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PM_{10} source apportionment at two urban sites in Southern Poland

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Abstract: The main aim of the study was to achieve a better understanding of the chemical composition, seasonal variation, and sources of ambient particulate matter in two mid-sized towns in Southern Poland, characterized by a significant air pollution issues: Nowy Targ and Zabierzów. Daily PM_{10} samples were chemically analyzed for the content of water-soluble ions, carbonaceous matter and trace elements. Positive Matrix Factorization (PMF) was applied for source apportionment. The annual mean PM_{10} concentrations were 38 μg/m³ and 41 μg/m³ in Zabierzów and Nowy Targ, respectively. Secondary species (SIA + SOC) constituted, on average, 23% of PM_{10} in Nowy Targ, while in Zabierzów, this share varied from 32% to 41% during the non-heating and heating seasons, respectively. The proportion of primary pollutants (EC + POC) in PM_{10} substantially increased during the heating season in both locations, reaching 24% and 37% of PM_{10} in Zabierzów and Nowy Targ, respectively. PMF analyses identifies four sources with similar profiles at both sites: residential coal combustion, residential wood combustion, road transport, and secondary aerosol. In both locations, residential coal and wood combustion were the largest contributing sources (on average 44% and 50% of PM_{10} in Zabierzów and Nowy Targ, respectively), followed by road transport (on average 14% and 21% of PM_{10}). Local sources were the dominant contributors to PM_{10} at both sites, accounting for 86% and 90% of PM_{10} in Nowy Targ and Zabierzów, respectively. These findings underscore the importance of implementing control strategies tailored to local factors to improve air quality in these towns.

Introduction

Air pollution is widely considered one of the most serious risks to human health and the environment, both locally and on a regional and global scale, taking into account both short- and long-term exposure (WHO 2021). According to the annual reports of the European Environment Agency (EEA), including the latest one (EEA 2023a), air quality in Europe has notably improved over the last decades due to the implementation of European legislation and technological advancements that have led to a reduction in air pollutant emissions. Between 2000 and 2021, emissions of TSP (total suspended particulate), PM_{10} and $PM_{2.5}$ (particles with an aerodynamic diameter not greater than 10 and 2.5 μm, respectively), and BC (black carbon) associated with the solid phase decreased by 27%, 29%, 31% and 44%, respectively (EEA 2023b). Despite these promising changes, exceedances of air quality standards remain common across the EU, with concentrations significantly above the latest WHO recommendations (WHO 2021). As a result, the discussion regarding the introduction of effective control measures remains a top priority.

The physicochemical properties and toxicity of ambient particles are determined not only by PM concentration and size distribution but also by its chemical composition. Consequently, differences in the chemical source fingerprints of PM across and within the urban areas are relevant for population risk assessment (e.g., Manousakas et al. 2021). The chemical composition of particulate matter, along with other PM characteristics, can vary significantly over time and space. These variations depend on primary emission sources, dispersion conditions, atmospheric chemical reactions, and the influence of air masses transported from both neighboring and remote areas (e.g., Błaszczak et al. 2020; Juda-Rezler et al. 2020). The specific components of aerosol particles provide valuable insights into air quality indicators, which, when combined with knowledge meteorological data - especially wind patterns – enable a reliable assessment of the origin of particles in the study area.

Estimating the contributions of various emission sources requires complex and often time-consuming source-apportionment studies. In most urban areas, the major sources of PM are traffic-related emissions, including both exhaust

and non-exhaust emissions. However, other anthropogenic activities, such as domestic heating and biomass burning, particularly during winter, industrial processes, energy production, and road dust resuspension may also affect air quality, which will strongly depend on the characteristics of the study area (e.g. Squizzato et al. 2017, Fachinger et al. 2021; Reizer et al. 2021). In addition, chemical profiles may vary over time, particularly between seasons (e.g., winter – summer differences). Particles and their gaseous precursors from specific sources often undergo chemical and physical transformations in the atmosphere, a process generally referred to as aerosol aging. These transformations include the formation of secondary aerosol and volatilization/condensation processes, causing the chemical fingerprint of the source found at the receptor site to differ significantly from the fresh source fingerprint (Manousakas et al. 2021.

In 2021, 10% of the EU urban population was exposed to PM_{10} concentrations above the EU annual limit value (40 $\mu g/m^3$), while as much as 97% was exposed to concentrations exceeding the stricter guideline level set by the World Health Organization (WHO) (20 $\mu g/m^3$) (EEA 2023a). It is well known that most Europeans live in urban areas, while the remaining 27% reside in local centers, villages and dispersed settlements. It seems that compared to large urban agglomerations, often considered hot spots for air pollution, or remote areas, which are typically regarded as natural background locations, the issue of air pollution in small and medium-sized cities does not receive sufficient attention (Tammekivi et al. 2023). On the other hand, small towns serve as important transport nodes between major cities and are often closely linked to rural areas (Squizzato et al. 2017; Tammekivi et al. 2023). Air quality in rural areas and small towns is often worse compared to neighboring urban areas, making them specific hot spots. The most frequently cited cause is the combustion of solid fuels, often in inefficient heating devices, leading to increased black carbon (BC) and organic carbon (OC) emissions. Traditional heating can be a large-scale, non-point source of air pollution in winter, which, in some cases, may substantially increase overall background levels of ambient particulate matter (e.g., Błaszczak et al. 2020).

Finally, it should be borne in mind that each large-scale air pollution event negatively impacts public health and well-being and contributes to the unsustainable development of society. Both observational data and model simulations indicated that unfavorable local meteorological conditions, combined with increased activity of local emission sources, are among the most direct factors influencing the formation and duration of PM episodes (Błaszczak et al. 2020; Fachinger et al. 2021). On the other hand, the advection of polluted air masses caused by regional and long-range transport events can significantly contribute to heavy PM pollution episodes (e.g., Reizer and Juda-Rezler 2016; Wiśniewska et al. 2019).

The phenomenon of smog is still observed in Poland, where poor air quality is primarily caused by exceeding the permissible PM_{10}, $PM_{2.5}$ and BaP concentrations (Reizer and Juda-Rezler 2016; Wiśniewska et al. 2019; Wielgosiński and Czerwińska 2020). An important source of particulate matter and its gaseous precursor emissions in the country is the so-called "low-level emission", i.e., the release of pollutants from emitters up to 40 m high, mainly from domestic furnaces (such as coal- and wood-fired boilers) and traffic. Scientific research has proven the existence of a specific type of smog known as "Polish smog", which differs from typical London-type smog in both atmospheric conditions (high pressure and negative temperatures) and chemical composition (low sulfur dioxide concentrations) (Wielgosiński and Czerwińska 2020). In general, the highest aerosol concentrations are recorded mainly in Southern Poland, where stable atmospheric conditions prevail and there is a high concentration of anthropogenic activities (Wielgosiński and Czerwińska 2020; Błaszczak et al. 2020).

A better understanding of the causes of poor air quality, not only in large cities but also in smaller towns, is a public health concern of significant importance. In this context, this paper presents the results of a one-year measurement campaign conducted in two mid-sized towns with different characteristics, located in Southern Poland. The main aim of the research was to assess the air quality of the studied areas based on recorded PM_{10} concentrations and its constituents, with particular attention to the seasonal variation of particulate matter pollution. Moreover, the sources of PM_{10} were identified by analyzing its chemical components, including carbonaceous species, water-soluble ions and trace elements. Analyses were carried out separately for pollution episodes, as high PM_{10} concentrations represent a complex phenomenon with particularly adverse effects. Additionally, since studies on the quantitative relationships between emission sources and the development of pollution episodes are relatively rare in Central-Eastern Europe, this study provides new insights by analyzing particulate composition and identifying emission sources during observed episodes in this region.

Material and methods

Study area

All analyses were conducted on archival 24-hour PM_{10} samples collected between 1 October, 2020, and 30 September, 2021, using reference low-volume samplers (PNS 15, Atmoservice). The samplers operated at two urban background monitoring sites located in Nowy Targ and Zabierzów in southern Poland (Fig. 1). Both sites are part of the national air quality monitoring network and are managed by the Voivodeship Inspectorate for Environmental Protection (VIEP) in Kraków.

Nowy Targ, located approximately 80 km south of Kraków in the Orava-Nowy Targ Basin, has a population of around 31,000 inhabitants. About 80% of the city's area is covered by agriculture land and forests, while residential areas occupy 18% of the total land. The measurement site is located in the central part of the city, in a mixed commercial and residential area. The immediate surroundings consist mainly of single-family houses, a secondary school complex, and an ice hall with a seating capacity of approximately 3,000. The nearest national roads are located about 600 m west and south of the site.

The village of Zabierzów has a population of approximately 6,000 inhabitants and is located about 20 km northwest of Kraków. The measurement site is situated in the northern part of the village. The immediate surroundings of the site consist mainly of single-family houses and a town square, while a 5-km^2 forest area is located 750 m west of the site. The nearest national, highway and express roads are located approximately 300 m and

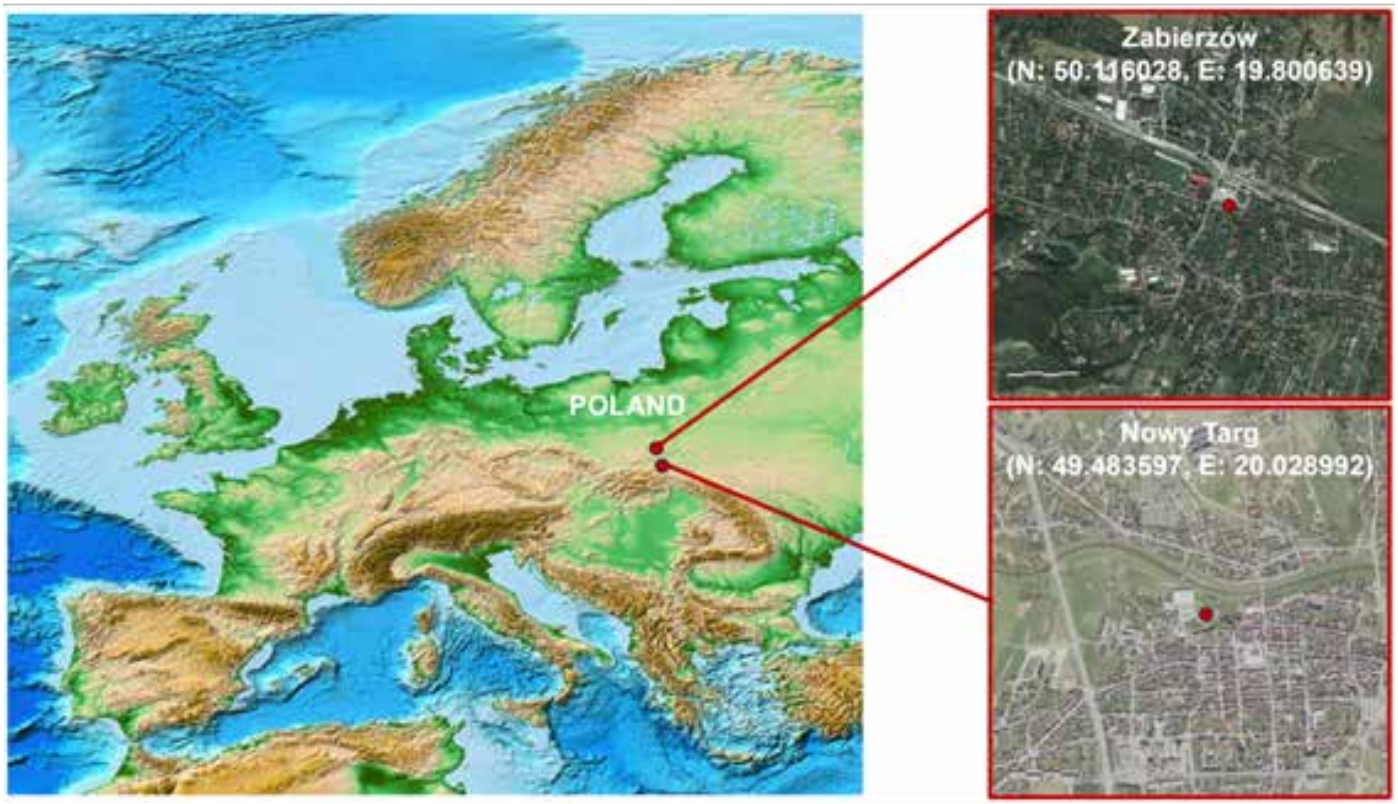

Figure 1. Location of the measurement sites in Nowy Targ and Zabierzów (Poland). Source of the maps: http://www.ngdc.noaa.gov/mgg/global/global.html; https://mapy.geoportal.gov.pl.

