (262–1535)	3516 (2328–4731)	1799 (285–3742)
oxalate	55.9 (32.2–72.8)	85.8 (19.0–148)	91.5 (50.2–109)	133 (28.4–262)

Table 3. *Cont.*

PM Component	Brno		Šlapanice	
	Winter	**Summer**	**Winter**	**Summer**
	Mean (range)	Mean (range)	Mean (range)	Mean (range)
PO_4^{3-}	3.00 (nd–8.84)	3.90 (1.00–10.7)	26.2 (13.0–48.1)	5.18 (nd–21.1)
Na^+	4.30 (nd–11.5)	50.1 (2.01–166)	30.4 (nd–148)	25.0 (1.01–57.1)
K^+	39.5 (10.5–72.7)	55.6 (17.3–109)	84.7 (18.7–175)	63.3 (18.2–119)
NH_4^+	1140 (616–1894)	395 (121–601)	2387 (1388–3989)	733 (134–1450)
Ca^{2+}	5.37 (2.11–10.3)	26.6 (15.0–46.3)	28.0 (11.9–43.7)	35.4 (25.9–45.8)
Mg^{2+}	nd (nd–nd)	nd (nd–nd)	nd (nd–nd)	3.52 (1.00–6.02)

nd—not detected.

Table 4. Summary of concentrations of elements and water-soluble ions (ng m^{-3}) in PM$_1$ aerosols collected during winter and summer campaigns in Brno and Šlapanice in 2010.

PM Component	Brno		Šlapanice	
	Winter	**Summer**	**Winter**	**Summer**
	Mean (range)	Mean (range)	Mean (range)	Mean (range)
V	0.57 (0.31–0.97)	nd (nd–nd)	0.98 (0.37–1.45)	0.08 (nd–0.58)
Cd	0.58 (0.38–1.17)	0.15 (0.07–0.26)	0.50 (0.42–0.62)	0.10 (0.02–0.32)
As	1.11 (0.54–1.68)	0.20 (nd–0.43)	1.06 (0.66–1.92)	0.88 (nd–2.44)
Sb	1.05 (0.67–1.72)	0.70 (0.44–1.13)	1.93 (0.84–4.96)	0.29 (0.09–0.39)
Cu	1.40 (0.45–3.47)	1.44 (1.04–2.15)	1.09 (0.31–3.02)	0.60 (nd–1.14)
Ni	1.38 (0.40–4.21)	0.10 (0.02–0.23)	0.72 (0.29–1.40)	nd (nd–nd)
Mn	5.90 (1.71–11.6)	1.24 (0.51–1.83)	2.14 (0.73–5.28)	2.37 (0.78–3.84)
Al	3.89 (0.90–11.1)	8.63 (7.21–11.4)	1.51 (0.45–2.90)	13.5 (nd–27.6)
Ba	12.6 (nd–69.6)	0.10 (nd–0.30)	nd (nd–nd)	0.87 (nd–4.87)
Fe	57.4 (20.6–86.0)	25.1 (20.8–31.5)	20.4 (10.6–53.0)	33.2 (7.44–70.1)
Zn	46.2 (19.8–73.7)	12.5 (4.54–19.7)	40.2 (27.4–51.4)	9.77 (4.45–12.9)

Table 4. *Cont.*

PM Component	Brno		Šlapanice	
	Winter	**Summer**	**Winter**	**Summer**
	Mean (range)	Mean (range)	Mean (range)	Mean (range)
Ca	20.7 (13.6–26.5)	13.0 (10.7–16.8)	6.87 (2.88–13.2)	6.15 (2.45–12.8)
K	273 (217–377)	44.0 (8.59–100)	353 (229–391)	25.7 (18.2–33.1)
Pb	76.7 (46.5–109)	3.05 (1.69–5.04)	81.1 (50.6–135)	3.36 (nd–7.18)
F^-	14.4 (7.65–27.3)	4.02 (nd–7.89)	43.4 (16.5–141)	0.27 (nd–1.91)
Cl^-	140 (37.8–194)	7.65 (nd–19.2)	315 (40.3–1129)	10.7 (2.61–21.6)
NO_2^-	23.4 (3.52–74.8)	2.06 (0.48–3.54)	16.7 (nd–46.5)	17.5 (0.30–82.6)
NO_3^-	3746 (2234–5422)	105 (8.20–519)	3156 (1727–4315)	137 (25.1–335)
SO_4^{2-}	1355 (518–2770)	577 (79.0–1315)	1591 (280–3228)	596 (178–1009)
oxalate	74.8 (51.9–112)	78.0 (7.29–190)	121 (2.82–234)	23.7 (0.50–46.6)
PO_4^{3-}	24.0 (5.48–37.2)	12.3 (1.75–44.0)	30.1 (nd–67.0)	3.01 (0.28–6.59)
Na^+	45.1 (13.1–70.2)	4.74 (nd–10.2)	75.9 (6.34–324)	2.58 (nd–6.68)
K^+	212 (171–278)	36.8 (10.1–105)	314 (191–352)	18.5 (12.8–21.7)
NH_4^+	3217 (2539–3942)	701 (117–1382)	3261 (1783–5475)	716 (211–1173)
Ca^{2+}	6.12 (3.35–9.05)	8.27 (4.49–13.7)	4.93 (2.03–9.48)	4.50 (1.85–9.43)
Mg^{2+}	1.00 (nd–3.08)	0.66 (0.06–1.37)	4.32 (nd–27.2)	0.10 (nd–0.68)

nd—not detected.

The concentrations of elements in the PM_1 samples from both the Brno and Šlapanice sites are comparable with those found in Granada [34], Bologna [46] and Frankfurt [53], but lower than those in samples from other European sites, such as Katowice [47] or Tito Scalo [54]. In other Polish cities, Zabrze and Racibórz, the concentrations of several elements (Al, Mn, Fe, Cu, Zn, As) in PM_1 were higher than those in Brno and Šlapanice, while the concentrations of other elements were comparable [48].