3 km south of the site, respectively. Additionally, the Kraków International Airport is located about 4 km south of the site.

The samples, collected on 47 mm quartz filters, were initially used by VIEP for PM_{10} concentration analysis, with only half of each filter archived. As a result, there was not enough material to perform all the desired chemical analyses with daily resolution. Therefore, 4-day composite samples were created for the analysis of most PM_{10} components (see Chapter 2.2), except for anhydro sugars, which required 8-day composite samples. The sampling scheme is presented in Fig. S1 in the Supplementary Material.

Chemical analyses

The collected samples were analyzed in the Central Laboratory of the Environmental Engineering of the Polish Academy of Sciences (Zabrze, Poland) to determine the mass concentration of PM_{10} and its chemical composition. The analyses included: water-soluble ions: SO_4^{2-}, NO_3^-, NH_4^+, K^+, Cl^-, Na^+, Ca^{2+}, Mg^{2+} (4-day composite samples), carbonaceous matter: OC and EC (4-day composite samples), trace elements (15 total): As, Al, Ba, Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, Sr, Ti, V, Zn (4-day composite samples), and main anhydro sugars: levoglucosan (LG), mannosan (MN), galactosan (GA) (8-day composite samples).

Water-soluble ions were extracted in a shaker using deionized water (12h, 60 cycles per minute), with a preliminary 1-hour ultrasound exposure in a water bath. Ion chromatography with conductometric detection was then applied (Dionex ICS-1100, Thermo Fisher Scientific, USA). For particular ions, the detection limit (DL) ranged from 0.010 to 0.224 mg/l, while the uncertainty of the results ranged from 5.95 to 17.3% (see Table S1 in the Supplementary Material).

Carbonaceous matter was determined using a flame ion detector (4L Main Oven Assembly, Sunset Laboratory Inc.) according to the "EUSAAR_2" protocol (Cavalli et al. 2010). The limit of detection (LOD) for EC was 0.1 μg/cm^2 and for OC was 0.47 μg/cm^2, while the uncertainty of the results was 5% for both fractions (Table S1). Based on the obtained EC and OC values, calculations following the method of Castro et al. (1999) allowed for determination of the primary organic carbon (POC) and secondary organic carbon (SOC).

The analysis of 12 trace elements (As, Cd, Ni, Pb, V, Mn, Cu, Sr, Ti, Ba, Zn, and Cr) was conducted using inductively coupled plasma mass spectrometry (ICP-MS, Elan 6100 DRC-e Perkin Elmer), while the remaining three elements (Al, Fe, and K) were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer AVIO 200). The mineralization of PM samples was conducted for 60 minutes in a mixture of HNO_3 and H_2O_2. During both the spectral analysis process and further result validation, only certified reference materials, solutions and gases were used. The detection limit (DL) for metals analyzed with ICP-MS ranged from 0.02 to 4.2 mg/l, while for ICP-OES it ranged from 33.4 to 42.2 mg/l. The uncertainty of the results ranged from 7.3% to 19% (Table S1).

To determine the contents of LG, MN and GA, gas chromatography (Thermo Scientific Trace 1300) coupled with a mass spectrometry detector (ISQ 7000) was used. The DL ranged from 0.0077 to 0.0500 μg/ml, and the uncertainty of detection was 19% (Table S1).

Prior to further statistical analyses, quality control of the dataset was performed. In particular, data completeness, basic statistics, box-an-whisker plots, as well as outlier test results

were analyzed for mass concentration time series of PM_{10} and all its components.

PM source apportionment

To identify the sources of PM_{10} and their contributions to PM_{10} concentrations observed in Nowy Targ and Zabierzów, the EPA PMF 5.0 software, developed by the United States Environmental Protection Agency (EPA), was applied. This software implements a receptor model based on positive matrix factorization (PMF) and is widely used in air quality studies aimed at the source apportionment of various PM fractions (e.g., Hopke et al. 2020).

PMF is a multidimensional factor analysis model used to estimate PM source profiles and determine theircontributions to total PM concentrations. The model solution is obtained using the least squares method, with the assumption that the apportioned source contributions, derived through an optimization procedure, are non-negative. Calculations are based on the concentrations of PM chemical components, weighted by their estimated measurement uncertainties (Paatero and Tapper 1994).

The input data for PMF was prepared following the procedure of Polissar et al. (1998). Concentrations of PM components below the DL were replaced with 1/2 DL, and their uncertainties were set at 5/6 DL. For measured concentrations above the DL, uncertainties (σ_{ij}) were calculated based on Zabalza et al. (2006) using following Equations (1) and (2):

$$\sigma_{ij} = 0.2x_{ij} + \frac{2}{3}(DL_j); \quad DL_j < x_{ij} < 3DL_j \qquad (1)$$

$$\sigma_{ij} = 0.1x_{ij} + \frac{2}{3}(DL_j); \quad x_{ij} > 3DL_j \qquad (2)$$

where x_{ij} represents the concentration of species j in the ith sample, and DL_j is the detection limit for species j. The coefficients 0.2 and 0.1 in Equations (1) and (2) were empirically determined by Zabalza et al. (2006).

To eliminate variables dominated by noise, the signal-to-noise (S/N) criterion proposed by Paatero and Hopke (2003) was used. Based on this criterion, Cu and V concentrations in Nowy Targ and Cr, Cu and V levels in Zabierzów with S/N < 0.2 were excluded from PMF analyses. Species with 0.2 < S/N < 2 were classified as "weak" and downweighted by a factor of 3. The remaining components were classified as "strong variables".

In order to improve the differentiation between primary and secondary PM sources, POC and SOC were introduced into the PMF model instead of OC. In total, 26 input variables were used for Nowy Targ: Strong variables - EC, POC, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, Cd, Ni, Pb, Mn, Sr, Ti, Ba, Zn, Cr, LG, MN, GA, and Weak variables - As, Al, Fe, and SOC. For Zabierzów, 25 input variables were considered: Strong variables - EC, POC, SOC, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, Cd, Ni, Pb, Mn, Sr, Ti, Ba, Zn, Al, Fe, LG, MN, GA, and Weak variable - As.

Similar to other receptor models, PMF does not yield a single, definite solution. Instead, it facilitates the exploration of multiple scenarios to identify a stable and physically interpretable outcome. In this study, for each location, various solutions were tested, assuming 3 to 10 PM sources. The results were carefully analyzed in both cases to determine the optimal solution. To assess the stability of the solutions, a bootstrap analysis was performed with 100 repetitions, setting the minimum correlation threshold at 0.6.

Results and discussion

PM_{10} concentrations and chemical composition

The summary of PM_{10} concentrations observed in both locations is presented in Table S2ł in the Supplementary Material. During the non-heating season, PM_{10} levels were similar in both locations, with an average concentration of 21-22 µg/m³ and almost no exceedances of the 50 µg/m³ daily limit value (LV_{24h}). However, significant differences were observed during the heating season: in Nowy Targ, the mean PM_{10}concentration reached 60.1 µg/m³, with 80 exceedances of the LV_{24h}. In Zabierzów the average PM_{10} level was 53.2 µg/m³, with 76 exceedances of the LV_{24h}. In both locations, the PM_{10}levels during the heating season were very high, with more than twice the allowable 35 exceedances per year. The highest daily concentration recorded in Nowy Targ was 234.9 µg/m³ and it was 67% higher than the maximum recorded in Zabierzów (140.9 µg/m³).

For the purposes of this study, a "PM episode" was defined as a period in which the LV24h was exceeded for at least 4 consecutive days. During the analyzed period, Nowy Targ experienced a total of 58 episodic days whereas Zabierzów recorded 50 episodic days. The average PM_{10} concentration during episodes was: 96 µg/m³ in Nowy Targ (3.3 times higher than the average of all non-episodic days across both seasons) and 83 µg/m³ in Zabierzów (2.8 times higher than the mean from non-episodic days) (See Fig. S2 in the Supplementary Material for details).

As shown in Fig. 2, the composition of PM_{10} in both locations show some differences, with more pronounced variations during the heating season. Carbonaceous matter concentrations were significantly higher in the heating season, a trend commonly observed Southern Poland (e.g., Błaszczak et al. 2023). No statistically significant differences were found between the two locations in the non-heating season. During the heating season, OC concentrations in Nowy Targ were around 25% higher than in Zabierzów. This was mainly due to very high POC levels in Nowy Targ (17.6 µg/m³, vs. 8.8 µg/m³ in Zabierzów). In contrast, SOC was the dominant fraction in Zabierzów (11.1 µg/m³, vs. 7.6 µg/m³ in Nowy Targ). During PM episodes, both POC and SOC levels increased significantly (see Fig. S1ł2 in the Supplementary Material). POC reached on average 22.5 µg/m³ in Nowy Targ and 11.3 µg/m³ in Zabierzów, while SOC 11.8 µg/m³ and 15.7 µg/m³, respectively.

In general, the share of secondary matter (SOC + SIA) is much higher in Zabierzów than in Nowy Targ: 31.9% vs. 21.9% in the non-heating season and 41.1% vs. 24.0% in the heating season. Conversely, the share of POC is substantially higher in both seasons in Nowy Targ: 27.2% vs. 18.2% and 29.3% vs. 16.5% in the non-heating and heating seasons, respectively. This might suggest that local sources play a more important role in PM_{10} levels in Nowy Targ, while air quality in Zabierzów is, to larger extent, influenced by sources located outside the town.