A comparison of the concentrations of elements in PM_1 aerosols collected in Brno in 2009 and 2010 with the concentrations of elements collected at the same location in summer 2014 and winter 2015 [21] does not show a marked drop in air pollution with heavy metals in Brno location during this period. Most of the elements measured simultaneously in this and in a later study (i.e., Fe, Mn, V, Ni, Cu, Zn, Cd) show approximately similar concentrations, with the exception of lead, as the concentrations of which in winter 2015 were much lower than the concentrations found in the corresponding season in

2009 and 2010. Similarly, the concentration of lead in summer of 2014 was much lower than in summer of 2009, but practically identical with the concentrations in summer of 2010.
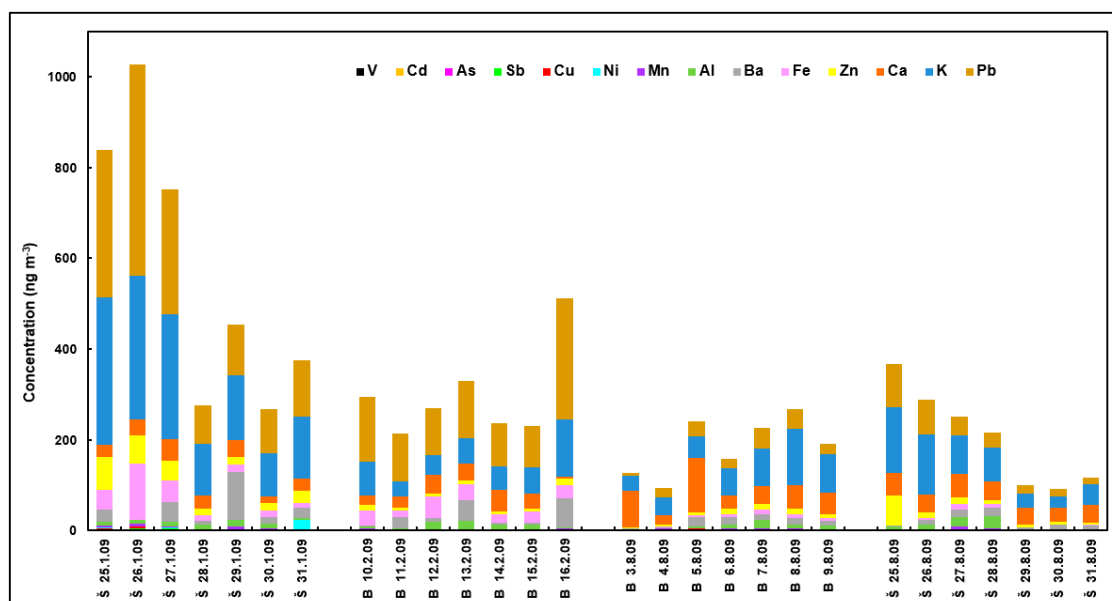

Figure 2. Daily variations in the concentrations of elements in the PM$_1$ aerosols in Brno and Šlapanice in 2009.
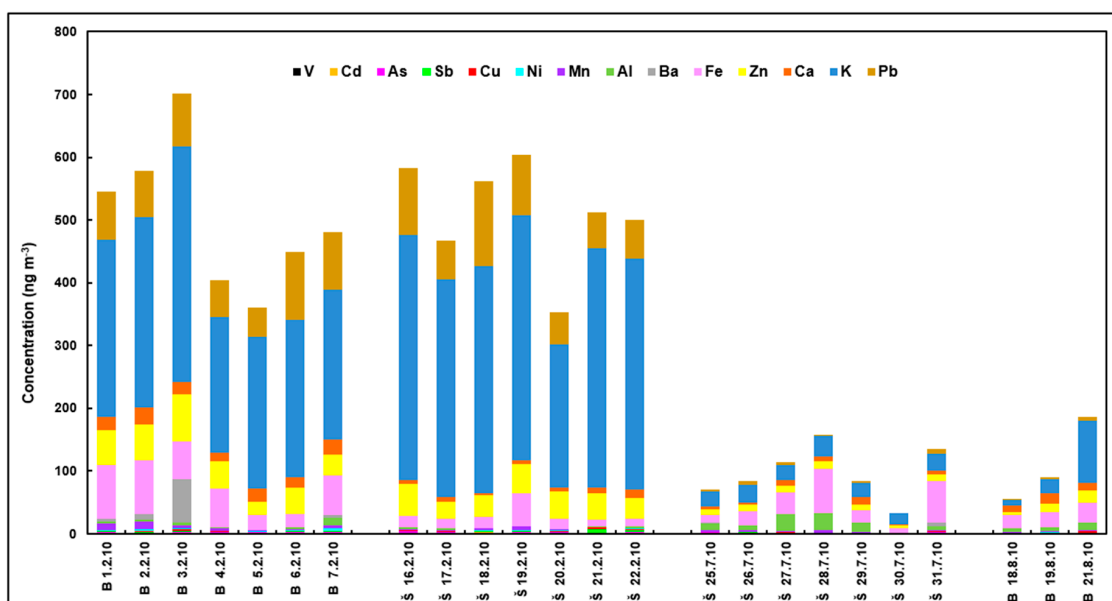

Figure 3. Daily variations in the concentrations of elements in the PM$_1$ aerosols in Brno and Šlapanice in 2010.

The enrichment factors (EFs) of elements in aerosols collected in Brno and Šlapanice were calculated to discriminate the anthropogenic and crustal (i.e., natural) origin of the studied elements. The EFs are defined by the equation

$$EF = (X/R)_{aerosol}/(X/R)_{crust} \qquad (2)$$

where X represents the considered element and R is the reference element, while the subscripts aerosol and crust indicate concentrations in PM$_1$ and in the Earth's crust, respectively [55]. The EFs were

calculated for Fe as the reference element [21]. Generally, EF < 5 indicates the crustal soil as the predominant source of the element, while the anthropogenic origin of the element may be considered at EF > 100 [56]. The enrichment factors calculated from the element concentrations determined in PM$_1$ aerosols collected in Brno and Šlapanice are shown in Table 5. Pb, Cd and Sb have the highest EFs, with Pb being the most enriched element for PM$_1$ particles both in Brno and Šlapanice followed by Cd, Sb, Zn and As with EF > 100, which indicates their anthropogenic sources. The EFs of Cu, Ba, Ni, K, Mn and V are within the range of 5–100, which suggests that these elements are of both anthropogenic origin and soil contribution. The EF of Al approaches to unity, which indicates crustal soil as a predominant source [54,57]. The EFs of most elements in the aerosols sampled in Šlapanice are larger than enrichment factors of elements in aerosols collected in Brno. The obtained value of the EFs from both localities are similar to those of the recent study in Brno [21], with the exception of V, Mn and Cd, the values of which in this study are approximately twice higher, and the EF of Pb is approximately 20 times higher.

Table 5. Enrichment factors calculated from the element concentrations determined in PM$_1$ aerosols collected in Brno and Šlapanice.

	Fe	Al	Ca	V	Mn	K	Ni	Ba	Cu	As	Zn	Sb	Cd	Pb
Brno	1.00	0.24	4.57	4.82	5.65	8.94	8.59	48.2	103	283	462	4356	5753	6393
Šlapanice	1.00	0.37	4.41	8.11	9.39	17.9	28.2	53.4	80.8	285	1096	7985	9717	11,722

Most of the elements exhibit distinct seasonal variability when the concentrations of elements in winter were higher than in summer. High seasonal differences were observed especially for K, Pb, Fe, As, V, Cd, Zn, Ni, Sb and Ba, and less for Mn and Cu. Potassium is produced largely during wood combustion [58]. Other metals can originate from several different sources. Arsenic and cadmium originate mainly from coal combustion and partly from industry. Zn, Mn, Cu, Fe or Pb are produced, next to various industrial sources and traffic, mainly by biomass (wood) burning and coal combustion [59–62]. Coal combustion and biomass burning are still frequently used for energy production and for residential heating in many European countries [36,63]. Hence, it is plausible that increased concentration of these elements (with exception of Al and Ca) in heating seasons when compared to the rest of the year is largely caused by wood and coal combustion in residential heating. Recent studies [11,15,18,19] and the results from the last census in the Czech Republic in 2011 [64] indicate that the combustion of coal and wood is used for heating only in a small part of households both in Brno (0.46%) and in Šlapanice (1.36%), but the proportion of households in small villages near Šlapanice and Brno using wood or coal for heating is much higher (up to 11%). In addition, elements, such as Cd, As, Mn, Ni, Pb, V, Cu, Zn, Sb and so on, can also originate from emission of a municipal solid waste incinerator [65,66] located directly on the connecting line between the sampling site in Brno and Šlapanice, or from the incineration of waste in households (Sb, Cu, Pb, Sn, Ti, and Zn) [67]. Another possible source of elements, in particular Ca, Zn, Fe, Mn, Pb, Cd, As, Cu and Ni, is a cement plant [68–70] located north of Šlapanice and east of Brno. To verify this hypothesis, we calculated one-day backward trajectories for all the sampling campaigns in both the Brno and Šlapanice sampling sites (Figures S1–S8). Detailed analysis revealed the transport of air masses from all directions, although during individual campaigns certain wind directions prevailed (Table 1). Moreover, the backward trajectory analysis shows the possibility of a long-range transport of air masses to Brno and Šlapanice from areas as far as several hundred kilometres.

3.3. Characterization of Water-Soluble Ions

We analysed 12 water-soluble ions in total (i.e., 5 inorganic cations, 6 inorganic anions and oxalate) in all submicrometre aerosol samples collected in Brno and Šlapanice. Average water-soluble ion concentrations in PM$_1$ aerosols from both Brno and Šlapanice are summarized in Table 3 (campaigns of 2009) and Table 4 (campaigns of 2010). Ion species were important constituents of submicrometre

aerosols both in Brno and Šlapanice, accounting for 27.5% and 26.8% of PM_1 mass in Brno and Šlapanice, respectively. Ion species on average accounted for 27.2% of mass of PM_1 aerosols. Ammonium, nitrate and sulphate were the three major ion species, contributing 32.3%, 36.2% and 23.4% of the total ion concentrations, respectively. SO_4^{2-}, NO_3^- and NH_4^+ are generally considered as secondary inorganic aerosol components (SIA; [71]). They derive from gas to particle conversion processes when SO_2 is transformed to H_2SO_4 and nitrogen oxides to HNO_3, followed by NH_3 neutralization to form $(NH_4)_2SO_4$ and NH_4NO_3. SO_2 and NO_X are products of combustion processes, whereas NH_3 originates mainly from anthropogenic sources, such as agricultural activity, industry and traffic [36,72]. The sum of SO_4^{2-}, NO_3^- and NH_4^+ accounted together for 91.9% on average (86.1–97.5%) of total ion concentration and for 25.1% of PM_1 mass. The concentrations of other analysed anions and cations were much lower. The daily changes in the concentrations of ions in 2009 and 2010 are shown in Figures 4 and 5, respectively.
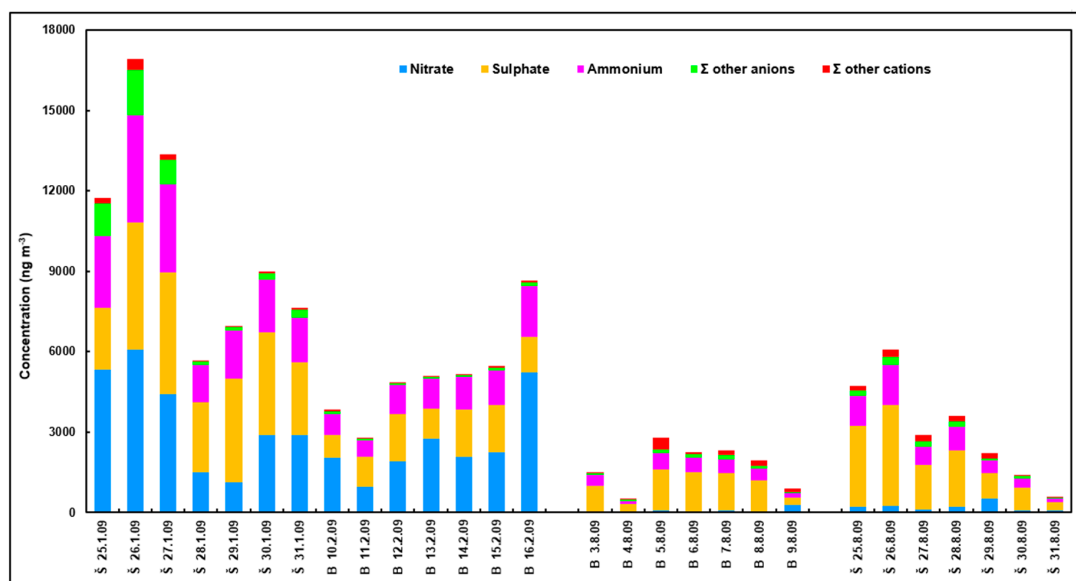
Figure 4. Daily variations in the concentrations of water-soluble ions in the PM_1 aerosols in Brno and Šlapanice in 2009.
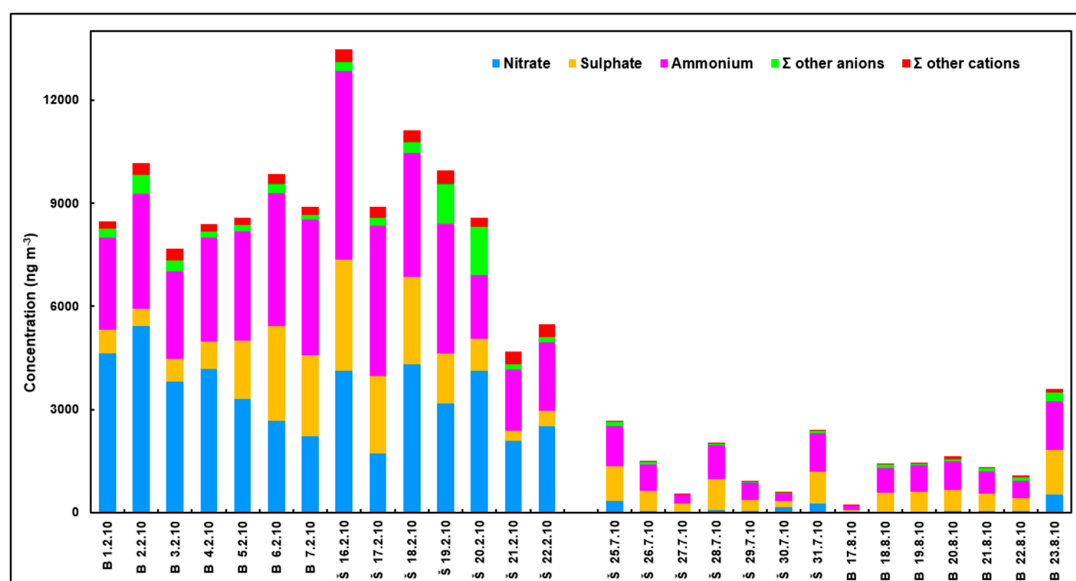