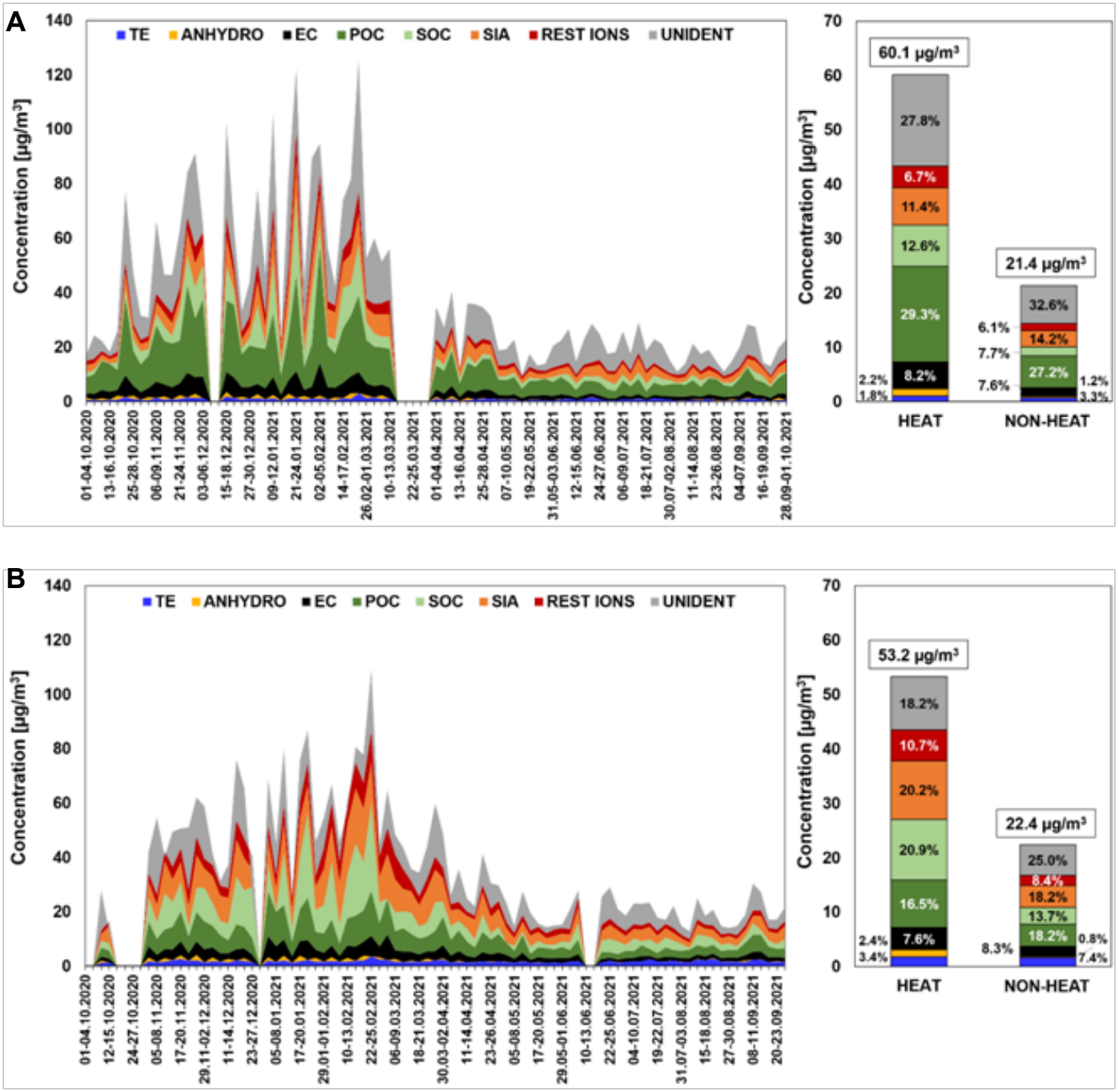

Figure 2. Time series of weekly concentrations of PM_{10} [µg/m³] main components in Nowy Targ (A) and Zabierzów (B) in the period of 1 October 2020 – 30 September 2021. The bar charts show the average shares [%] in PM_{10} mass in the heating (01 October 2020 – 31 March 2021; HEAT) and non-heating (1 April 2021 – 30 September 2021; NON-HEAT) seasons. TE – trace elements, ANHYDRO – anhydrosugars (sum of levoglucosan, mannosan, galaktosan), OC – organic carbon, EC – elemental carbon, SIA – secondary inorganic aerosols (sum of SO_4^{2-}, NO_3^-, NH_4^+), REST IONS – rest of ions (sum of Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}), UNIDENT – unidentified PM_{10} components.

Another difference can be observed in the case of trace elements: both their aggregate share in PM_{10} mass and their total concentrations (not shown) are approximately twice as high in Zabierzów than in Nowy Targ. The largest seasonal differences (over 2.5-fold) were observed for As, Cu, and Pb. During pollution episodes, the aggregate concentration of all analyzed trace elements increased by 90% in Nowy Targ compared to non-episodic days, whereas in Zabierzów, this increase was only 24%. In both locations, the largest increases (over 2-fold) during episodes were observed for Cu, As, and Pb – elements associated with coal combustion and, in the case of Pb, road transport.

Crustal matter (CM) content was estimated based on the contributions of main crustal element compounds (SiO_2, Al_2O_3, Fe_2O_3, FeO, CaO, $CaCO_3$, Na_2O, MgO, K_2O, TiO_2), using factors available in the literature (e.g. Trippetta et al., 2016):

$$[CM]=2.14[Si]+1.89[Al]+2.42[Fe]+1.95[Ca]+1.35[Na]+1.67[Mg]+1.21[K]+1.67[Ti] \quad (3)$$

Since Si concentrations were not measured in the samples, SiO_2 was indirectly estimated using empirical factors (see Querol et al., 2001). All other trace elements used in this calculation are characterized by enrichment factors <10 (see Table S3 in Supplementary Materials), indicating their predominantly crustal origin (Juda-Rezler et al., 2020). The resulting mean concentrations of CM are presented in Table 1. Following the concentrations of TE, average CM concentrations were higher in the heating season, however its relative (%) contribution to total PM_{10} mass was approximately twice as high in the non-heating season than in the heating season (not shown). This aligns with the fact that anthropogenic sources have a greater influence on PM_{10} concentrations in colder months, while crustal contribution becomes more important in the warmer months. During episodic days, the average CM level tended to increase slightly, but its relative contribution to PM_{10} mass decreased about 2-fold as compared to non-episodic days.

In terms of secondary inorganic aerosol (SIA: NO_3^-, SO_4^{2-}, NH_4^+), the concentrations in both locations were significantly higher in the heating season, ranging from a 1.5-fold increase for SO_4^{2-} to a 4-fold increase for NH_4^+. The higher SIA concentration in Zabierzów (in both seasons) was primarily driven by the NO_3^- anion, whose levels were approximately twice as high as in Nowy Targ. Consequently, NO_3^- accounted for 40% of the total SIA in Zabierzów during the heating season, compared to 30% and 24% in Nowy Targ, respectively. This suggests that road transport (the main source of NOx, the precursor of NO_3^-) has a greater impact on PM_{10} levels in Zabierzów than in Nowy Targ. During pollution episodes, however, the largest concentrations increase in both locations was observed for NH_4^+, with a 3.4-fold rise in Nowy Targ and 2.6-fold rise in Zabierzów.

The seasonal variance in the proportions of the three ions contributing to SIA is presented in Fig. S3 in the Supplementary Material. The reconstruction of the major components of this aerosol, namely ammonium sulfate and ammonium nitrate, is based on the analysis of the ratios of equivalent concentrations [neq/m³] of NH_4^+, SO_4^{2-} and NO_3^-. Since the sites are located more than 500 km from the seaside, it was assumed that all SO_4^{2-} is non-sea salt sulfate. If the equivalent concentration of $[NH_4^+]_{eq}$ exceeds that of $[SO_4^{2-}]_{eq}$, all sulfate is considered fully neutralized to form ammonium sulfate. The remaining ammonium then contributes to the formation of ammonium nitrate. The computation method is well known and has been described elsewhere (e.g., Cheng et al., 2005). The resulting average concentrations of the two main inorganic salts are presented in Table 1.

Table 1. Estimated mean concentrations of crustal matter (CM), ammonium sulfate and ammonium nitrate in Nowy Targ and Zabierzów in the heating and non-heating periods.

	Nowy Targ HEAT	Nowy Targ NON-HEAT	Zabierzów HEAT	Zabierzów NON-HEAT
CM [µg/m³]	4.77	3.83	10.91	9.04
$(NH_4)_2SO_4$ [µg/m³]	3.99	1.69	5.79	1.66
NH_4NO_3 [µg/m³]	1.92	0.00	2.09	0.00

In both locations, ammonium nitrate was present in the aerosol only during the heating season, with similar mean concentrations of around 2 µg/m³. Ammonium sulfate, however, was present in the aerosol year-round in both locations, with levels in the heating season approximately 2.5 and 3.5 times higher than in the non-heating season in Nowy Targ and Zabierzów, respectively. In both locations, the contribution of ammonium sulfate to total PM_{10} mass remained similar on episodic and non-episodic days. In contrast, the contribution of ammonium nitrate was 6 times higher during episodes in Nowy Targ and 4 times higher in Zabierzów.

Among other inorganic ions, higher concentrations of Na^+ and Ca^{2+} were observed in Zabierzów in both seasons, while Mg^{2+} showed increased levels only in the heating season. All ions presented higher concentrations during episodes, but the most significant increases were observed for Cl^- (5.3-fold in Nowy Targ and 3.4-fold in Zabierzów) and K^+ (3.0-fold and 2.3-fold, respectively). Both of these ions are associated with emissions from coal and biomass combustion in the residential sector.

The total concentration of anhydro-sugars was significantly higher (4- to 8-fold) in both locations during the heating season, because they are emitted from biomass combustion, which occurs in fall and winter. Significant differences between locations were observed only for mannosan, with concentrations 60% and 45% higher in Nowy Targ than in Zabierzów during the non-heating and heating seasons, respectively. During episodes, the total concentration of anhydro-sugars was over 2.5-times higher than on non-episodic days, with the largest differences (over 3-fold) observed for mannosan in both locations.

Identification of different PM_{10} types

In Nowy Targ and Zabierzów, the PMF model identified five and seven sources contributing to PM_{10} mass, respectively. Among them, four sources exhibited similar chemical profiles in both locations: residential coal combustion, residential wood combustion, road transport, and secondary aerosol (Fig. 3).

In both locations, the residential coal combustion factor is characterized by high contributions of Cl^-, SOC, and NH_4^+, with As, K^+, and, to a lesser extent, NO_3^- (in Nowy Targ) also playing a role. Although water-soluble K^+ and Cl^- ions are emitted in significant quantities from the combustion of wood, straw, and agricultural waste (e.g., Nava et al. 2015), they can also originate from coal combustion processes (e.g. Błaszczak et al. 2020). It is unclear whether the presence of K^+ and Cl^- ions in this source profile results partly from the co-combustion of coal and biomass in the residential sector. However, the high arsenic content indicates that coal combustion is the dominant source (e.g., Nava et al. 2015; Zhao and Luo 2018). Notably, Polish hard coal is known for its high chlorine content (e.g., Mazurek et al. 2021). The Lesser Poland region has many houses heated with solid fuels, mainly coal (Godłowska et al. 2022). The high contributions of secondary inorganic ions (NH_4^+ and NO_3^-) and SOC indicate a significant influence of regional transport of transformed aerosols from outside both locations.