Figure 5. Daily variations in the concentrations of water-soluble ions in the PM_1 aerosols in Brno and Šlapanice in 2010.

The majority of the analysed ions show significant seasonal variability with winter concentrations, significantly exceeding those in the summer (Tables 3 and 4). The SIA contribution decreased from a share of 32.4% in PM_1 mass in winter to 17.8% in summer. The concentration of NO_3^- was much higher in winter than in summer, which may be due to the low thermal stability of ammonium nitrate in the summer, favouring the conversion of particulate ammonium nitrate to gaseous nitric acid and ammonia [1,73]. In contrast, the difference between the winter and summer SO_4^{2-} concentrations was much smaller compared to that of NO_3^-, which indicates an active photochemical production of SO_4^{2-} in summer [74].

Increased concentrations of F^-, Cl^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, NH_4^+ and K^+ in winter are mostly associated with burning of wood and coal in residential heating [11,18,19,36]. Combustion processes are the main sources of fluoride (i.e., coal), chloride (i.e., wood, coal, solid waste) and phosphate (i.e., coal, wood, traffic). K^+, considered an inorganic tracer for biomass burning [14,62], formed the majority (i.e., 73.9%) of the total potassium in submicrometre aerosol. Enhanced winter concentrations of Cl^-, F^-, PO_4^{3-} and K^+ were observed especially in Šlapanice, which is likely associated with local and regional combustion of wood and coal in residential heating [11,18,19]. Moreover, Cl^- and F^- may also be emitted from the brickworks [75,76] located directly in Šlapanice. Cl^- and PO_4^{3-} serving as markers of plastic waste combustion may also originate from a large municipal waste incinerator located east of Brno or from the combustion of solid waste by households [67].

The concentrations of oxalate in winter were similar to those during summer campaigns, with the exception of Šlapanice in 2010. Oxalates, considered a major water-soluble organic compound in the aerosols, were reported as both a product of primary emissions from combustion processes (traffic, biomass burning, biogenic activity) and as a secondary product of atmospheric chemistry [77,78]. Oxalate correlated both with sulphate and K^+ (Tables S1 and S2), which suggests that oxalate found in PM_1 aerosols in Brno and Šlapanice originated from both biomass burning and secondary oxidation.

The concentration of ions in PM_1 in Brno and Šlapanice were comparable with those found in Granada [34] and Katowice [47], while in other Polish cities, Zabrze and Racibórz, the concentrations of several ions (Cl^-, K^+, Na^+, Ca^{2+}, Mg^{2+}) were higher and others (NH_4^+) were lower [48]. The concentrations of ions at background station in Melpitz were comparable with the exception of a higher concentration of Mg^{2+} and a lower concentration of Ca^{2+} in comparison with results of this study [45]. A recent study from Prague reported generally higher concentrations of the analysed Cl^-, SO_4^{2-}, NO_3^- and NH_4^+ in comparison with those from Brno and Šlapanice [20]. Recently, Cl^-, NO_2^-, SO_4^{2-} and NO_3^- have been analysed in Brno in $PM_{2.5}$ particles, using the continuous aerosol sampler [16]. The concentrations of Cl^- and SO_4^{2-} found by the aerosol sampler were comparable with filter-based concentrations in this study, but the concentrations of NO_2^- and NO_3^- from the aerosol sampler were higher. This difference can be explained by the bimodal distribution of nitrate in PM_1 and $PM_{2.5}$ [6] and by sampling artefacts observed during the sampling of nitrite on filters [16].

3.4. Correlation Analysis

Pearson correlation coefficients provide another way to assess the sources of the analysed components in PM_1 aerosols. The possible sources can be identified from the correlation matrix by analysing the value, which represents the linear coefficient of correlation between the species. The high correlation of two species suggests their identical sources. The results of correlation analysis of the studied elements and water-soluble ions and their relationship to the mass concentration of PM_1 and temperature of air are shown in Table S1 (Šlapanice) and Table S2 (Brno), and are discussed in detail below.

Several elements (V, Cd, As, Fe, Zn, K) and most ions (NO_3^-, Cl^-, F^-, PO_4^{3-}, K^+ and NH_4^+) both in Šlapanice and Brno ($p < 0.01$) significantly positively correlated with PM_1, but negatively correlated with temperature, which indicates a strong association of the mentioned elements and ions with combustion sources, especially in heating seasons.

Many elements and ions have the same overlapping sources. For example, Zn, Cu, Mn, Pb, As, Cd were found in the emissions from several combustion processes, such as coal combustion, biomass burning, an incinerator or vehicle emissions. The effect of biomass burning on the studied elements and ions was investigated through the correlation with K^+, which is used as a marker of biomass (especially wood) burning [14,62]. K^+ correlated significantly ($p < 0.01$) in Brno with V, Cd, As, Sb, Cu, Ni, Mn, Fe, Zn, K, NO_3^-, Cl^-, F^-, PO_4^{3-}, NO_2^- and NH_4^+, and in Šlapanice with V, Cd, Sb, Zn, K, NO_3^-, F^-, NH_4^+ ($p < 0.01$) and with As and PO_4^{3-} ($p < 0.05$), which suggests that wood burning was one of the major sources of the PM_1 constituents during the campaigns in Brno and Šlapanice. This finding is in good agreement with the list of elements found in the emissions from the combustion of various biomass fuels [61,62]. Other elements (i.e., Zn, Cu, Cd and As) are important markers of coal combustion [60]. Significant cross-correlations among these elements ($p < 0.01$) confirm their common origin in combustion of coal. Moreover, some elements and ions originated from the municipal waste incinerator, such as Sb, Zn, Cd, As, Mn, Ni, Cl^-, F^-, and PO_4^{3-} correlated significantly with other elements and ions in Brno more than in Šlapanice, which suggests a stronger effect of emissions from the municipal incinerator on the composition of PM_1 in Brno than in Šlapanice. Ni did not correlate with any other element or ion in Šlapanice, but in Brno, Ni correlated significantly with V, Mn, Fe, K, NH_4^+, PO_4^{3-} ($p < 0.01$), Cd, NO_3^- and Cl^- ($p < 0.05$), which indicates the municipal incinerator as a predominant source of Ni in Brno. A similar difference in the correlations between the Brno and Šlapanice was also observed for Mn. The opposite situation was observed for Pb, which highly correlated with other PM_1 components more in Šlapanice (i.e., Cd, Cu, Fe, Zn, K, SO_4^{2-}, NO_3^-, Cl^-, F^-, PO_4^{3-}, NH_4^+ ($p < 0.01$), Mn, F^- ($p < 0.05$) than in Brno (Ba, NO_3^- ($p < 0.01$), V ($p < 0.05$)). No apparent correlation with other constituents in the PM_1 samples collected in the Brno and Šlapanice sites was observed for Al and Ca, suggesting that Al and Ca have different sources compared to other elements and ions in PM_1, such as soil dust resuspension for Al or emissions from a cement factory for Ca and Ca^{2+}.

3.5. Source Apportionment

The correlation analysis groups the elements and ions on the basis of high pair correlations. The method provides only general information about the possible sources. Moreover, it does not evaluate the relationship between various sources, so overlapping of sources is problematic. To enhance the accuracy of emission source identification and their relative contribution, the method of factor analysis was also applied. The factor analysis belongs to multivariate statistical methods and is commonly used to identify the sources of PM aerosols [29,31,32,79].

In order to identify the aerosol emission sources, the factors were extracted by using the principal component analysis method (PCA) [41] and further rotated by using the varimax criterion, which achieves a simpler structure of the orthogonal factor model and also better interpretable factors. The optimal number of factors was estimated based on the Kaiser criterion and scree plot [41]. All computations were performed by using the software R version 3.6.1.

The principal component analysis was performed on the concentrations of elements and ions in PM_1 aerosols collected in Šlapanice and Brno sites. The six extracted factor loadings from PCA analysis in Šlapanice and Brno dataset are given in Tables 6 and 7, and Figures 6 and 7, respectively. Only factor loadings above 0.1 are shown and values greater than 0.5 are in bold. The last lines in the tables (Variance and Cumul. Var., %) show the proportions of the total data variance explained by each individual factor and total explained variance, respectively.

Table 6. Principal component analysis results of PM_1 components in Šlapanice.

	F1	F2	F3	F4	F5	F6
V	**0.79**			0.24		0.1
Cd	**0.7**	0.46	0.14	0.33	0.3	0.16
As	0.32	0.49				
Sb	0.38				**0.88**	
Cu		0.43		0.26	**0.84**	
Ni						0.5
Mn	0.1	**0.59**	0.19	0.19		
Al		0.3	0.17			
Ba			0.44			0.42
Fe		**0.84**		0.28	0.16	
Zn	**0.6**	0.28	0.1	0.43	0.3	0.16
Ca				**0.98**		
K	**0.89**	0.11		0.25	0.34	
Pb	0.34	0.59	0.31	0.4	0.27	0.39
NO_3^-	**0.6**	0.35		**0.51**	0.22	0.38
SO_4^{2-}	0.39	0.48	**0.51**			0.44
Oxalate	**0.57**	0.1	0.45			
F^-		0.44	0.19		**0.77**	
Cl^-	0.18	0.45		**0.84**	0.2	0.12
NO_2^-	0.1			0.27		
PO_4^{3-}	0.41	0.25		**0.6**		0.12
NH_4^+	**0.87**	0.39		0.14		0.15
Na^+	0.25	**0.59**	0.28	0.41	0.18	
K^+	**0.89**			0.15	0.31	
Ca^{2+}			**0.98**			
Variance (%)	23	14	13	12	9	5
Cumul.Var. (%)	23	37	50	62	71	76

Table 7. Principal component analysis results of PM_1 components in Brno.