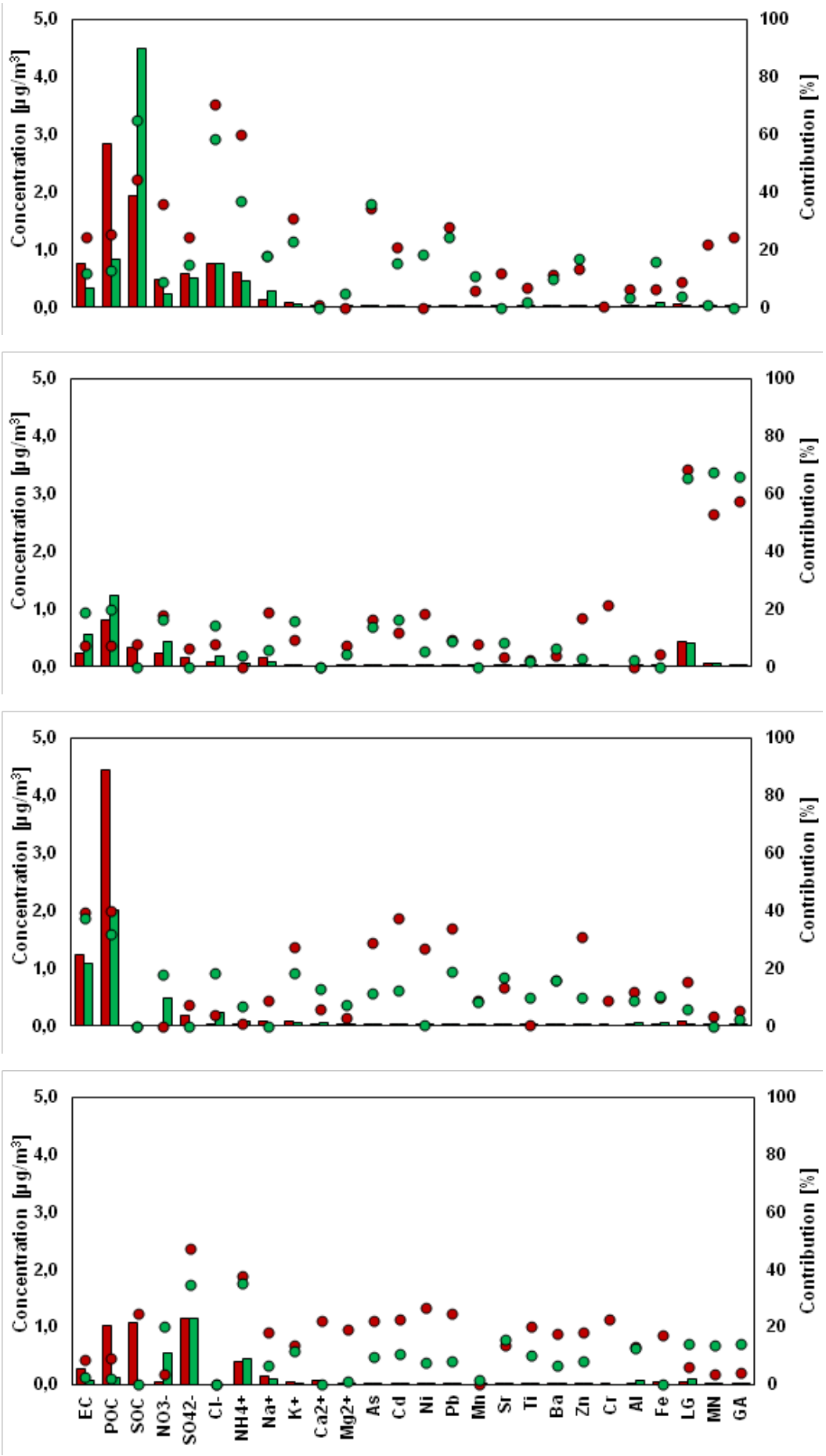

Figure 3. PMF profiles (bars, left y axis) and explained variations (dots, right y axis) of the PM_{10} sources identified in both cities – Nowy Targ (red) and Zabierzów (green).

The road transport factor is characterized by high loadings of EC and POC, with Cd, Pb, and Zn to a lesser extent. The presence of EC and POC highlights the primary contribution of fuel combustion in vehicle engines, while the trace elements can originate from both liquid fuel combustion (diesel oil, gasoline, lubricating oil) and the abrasion of brake linings, pads, and engine components (e.g. Banerjee et al. 2015).

The third factor is characterized by anhydro sugars (levoglucosan, galactosan, mannosan) suggesting an association with residential wood combustion (e.g., Klyta et al. 2023). The ratios of levoglucosan and mannosan concentrations (6.4 in Nowy Targ and 8.7 in Zabierzów) and the ratio of levoglucosan to the sum of mannosan and galactosan concentrations (5.2 in Nowy Targ and 7.2 in Zabierzów) indicate that in Nowy Targ, anhydro sugars are most likely emitted from the combustion of coniferous wood, while in Zabierzów, they result from the simultaneous combustion of coniferous and hardwood wood (Fabbri et al. 2009).

The secondary aerosol factor is characterized by the highest share of inorganic ions SO_4^{2-}, NH_4^+ and NO_3^-, which are well-known markers of long-range transport of particles (e.g., Banerjee et al. 2015). The air pollution levels in the Lesser Poland region can be affected by the inflow of pollutants from the neighboring Silesia region. Which is home to numerous industrial plants related to power engineering, coal mining, and heavy industry (e.g., Godłowska et al. 2022).

Mineral dust factors were identified in both locations, however, they exhibited different chemical profiles (see Fig. S4 in the Supplementary Material). In Nowy Targ, this factor is characterized by contributions from typical crustal elements such as Ca^{2+}, Mg^{2+}, Al, Fe, Ti and Sr, (e.g. Banerjee et al. 2015). In addition, high loadings of Ca^{2+} and Mg^{2+} may also be linked to dust emitted from renovation and construction works in the city (e.g., Cesari et al. 2018). Alongside crustal elements, notable contributions from species associated with non-exhaust and exhaust traffic emissions, such as Mn, Ba, Cr, Ni, and Zn, are observed. These elements are likely emitted from the abrasion of road surface, brake linings, pads, tires, as well as from fuel combustion, lubricants, catalytic converters, particulate filters, and engine corrosion (e.g. Banerjee et al. 2015). Therefore, this factor can be attributed to a mixed source, consisting of mineral dust with substantial contributions from construction dust and the abrasion of road surface and vehicle parts.

In Zabierzów, the mineral dust source was divided into two separate factors. The first factor is associated with typical crustal elements (Ca^{2+}, Mg^{2+}, Ti, Mn, and Fe), with high contributions of Ca^{2+} and Mg^{2+} that may also come from renovation and construction works. Therefore, this factor can be identified as a mixed source of mineral dust and construction dust (Mineral dust & Construction works). The second factor is characterized by contributions from typical crustal elements (Sr, Al, Fe, and Mn) and traffic emissions (Ba, Ni, Cd, Zn, and Pb), so it can be assigned as a mixed source of mineral dust and road dust (Mineral dust & Road transport).

Finally, a factor associated with Na^+, and to a lesser extent Mg^{2+}, NO_3^-, and Ca^{2+} representing road de-icing was identified only in Zabierzów (Fig. S4). The dominant contribution of Na^+ ion may be related to the use of chemical de-icing agents used for road surface maintenance in winter. Sodium chloride (NaCl) is most commonly used, while at lower temperatures, magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$) are also used. The presence of these compounds in the source profile may be

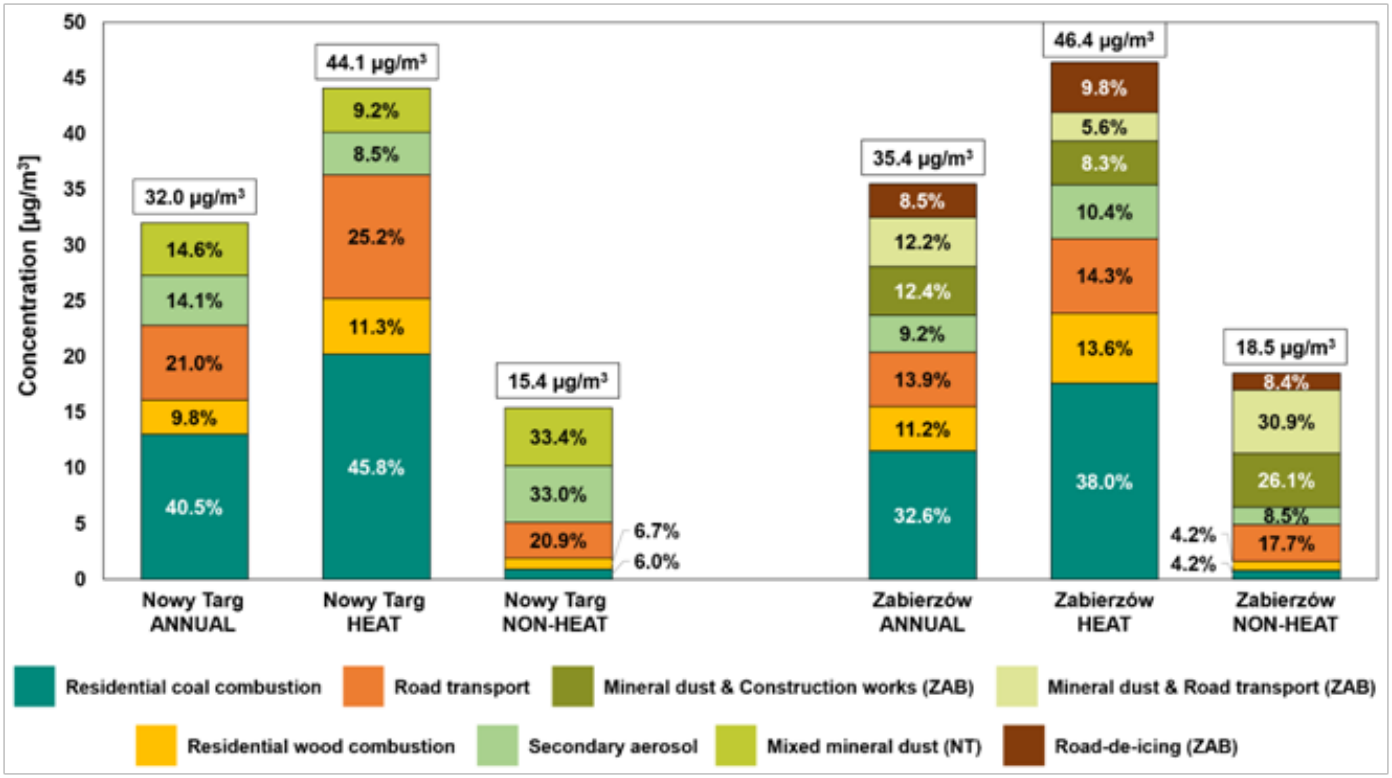

Figure 4. Contributions [%] of PM_{10} sources identified by the PMF model in Nowy Targ and Zabierzów averaged for the period of 01 October 2020 – 30 September 2021 (ANNUAL), as well as for heating (01 October 2020 – 31 March 2021; HEAT) and non-heating (1 April 2021 – 30 September 2021; NON-HEAT) seasons.

related to the winter maintenance of pavements and roads in Zabierzów, as well as the nearby expressway and the highway (approx. 3 km from the station). Additionally, this source may be related to the use of chemical de-icing agents at the Kraków-Balice International Airport, located approximately 4 km from the station. The PM components present in the source profile do not allow for a precise assignment of the source in the summer, so the source was primarily identified as dust related to de-icing agents used in winter road maintenance.