	F1	F2	F3	F4	F5	F6
V	**0.61**		0.5		0.24	
Cd	0.26	**0.58**	**0.66**	0.11		
As	0.45	0.32	0.38	0.18		
Sb	0.32	**0.87**	0.16	0.16		
Cu	0.26	**0.86**		0.2	0.11	
Ni	**0.59**	0.15	**0.51**			
Mn	**0.9**	0.38				
Al			0.1	0.13		
Ba		0.31			**0.71**	
Fe	**0.88**	0.3	0.16		0.15	
Zn	**0.65**	**0.68**	0.2		0.14	0.15
Ca				**0.74**		
K	**0.61**	**0.63**	0.35		0.21	0.2
Pb	0.26		0.27		**0.8**	
NO_3^-	**0.73**	0.11	0.25		**0.57**	0.18
SO_4^{2-}			**0.84**	0.28	0.19	
Oxalate			0.27	**0.52**		0.31
F^-	0.27	**0.54**	0.16			0.29
Cl^-	**0.79**	0.4				0.32
NO_2^-	0.47	0.37				0.38
PO_4^{3-}	0.13	0.27	**0.6**			**0.51**
NH_4^+	**0.6**	0.25	**0.69**		0.13	0.24
Na^+	0.2	0.3	0.23	**0.75**		
K^+	**0.55**	**0.53**	0.38			0.48
Ca^{2+}		0.1		**0.92**		
Variance (%)	23	18	13	10	8	7
Cumul.Var. (%)	23	41	54	64	72	79
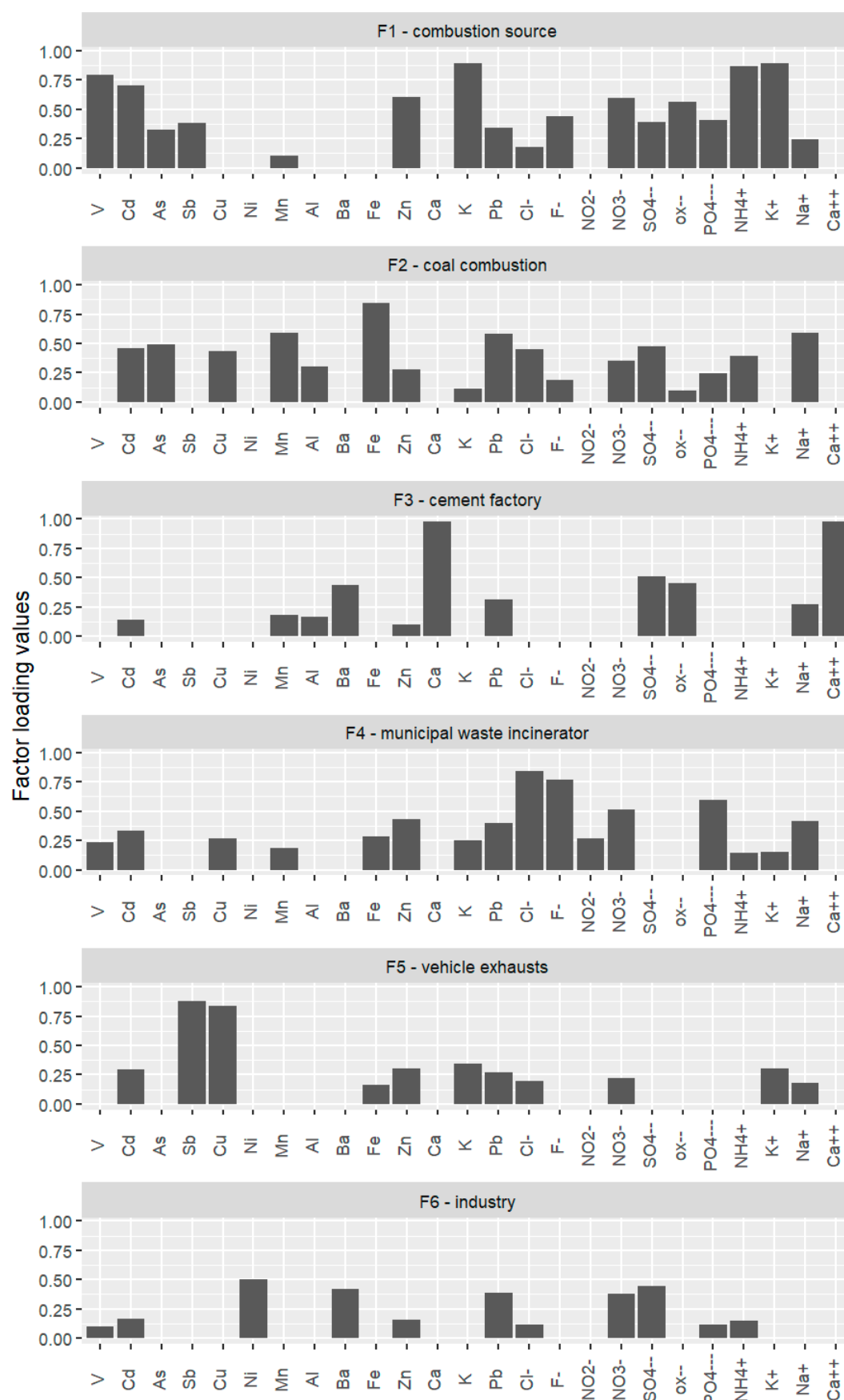
Figure 6. Source profiles for PM_1 in Šlapanice.
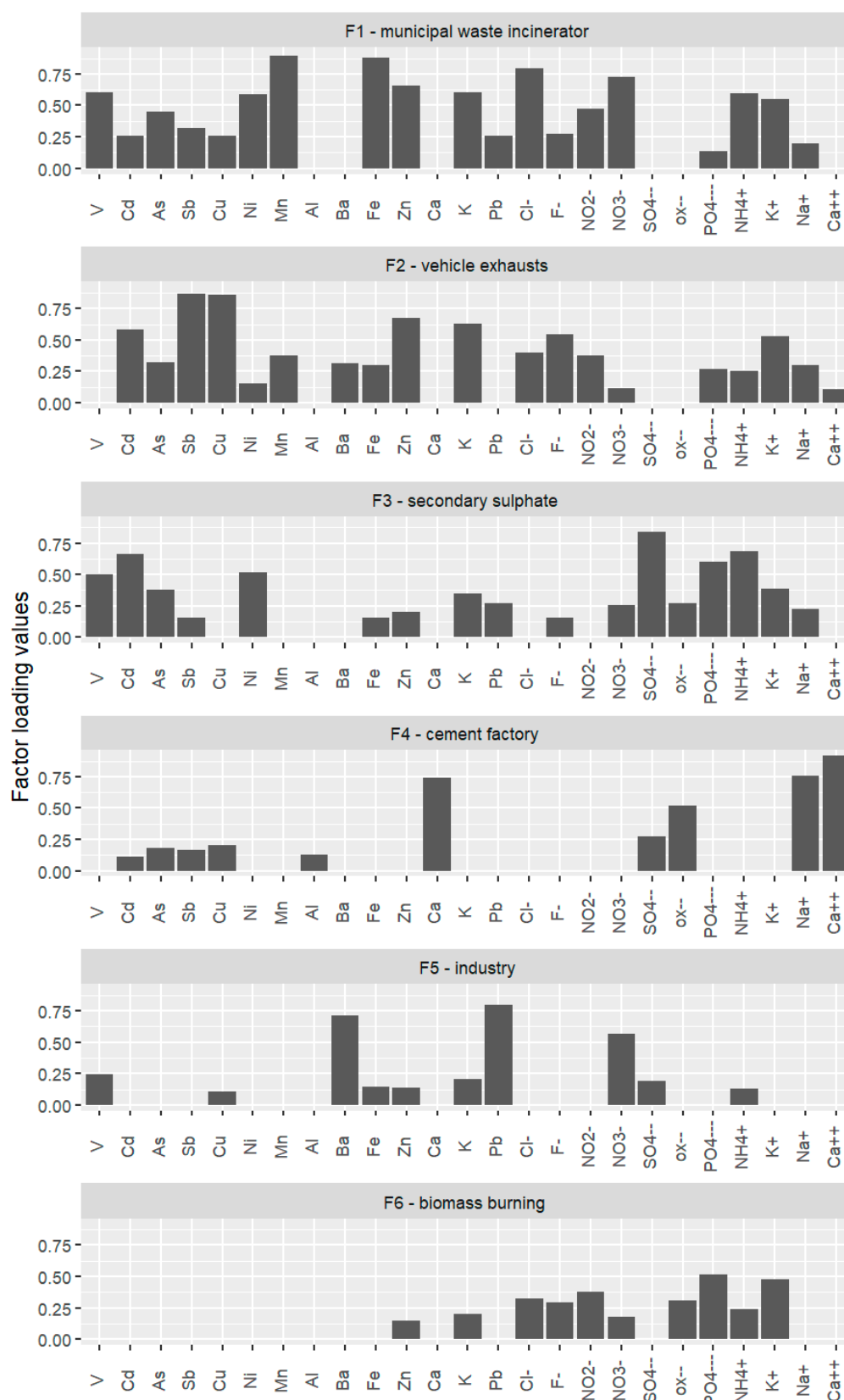
Figure 7. Source profiles for PM$_1$ in Brno.

3.5.1. Analysis for Šlapanice

Six independent sources identified in Šlapanice dataset (F1–F6 in Table 6 and Figure 6) include a combustion source (23%), coal combustion (14%), a cement factory (13%), a municipal waste incinerator (12%), vehicle exhausts (9%) and industry (5%). The identified factors together explained 76% of the total variance.

The first factor was identified as a combustion source. It is dominated by K^+, K, NH_4^+, V and Cd, followed by NO_3^-, oxalate and Zn. Other identified tracers are As, Sb, Pb, PO_4^{3-} and SO_4^{2-}. These can be related to biomass (mainly wood) burning and coal combustion in residential heating [11,18,19,35] or in a power plant burning coal and biomass located 50 km southeast of Šlapanice. The factor may also include local sources, such as engine vehicle emissions (Zn, Pb, Mn) [80] or emissions from brickworks built on a small hill at the north side of Šlapanice.

The second factor was identified as coal combustion. The factor was associated with high loadings of Fe, Mn, Pb and Na^+ and moderate loadings of Cd, As, Cu, SO_4^{2-}, Cl^-, NO_3^- and NH_4^+. Coal is used for household heating to some degree in Šlapanice and, in particular, in villages around Šlapanice. Moreover, a coal-fired power plant is located in a distance of 50 km southeast of Šlapanice.

The third factor with high loadings of Ca and Ca^{2+} may be explained mainly by emissions from a cement factory [68–70,81]. The cement factory in Mokrá is situated in a short distance, about 6.5 km northeast of Šlapanice.

The fourth factor with high loadings of Cl^-, F^-, PO_4^{3-} and NO_3^- and moderate loadings of Cd, Cu, Zn, Pb, K and Na^+ was identified as emissions from a municipal waste incinerator [65,66]. The large municipal waste incinerator, located at the southeast side of Brno and at a distance of 5 km northwest of Šlapanice, is used for the entire agglomeration of Brno. It is also necessary to take into account a partial contribution from waste incineration in households in Šlapanice and surrounding villages [67].

The fifth factor identified as vehicle exhausts was characterized with high loadings of Sb and Cu and moderate loadings of Cd, Zn, K, Pb and K^+. Cu, Sb and Zn are used as markers of vehicle-related sources [57]. They generally originate from abrasions of tires or break wear. However, Cu, Zn and Sb present in PM_1 aerosols, originating probably from the exhaust emissions from diesel and petrol engines as Cu, Zn and Sb, along with other elements, are present directly in the fuel or lubricating oils [36,57,80,82].

The sixth factor with moderate loadings of Ni, Ba, Pb, SO_4^{2-} and NO_3^-, represented emissions from industry. Several small production workshops dealing with the processing of metals are located on the outskirts of Šlapanice or nearby.

3.5.2. Analysis for Brno

Six independent sources identified in the Brno dataset (F1-F6 in Table 7 and Figure 7) included a municipal waste incinerator (23%), vehicle exhausts (18%), secondary sulphate (13%), a cement factory (10%), industry (8%) and biomass burning (7%). Identified factors together explained 79% of the total variance.

The first factor was identified as the municipal waste incinerator [65,66] situated about 6 km southeast of the sampling site. The factor is associated with high loadings of Mn, Fe, Cl^-, Ni, Zn, V, K, NO_3^- and NH_4^+ and moderate loadings of K^+, As, Sb, Cu, Cd, Pb and F^-.