The solution obtained provides a reasonable physical interpretation and reproduces the measured PM_{10} concentrations reasonably well, with $R^2 = 0.96$ for Nowy Targ and $R^2 = 0.91$ for

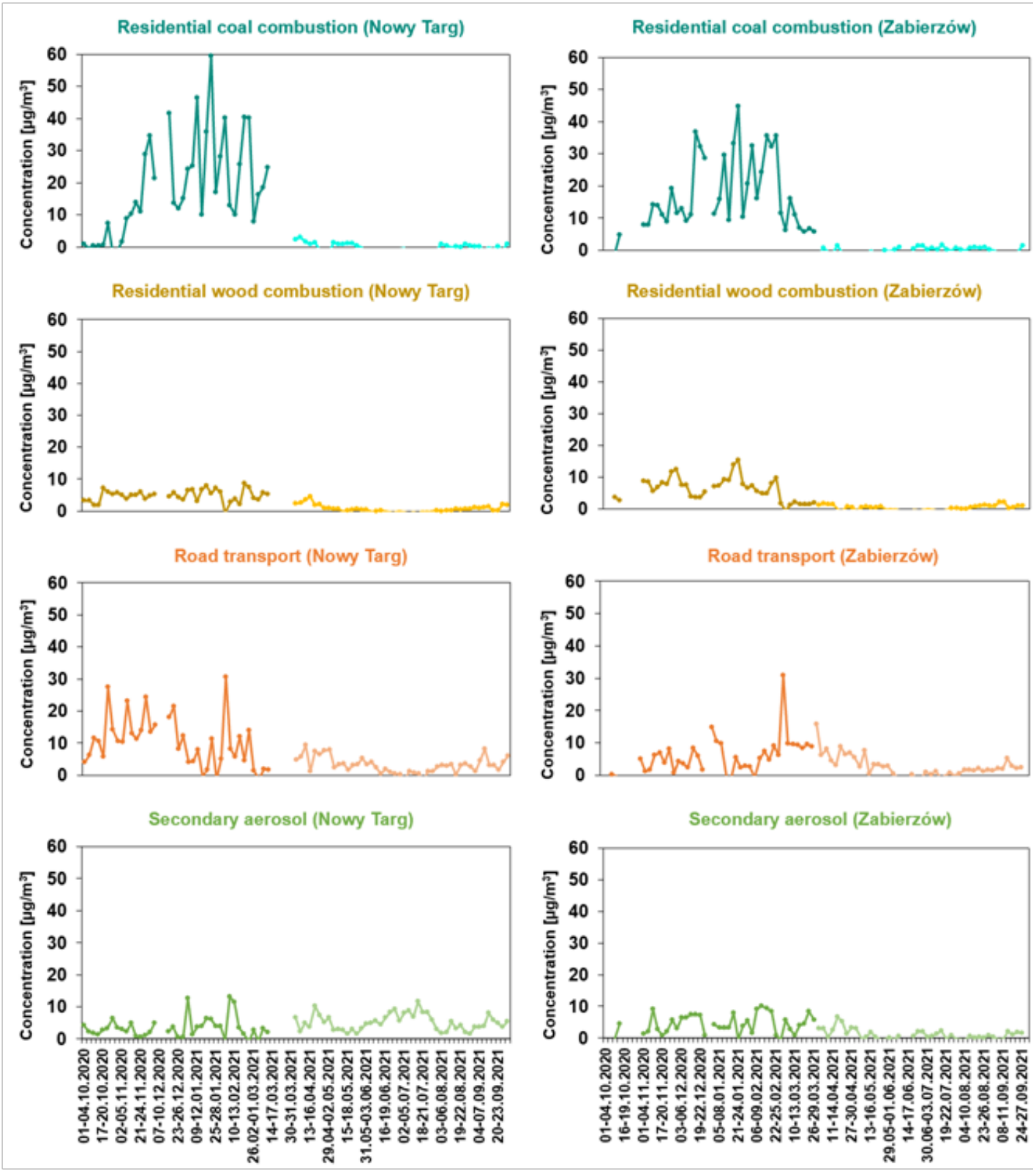

Figure 5. Annual patterns of the PM_{10} source concentrations commonly identified in Nowy Targ and Zabierzów in the period of 01 October 2020 – 30 September 2021. Dark and light colors indicate the heating (01 October 2020 – 31 March 2021) and non-heating (1 April 2021 – 30 September 2021), respectively.

Zabierzów (Fig. S5 in the Supplementary Material). For almost all variables, the scaled residuals estimated by the PMF were distributed between −3 and +3. The bootstrap (BS) analysis (100 runs, minimum correlation R-value of 0.6) showed that in Nowy Targ, 4 out of 5 sources, and in Zabierzów, for 6 out of 7 sources, were assigned to base case factors in 97 – 99% and 92 – 99% of the BS resamples, respectively (Table S4-S5). The Road Transport factor in Nowy Targ and the Mineral dust/ Construction Works factor in Zabierzów were mapped to base factors in 82% and 84% of the runs, respectively, still meeting the overall reproducibility criteria suggested by EPA PMF guide (80%). Furthermore, the displacement analysis revealed no factor swaps for any values of *dQmax*, indicating that the PMF solutions were well-defined in both locations.

Temporal variability of the identified PM_{10} sources

The annual and seasonal mean concentrations and relative contributions of PM_{10} sources identified by the PMF model are shown in Fig. 4, while their concentrations and contributions during episodic and non-episodic periods are presented in Fig. S64 in the Supplementary Material.

The average PM_{10} concentrations reproduced by the PMF model account for approximately 70% and 80% of the measured concentrations in Nowy Targ and Zabierzów, respectively. On an annual basis, the average concentrations of total identified PM_{10} are 32.0 μg/m³ in Nowy Targ and 35.4 μg/m³ in Zabierzów. During the heating period, these concentrations increase to 44.1 μg/m³ and 46.4 μg/m³, respectively (Fig. 5), while on episodic days, they reach 57.2 μg/m³ in Nowy Targ and 58.2 μg/m³ in Zabierzów (Fig. S6). In the non-heating period, the total concentrations are 15.4 μg/m³ and 18.5 μg/m³, respectively (Fig. 4).

On an annual basis, the main sources of PM_{10} in both locations are factors related to the solid fuel combustion in residential sector, i.e., Residential coal combustion and Residential wood combustion, which together contribute 43.8% (14.8 μg/m³) and 50.3% (16.1 μg/m³) of total PM_{10} in Zabierzów and Nowy Targ, respectively. Both sources show the strongest seasonal variation among all identified factors, accounting for over 50% of PM_{10} mass during the heating season (51.6%, 22.4 μg/m³ in Zabierzów and 57.1%, 25.2 μg/m³ in Nowy Targ) and between 8.0% (2.4 μg/m³) and 12.7% (1.9 μg/m³) during non-heating season in Zabierzów and Nowy Targ, respectively. On episodic days, the contribution of both sources increases to 54.9% (32.0 μg/m³) in Zabierzów and 62.5% (35.7 μg/m³) in Nowy Targ (Fig. S6). It is important to note that the non-negligible presence of these factors in the non-heating season may indicate the burning of green waste, fuel combustion in restaurants with wood-fired ovens, or coal and wood combustion at the beginning and the end of the non-heating season (April, September) when unfavorable meteorological conditions occur.

The second most significant PM_{10} source is road transport, contributing 13.9% (4.9 μg/m³) in Zabierzów and 21.0% (6.7 μg/m³) in Nowy Targ annually. During the heating season, its share rises to 14.3% (6.7 μg/m³) in Zabierzów and 25.5% (11.1 μg/m³) in Nowy Targ, while in the non-heating season, it accounts for 17.7% (3.3 μg/m³) in Zabierzów and 20.9% (3.2 μg/m³) in Nowy Targ (Fig. 4). The higher concentrations observed in Nowy Targ during the heating season may be attributed to increased tourist traffic in the Podhale region, a major winter sports destination, as well as adverse meteorological and road conditions (e.g., lower temperatures, snowfall, slippery road surface, and traffic congestion), which lead to higher emissions from individual vehicles. Overall, the joint contribution of all sources of residential fuel combustion and road transport accounts for over 66% (30.6 μg/m³) of total PM_{10} in Zabierzów and 82% (36.3 μg/m³) in Nowy Targ during the heating season.

The Secondary aerosol source contributes more significantly in Nowy Targ, where factor concentrations average 4.5 μg/m³ (14.1% of PM_{10} mass) over the entire study period and increase to 5.1 μg/m³ (33.0% of PM_{10} mass) during the non-heating season. On the contrary, Zabierzów experiences higher concentration of 4.8 μg/m³ (10.4% of PM_{10} mass) during the heating season. This variability is likely due to the nature of distant sources contributing to Secondary aerosol transport to Zabierzów, which are at least partially associated with residential solid fuel combustion for heating purposes. These sources exhibit significantly higher activity during the heating season, leading to increased secondary aerosol formation and transport.

Sources related to mineral dust show different characteristics. In both locations, their concentrations and contributions to PM_{10} are much higher during the non-heating season (Fig. 4). In Nowy Targ, the Mixed source of mineral dust accounts for 33% of total PM_{10} (5.1 μg/m³) in the non-heating season. In Zabierzów, the combined contribution of Mineral dust & Construction works, and Mineral dust & Road transport reaches 57% (10.5 μg/m³) during the same period.

The local Road de-icing source in Zabierzów contributes consistently across seasons, accounting for 8.4% (1.6 μg/m³) of total PM_{10} in the non-heating and 9.8% (4.5 μg/m³) in heating season (Fig. 4).

The annual source concentration profile in both locations reveal a stronger contributions from solid fuel combustion sources (Residential coal combustion and Residential wood combustion) during the heating season, when heat demand is the highest. Similarly, Road transport emissions increase in this period due to higher activity (Fig. 5). In Zabierzów, the Road de-icing source also shows elevated concentrations in the heating season (Fig. S7, Supplementary Material). In contrast, other sources in both Nowy Targ and Zabierzów show no clear seasonal trends, maintaining relatively stable levels with frequent narrow peaks across seasons (Fig. 5 and Fig. S7).

Conclusions

The comparative study of PM_{10} chemical composition and source apportionment at two distinct sites in Southern Poland provides valuable insights into the variability and origins of particulate matter in different urban environments. Using the PMF receptor model, we successfully identified and quantified key sources contributing to PM_{10} levels at both sites.

Both analyzed locations experience high PM_{10} concentrations, in particular during the heating season. In Nowy Targ, the average PM_{10} concentration reaches 60.1 μg/m³, with 80 exceedances of the EU daily limit value (50 μg/m³), while in Zabierzów, the average PM_{10} level is 53.2 μg/m³, exceeding the limit 76 times. Maximum daily concentrations reach 234.9 μg/m³ in Nowy

Targ and 140.9 μg/m^3 in Zabierzów. Organic carbon (OC) and Secondary Inorganic Aerosol (SIA) are major contributors to annual PM_{10} levels, accounting for 52% of PM_{10} in Nowy Targ and 55% in Zabierzów. The total share of secondary pollutants (SOC + SIA) remains relatively stable in Nowy Targ (average 23%), while in Zabierzów, the impact of distant emission sources is more pronounced (from 32% in the non-heating to 41% in heating season. In both locations, secondary inorganic ions exist as ammonium sulfate during the non-heating season, while during the heating season both ammonium sulfate and ammonium nitrate are present. The share of primary pollutants (POC + EC) is higher in both locations during the heating season, ranging from 24% in Zabierzów to 37% in Nowy Targ.

The study identifies residential coal and wood combustion as the dominant source of PM_{10} pollution, contributing 44% in Zabierzów and 50% in Nowy Targ. Road transport follows as the second major source, accounting for 14% of PM_{10} in Zabierzów and 21% in Nowy Targ. Among all identified sources, residential emission exhibits the strongest seasonality, with significantly higher contributions during the heating season. However, the non-negligible contribution of wood combustion during the non-heating season suggests additional sources of wood combustion, such as burning green waste and fuel combustion in restaurants with wood-fired ovens may influence PM_{10} levels. Road transport emissions show only slight seasonal variation, with higher contributions in Nowy Targ during the heating season (25% of PM_{10}) and in Zabierzów during the non-heating season (18% of PM_{10}). The remaining sources in both locations contribute less than 15 % of total PM_{10} annually.

The contribution of regional transport to PM_{10} pollution is approximately 10% in Zabierzów and 14% in Nowy Targ, when secondary aerosol increases to over 33%. This highlights the significant role of local factors in determining air quality and underscores the need for tailored control strategies.

The analyses of PM_{10} composition during air pollution episodes (PM_{10} > 50 μg/m^3 for at least 4 consecutive days) and the sources of these exceedances show that, on episodic days, the contribution of both main PM components and the sources responsible for elevated PM concentrations is even higher than during the entire heating season.

The overall findings of this study provide valuable scientific data that can assist policymakers in designing effective control strategies, including urban planning and relevant source emission regulations.

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Identyfikacja źródeł PM_{10} w dwóch lokalizacjach miejskich w południowej Polsce

Streszczeanie. Głównym celem badań było lepsze zrozumienie składu chemicznego, zmienności sezonowej i źródeł pyłu zawieszonego w powietrzu w dwóch środowiskach miejskich charakteryzujących się znacznym problemem zanieczyszczenia powietrza, położonych na południu Polski, tj. w Nowym Targu i Zabierzowie. Dobowe próbki pyłu PM_{10} scharakteryzowano chemicznie pod kątem zawartości jonów rozpuszczalnych w wodzie, materii węglowej i pierwiastków śladowych. Do identyfikacji źródeł PM_{10} zastosowano dodatnią faktoryzację macierzy (Positive Matrix Factorization – PMF). Średnie roczne stężenie PM_{10} wynosiło 38 µg/m^3 i 41 µg/m^3, odpowiednio w Zabierzowie i Nowym Targu. Zanieczyszczenia wtórne (SIA + SOC) stanowiły średnio 23% PM_{10} w Nowym Targu, natomiast w Zabierzowie wahały się od 32% do 41% PM_{10}, odpowiednio w sezonie niegrzewczym i grzewczym. Udział zanieczyszczeń pierwotnych (EC + POC) w PM_{10} znacznie wzrastał w obu lokalizacjach w sezonie grzewczym, stanowiąc od 24% do 37% PM_{10}, odpowiednio w Zabierzowie i Nowym Targu. Analiza PMF pozwoliła na zidentyfikowanie w obu lokalizacjach czterech źródeł o podobnych profilach, obejmujących spalanie węgla w

sektorze komunalno-bytowym, spalanie drewna w sektorze komunalno-bytowym, transport drogowy i aerozol wtórny. W obu lokalizacjach największym źródłem emisji PM_{10} było spalanie węgla i drewna w sektorze komunalno-bytowym (łącznie 44% i 50% PM_{10}, odpowiednio w Zabierzowie i Nowym Targu), a następnie transport drogowy (średnio 14% i 21% PM_{10}). W obu lokalizacjach największy udział w stężeniach PM_{10} miały źródła lokalne (średnio 86% i 90% PM_{10}, odpowiednio w Nowym Targu i Zabierzowie), co podkreśla znaczenie strategii działań naprawczych dostosowanych do lokalnych czynników kształtujących jakość powietrza w miastach.

Supplementary Material

Enrichment factors (EF)

The EF for element *X* with respect to a reference crustal element *Y* is defined as:

$$EF_X = \frac{\left(\frac{X}{Y}\right)_{air}}{\left(\frac{X}{Y}\right)_{crust}} \quad \text{(S1)}$$

where $(X/Y)_{air}$ is the concentration ratio of *X* to *Y* in the PM sample and $(X/Y)_{crust}$ is the average concentration ratio of *X* to *Y* in the crust. Al was used as reference crustal element, and the chemical composition of the upper continental crust was taken from McLennan (2001). Relationships between the trace element composition of sedimentary rocks and upper continental crust, Geochemistry, Geophysics, Geosystems, 2, 2000GC000109. DOI:10.1029/2000GC000109)

Table S1. Detection limits (DL) and uncertainties (UNC) for PM_{10} components.

PM_{10} component	DL	UNC
EC	0.1 µg/cm²	5%
OC	0.47 µg/cm²	5%
LG	0.0496 µg/ml	19%
MN	0.0231 µg/ml	19%
GA	0.0183 µg/ml	19%
Cl^-	0.072 mg/l	7.77%
NO_3^-	0.055 mg/l	17.3%
SO_4^{2-}	0.114 mg/l	8.96%
Na^+	0.012 mg/l	9.75%
NH_4^+	0.010 mg/l	5.95%
K^+	0.047 mg/l	12.2%
Mg^{2+}	0.024 mg/l	7.10%
Ca^{2+}	0.224 mg/l	10.5%
Al	42.2 mg/l	18.0%
As	0.22 mg/l	14.7%
Ba	0.36 mg/l	10.2%
Cd	0.02 mg/l	8.0%
Cr	2.0 mg/l	10.6%
Cu	4.2 mg/l	9.5%
Fe	37.6 mg/l	17.0%
K	33.4 mg/l	19.0%
Mn	0.18 mg/l	7.3%
Ni	0.12 mg/l	18.2%
Pb	0.44 mg/l	17.7%
Sr	0.16 mg/l	15.0%
Ti	0.74 mg/l	18.0%
V	0.5 mg/l	9.9%
Zn	3.2 mg/l	14.8%

Table S2. Statistics of 24h PM_{10} concentrations observed in Nowy Targ and Zabierzów.

	Heating season 2020/2021*		Non-heating season 2021**	
	Nowy Targ	Zabierzów	Nowy Targ	Zabierzów
N [-]	177	181	183	177
Data coverage [%]	97.3	99.5	100.0	96.7
Min [µg/m³]	6.5	6.1	6.8	5.5
Max [µg/m³]	234.9	140.9	51.4	51.8
Average [µg/m³]	60.1	53.2	21.4	22.4
Standard deviation [µg/m3]	38.6	27.1	9.1	8.2
No. Of days > LV_{24} [-]* **	80	76	1	1

*** Heating season 2020/2021**: 01.10.2020 – 31.03.2021; **** Non-heating season 2021**: 01.04.2021 – 30.09.2021;
***** No of days >LV_{24h}** – number of days with exceedance of the 24h limit value for PM_{10}

Table S3. Enrichment Factors (EF) calculated for trace elements measured in PM_{10}.

Element	EF Nowy Targ	EF Zabierzów	EF_mean
Al	1.0	1.0	1.0
Mg	1.3	0.7	0.9
Ti	1.6	0.6	0.9
V	2.3	0.7	1.1
Fe	2.9	2.2	2.4
Sr	3.5	4.3	4.1
Ca	3.8	2.0	2.4
K	4.4	1.6	2.3
Ba	5.4	3.5	4.0
Mn	8.8	3.4	4.7
Na	12.2	7.4	8.6
Ni	34.5	15.4	20.1
As	98.2	38.7	53.5
Cu	112.8	39.0	57.3
Cr	217.1	10.1	61.3
Zn	243.0	116.2	147.5
Pb	269.9	114.6	153.0
Cd	1126.8	512.1	664.1

Table S4. Results from PMF bootstrap runs for Nowy Targ.

	Residential coal combustion	Secondary aerosol	Residential wood combustion	Mixed mineral dust	Road transport	Unmapped
Residential coal combustion	99	0	1	0	0	0
Secondary aerosol	1	97	0	0	2	0
Residential wood combustion	1	0	98	1	0	0
Mixed mineral dust	0	2	0	98	0	0
Road transport	5	1	3	9	82	0

Table S5. Results from PMF bootstrap runs for Zabierzów.

	Road deicing	Mineral dust/Road transport	Secondary aerosol	Residential coal combustion	Mineral dust/ Construction works	Road transport	Residential wood combustion	Unmapped
Road deicing	96	1	0	3	0	0	0	0
Mineral dust/Road transport	1	94	0	1	1	2	1	0
Secondary aerosol	0	1	96	2	0	1	0	0
Residential coal combustion	1	5	0	93	0	0	1	0
Mineral dust/ Construction works	2	1	2	2	84	7	2	0
Road transport	0	3	0	2	0	92	3	0
Residential wood combustion	0	0	0	1	0	0	99	0

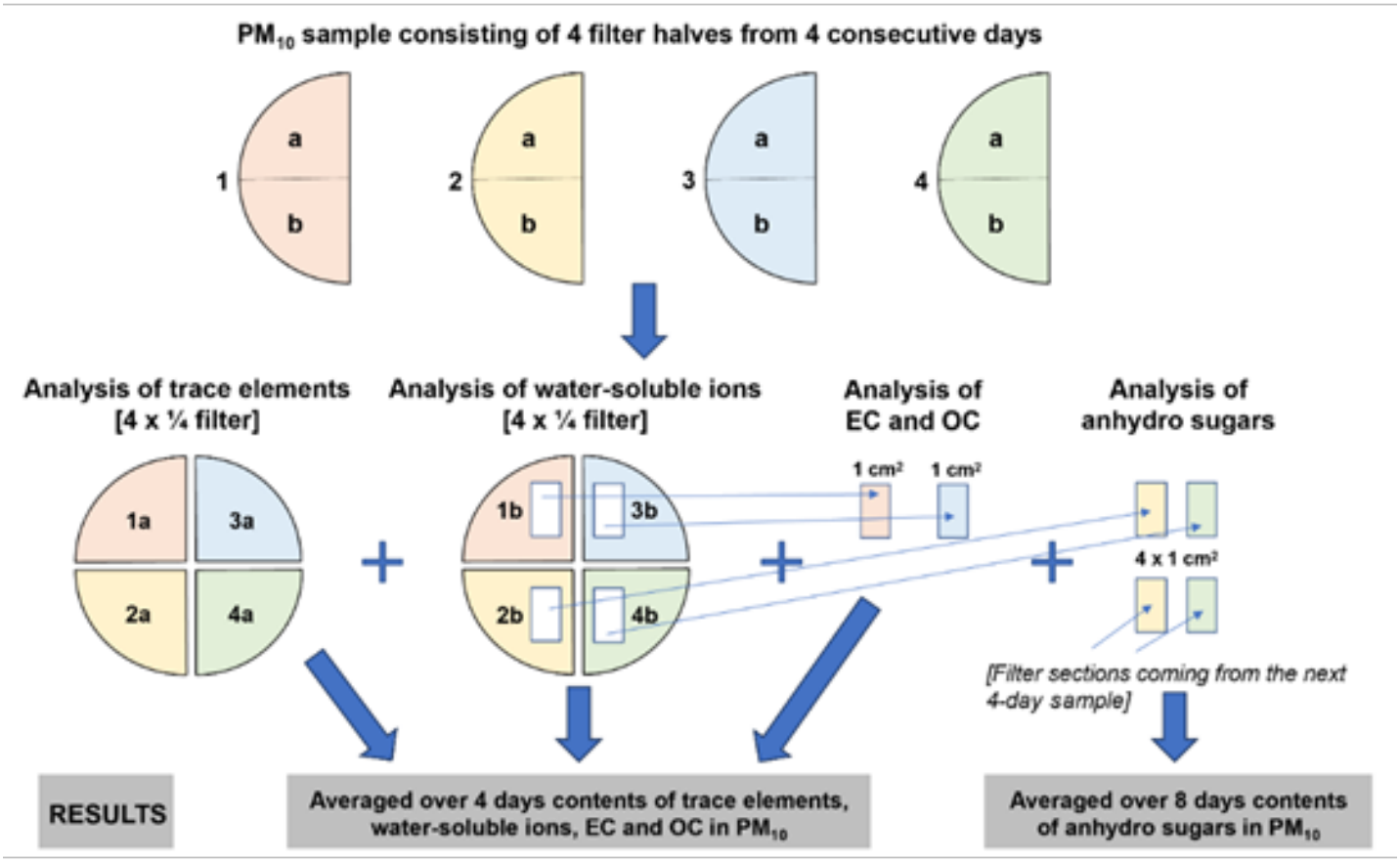

Figure S1. Scheme of combining PM_{10} samples for chemical analyses.