The second factor was identified as vehicle exhausts. It is dominated by Sb and Cu and by moderate loadings of Zn, K, Cd, F^-, K^+, Mn, As, Ba, Cl^- and Fe [35,36,57]. The intensity of traffic, including cars and trams on the Veveří street, is quite high, with frequent queues of standing cars in front of the sampling site due to a nearby intersection.

The third factor representing the secondary aerosol production was identified as a secondary sulphate with SO_4^{2-} and NH_4^+ as the two main markers. They derive from gas to particle conversion processes from SO_2 oxidation and NH_3 neutralization [30,57]. SO_2 originates largely from coal and

biomass combustion, while NH_3 results from agricultural and traffic emissions [36,72]. This factor represents regional or long-range transport of aerosols.

The fourth factor was dominated by high loadings of Ca^{2+}, Ca and Na^+, followed by moderate loadings of oxalate and SO_4^{2-}, and represented the emissions from a cement factory [68–70] situated about 14 km east of the Brno sampling site.

The fifth factor was identified as an industry source. It was characterized with high loadings of Pb and Ba and moderate loading of NO_3^- [57]. The factor is associated with emissions from various industrial plants around Brno.

The sixth factor with PO_4^{3-}, K^+, Cl^-, F^-, oxalate, NH_4^+ and Zn, as the main indicators, was related to biomass burning [30,35]. The factor relates mainly to the regional transport of emissions from biomass (mainly wood) burning within residential heating in villages near Brno.

3.5.3. Comparison of Results for Šlapanice and Brno

The major sources of PM_1 components identified by PCA in both localities are quite similar, but they differ with their contribution. PCA showed that local pollution from the municipal waste incinerator (accounting for 23%) and vehicle exhausts (18%) prevailed in Brno, while Šlapanice was more burdened by the transport of pollution from regional sources, such as the municipal waste incinerator in Brno (12%), the cement factory in Mokrá (13%) or coal and wood combustion (14 and 23%) in the nearby villages. This hypothesis was confirmed by one-day backward trajectories (Figures S2, S4, S6 and S8) that indicate possible regional transport of air masses to Šlapanice from all directions, although the transport from east is less frequent. Villages, predominantly south or north of Šlapanice could thus be an important source of air pollution originated from biomass and coal combustion in the frame of residential heating. Moreover, there is a coal and biomass burning power plant located southeast of Šlapanice within a distance of 1 day of transport. Trajectories also confirmed the transport of air masses to Šlapanice from a northeast or northwest direction, where the cement factory and municipal incinerator are located. One-day backward trajectories calculated for Brno location (Figures S1, S3, S5 and S7) also indicated possible regional transport of air masses to Brno from all directions, which confirms findings of the factor analysis which identified the cement factory and biomass burning (i.e., within residential heating in surrounding villages or in a biomass-burning power plant located southeast of Brno) as regional sources of air pollution in Brno. Finally, we cannot neglect the contribution of long-range transport of polluted air from remote areas at distances of as far as several hundred kilometres to the pollution of both locations.

It should be borne in mind that, due to the limited sampling period at both locations, the findings concerning the source apportionment are valid only for the sampling period, while for the rest of the year, the PM_1 sources or their contribution may vary.

4. Conclusions

The concentrations of elements and water-soluble ions in PM_1 aerosols in Brno and Šlapanice, representing a large city and a small town in the Czech Republic, were compared in heating and non-heating seasons in 2009 and 2010. The average PM_1 mass concentration was 19.1 and 9.65 $\mu g\,m^{-3}$ in winter and summer in Brno, respectively, and 30.8 and 10.0 $\mu g\,m^{-3}$ in winter and summer in Šlapanice, respectively. In the winter season, ions formed a significant part of PM_1 mass of aerosols, accounting for 34.6% (26.8–41.6%), while in the summer season the contribution of ions to PM_1 mass decreased to 19.7% (14.8–24.9%). Ammonium, nitrate and sulphate, the three major ion species, accounted for 91.9% of a total ion concentration and 25.1% of PM_1 mass. The contribution of elements to PM_1 mass was much smaller: 2.17% (1.70-2.76%) in winter and 1.37% (0.92–1.97%) in summer. A more recent seasonal studies in Brno and Šlapanice [11,18,19] ascribed the rest of PM_1 mass to other components: organic material and elemental carbon that accounted for 38.8% and 7.00% of PM_1 mass in winter, respectively, and for 36.5% and 8.62% of PM_1 mass in summer, respectively.

The differences in the concentrations of PM_1 aerosols, elements and water-soluble ions in the corresponding seasons (especially winter) in 2009 and 2010 may have mainly been due to different meteorological and dispersal conditions in those two years. The variations in the concentrations of PM_1, elements and water-soluble ions in Brno and Šlapanice during the same season result from a change in the actual emission and meteorological and dispersal situation at the relevant site.

The backward trajectory analysis confirmed that the concentrations of elements and ions in aerosols collected in Brno or Šlapanice do not depend only on local emission sources but are affected significantly also by regional transport of polluted air from various sources both nearby (e.g., surrounding villages, cement factory etc.) and by a long-range transport of polluted air from sources at larger distances from both the studied locations, such as a power plant southeast of Brno and Šlapanice, or even from more distant areas, such as a heavily polluted region in Ostrava or southern Poland situated north of Brno and Šlapanice.

The source apportionment of the PM_1 samples collected in Brno and Šlapanice was performed using PCA. The six major sources of PM_1 components identified by PCA in both localities are quite similar in composition, although differing in their fractional contribution. Coal and biomass (largely wood) combustion, a municipal waste incinerator, vehicle exhausts, a cement factory and industry were identified as major sources at both localities. Both sampling sites were burdened by both local and regional pollution. The municipal waste incinerator (23%) and vehicle exhausts (17%) identified as the two major sources of PM_1 in Brno indicate a predominant effect of local sources in Brno, while Šlapanice was more burdened by the transport of pollution from regional sources, such as the municipal waste incinerator in Brno (12%) or the combustion of wood and coal in the nearby villages (37%). The transport of aerosols from sources at larger distances from Šlapanice (for example a coal- and biomass-fired power plant near the border with Slovakia) or a long-range transport of PM_1 from neighbouring countries should also be taken into account. However, the short sampling period at both locations restricts the validity of conclusions concerning the sources of PM_1 aerosols at both locations only to the sampling period, while in rest of year, the PM_1 sources or their contribution may vary.

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