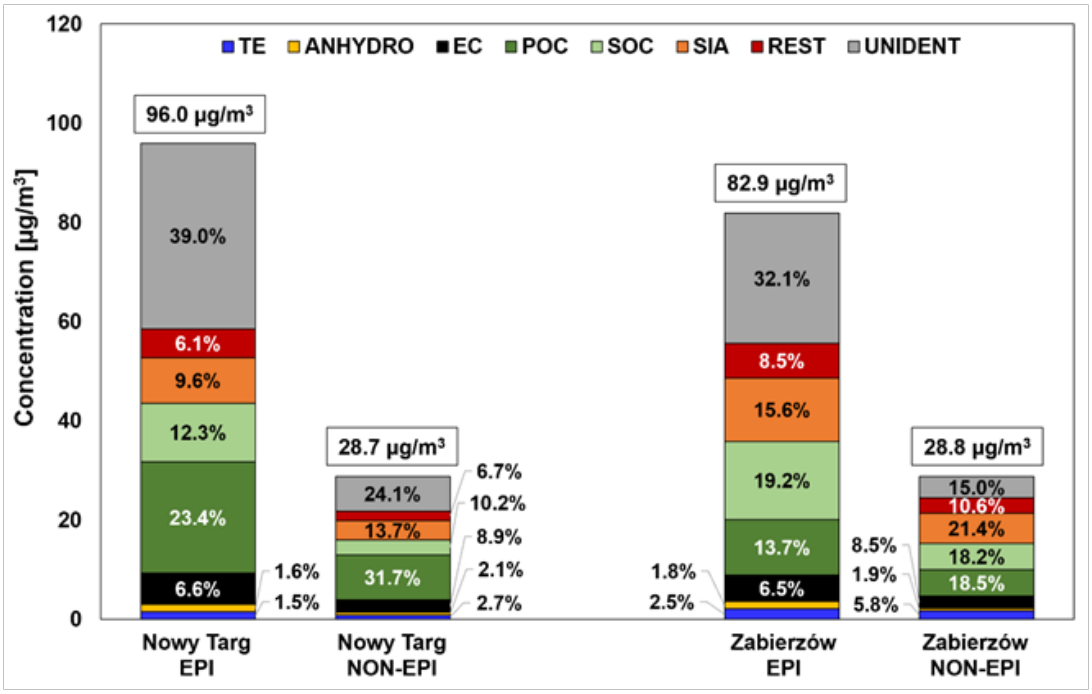

Figure S2. Average contributions [%] of PM_{10} components in Nowy Targ and Zabierzów in the episode (EPI) and non-episode (NON-EPI) periods. TE – trace elements, ANHYDRO – anhydrosugars (sum of levoglucosan, mannosan, galaktosan), OC – organic carbon, EC – elemental carbon, SIA – secondary inorganic aerosols (sum of SO_4^{2-}, NO_3^-, NH_4^+), REST IONS – rest of ions (sum of Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}), UNIDENT – unidentified PM_{10} components.

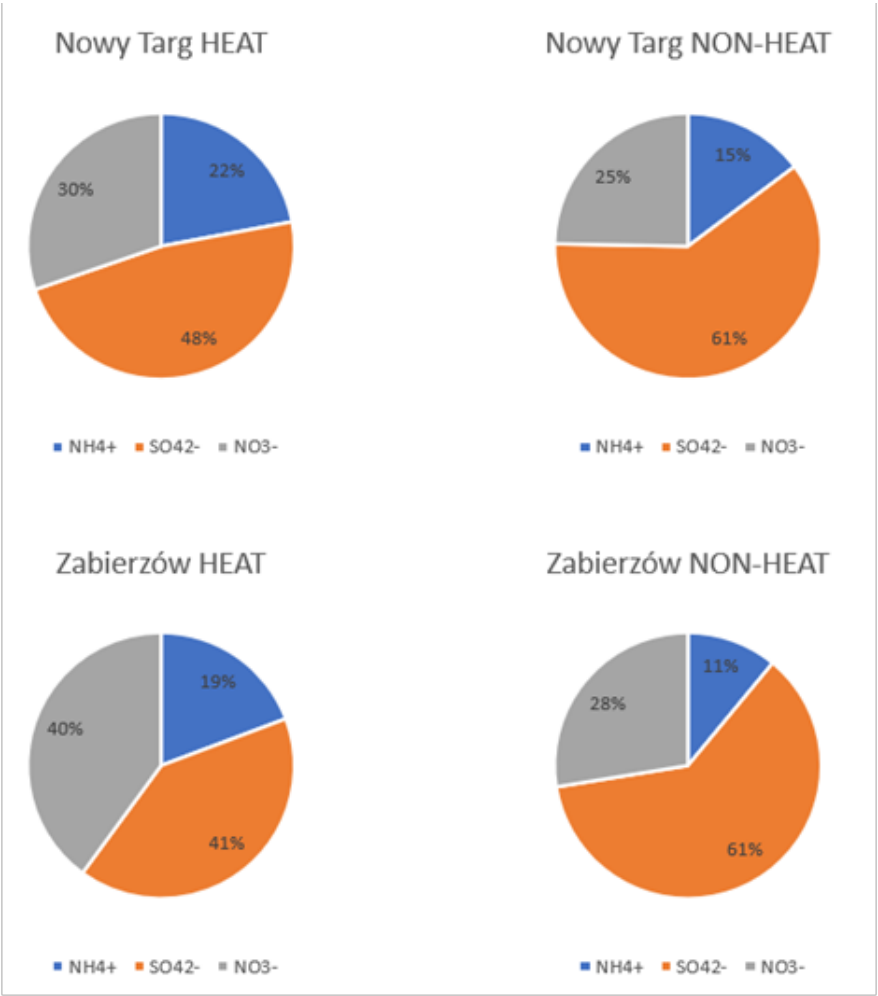

Figure S3. Comparison of relative contributions of ammonium, sulfate and nitrate ions in the secondary inorganic aerosol in Nowy Targ and Zabierzów during the heating and non-heating periods.

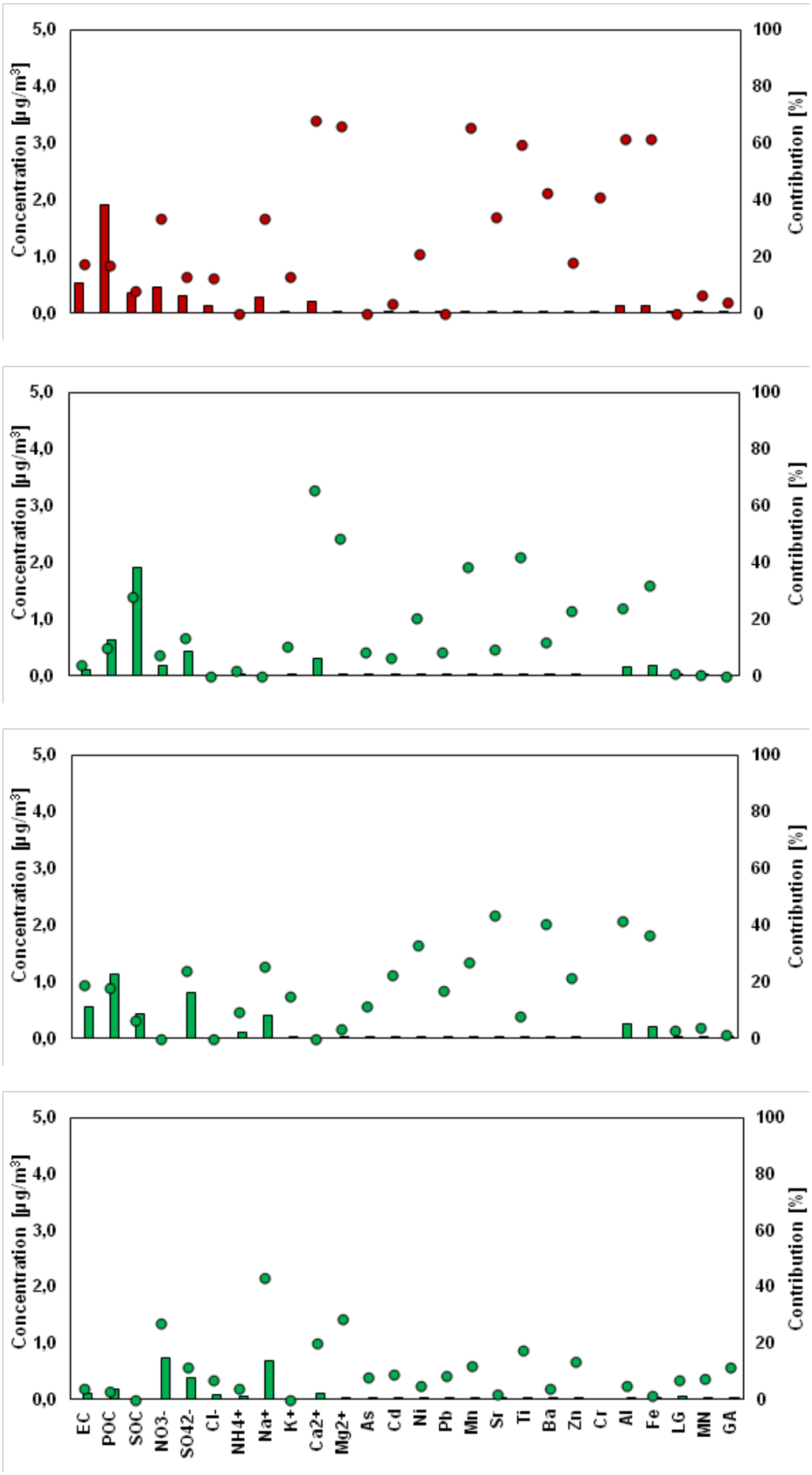

Figure S4. PMF profiles (bars, left y axis) and explained variations (dots, right y axis) of the PM_{10} sources identified solely in Nowy Targ (red) and Zabierzów (green).

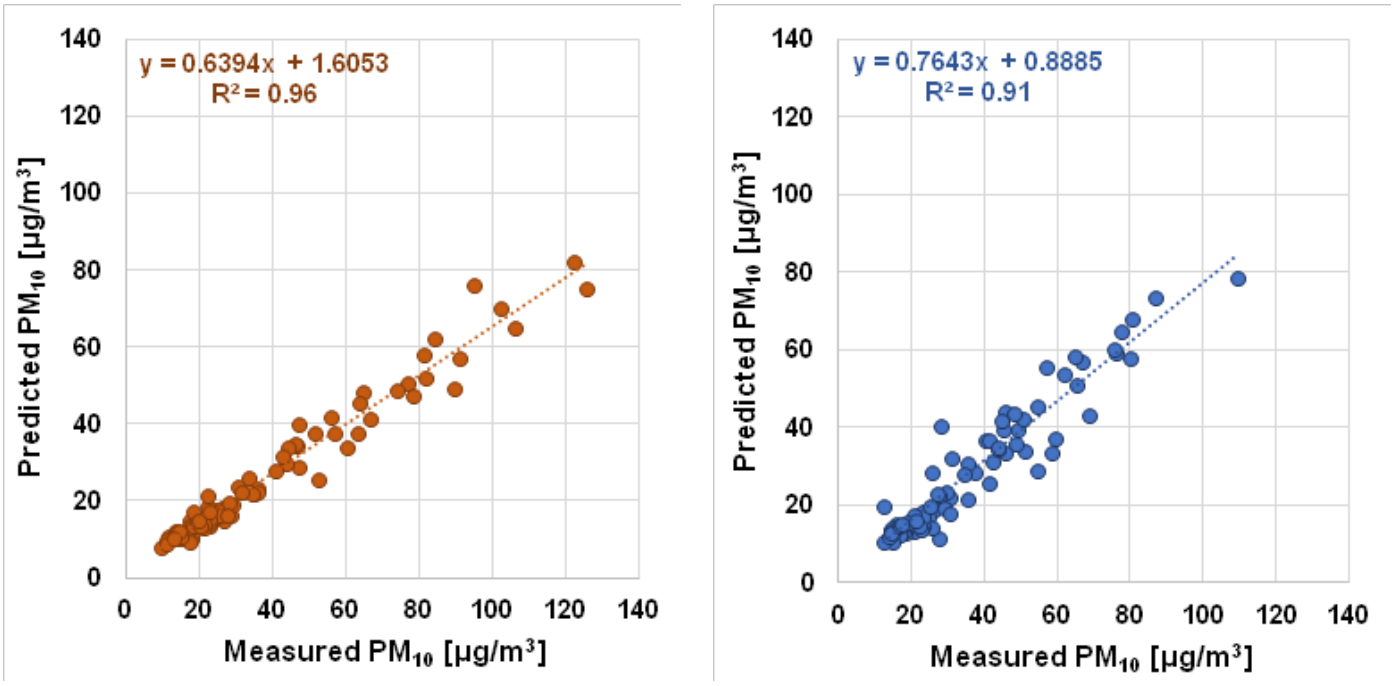

Figure S5. Scatter plots of predicted and measured PM_{10} in Nowy Targ (left) and Zabierzów (right).

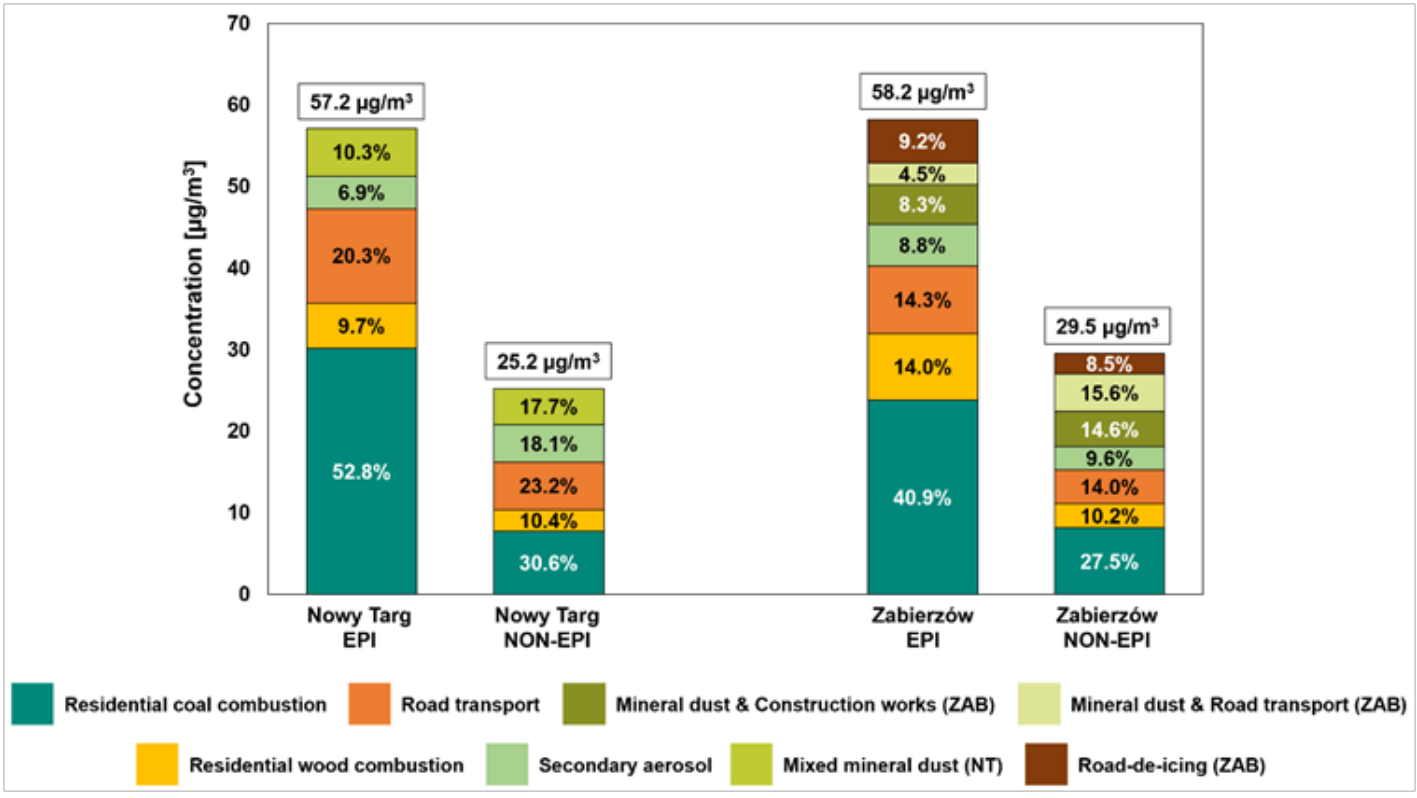

Figure S6. Contributions [%] of PM_{10} sources identified by the PMF model in Nowy Targ and Zabierzów averaged for the episode (EPI) and non-episode (NON-EPI) periods.

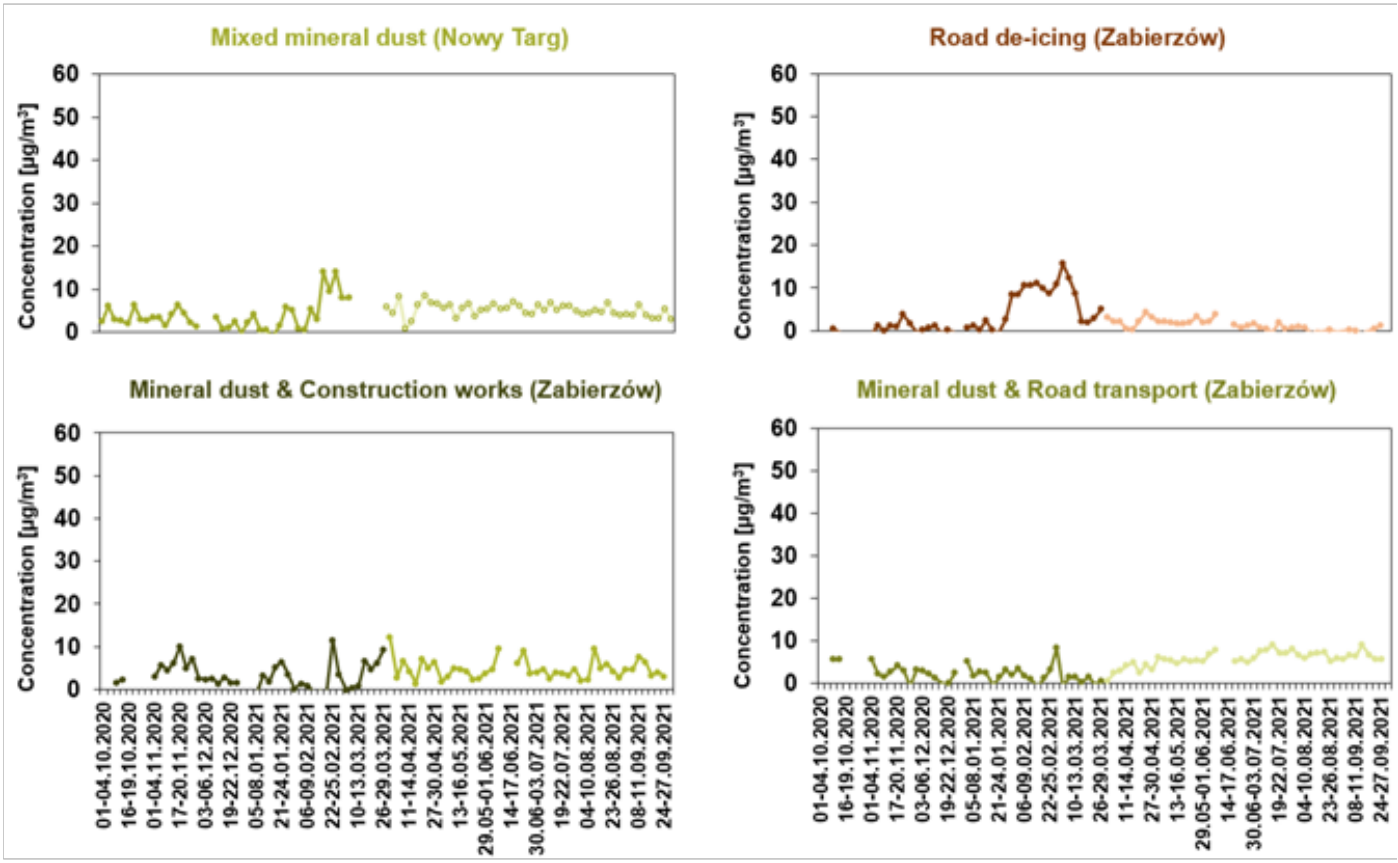

Figure S7. Annual patterns of the PM_{10} source concentrations solely identified in Nowy Targ and Zabierzów in the period of 01 October 2020 – 30 September 2021. Dark and light colors indicate the heating (01 October 2020 – 31 March 2021) and non-heating (1 April 2021 – 30 September 2021), respectively.